



Magnetic imaging with nitrogen-vacancy defects in diamond

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Magnetic imaging with Nitrogen-Vacancy defects in diamond

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Le 29 Octobre 2020

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Introduction

The ability to image magnetic field patterns with a high sensitivity and nanoscale spatial resolution, has become of prime importance in a large number of research areas. It can be applied to the study of biomagnetic species (such as neurons, cardiac cells...), geomagnetism, condensed matter or micro-electronics, to name a few. Multiple techniques have been developed to image magnetism at the nanoscale in the last decades. These techniques can be classified in two different branches; one maps directly the magnetization of the sample, the other relies on mapping stray field emanating from the sample.

The first category of magnetic microscopes relies on sending and collecting particles that interact with matter via a magnetization dependent term. Spin polarized scanning tunneling microscopy [1] is an example where a spin polarized current flows from the probe towards the substrate and through the investigated sample. This technique enabled magnetic imaging of antiferromagnetic ordering of an *Fe* monolayer on *W*(001) with an atomic resolution [2]. Nevertheless, the need for highly controlled work environment (Ultra High Vacuum) with samples fabricated in situ, combined to their required conductivity, restricts the array of materials that can be investigated. X-ray transmission microscopy also falls into this category and uses photons instead, enabling a spatial resolution down to the nanometer [3] when using synchrotron radiation, therefore requiring highly complex experimental apparatus.

The second branch of magnetic imaging techniques relies on mapping the stray field emanating from the sample. In this case, the spatial resolution is usually limited by the probe dimensions and the distance to the sample. A prominent example is the on-tip Nano-Superconducting quantum interference device (Nano-SQUID) [4] developed in the labs of *E. Zeldov* in Tel Aviv. These nano-devices fabricated at the apex of a tip enabled access to imaging of exotic phases (super paramagnetic single domain islands in presence of anomalous quantum hall effect) in Cr doped $(Bi, Sb)_2Te_3$ [5] with a spatial resolution of 20 nm and a single spin sensitivity [6]. However, this technique amongst many others (such as Hall bars [7]) requires operation at cryogenic temperatures therefore hampering their implementation and operation. Magnetic Force Microscopy (MFM) technique is one of the most commonly used tech-

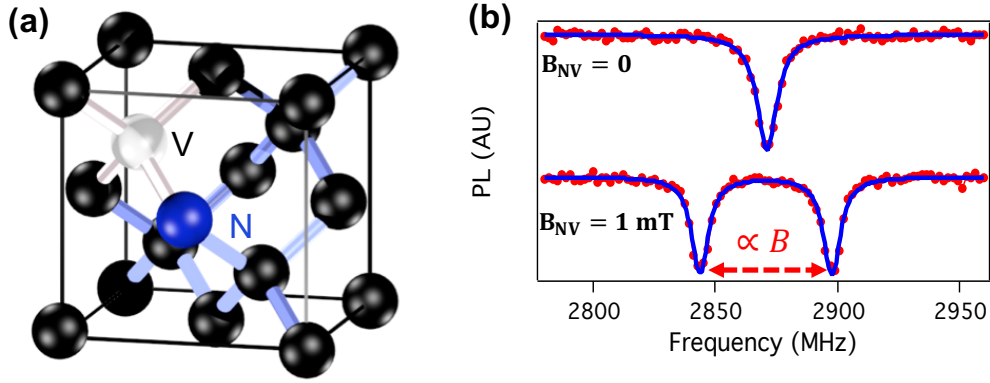


Figure 1: The NV center as a magnetometer (a) Sketch of the atomic structure of the NV defect inside the diamond lattice consisting of a substitutional nitrogen atom (Blue sphere) and a carbon vacancy (White sphere) on an adjacent site. (Black spheres represent the carbon atoms). (b) Optically detected Electron Spin Resonance spectra of a single NV center obtained at zero magnetic field (upper) and under an external magnetic field of 10 G (lower). The photoluminescence signal is plotted here as a function of the MW excitation frequency.

niques for magnetic characterization. It relies on the interaction between a magnetically coated probe and the stray field created by the magnetic sample underneath the probe. With its < 50 nm spatial resolution and versatility of operation temperature, it remains a technique of choice for the investigation of magnetic multilayers. However, the use of a magnetically coated probe renders this technique highly perturbative [8]. This is an important drawback for the investigation of ultrathin magnetic layers.

In 2005, a proposition involving the integration of a single electronic spin into a scanning probe configuration was presented by Chernobrod et al [9] in order to implement a scanning magnetic imager with nano-scale resolution and high sensitivity. Tracking the Zeeman splitting induced by the magnetic field would transform this single spin into an atomic sized magnetometer with a nanometric spatial resolution. Using a single Nitrogen-Vacancy (NV) defect in diamond, this proposition came to reality in 2008 [10, 11]. The NV center in diamond consists in a carbon vacancy associated to a substitutional nitrogen impurity [See Fig.1(a)]. This point defect acts as a fluorescent molecule lodged inside the diamond matrix. Associated to this defect is a single spin, that can be addressed optically. As shown in Figure 1(b) [12], the associated spin resonance can be detected optically and the Zeeman splitting observed under magnetic field is proportional to the local magnetic field [10]. Recent progress in diamond engineering has led to the development of full diamond cantilevers, that contain an NV defect located at their apex [13]. As shown in Figure 2(a), these cantilevers used in a scanning configuration enable the mapping of stray fields at distances down to few tens of nanometers [14] and with sensitivities down to $200 \text{ nT}/\sqrt{Hz}$ [13]. Applications of this technique are exemplified by the imaging of stray fields emanating from un-compensated moments in antiferromagnetic materials [15], images of superconducting vortices at low temperatures [16, 17] or the investigation of atomically thin magnetic CrI_3 crystals [18].

Besides the scanning configuration, magnetic imaging can also be performed with NV defects in a

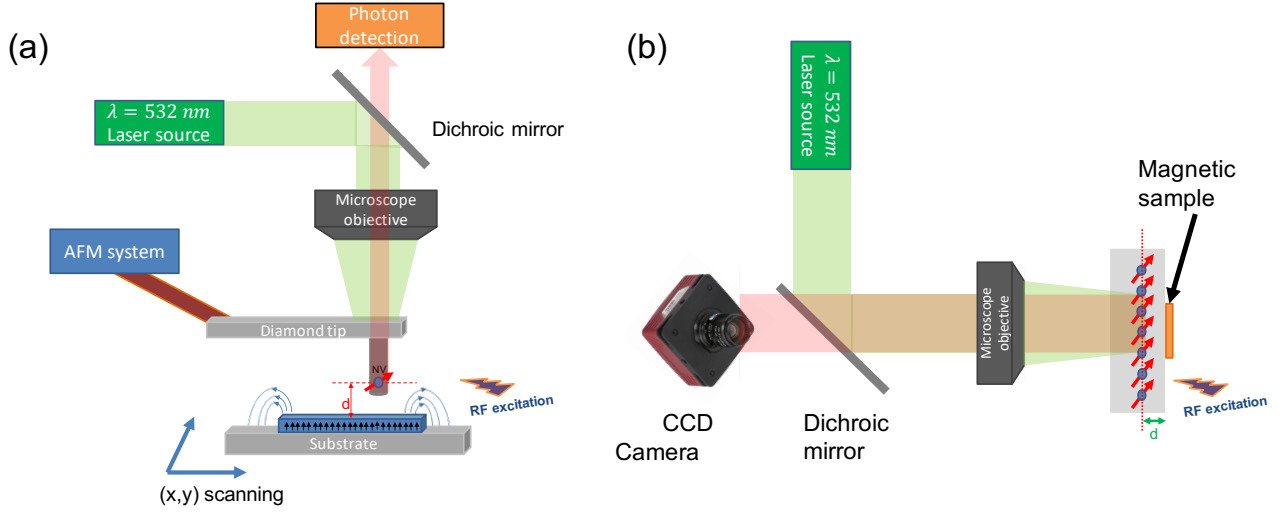


Figure 2: Magnetic imaging with NV centers (a) A scanning probe configuration, where an NV defect is created at the apex of a scanning cantilever. The Zeeman shift induced by the stray field from the sample of interest is mapped by recording a spin resonance spectrum in each point of the scan. (b) A diamond sample containing a dense layer of near-surface NV centers. The NV centers are addressed as an ensemble in a widefield configuration and their photoluminescence response is directly imaged on a CCD camera. By recording a resonance spectrum at each pixel, a full map of the magnetic field created by the sample deposited on-top of the diamond is obtained.

wide-field detection scheme, as shown in Figure 2(b). Here an array of near-surface NV centers is created at a close distance from the diamond surface. The sample to investigate is then deposited directly on top of diamond and a dedicated experimental apparatus enables mapping of the stray field. This technique was employed for multiple applications such as mapping of the magnetic field produced by magnetotactic bacteria [19], characterization of ferromagnetic mineral samples that were saturated by ancient magnetic fields [20] and imaging of current flow in graphene [21]. Although this approach is easier to implement experimentally, the spatial resolution remains limited by diffraction to the micron scale.

In this context, the work performed in the framework of this thesis can be divided in two main parts. During the first year of my thesis, I worked on extending scanning magnetometry using single NV centers towards cryogenic operation. I have implemented an experimental setup operating at 4 K. We then used this setup under ambient conditions to investigate the physics of ferromagnetic skyrmions in multiple thin film hosts. In the last part of this manuscript, we took interest into the optimization of diamond samples for wide-field imaging applications by controlling the preferential orientation and in-depth localization of the created NV centers during CVD growth.

This manuscript is divided in three chapters.

In the first chapter we will start by introducing the NV center main properties (§1.1). We will afterwards present how a single NV defect can be engineered in a scanning-probe configuration in order

to finally present a low temperature NV magnetometry setup that was mounted in the first year of this thesis. We also give a glimpse of the imaging modes that can be performed with this non-invasive magnetic microscope (§1.3.3).

In the second chapter, we use scanning-NV magnetometry to investigate the physics of topological spin structures with a whirling configuration known as magnetic skyrmions in ultrathin magnetic layers under ambient conditions. This experimental work was done in collaboration with:

- A. Hrabec, A Thiaville and S. Rohart at the Laboratoire de physique des solides (LPS, Orsay) - France
- M. Belmegnenai at the Laboratoire des Sciences de Procédés et des Matériaux - Université Paris 13 - France
- M.S. Gabor at the Center for Superconductivity, Spintronics and Surface Science - Technical University of Cluj Napoca - Romania
- K. Gaurav Rana, L.D. Buda-Prejbeanu, O. Fruchart, G. Gaudin and O. Boulle at Spintec - Grenoble - France
- R. E. Dunin-Borkowski at the Peter Grunberg Institute - Jülich - Germany

The chapter is divided into three sections. We first investigate the impact of structural disorder and magnetic history on the morphology of skyrmions in an ultrathin magnetic sample relevant for spintronic applications (§ 2.1). We then study the properties of magnetic skyrmions in an Heusler alloy, a class of ferromagnetic materials with an intrinsically low magnetic damping coefficient (§ 2.2). In a last section, we finally demonstrate the stabilization of sub-100 nm skyrmions at zero external magnetic field in an exchange-biased magnetic structure (§ 2.3)

The last chapter of this thesis focuses on the optimization of diamond samples for widefield imaging applications [19, 20, 21], and lies into the improvement of the second branch of imaging techniques based on the use of ensembles of NV defects. In the first section (§3.1), we will recall its operation principle and the related requirement specifications to boost its performances. These include

- Control over the orientation of the NV centers;
- Maximizing their density;
- Localizing them spatially;
- Maximizing their spin coherence times.

In the second section (§3.2), we will introduce the various approaches currently pursued to produce quantum-graded diamonds hosting NV centers and will focus on the most favourable one, that is Chemical Vapour Deposition (CVD) growth. The strategies that have been implemented up to now to control the

NV centers orientation during CVD growth, will be summarized. In a third section (§3.3), I will detail our results on the tailoring of the NV centers orientation by tuning the CVD chamber temperature on a (113)-oriented diamond substrate. Last in §3.4, we will apply this tuning parameter to localize in-depth dense and preferentially-oriented NV centers, thanks to the temperature-dependent incorporation of NV defects during the CVD growth. All of the investigated diamond samples were grown by;

- O. Brinza, A. Tallaire and J. Achard at the Laboratoire des Sciences des Procédés et des Matériaux in Villetaneuse - France

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Quantum sensors based on the single spin of the nitrogen vacancy defect (NV) in diamond have emerged during the last few years as a challenger to the pre-existing magnetic imaging techniques, owing to the unique combination of capabilities they feature. These capabilities include a high sensitivity (down to $nT/\sqrt{Hz}$), a large operational temperature range (from thousands of degrees celsius down to cryogenic temperatures), a high spatial resolution (down to few tens of nanometers) and a non-perturbative operation. NV magnetometers are in addition suited for quantitative vector measurements of the magnetic fields [22, 23].

After first proof-of-principle demonstrations of its capabilities [10], NV magnetometry has started during the last years to be exploited to explore various open questions in condensed matter systems. It in particular enabled to achieve various breakthroughs in nanomagnetism. These are exemplified by the mapping of the extremely low stray magnetic fields emanating from un-compensated moments in anti-ferromagnetic materials [15], the quantitative imaging at nanoscale of superconducting vortices at low temperatures [16, 17], the investigation of atomically-thin magnetic CrI_3 crystals [18] or the imaging of current flows in graphene ribbons [21]. Furthermore, the bio-compatibility and non-toxicity of diamond

make it suitable for biology applications, as illustrated by the optical magnetic imaging of living cells with sub-cellular spatial resolution [19].

NV magnetometers measure the stray field produced by the probed magnetic samples. The interaction between the NV center and the sample is usually carried out in two different ways: (i) placing the sample in the proximity of a diamond chip that hosts single or an ensemble of near-surface NV centres, or (ii) holding the NV center probe on a scanning unit and moving it across the sample surface. The second configuration is usually referred to as scanning NV magnetometry. It is achieved either by grafting a functionalized nanodiamond with single NV centres at the apex of an atomic force microscope (AFM) tip or by engineering full-diamond tips hosting single NV centres that are mounted on an AFM set-up. This latter architecture is the one used in this PhD work. Among all the capabilities provided by scanning NV magnetometry, the main advantages featured by this architecture, lie in its ultimate nanoscale spatial resolution and its high sensitivity, even under ambient conditions.

In this chapter we will first describe the main optical and spin properties of such NV centers, and how these can be used for magnetic sensing applications. We will afterwards present how this sensor can be integrated in a scanning-probe configuration (§1.2.1) in order to finally present a low temperature NV magnetometry setup that was mounted in the first year of this thesis (§1.3). The chapter will end with an overview of the scanning operation modes that can be performed with this non-invasive tool, with a particular focus on the photoluminescence quenching mode (§1.3.3).

1.1 The NV defect as a magnetic field sensor

The goal of this section is to introduce how the Nitrogen Vacancy defect in diamond can be used as a quantum sensor to probe magnetic fields. We will first start by examining the electronic structure and optical properties of such point defect in §1.1.1. We will then explain the procedure to optically detect the resonance of the associated electronics spin in §1.1.2 paving the way towards the detection of magnetic stray fields using the defect's single spin in §1.1.3. At last we will evaluate the sensor's sensitivity.

1.1.1 Electronic structure and optical properties

Unparalleled since the dawn of times for its sturdiness, diamond is a face-centered cubic arrangement of carbon atoms. This semi-conductor has a large band-gap ($E_g = 5.5$ eV) that makes it transparent to visible light. Diamond can also host several hundreds of impurities, commonly referred to as colour centres, which are responsible for the great diversity of diamond colours. Among the large variety of optically-active impurities, the nitrogen-vacancy (NV) defect has been intensively studied during the last decades owing to its outstanding optical and spin properties [12, 24, 25]. It consists of a substitutional nitrogen atom (N) and a carbon vacancy (V) in a neighbouring lattice site of the diamond matrix and

it exhibits a C_{3v} symmetry, as shown in figure 1.1(a).

Like most of solid-state point defects, the NV center can be found in different charge states. The neutral form, denoted NV^0 , consists of five electrons localized at the defect position: three electrons are provided by the carbon atoms adjacent to the vacancy, and the other two come from the nitrogen atom. An additional electron can also be provided by a donor impurity placed in the vicinity of the NV defect, for example a substitutional nitrogen atom (P1 center). The NV defect is then stabilized in its negatively-charged form, denoted NV^- , which corresponds to a system of six electrons, as sketched in figure 1.1(a). Applications of NV defects in quantum technologies mostly rely on the negatively-charged state, because it features a spin triplet ground level, which can be initialized by optical pumping, coherently manipulated with long coherence time through microwave excitation, and readout by pure optical means. In this thesis, we will only focus on the negatively-charged form NV^- of the defect, which will be denoted NV for the sake of simplification.

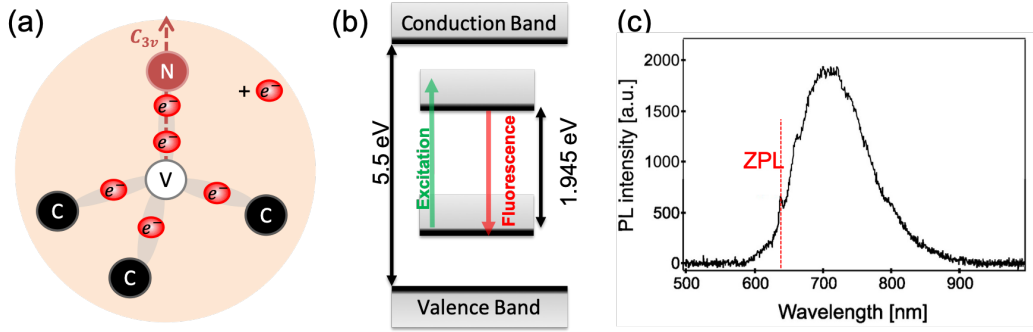


Figure 1.1: Electronic structure and optical properties of the NV defect in diamond. (a) Crystal and electronic structure of the NV defect. (b) Simplified energy levels of the NV defect buried inside the Diamond bandgap. (c) Typical photoluminescence spectrum of the NV defect at 300 K showing its ZPL at 637 nm.

The NV defect gives rise to localized electronic states with energy levels deeply buried inside the bandgap of diamond. As a result, the NV centre can be considered as an artificial atom, *i.e.* mostly decoupled from the valence and conduction bands of the host material. A simplified structure of the energy levels is shown in Figure 1.1(b). The ground level and the first excited level are coupled by an electric dipolar transition with a zero phonon line (ZPL) at 1.945 eV, corresponding to a wavelength $\lambda_{ZPL} = 637$ nm. This transition is commonly excited off-resonance by a green laser at the wavelength $\lambda_{ex} = 532$ nm, leading to an efficient photoluminescence (PL) signal in the red. A typical photoluminescence spectrum of a single NV defect at room temperature is shown in Figure 1.1(c). It exhibits a broadband emission with a spectral width around 100 nm, resulting from an efficient coupling with phonons. Importantly, the PL signal is perfectly photostable, even under ambient conditions. This property enabled the development of highly robust single photon sources operating at room temperature [26] and is currently exploited in biology where NV defects hosted in diamond nanocrystals are used as fluorescent labels [27]. In the next section, we focus on the spin properties of the NV defect.

1.1.2 Optical detection of the electron spin resonance

The purpose of this section is to briefly explain another remarkable property of the NV defect, namely the possibility to detect its electron spin resonance by optical means. This property is at the heart of a wide variety of applications of NV defects, ranging from quantum information processing to the development of ultra-sensitive quantum sensors for metrology [28].

Among the six electrons localized at the NV defect, two are unpaired thus leading to either triplet ($S = 1$) or singlet ($S = 0$) states for the electronic spin. The structure of the energy levels including electronic spin states at room temperature is described in Figure 1.2(a). The ground level of the NV defect is a spin triplet state, whose degeneracy is partially lifted by spin-spin interaction into a doublet state with spin projection $m_s = \pm 1$ and a singlet $m_s = 0$, which are separated by $D_g \sim 2.87$ GHz in the absence of magnetic field. Here the quantum number m_s denotes the spin projection along the intrinsic quantization axis of the NV defect, $\mathbf{u}_{NV}$, corresponding to the axis joining the nitrogen and the vacancy. This axis lies along the $\langle 111 \rangle$ direction of the diamond crystal, and can therefore have four possible orientations.

The excited level is also a spin triplet characterized by a zero-field splitting $D_e \sim 1.4$ GHz between the $m_s = 0$ and $m_s = \pm 1$ spin sublevels [29]. Once promoted to the excited level with a green laser at $\lambda = 532$ nm, the NV defect relaxes back to the ground level either in a radiative way by emitting a broadband red photoluminescence, or through a secondary path involving non-radiative transitions to a metastable singlet state as shown in Figure 1.2(a) [30]. While optical transitions are mainly spin conserving ($\Delta m_s = 0$), the non-radiative decays through the metastable state are strongly spin selective. More precisely, the shelving rate from the $m_s = 0$ excited state is much smaller than those from the $m_s = \pm 1$. Conversely, the decay from the metastable state occurs preferentially towards the $m_s = 0$ spin sublevel of the ground state. These spin selective processes have two important consequences:

1. The NV defect is efficiently polarized in the $m_s = 0$ spin sublevel by optical pumping after few (tens to hundred) optical cycles.
2. The NV defect exhibits a spin-dependent PL signal. More precisely, the PL intensity is significantly higher when the $m_s = 0$ spin sublevel is populated; the $m_s = 0$ states are bright levels, while the $m_s = \pm 1$ states are "dark" states emitting typically 30 % less photons.

These two properties enable the detection of the electron spin resonance (ESR) on a single NV defect by optical means. To do so, the NV defect is initialized in the $m_s = 0$ sublevel by optical pumping with a green laser, and a microwave excitation is used to drive the electron spin transition. When the microwave frequency is resonant with the electron spin transition, populations are efficiently transferred from $m_s = 0$ to $m_s = \pm 1$ spin sublevels, leading to a reduction of the PL signal as shown in Figure 1.2(b).

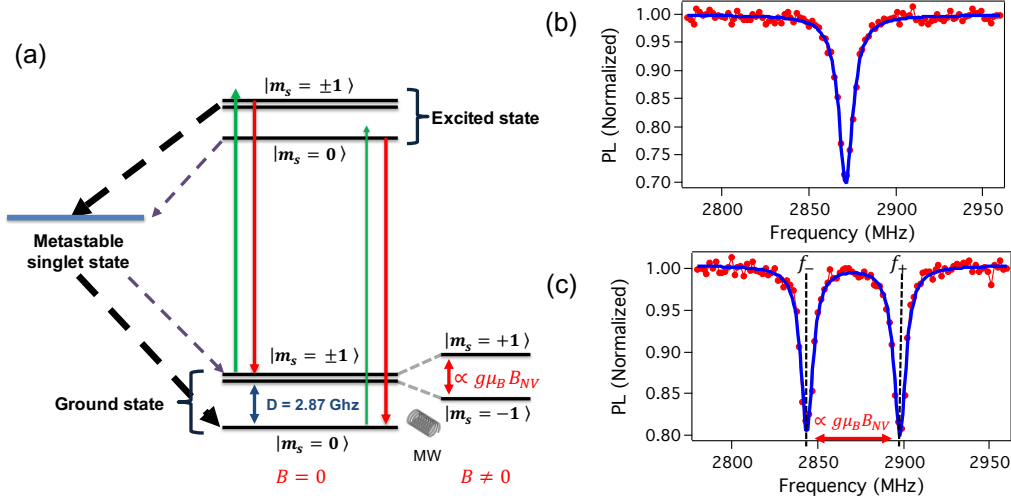


Figure 1.2: Energy diagram and effect of an external magnetic field on the NV center's optically detected magnetic Resonance. (a) Energy diagram of the NV center. Green laser excitation promotes the NV defect to the excited level. It relaxes back to the ground level either in a radiative way (solid red arrows) or non-radiatively through the metastable singlet state (dashed arrows). Under application of an external magnetic field, the spin degeneracy is lifted between the $m_s = -1$ and $m_s = +1$ due to Zeeman splitting. (b) ESR spectrum of an NV center at zero field. Solid lines are fits using a Lorentzian function, dots are data points. (c) ESR spectrum of an NV center under external magnetic field $B_{NV} = 10 \text{ G}$. Solid lines are fits using a Lorentzian function, dots are data points.

The first demonstration of optically-detected ESR on a single NV defect was reported in 1997, using a natural diamond sample and a confocal optical microscope operating under ambient conditions [12]. About ten years later, it was realized that these properties can be exploited for the design of a new generation of magnetometers [22], providing an unprecedented combination of spatial resolution and magnetic field sensitivity, even at room temperature. Indeed, in the presence of an external magnetic field, the degeneracy of the $m_s = \pm 1$ spin sublevels is lifted by the Zeeman effect and two resonances can be observed in the ESR spectrum, corresponding to the transitions $m_s = 0 \Leftrightarrow m_s = -1$ and $m_s = 0 \Leftrightarrow m_s = +1$ as shown in Figure 1.2(b). The Zeeman shift of the ESR frequencies is directly linked to the projection B_{NV} of the external magnetic field along the NV defect quantization axis $\mathbf{U}_{NV}$. As such, by recording the spectral shift of one of the two ESR lines, one can retrieve the component of the magnetic field in the vicinity of the NV center along its quantization axis. This measurement is at the core of NV-center enabled magnetometers.

1.1.3 DC magnetic field sensing

In order to fully describe the operating principle of such magnetometer, one needs to examine in more details the ground state spin Hamiltonian of the NV center in order to establish how the ESR frequencies are evolving with an external magnetic field $\mathbf{B}$.

In the presence of a magnetic field, the spin Hamiltonian of the NV defect in the ground state

writes [31];

$$H = hD\hat{S}_Z^2 + hE(\hat{S}_X^2 - \hat{S}_Y^2) + g\mu_B \mathbf{B} \cdot \mathbf{S} \quad (1.1)$$

where μ_B is the Bohr magneton, $g \approx 2$ is the Landé g-factor, $\hat{S}_X$ $\hat{S}_Y$ $\hat{S}_Z$ are the spin operators, h is the Plank constant. The NV quantization axis $\mathbf{u}_{NV}$ is along the Z direction, D and E are the zero-field splitting parameters.

The axial zero-field splitting parameter $D \approx 2.87$ GHz results from spin-spin interaction between the two unpaired electrons of the NV defect. This parameter is sensitive to temperature fluctuations with a thermal shift, $\frac{dD}{dT} = -75$ kHz.K⁻¹ [32]. We note that these variations can be exploited for nanoscale thermometry [33]. The off-axis zero-field splitting parameter E results from local strain in the diamond matrix which lowers the symmetry of the NV defect. It is therefore heavily influenced by the properties of the host matrix. In high purity diamond crystal $E \approx 100$ kHz, while it can reach values up to 10 MHz for NV defects hosted in nanodiamonds, where strain effects are more pronounced. We note that the condition $E \ll D$ is always fulfilled.

The Hamiltonian can be rewritten as follows

$$H = H_{\text{perp}} + H_{\text{para}} , \quad (1.2)$$

with

$$H_{\text{perp}} = g\mu_B(B_X S_X + B_Y S_Y) \quad (1.3)$$

$$H_{\text{para}} = hD\hat{S}_Z^2 + hE(\hat{S}_X^2 - \hat{S}_Y^2) + g\mu_B B_Z S_Z . \quad (1.4)$$

By computing the eigenenergies of this Hamiltonian, the two ESR frequencies $f_{\pm}$ of the NV defect can be calculated for any magnetic field. Two regimes can be distinguished, depending on the value of the transverse component of the magnetic field $B_{\text{perp}} = \sqrt{B_X^2 + B_Y^2}$.

Weak transverse magnetic field regime $H_{\text{perp}} \ll H_{\text{para}}$

For magnetic field amplitudes such that $B_{\text{perp}} \ll |\frac{hD}{g\mu_B} - B_{NV}|$, the Hamiltonian H_{perp} can be neglected and the ESR frequencies $f_{\pm}$ are simply given by [34]

$$f_{\pm} = D \pm \sqrt{(\frac{g\mu_B}{h} B_{NV})^2 + E^2} \quad (1.5)$$

We consider here that the Z direction corresponds to the direction of the NV axis $\mathbf{u}_{NV}$, therefore $B_Z = B_{NV}$ is the projection of the external magnetic field along the NV axis. As long as $B_{NV} \gg \frac{Eh}{g\mu_B}$, the expression (1.5) of the ESR frequencies can be further simplified into

$$f_{\pm} = D \pm \frac{g\mu_B}{h} B_{NV} \quad (1.6)$$

We note that the evolution of the ESR frequency becomes linear as a function of the on-axis stray field.

However, for small magnetic fields, ie when $B_{NV} \ll \frac{Eh}{g\mu_B}$, the magnetometer is no longer sensitive to field variations. For nanodiamonds, this regime occurs for relatively high magnetic fields amplitudes of the order of hundreds μT typically. To avoid this blind zone, one solution consists of applying a known supplementary magnetic field B_{bias} of about $\approx 2\text{mT}$ along $\mathbf{u}_{NV}$ so that $\mathbf{B} \cdot \mathbf{u}_{NV} = B_{bias} + B_{NV} \gg \frac{Eh}{g\mu_B}$. In this expression, B_{NV} denotes the projection along $\mathbf{u}_{NV}$ of the stray field emanating from the probed magnetic sample. This strategy enables to achieve sensitivities down to $\mu T/\sqrt{Hz}$ or even less.

These sensitivities can be estimated from the characteristics of the optically detected spin resonance. The model is described in the next paragraph.

DC Magnetic field sensitivity

In order to retrieve the magnetic field, the measurement consists in recording optically the ESR spectrum of the NV center electron spin. This experiment relies on the measurement of photoluminescence signal S_{PL} as a function of the microwave excitation frequency as shown in Figure 1.3.

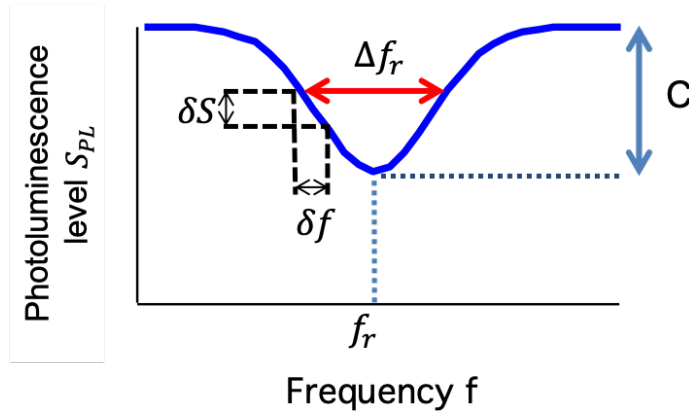


Figure 1.3: ESR spectrum modeled using a gaussian function. The resonance occurs at a frequency f_r with a Full Width at Half Maximum (FWHM) Δf_r and a contrast C . Fluctuations δf of the ESR resonance frequency f_r , for instance due to a magnetic field, translates into a fluctuation δS of the photoluminescence signal at a fixed frequency f

The sensitivity in such measurement corresponds to the smallest magnetic field variation that can be detected with a signal to noise ratio equal to 1. It writes $\eta = \delta B_{min} \cdot \sqrt{\Delta t} [T/\sqrt{Hz}]$, where Δt is the acquisition time. It thus relates to the noise in the measurement process. In our case, this noise arises mainly from photon shot noise during the photo-detection process. This noise is poissonian. As such, for a given PL signal S_{PL} , the noise level equals $\sqrt{S_{PL}}$. Let's now relate η to the parameters of the ESR spectrum.

The photon count rate I corresponding to the ESR lineshape as a function of the microwave excitation frequency f can be described by

$$I(f) = R(1 - C \times L(\frac{f - f_r}{\Delta f_r})) \quad (1.7)$$

Here L is a function that describes the resonance profile¹, R is the counting rate out of resonance, C is the resonance contrast, Δf_r its width at half maximum and f_r its central frequency [see Fig 1.3]. In order to estimate the magnetic measurement sensitivity, we place ourselves at a fixed frequency f .

During an acquisition time Δt , the photoluminescence level is the sum of the signal level $S_{PL} = I\Delta t$ and the associated shot noise $\sqrt{I\Delta t}$. A variation of the probed magnetic field induces a modification of the spin resonance frequency f_r and as such a variation δS of the signal level at a fixed microwave frequency f . Such signal variation can be written in the first order as :

$$\delta S = \frac{\partial S_{PL}}{\partial B} \delta B \quad (1.8)$$

$$= \frac{\partial I}{\partial B} \delta B \Delta t \quad (1.9)$$

The corresponding signal to noise ratio then writes as follows,

$$SNR = \frac{\delta S}{\sqrt{I\Delta t}} = \frac{\frac{\partial I}{\partial B}}{\sqrt{I(B)\Delta t}} \delta B \Delta t \quad (1.10)$$

Since the sensitivity η is by definition the minimal DC magnetic field detectable in a time Δt for a signal to noise ratio of 1 , it reads as:

$$\eta = \delta B_{min} \sqrt{\Delta t} = \frac{\sqrt{I(B)}}{\frac{\partial I}{\partial B}} \quad (1.11)$$

This result can be simplified by assuming that the contrast C is low enough so that $\sqrt{I(B)} \approx \sqrt{R}$. Moreover, let's consider the linear regime for which the dependance of the spin resonance frequency on the magnetic field is linear, that is : $f_{\pm} = D \pm \frac{g\mu_B}{h}.B_{NV}$. In this context, any small variation of the magnetic field δB translate into a small variation of the resonance frequency $\delta f = \frac{g\mu_B}{h}.\delta B$. The sensitivity can then be rewritten as;

$$\eta \approx \frac{h}{g\mu_B} \frac{\sqrt{R}}{|\frac{\partial I}{\partial f}|} \quad (1.12)$$

The maximum value of $\frac{\partial I}{\partial f}$ is achieved at the inflexion point of the ESR line, which leads to;

$$\eta \approx \frac{h}{g\mu_B} \frac{\sqrt{R}}{\max_f |\frac{\partial I}{\partial f}|} \quad (1.13)$$

$$\approx \beta \frac{h}{g\mu_B} \frac{\Delta f_r}{C\sqrt{R}} \quad (1.14)$$

¹Lorentzian or Gaussian profiles are commonly used [35]

The factor β is a numerical parameter related to the spin resonance profile. For a Lorentzian profile $\beta_{Lor} = \frac{4}{3}\sqrt{3} \approx 0.77$ whereas a Gaussian one leads to $\beta_{Gauss} = \sqrt{e/8\ln 2} \approx 0.70$ [36].

We note that the sensitivity depends on three parameters : the ESR contrast C , the count rate R and the ESR linewidth Δf_r . The ESR contrast C is fixed by the intrinsic photophysical properties of the NV defect and reaches around 30% for a single NV defect [37]. The parameter R is affected by two parameters: the radiative transition rate of the NV center and the collection efficiency of the optical setup. The transition rate can be enhanced via the Purcell effect by integrating the NV defect into resonant cavities [38], whereas the collection efficiency can be optimized by engineering diamond nanostructures that can guide the PL signal, such as nanowires [26], nanopillars [13] or by tailoring the diamond surface in a way that eliminates surface refraction [39]. Counting rates $R \approx 10^6 \text{ s}^{-1}$ can be obtained in the case of structured diamonds, as we will see in the following sections. The ESR linewidth Δf_r is highly dependent on the measurement protocol. Its intrinsic lower bound value is set by the inverse of the electron spin coherence time T_2^* . This relaxation is mainly governed by spin-spin interactions with the paramagnetic impurities contained in the host diamond. For single NV defects hosted in high purity diamond crystals, the coherence time reaches few microseconds, corresponding to an optimal ESR linewidth of about 200 kHz. Such ultimate limit can not however be reached when recording an ESR spectrum under continuous laser and microwave excitation. Indeed, these induce a power broadening of the ESR line [35], so that typical ESR linewidths are on the order of $\Delta f_r \approx 10 \text{ MHz}$. A way to avoid power broadening and reach the limit fixed by the coherence time of the NV spin is described in (§1.3), where pulsed-ESR spectroscopy is performed. In the same paragraph, the magnetometer's sensitivity η_{pulsed} in pulsed regimes will be estimated and compared to the continuous wave regime sensitivity η .

1.1.4 High transverse magnetic field regime

When the condition $H_{perp} \ll H_{para}$ is not fulfilled, *i.e.* for magnetic fields with an off-axis component larger than 5 mT, the ESR frequencies $f_{\pm}$ are not only affected by the value of the magnetic field, but also by the angle it makes with the NV quantization axis. The evolution of the ESR frequencies under magnetic field is no longer linear, as illustrated by Figure 1.4(a). Nevertheless, even if the relation is more complex, one can still deduce information about the magnetic field amplitude and orientation by measuring the position of the two ESR frequencies. The eigenvalues of the spin Hamiltonian can be obtained by solving the following characteristic equation [10]

$$x^3 - \left(\frac{D^2}{3} + E^2 + \zeta^2\right)x - \frac{\zeta^2}{2}\Delta - \frac{D}{6}(4E^2 + \zeta^2) + 2\frac{D^3}{27} = 0. \quad (1.15)$$

Here $\zeta = \frac{g\mu_B}{h}B$ and $\Delta = D \cos(2\theta) + 2E \cos(2\phi) \sin^2(\theta)$, where (θ, ϕ) are the polar angle characterizing the magnetic field orientation in the (X, Y, Z) reference frame. Making the assumption that $\Delta \approx D \cos(2\theta)$ as long as $E \ll D$, solving this equation provides us with the expression of ζ^2 and Δ as a function of f_{-}

and f_+

$$\begin{aligned}\zeta^2 &= \frac{1}{3}(f_+^2 + f_-^2 - f_+f_- - D^2 - 3E^2) \\ \Delta &= \frac{7D^3 + 2(f_+ + f_-)(2(f_+^2 + f_-^2) - 5f_+f_- - 9E^2) - 3D(f_+^2 + f_-^2 - f_+f_- + 9E^2)}{9(f_+^2 + f_-^2 - f_+f_- - D^2 - 3E^2)}\end{aligned}\quad (1.16)$$

Once a full ESR spectrum is recorded, the magnetic field amplitude and θ can then be deduced respectively from ζ^2 and Δ with a π uncertainty for the polar angle.

However, in the regime of large magnetic fields, the quantization axis is no longer fixed by the NV defect axis, since the transverse component of the magnetic field B_{perp} induces mixing of the electron spin states. In that case, the eigenstates of the spin Hamiltonian are given by superpositions of the $m_s = 0$ and $m_s = \pm 1$ spin sublevels. Such a mixing leads to strong modifications of the NV defect spin dynamics under optical illumination. This is illustrated by Figure 1.4, adapted from a work by Tetienne *et al.* published in 2012 [37]. In this work single NV centres in bulk diamond were investigated by optically detected magnetic resonance under the application of high magnetic fields at room temperature. Figure 1.4(a) shows ESR spectra recorded from a single NV defect for increasing values of an external magnetic field applied with an angle $\theta = 74^\circ$ with respect to the NV axis. As soon as the off-axis component overcomes the condition $H_{\text{perp}} \gg H_{\text{para}}$, spin mixing efficiently inhibits both optically-induced spin polarization and spin-dependent PL of the NV defect, and the ESR contrast vanishes [Fig. 1.4(b)]. In this field regime, the NV defect can no longer be used for quantitative magnetic field sensing.

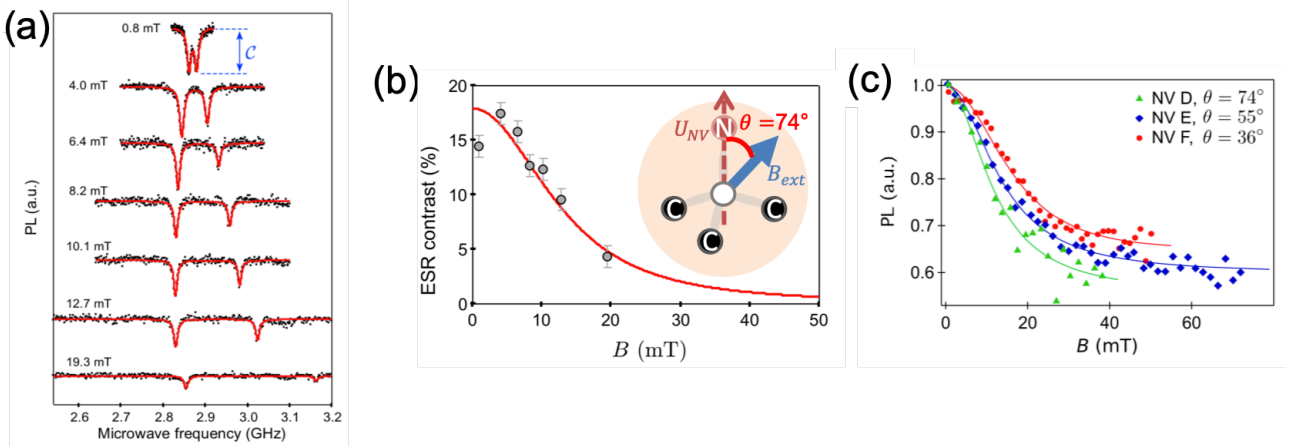


Figure 1.4: ESR properties of an NV center under off axis magnetic field. (a) ESR spectra of a single NV for different values of external magnetic field applied along $\theta = 74^\circ$. from ref [37] (b) Relative contrast C of the ESR resonance as a function of magnetic field value. The solid line is a fit based on the model proposed in the same paper, and that will be used in this thesis for the simulation of quenching images in chapter 2. (c) Photoluminescence signal as a function of off axis magnetic field intensity for multiple single NV's with different orientations. The angle presented in the inset is the angle between the NV's direction and the applied magnetic field. Increasing the magnetic field value quenches the photoluminescence signal. The quenching increases faster for higher θ . Solid line are fits using the same model. From ref. [37]

The decreased ESR contrast is accompanied by an overall reduction of the NV defect PL intensity when the off-axis component of the magnetic field increases. As shown in Figure 1.4 (c), the PL signal drops by more than 30% for $B_{\text{perp}} \geq 20 \text{ mT}$. This PL quenching is due to spin mixing, which increases the mean probability for non-radiative transitions through the metastable state. This effect can be used as a resource to qualitatively map high magnetic field regions without the need for microwave excitation. Although not quantitative, we will show in Chapter 2 that such an all-optical imaging mode is ideally suited to study the physics of ferromagnetic skyrmions. In order to understand in more details this magnetic-field-dependent PL quenching effect, we will rely on the model introduced in Ref. [37], which describes the NV center's photodynamics in the presence of a transverse magnetic field. This model will be used in this manuscript for simulation of the quenching images of spin textures in ferromagnets in Chapter 2 of this thesis. It is described in details in the following section.

Photodynamics of a single NV center in a static magnetic field

Optical transitions take place between the two triplet states and non radiative transitions occur via the metastable singlet state. States $|1^0\rangle, |2^0\rangle, |3^0\rangle, |4^0\rangle, |5^0\rangle, |6^0\rangle$ and $|7^0\rangle$ here denote the eigenstates in zero magnetic field, as shown in Figure 1.5(a). These eigenstates are the spin projections along the quantization axis of the NV defect. $|1^0\rangle, |2^0\rangle$ and $|3^0\rangle$ correspond to the ground state, and $|4^0\rangle, |5^0\rangle$ and $|6^0\rangle$ to the excited one. The remaining one $|7^0\rangle$ is the metastable state. Zero-field transition rates from $|i^0\rangle$ to $|j^0\rangle$ are noted k_{ij}^0 . At zero magnetic field, the number of levels reduces to five, since $|5^0\rangle$ and $|6^0\rangle$ ($|2^0\rangle$ and $|3^0\rangle$) are degenerate. This 5-level model at zero field and at room temperature has been previously used in literature [30, 40, 37]. Some assumptions are made:

- Optical transitions between the two spin triplet states are spin conserving, $\Delta m_s = 0$;
- The radiative transition rates are independent of the spin projection value m_s ($k_{41}^0 = k_{52}^0 = k_{63}^0 = k_r^0$);
- The optical pumping rates from the fundamental to the excited state are proportional to the corresponding decay rates. These write $k_{ji}^0 = \alpha k_{ij}^0$ for $j = 1..3$ and $i = 4..6$ where α is the optical pumping parameter. This parameter can be time dependent $\alpha(t)$.
- Non radiative transition rates between the metastable state and the triplet states only depend on the absolute value of m_s , $k_{57}^0 = k_{67}^0$ and $k_{72}^0 = k_{73}^0$

The dynamics of the NV center under optical pumping and in zero field is thus described by five parameters which are intrinsic to the defect ($k_r^0, k_{47}^0, k_{57}^0, k_{71}^0$ and k_{72}^0), and α an extrinsic parameter linked to the optical pumping intensity, as presented in Figure 1.5(a).

This dynamics is modified under strong magnetic field. The transverse component of the external magnetic field induces spin mixing in both the ground and the excited levels. The new k_{ij} transition

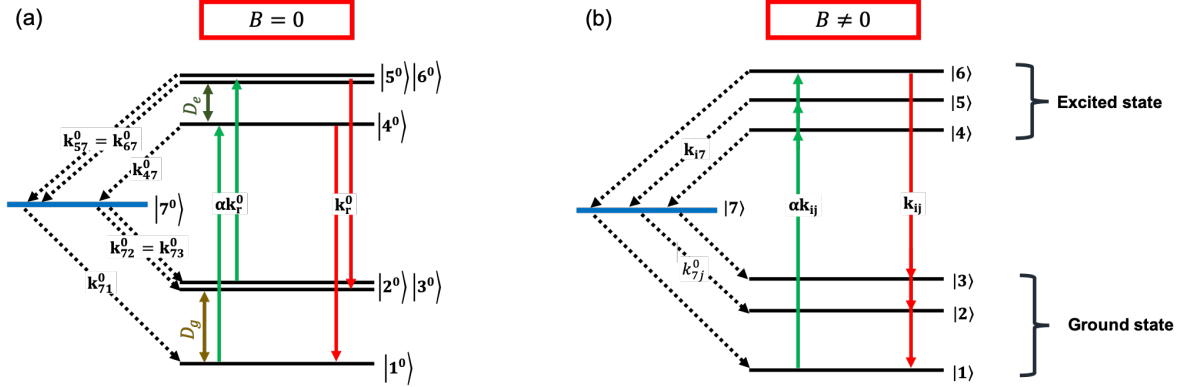


Figure 1.5: Modeling of the photodynamics of an NV center. A seven level model is used to describe the photodynamics of the NV center : the excited and ground states are composed of spin triplets and are linked via radiative transition rates assuming spin conservation (in solid arrows). Transitions via the metastable state are non-radiative (in dashed arrows). (a) In zero field the k_{ij}^0 and k_r^0 parameters describe the transition rates between these levels, and α is the optical pumping parameter. (b) In the presence of an external magnetic field, the induced spin mixing in both ground and excited states affects the transition rates.

rates are thus likely to be different from k_{ij}^0 . Under strong magnetic field, the NV center can still be described along a 7 level model as depicted in Figure 1.5(b). The new k_{ij} transition rates shall depend only on the zero-field transition rates k_{ij}^0 , the optical pumping parameter α and the external magnetic field $\mathbf{B}$. Resolving the classical rate equations shall then allow to predict the emission rate and the populations of each state. Here we use the same spin Hamiltonian for the ground and excited levels, in the form

$$H_\lambda = hD_\lambda \hat{S}_Z^2 + g\mu_B \mathbf{B} \cdot \mathbf{S} \quad (1.17)$$

where $\lambda = g$ (respectively $\lambda = e$) is an indication of the ground level (respectively excited level). D_λ is the zero field splitting which depends on the considered level ($D_g = 2.87 \text{ GHz}$ and $D_e = 1.42 \text{ GHz}$ [41]). The transverse splitting term E is neglected since its contribution is only relevant at very low fields $B < 1 \text{ mT}$.

For a given magnetic field, the eigenstates $\{|i\rangle\}$ can be described as linear combinations of the zero field eigenstates $|i^0\rangle$

$$|i\rangle = \sum_{j=1}^7 \kappa_{ij}(\mathbf{B}) |j^0\rangle \quad (1.18)$$

where the $\kappa_{ij}(\mathbf{B})$ coefficients are calculated using the expressions of H_e and H_f and while supposing $|7\rangle = |7^0\rangle$. Applying Fermi's golden rule, we obtain an expression of the new transition rates $\{k_{ij}(\mathbf{B})\}$

in terms of the zero field transition rates $\{k_{ij}^0\}$ as follows

$$\begin{aligned} k_{ij}(\mathbf{B}) &= \Gamma_0 |\langle j | \mathbf{W} | i \rangle|^2 \\ &= \Gamma_0 \left| \sum_{p=1}^7 \sum_{q=1}^7 \kappa_{ip} \kappa_{jq}^* \langle q^0 | \mathbf{W} | p^0 \rangle \right|^2 \end{aligned} \quad (1.19)$$

where Γ_0 is a normalization factor that includes the density of states and $\mathbf{W}$ is the perturbation Hamiltonian responsible for the transition. The cross terms in Equation (1.19) can be neglected since they only affect the coherence times. Eq 1.19 becomes

$$k_{ij}(\mathbf{B}) = \Gamma_0 \sum_{p=1}^7 \sum_{q=1}^7 |\kappa_{ip}|^2 |\kappa_{jq}|^2 |\langle q^0 | \mathbf{W} | p^0 \rangle|^2 \quad (1.20)$$

The transition rates at zero field are given by $k_{pq}^0 = \Gamma_0 |\langle q^0 | \mathbf{W} | p^0 \rangle|^2$. Therefore Equation (1.20) becomes

$$k_{ij}(\mathbf{B}) = \sum_{p=1}^7 \sum_{q=1}^7 |\kappa_{ip}|^2 |\kappa_{jq}|^2 k_{pq}^0. \quad (1.21)$$

These transition rates allow us to describe the time evolution of the populations $\{n_i\}$ for a given optical pumping rate $\alpha(t)$ by solving the rate equations,

$$\frac{dn_i}{dt} = \sum_{j=1}^7 (k_{ji} n_j - k_{ij} n_i) \quad (1.22)$$

with $\sum_{j=1}^7 n_j = 1$, the normalization for a closed system. Finally, the steady state fluorescence rate is given by

$$R(\mathbf{B}) = \sigma_e \sum_{i=4}^6 \sum_{j=1}^3 k_{ij}(\mathbf{B}) \bar{n}_i \quad (1.23)$$

where σ_e is the collection efficiency of the optical detection system (typically $\sigma_e \approx 10^{-3}$) and $\bar{n}_i$ is the mean population in level $|i\rangle$.

In Figure 1.6 the variation of the photoluminescence signal as a function of the magnetic field components B_{perp} and B_{para} is plotted following such model. Figure 1.6(a) represents a photoluminescence map of an NV center as a function of the magnetic field components B_{perp} and B_{para} for a given orientation of the NV center. As long as $B_{perp} \leq 2$ mT, the photoluminescence signal of the NV center is not affected by quenching. When B_{perp} is further increased, the PL signal is reduced with a characteristic quenching contrast that reaches a maximum value of 40 %. In figure 1.6(b) a linecut of the map for $B_{para} = 0$ mT is shown. Again, it reveals a 40 % quenching of the PL signal for increasing values of B_{perp} .

To summarize, we have seen in this section that a single NV center can be exploited as a non-perturbative magnetic field sensor in two configurations;

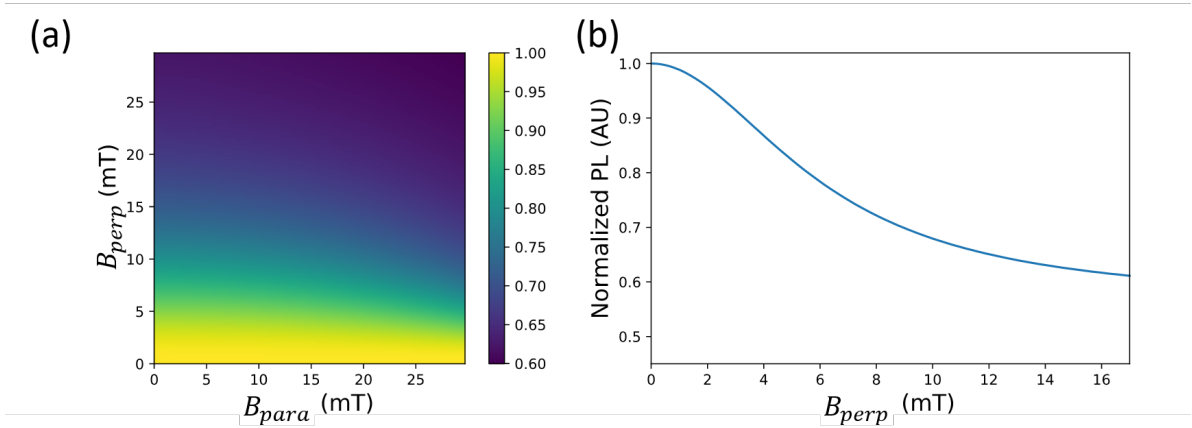


Figure 1.6: Modeling the photoluminescence quenching of an NV center under external magnetic field for a given orientation of an NV center. (a) Photoluminescence map of an NV center (for $\theta = 55^\circ$) as a function of B_{perp} and B_{para} . (b) Linecut of the map for $B_{\text{para}} = 0$ mT showing the effect of pure perpendicular magnetic field on the photoluminescence signal of the NV center. Both data are obtained using the photoluminescence quenching model with photophysical parameters extracted from Ref [37]

- The first is a mode that relies on the tracking of the Zeeman shift relative to its ESR frequency. Such shift is proportional to the projection of the perceived stray field on the NV's quantization axis. It is quantitative and can be used as long as the off-axis magnetic fields keep smaller than 5 mT.
- The second is a qualitative mode that relies on the photoluminescence quenching induced by the off-axis component of the detected stray field.

In the next section, we will address the integration of a NV center into a scanning configuration, in order to perform magnetic imaging.

1.2 Nanoscale magnetic imaging with a single NV defect

In this section we first introduce the experimental setup configuration in which a single NV center's spin properties can be harvested for magnetic imaging. Such set-ups can operate at room temperatures or cryogenic temperatures. I mounted such an experimental setup in our labs for low-temperature magnetic imaging down to 4K. This in itself was one of the challenges of this thesis project. When I joined the labs, our team had just arrived in Montpellier University, and establishing reliable low temperature scanning NV magnetometry was a challenge not only for us, but for multiple group in NV community. Various scanning NV-magnetometers operating at room temperature are now settled and applied to open questions in nanomagnetism around the world including in our team. This experimental setup operating at 4 K is yet one of the only four operating cryogenic scanning NV magnetometers worldwide (A. Blejkyński's Group in UCSB -USCA, P. Maletinsky's group in Uni-Basel-Switzerland and J.F. Roch's group in Laboratoire Aimé Cotton-France).

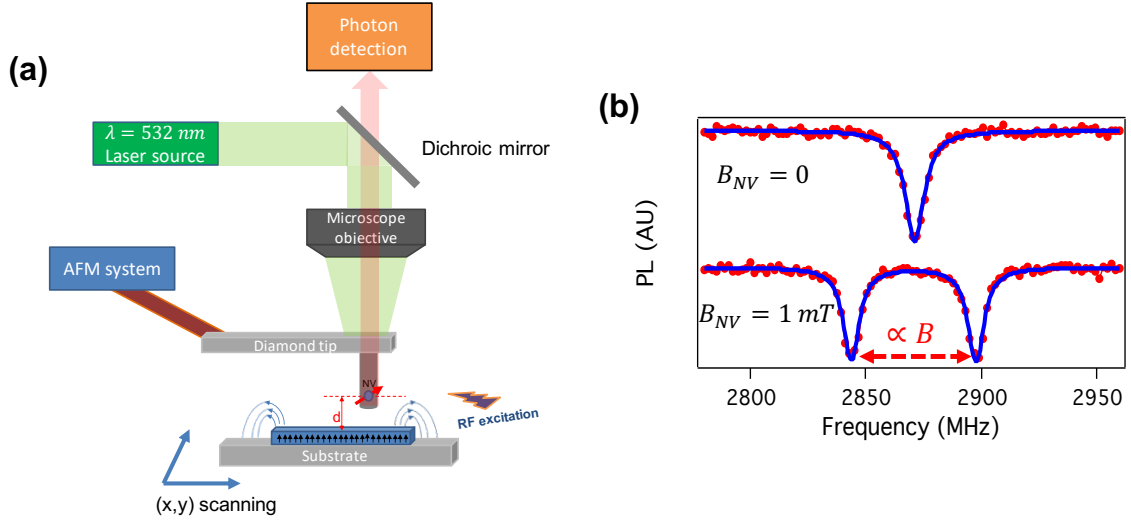


Figure 1.7: Sketch of the experimental setup for single spin scanning NV magnetometry. (a) Scheme depicting the setup as installed in our labs. A cantilever containing a single NV center is mounted on an AFM setup, and a microscope objective is used to collect the photoluminescence signal and for optical polarization. The Sample of interest is scanned in (x,y) under the cantilever and microwave excitation is provided using antennas patterned close to the area of interest. (b) ESR spectra obtained at zero field (up) and under $B_{NV} = 10 \text{ G}$ (bottom). Tracking the Zeeman shift of the NV's spin resonance while scanning the sample enables stray field mapping,

After a short introduction on the principle of the technique and its advantages and characteristics §1.2.1, we will address the engineering of the probes used in this configuration in §1.2.2. We will move on afterwards into integrating these probes into a low temperature operating setup in §1.3 and end up by showing the characterization procedure and the imaging modes of our magnetometer.

1.2.1 Principle of scanning NV-Magnetometry

The architecture of a scanning NV magnetometer is described in Figure 1.7. The magnetic field mapping is here achieved as follows :

- An NV center located at the apex of an Atomic Force Microscope (AFM) probe is scanned over the sample of interest.
- A confocal setup is integrated to the AFM to enable optical detection of the NV PL level and spin resonance.
- At each point of the scan, an ESR spectrum is recorded giving the Zeeman splitting proportional to the locally sensed magnetic field.

The scheme shown in Figure 1.7(a) gives an idea on how our actual setups are built. It is composed of two main parts, an Atomic Force Microscope and a confocal setup that enables measurement of the ESR spectrum. The magnetic sample is mounted over a stack of piezo-electric crystals that allow scanning

in the (x,y) directions, and the AFM system closed loop tracking ensures that the tip stays at a constant distance from the sample. While the sample is scanned under the probe, the NV center is excited using a $\lambda = 532$ nm laser beam focused using a microscope objective. The same objective collects the red photoluminescence signal which is redirected using a dichroic mirror into the optical detection apparatus consisting of Avalanche Photodiodes. Finally, adding RF excitation using patterned dedicated antennas on the sample enables optical detection of the magnetic resonance recorded in each pixel of the scanned area. As an example in 1.7(b) two resonance spectra obtained at zero field, and under a magnetic field of $B_{NV} = 10$ G are shown. Tracking the Zeeman shift then enables a mapping of the stray field generated by the sample. The main characteristics of such an experimental setup can be summarized as follows;

- Quantitative B-field measurement with $\eta \approx 1 \mu T / \sqrt{Hz}$, as estimated in (§1.3.2).
- High spatial resolution. The effective resolving power of the probe is dependent on the flight distance of the NV center over the sample of interest, which can reach values down to down to few tens of nm. Its measurement will be addressed in (§1.3.2).
- Operation at ambient conditions but also at low temperatures.
- Non-perturbative stray field measurement.

The cornerstone of this experimental setup is the probe. We will describe in the next section the fabrication procedure of the scanning NV probe, performed by our collaborators : the Patrick Maletinsky's group at the University of Basel.

1.2.2 Engineering of the sensor

Two main schemes are currently used to incorporate the NV's single spin into a scanning probe. Those are shown in Figure 1.8. We will first start by describing both methods by giving their advantages and drawbacks. We will afterwards move on to a detailed description of the method I used during my PhD thesis to prepare the probes for our experimental setup. The engineering of the probes was performed in Patrick Maletinsky's labs in Uni-Basel - Switzerland.

A first scheme is shown in Figure 1.8(a). This straightforward approach consists in grafting a nanodiamond containing a single NV defect at the apex of an AFM tip [42, 43]. These nanocrystals are obtained by milling type-1b High Purity High Temperature diamond crystals which contain a high concentration of paramagnetic nitrogen impurities (typically 100 ppm). NV defects are obtained after carrying high energy electron irradiation and annealing at 800° C and under vacuum. These NV hosting nanodiamonds are afterwards spreadout on a sample, and grafted to the AFM probe using a UV curable glue or a polymer (L-Lysine). This procedure is simple and robust, but exhibits two main disadvantages;

- Precise control on the position of the nanodiamond cannot be obtained, therefore limiting the NV-sample distance. Indeed, the nanodiamond is usually not grafted at the apex but tends to migrate

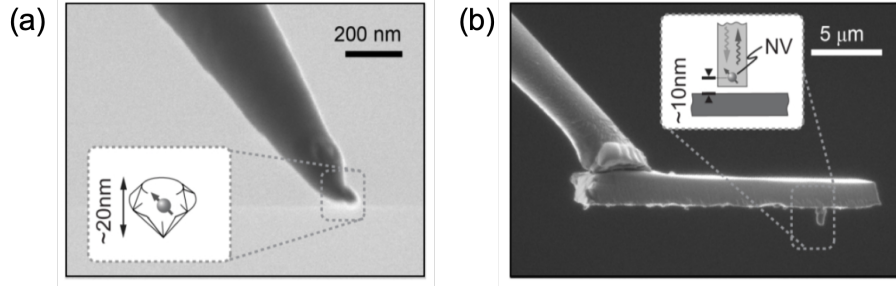


Figure 1.8: Incorporating the NV single spin into a scanning configuration. (a) Nanodiamond hosting a single NV center and grafted on the apex of an AFM probe. (b) Full diamond cantilever with a near-surface NV center located inside the nanopillar. From Ref [31]

slightly upwards, enhancing the NV-sample distance and consequently the spatial resolution of the sensor above 100 nm.

- NV centres in nanodiamonds exhibit short coherence times, typically $T_2^* \approx 1 \mu\text{s}$ [44] which limits the sensitivity of such probes as seen in (§1.1.3).

In order to surpass such disadvantages, tremendous efforts on material engineering were made to introduce a new kind of sensors: full diamond probes as shown in Figure 1.8(b). These probes consist of micrometric sized diamond cantilevers integrating diamond nanopillars that host single NV defects created by implantation at the pillar's apex. The scanning pillars have a cylindrical shape with a typical diameter of $\approx 200 \text{ nm}$ and a length of $1 \mu\text{m}$ and act as the scanning probe. These photonic structures also serve as a waveguide for the photoluminescence signal of the NV center therefore improving the collection rate by a factor 10 compared to an NV defect in bulk diamond [13]; this enhancement of the collection efficiency translates into a significant enhancement of the sensitivity. More importantly, since the NV center is created by ion implantation at the apex of the pillar, the created NV's are closer to the investigated sample, providing a higher spatial resolution than grafted nanodiamond probes. This spatial resolution can reach values down to few tens of nanometers.

During my thesis, I have used diamond tips produced by the group of P. Maletinsky at Uni-Basel Switzerland, and I had the opportunity on multiple occasions to visit his labs in order to mount all-diamond scanning probes compatible with our experimental setup. I will first start by introducing the nano-fabrication procedure performed by our collaborators. I will afterwards present the details of the mounting procedure.

Fabrication of diamond cantilevers

The first step consists in thinning down $500 \mu\text{m}$ thick diamond plates (Element 6, $[N] \leq 5 \text{ ppm}$, (001) oriented.) down to $\approx 50 \mu\text{m}$ by laser cutting and polishing. Since these mechanical procedures highly affect surface quality, the surfaces are further polished for a few microns using reactive ion etching

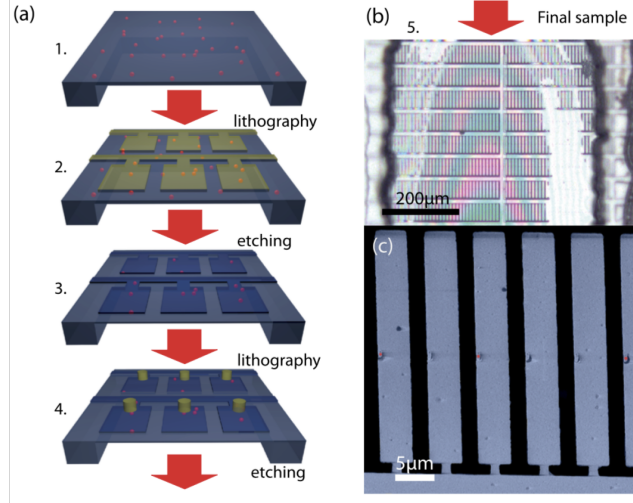


Figure 1.9: Fabrication procedure of diamond cantilevers. (a) Sketch of the successive mask lithography and reactive ion etching steps needed to fabricate the cantilevers and the pillars; The membrane is first implanted with shallow NV centres, this step is followed by Electron Beam lithography to pattern the cantilever and the holding bridge pattern. The pattern is imprinted in the membrane using induced coupled plasma reactive ion etching (ICP RIE). Finally the nanopillars are created using lithography and subsequent etching, followed by thinning down the cantilever. (b) Photo of a batch of full diamond cantilevers after their processing. (c) Zoomed image of the membrane showing some of the fabricated cantilevers, which are still attached to the diamond frame by the bridges at the bottom of the image. From Ref [13]

(RIE).

The second step is the creation of the NV defects. This is done by first implanting Nitrogen ions using an energy of 6 keV and a dose of $3 \times 10^{11} \text{ cm}^{-2}$. Simulations using Stopping and Range of Ions in Matter (SRIM) software [45] give an expected stopping depth of $\approx 9 \pm 4 \text{ nm}$ from the surface. Annealing the diamond at 800° C results in the formation of NV centers by combination of the mobile vacancies and the implanted Nitrogen ions.

The diamond plate is then thinned down to few microns and remains suspended in the surrounding $50 \mu\text{m}$ thick diamond. After consecutive electron beam lithography and Induced Coupled Plasma Reactive Ion Etching (ICP-RIE), the cantilevers and scanning pillars are fabricated as sketched in Figure 1.9(a). Figure 1.9(b) shows the final sample obtained after this procedure, in which a batch of diamond cantilever is held by bridges enabling their subsequent individual breakout as shown in the zoomed image in Figure 1.9(c).

In order to use these diamond probes in our imaging setup, they first need to be broken out of the diamond plate, and integrated into an Atomic Force microscope tuning fork.

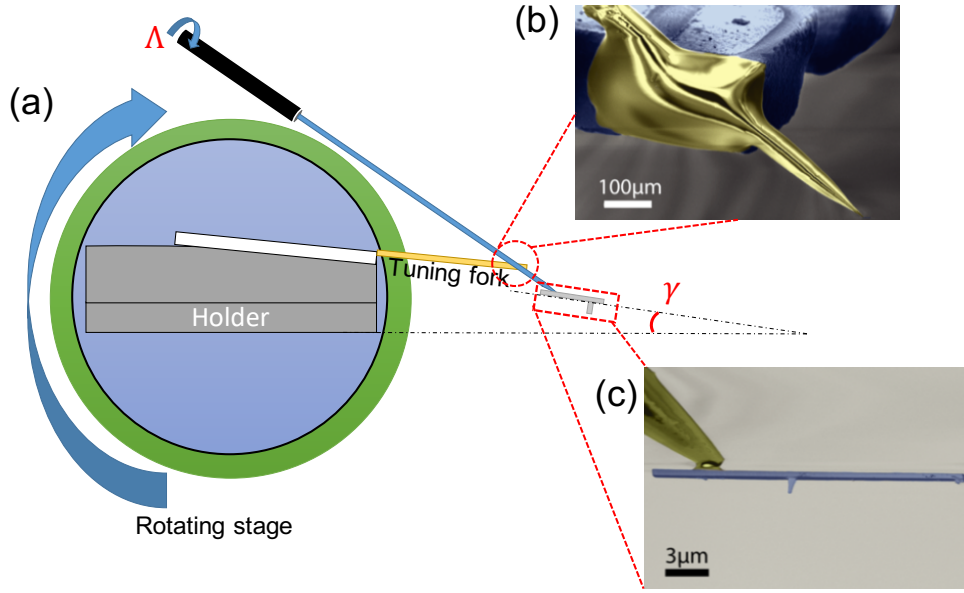


Figure 1.10: Mounting the diamond probe onto an AFM tuning fork. (a) Scheme showing the mounting procedure. The diamond cantilever is attached to the side of a tuning fork using a thinned down quartz rod (in blue). The two angles (Δ, γ) are controlled using two goniometers, one on the tuning fork holder, and the other on the quartz rod holder. (b) SEM image of the scanning probe attached to an AFM tuning fork. From Ref [13]. (c) SEM image of the scanning probe attached to the end of the quartz tip. From Ref [13]

Integrating the scanning probe into an AFM tuning fork

To integrate a scanning probe obtained following the procedure presented in the previous section into our scanning setup, it first needs to be detached from the diamond wafer, and then glued to an AFM tuning fork as schematized in Figure 1.10(a). We will address each of these steps in the following.

- Detaching a cantilever from the diamond wafer

The diamond chip (Figure 1.9(c)) is first placed under a microscope equipped with micro-manipulators. A quartz-rod is prepared using a dedicated setup that locally heats the center of the rod and then pulls it from both sides. This results in breaking and sharpening of the quartz rod with typically $\approx 2\mu\text{m}$ diameter at the apex and a length of $\approx 3\text{ cm}$. The quartz-rod is then dipped into UV glue and fixed to the support of the micro-manipulators. Using the lowest magnification for safety, the quartz-rod is approached cautiously to the diamond chip until its shadow can be seen on the diamond surface. A test procedure is performed by gently approaching the wafer surface in order to check if the rod apex has a convenient size to hold the cantilever. The rod is then lifted in the (Z) direction, then moved on top of the target cantilever and cautiously brought down to its free standing end while being careful not to apply pressure. As soon as contact is made, a UV glue droplet appears on the contact area. The next step is curing the UV glue using a UV lamp focused on the cantilever for a few minutes. Once the curing is done, the cantilever is detached from the wafer by gently moving in the Z direction with the rod and

if needed in Y . In this way, the bridge [See Fig 1.9(c)] is broken and a diamond cantilever held by the quartz tip is obtained, as shown in the SEM image presented in Figure 1.10(c).

- Gluing the diamond cantilever to an AFM tuning fork

The next step is to glue the second end of the quartz rod to the side of an AFM tuning fork. During this step, the angles describing the cantilever's orientation (γ and Λ shown in 1.10(a)) are controlled by the use of goniometers. The goal is to obtain a cantilever perfectly parallel to the sample plane ($\gamma \simeq 0$) once mounted on the tuning fork. This alignment procedure is made with a precision of a few degrees.

Once the alignment is satisfactory, the quartz tip holding the diamond cantilever is brought to the side of the tuning fork and a slight contact is made. A second quartz tip is used to apply UV glue locally at the contact location, and is then retracted. This is followed by a 5 minute curing using a UV source.

Once the curing is done [see Fig 1.10(b)], the quartz rod is detached from its holder by breaking it using a diamond scribe. The quartz rod is broken close to the glue location on the tuning fork in order to avoid touching the microscope objective once mounted on the magnetometer setup. The SEM image presented in Figure 1.10(c) shows a broken quartz-tip holding a diamond cantilever glued to an AFM tuning fork. These probes are afterwards shipped to our labs to be used in the scanning magnetometer.

In the next section, I will detail the experimental setup that I settled during the first year of this PhD thesis : a low-temperature scanning NV magnetometer. I will discuss its architecture, its characteristics and the procedures we developed in order to perform scanning magnetometry at 4 K.

1.3 Scanning NV magnetometry at 4 K

In this section, we address the installation of a 4 K operating scanning NV magnetometry setup. The setup combines an AFM (Atomic Force Microscope) and a Confocal Microscope (CFM). It can be operated in a liquid helium bath. We will first start by reviewing the main parts of the experimental setup by giving a description of their specifications and operation procedures.

1.3.1 Experimental setup

In order to establish a scanning NV magnetometer based on the scheme presented in Figure 1.7(a), the AFM-based scanning probe needs to be placed between the sample and the microscope objective. It is therefore mandatory to find a suitable compromise between the microscope objective's numerical aperture, that needs to be maximized to maximize the photoluminescence collection, and a working distance that enables the diamond probe's placement at the focal plane. The microscope objective we use for our experiment is an LT-APO/VISIR objective with a numerical aperture $NA = 0.82$. The microscope objective is located directly on top of the AFM head and its working distance of 0.65 mm enables the operation of the AFM probe and its placement at its focal plane. The probe can also be lifted from its

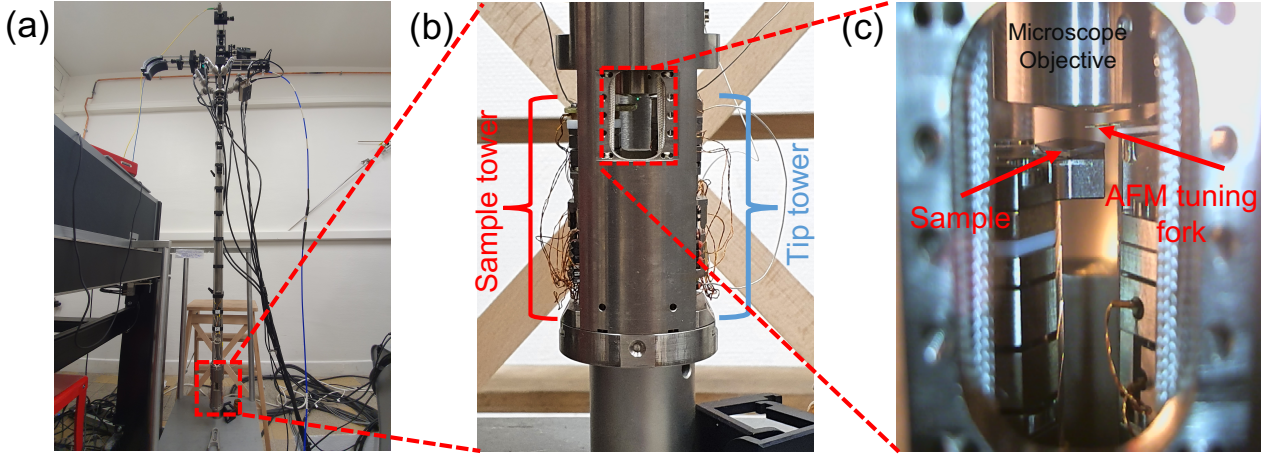


Figure 1.11: Photo of the suspended microscope stick. (a) Photo of the whole microscope stick. (b) Zoomed photo of the measurement head showing the tower holding the tip (right) and the tower holding the sample (left). (c) Zoomed photo showing the sample and the tuning fork under the microscope objective.

focal plane (typically up to $100\mu\text{m}$) to enable safe inspection of the sample surface.

The microscope, AFM tip and sample holder are placed inside a housing suspended on the lower end of a stick as shown in Figure 1.11(a), which itself is placed in a vacuum tube. Before cooling down the system, this vacuum tube is evacuated and backfilled with He exchange gas. This vacuum tube is then cooled by insertion into a Helium bath cryostat.

The main parts of the measurement head are the AFM sensor head, based on a tuning fork shear-force detection scheme, and the low temperature microscope objective as shown in Figure 1.11(b) and (c). In the next paragraphs, we will detail these two building blocks.

The Atomic Force Microscope

In this scanning setup, the probe-to-sample distance regulation is achieved with a piezo-electric tuning fork mounted on the AFM sensor head. The AFM tip is directly integrated onto one of the tuning fork prongs. The working principle of the tuning fork AFM is as follows: a small dither piezo stack glued in proximity of the tuning fork sensor excites the tuning fork at its fundamental resonance frequency. The oscillation response of the tuning fork is converted into a small charge accumulation picked up at the electrodes of the tuning fork. This charge signal is converted into a voltage and amplified by a charge amplifier (FEMTO). The output signal of the amplifier can then be monitored. The oscillation amplitude provides the signal for the feedback control. While approaching the probe to the sample surface, the oscillation amplitude reduces and is kept constant at a certain setpoint by the feedback loop acting on the (Z) scanner.

The tuning fork probe is mounted to a Titanium probe holder shown in Figure 1.12(a) and screwed

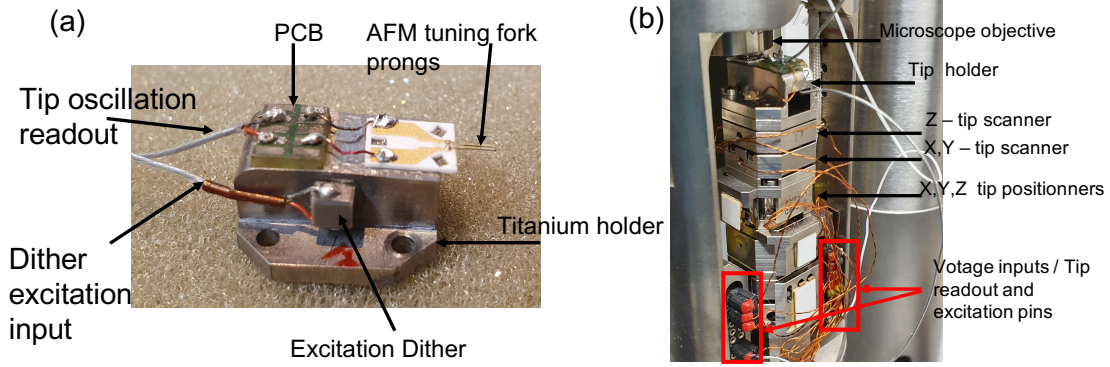


Figure 1.12: AFM tower and Tip holder (a) Photo of the tip holder showing the cable connections (readout and dither excitation to the left), the excitation dither glued to the side of the titanium holder and the AFM tuning fork mounted on top of the holder. Excitation and readout wires are soldered on a Printed Circuit Board (PCB) that is connected to the tuning fork's gold plated pads via micro-wires. (b) Photo of the tip tower showing the stacking order of its components. The tip holder is mounted on top of a stack of 3 axis positioners and a second stack of scanners. At the bottom of the tower multiple pins are used as a gateway to provide voltage excitation for the piezos, readout of their positions and readout and excitation of the Tip oscillation.

on top of the tip stack. It is connected via small wires to a little PCB (Printed Circuit Board). From the PCB the connection is realized by pico-coax wires attached to dedicated slots on the sides of the tip stack shown in Figure 1.12(b).

The sample to be examined and the AFM sensor head are each placed on (x, y, z) piezo-electric positionner (ANPxyz51) stack for coarse motion ($3 \times 3 \times 2.5 \text{ mm}^3$) and (x, y, z) scanners (ANSxyz50) (with ranges of $20 \times 20 \times 2 \mu\text{m}^3$ at 4 K and $32 \times 32 \times 2.6 \mu\text{m}^3$ at room temperature.) for fine motion. A temperature sensor and a heater that allow precise control of the sample temperature, are located underneath the sample.

The sample holders we use are printed circuit boards divided into two copper pads at the surface and separated by a insulating ledge. When in need of microwave excitation, the microwave line pads on the sample are connected using ball-bonding to these two pads, and microwave excitation is connected to the sample pad using Pico-Coax cables.

The Confocal setup

The confocal setup that combines laser excitation, photoluminescence signal collection and optical inspection, is mounted on the microscope stick as shown in Figure 1.13(a), and is coupled to a collection and an excitation fibers. Let's examine now in more details both of the excitation and detection systems.

- The excitation path

The $\lambda = 532 \text{ nm}$ excitation laser source is located on the optical table. The laser beam passes first through a double pass Acousto-Optic Modulator, thus enabling pulsed laser sequences. The output laser

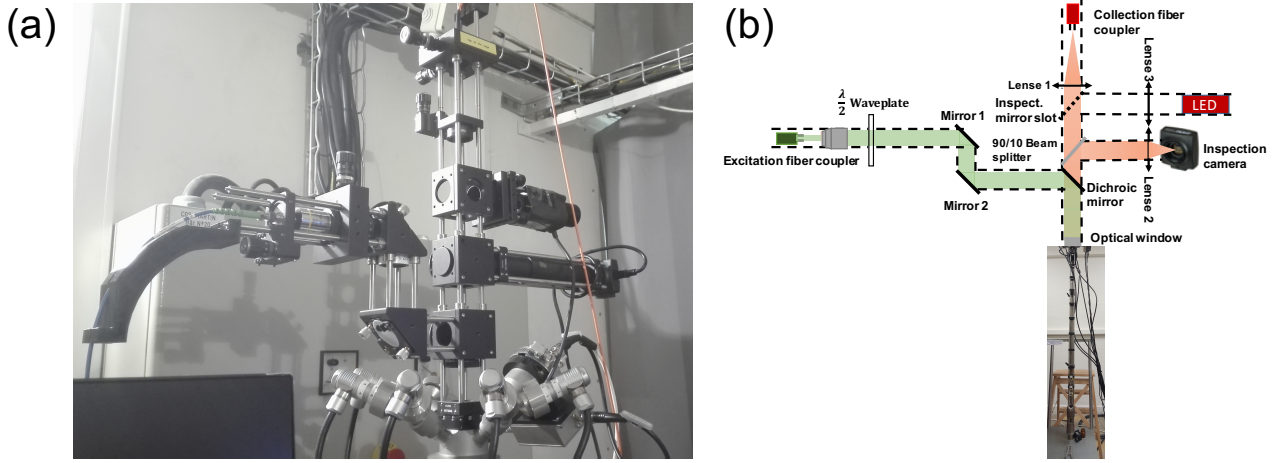


Figure 1.13: Photo and sketch of the optical set-up. (a) Photo of the upper part of the microscope stick showing to the left the excitation fiber input and the two mirrors guiding the excitation beam. To the right, the inspection camera and the inspection LED are visible. At the top of the stick, one can see the collection fiber output. (b) Optical scheme of the microscope stick: the incoming excitation laser beam is brought to the microscope stick by a fiber, it is then guided to the microscope objective at the bottom end of the stick using the combination of two mirrors and a dichroic mirror. The photoluminescence signal goes through the same objective and passes through the dichroic mirror to be focalized into the collection fiber that atop from guiding the signal towards the table-top detection apparatus, acts as a confocal pinhole.

beam is then focalized into a polarization maintaining fiber and sent towards the microscope stick. As shown in Figure 1.13(b), the incoming laser beam is reflected through the combination of two 2 mirrors towards a dichroic mirror (Semrock) mounted on the stick and then sent to the objective.

- The optical detection system

The photoluminescence signal passes through the same objective. It is guided along the same path until it hits the dichroic mirror, passing through it. It is then focused using a lens into the collection fiber (Multimode, $50\ \mu\text{m}$) entry which also plays the role of a pinhole. This pinhole allows the transition from a standard to confocal microscopy by providing spatial filtering, thus increasing the signal to noise ratio and decreasing the detection volume. The photoluminescence signal is directed back using the fiber towards the optical table. At the other end of the collection fiber, the beam goes through a bandpass filter, and is split in two with a polarized beam splitter. These two beams arrive on two separate avalanche photodiodes (APDs) which can be used in a Hanbury-Brown and Twiss configuration to identify single photon emitters. This detection configuration will be described in more detail in §1.3.2.

Note that the microscope stick also includes a 90/10 splitter that enables optical inspection in a widefield configuration while a red LED can be used for illumination owing to a removable mirror.

Liquid Helium Cryostat

To be operated at low temperatures, the inset lodging the AFM head and the microscope objective is cooled by a controlled exchange gas atmosphere in a liquid helium bath cryostat. In the following we describe the characteristics of this cryostat, and its operational procedure.

The attoLiquid 1000 is a 50 L liquid helium bath cryostat equipped with a He gas vent that is connected to the University's recovery system, and a Quench pressure relief Valve that allows helium gas to vent safely out of the helium reservoir in case of an accidental magnet quench. The cooldown procedure to 4K of the helium reservoir is divided in three main steps.

The first is a pre-cooling to 77.6 K using liquid Nitrogen. To do so, a 100 L self-pressurized liquid nitrogen dewar is connected via a rubber hose to a dedicated transfer cane which is inserted into the cryostat. A steady flow of liquid into the cryostat is maintained while avoiding spattering. During this process, a multimeter can be connected to a carbon resistance located inside the cryostat. Its readout value depends on the temperature of the cryostat which has a value of $402\ \Omega$ at room temperature and reaches $492\ \Omega$ at 77 K. Once the transfer complete, the setup is left to thermalize overnight.

On the next day, the liquid nitrogen is removed. A transfer cane that reaches the bottom of the cryostat is used as an exit while the cryostat is pressurized using a Nitrogen gas reservoir. When liquid nitrogen is no longer flowing, the Nitrogen gas reservoir is disconnected and replaced by an industrial grade Helium gas reservoir. Flushing the cryostat with Helium gas is mandatory to avoid the presence of hot spots once liquid Helium is transferred.

The last part of the cooldown procedure is the liquid Helium transfer. The dedicated transfer cane is first progressively inserted into the Liquid helium Dewar equipped with a conical reducer until the bottom is reached. At this point, the Helium gas reservoir is connected to the Dewar. While making sure that helium gas is flowing out of the cryo-side of the transfer cane, the latter is progressively inserted into the dedicated aperture in the cryostat. Liquid helium is afterward transferred from the Dewar at a pressure of $\approx 70\ mbar$. The LM-510 liquid Cryogen level monitor provides a digital readout of the liquid Helium level inside the cryostat owing to the integrated capacitive sensors located inside the reservoir. At this point, the carbon resistor's value should have a reading of $5.52\ k\Omega$. The first transfer usually takes four to five hours, with a use of $\approx 80\ L$ of liquid Helium for a complete fill of the Helium bath. Once this procedure complete, the transfer cane is carefully removed, the cryostat is connected to the He recovery line and the system is left to thermalize for a few hours. The same procedure is followed to refill the liquid helium bath, except that the refill is faster (two to three hours) and requires less liquid helium.

Cooling down the magnetometer and samples

In order to be inserted into the liquid helium bath, the inset needs to be fitted into the Vacuum tube. This procedure involves three main steps.

In a first step, once the sample of interest and the probe are in place, the sample is brought down in the (z) direction for at least $200\text{ }\mu\text{m}$ to ensure that the cantilever is safe during the procedure. The cantilever is brought to the focal plane of the microscope objective, and is kept there. All sources and cables are disconnected except the LED power source and the camera used to monitor the tip during the insertion procedure. The microscope stick is then carefully slid into the chamber, whilst monitoring the cantilever on the inspection camera. The chamber is afterwards connected to the turbo pump, and pumped until reaching 10^{-4} mbar. This procedure usually takes ≈ 2 hours.

The next step consists in inserting the He exchange gas into the chamber. The tubes and the connections are first flushed using the He gas. The turbo pump's main valve is afterwards closed and the pump is turned off. The needle valve is slightly rotated with the He bottle open until a value of ≈ 60 mbar is read on the analog gauge. At this point, the integrity of the tip and of the tuning fork is checked by measuring the resonance curve in the AFM interface (Daisy Software).

The last step is cooling down the chamber, by inserting the vacuum tube into the cryostat. To do so, all the cables need to be plugged back into the microscope (Voltage sources, Tip readout and ground). The chamber is slid into the cryostat by steps of ≈ 15 cm separated by few minutes of wait until the sample temperature readout stabilizes. At a chamber temperature of 120K , the traveled distance at each step is reduced to ≈ 8 cm. Once in contact with the liquid helium bath, a quick drop in temperature is observed accompanied with a gas pressure release. When waiting for temperature to stabilize, it is recommended to verify the tip status by checking the tuning fork resonance curve, and recentering the tip position in the inspection camera using the room temperature voltages for the positionner's excitation. The piezo-electric stacks are indeed affected by the cooldown and piezo-drift is observed during this procedure. Once the chamber is fully inside, the setup is left to thermalize for $\approx 1 - 2$ hours before operation. After this duration, when the temperature has stabilized at 4.13 K , the 0.5 T vectorial magnetic field sources can be used.

0.5T vectorial field through the 3 axis superconducting coils

Three superconducting coils are lodged inside the cryostat. They consist of a vertical field solenoid magnet with a rated central field of 0.5 T , and two horizontal split coil magnets along the (x) (0.5 T) and (y) (0.5 T) directions. Their independent power supplies allow precise and smooth magnetic field sweeps to be made.

Charging the superconducting coils relies on the use of 3 independent power units (APS100) that provide a low voltage high current DC power supply. The superconducting coils can be used in a persistent mode owing to the presence of individual switch heaters. These consist in a combination of a superconducting wire and a heater short-circuiting the coil's winding. In order to inject current into the windings, the heater is first turned on. By doing so, current flows directly from the power supply to the windings. Once the desired magnetic field value is reached and stabilized, turning the switch heater off cools it down to its superconducting temperature. In this way, the current no longer flows back to the power supplies which can be ramped down to zero output. The short-circuited winding becomes a closed loop that preserves the established magnetic field. These procedures need to be performed with caution to avoid magnet quenching, and the charging rates specific to each coil need to be respected. In order to perform magnetic field dependence measurements, I developed an interface using Labview that allows safe remote control of the power supplies and readout of the magnetic field values.

In the next paragraph, we present a characterization of a full diamond probe (§1.2.2) performed at low temperature using the previously introduced setup.

1.3.2 Characterization of a Full-diamond cantilever at 4 K

A diamond probe is mounted under the microscope objective, its performances and characteristics can be extracted by optical means via the PL produced by the NV centre. Various points are checked: the location of the NV center, its unicity, the level of the collected signal (related to the sensitivity η of the measurement), the contrast and FWHM of the ESR spectrum (also impacting the sensitivity). The first step is to locate the NV center by scanning the tip in (x,y) under the microscope objective while the cantilever is nearly at the focal point. In Figure 1.14(a) a photoluminescence scan of the diamond cantilever is shown. The NV center is located in the pillar integrated to the cantilever and its position is circled in red in the scan.

Unicity of the NV center

In order to verify that the cantilever contains a single NV center, we perform a measurement of the intensity correlation function $g^2(\tau)$ defined by

$$g^2(\tau) = \frac{\langle I(t+\tau)I(t) \rangle}{\langle I(t) \rangle^2} \quad (1.24)$$

where $I(t)$ is the photoluminescence intensity, and τ is a delay time. This function is related to the probability of first detecting a photon at a time t followed by a second one with a delay τ . Since we operate with single NVs, the PL signal shall correspond to the emission of at most one single photon per each excitation cycle. The probability of detecting 2 simultaneous single photons shall be null, that is $g^2(0) = 0$. This **anti-bunching** effect is the signature of single photon emission. This measurement makes use of a Hanbury-Brown and Twiss (HBT) experimental setup. The emission detected by the confocal microscope is sent towards a 50/50 beam splitter. Two avalanche photodiodes are placed

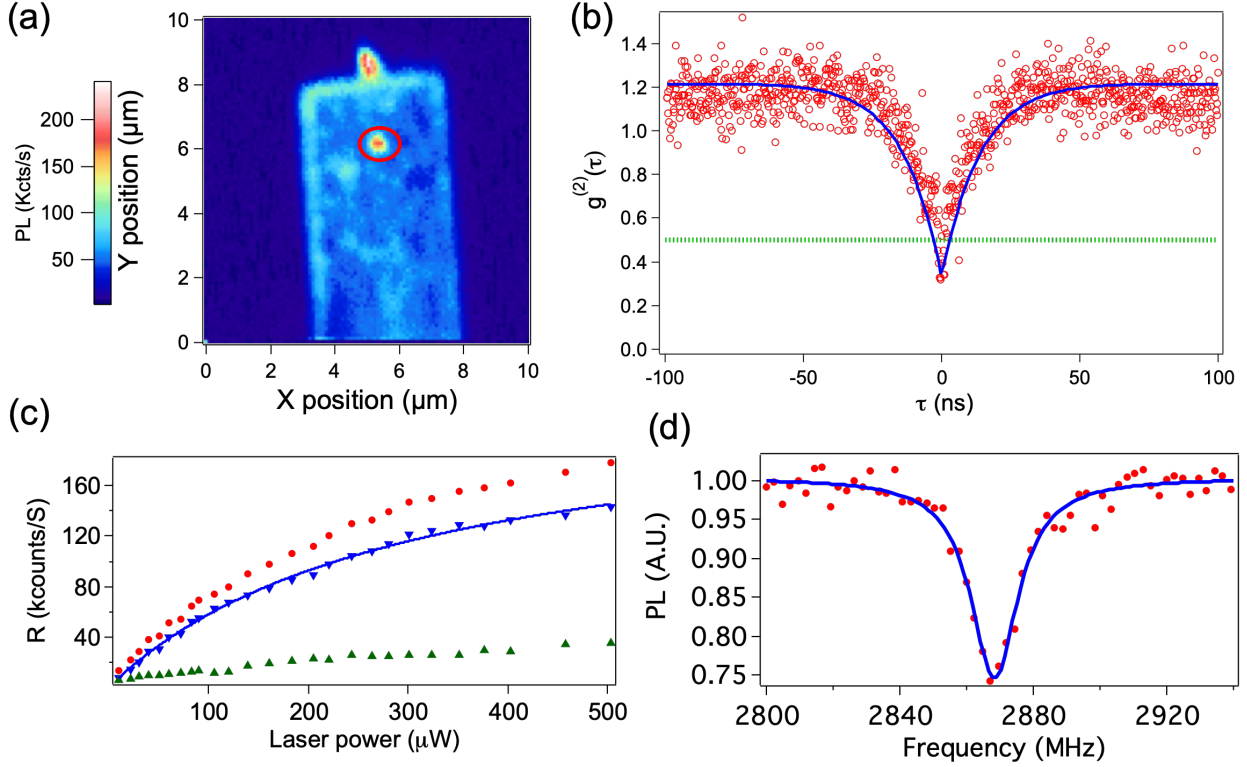


Figure 1.14: Characterization of the diamond cantilever. (a) Photoluminescence map of the diamond tip at 4 K. This image is obtained by scanning the diamond probe using the tip scanner under the microscope objective. The location of the NV center is circled. (b) Experimental $g^{(2)}(\tau)$ function recorded for the NV center in the diamond tip. The green line shows the 0.5 threshold for a single photon source, the blue solid line is a guide to the eye proving that the anti-bunching goes lower than 0.5. Red dots show data points. (c) Saturation curve of the single NV center. In red markers are the photoluminescence signal of the NV center, the green ones are the background counts and the blue dots are the background corrected photoluminescence. The solid blue line is a fitting using a function of the type $R(P) = R_{\infty} * \frac{1}{1 + P_{sat}/P}$ with $R_{\infty} = 120$ kcts/s and $P_{sat} = 300$ μW. (d) ESR spectrum at zero field of the NV's single spin. Red dots are data points while the blue solid line is a Lorentzian fitting.

respectively at each output of the splitter. The detector's outputs are connected to a time correlated single photon counting unit (FastComtech P7887). This unit records all of the detection events on both detectors and after post-processing gives the intensity correlation function for a given time binning parameter. In our measurement [See Fig. 1.14(b)], we indeed observe a dip in the measured $g^2(\tau)$ function, with a value at $\tau = 0$ below 0.5. This confirms the unicity of the NV defect.

Maximum count rates

A saturation curve of the NV's is afterwards recorded to estimate the maximum count rate. It is shown in Figure 1.14(c). Here we monitor the photoluminescence response in kcounts/s, as a function of the excitation laser power. Both the counts on the NV center and the background are recorded at each step. The latter has a linear variation, and is subtracted from the signal. The obtained difference plotted in blue can be fitted using a function of the type : $R(P) = R_\infty * \frac{1}{1+P_{sat}/P}$ where P is the excitation power, $R_\infty = 120$ kcts/s is the saturation photoluminescence count rate and $P_{sat} = 300 \mu\text{W}$ is the power at saturation.

Sensitivity of the probe

Using a sample containing a microwave excitation line (typically ≈ 100 nm thick gold patterned line), the cantilever is approached to the line and the ESR spectrum is recorded [See Fig1.14(d)]. As seen in (§1.1.2), a dip is observed when the microwave frequency matches the transition frequency from the bright $|m_s = 0\rangle$ to the dark state $|m_s = \pm 1\rangle$ with a contrast of $C = 25.7\%$ and a linewidth $\Delta f_r = 17.28$ MHz. With a typical number of counts of $R_\infty = 120$ kcounts/s and assuming a Lorentzian profile of the ESR, we can estimate the sensitivity as follows

$$\eta = \frac{4}{3} \sqrt{3} \frac{h}{g\mu_B} \frac{\Delta f_r}{C\sqrt{R}} = 16 \mu\text{T}/\sqrt{Hz} \quad (1.25)$$

This sensitivity here is estimated under CW laser and microwave excitation. Pulsed ESR measurements can be an alternative that yields a higher sensitivity due to the potentially smaller observed resonance linewidth. The latter is indeed increased by power broadening caused by the continuous wave excitation both from the laser and the microwave. Pulsed ESR measurements rely on specific sequences of laser and microwave pulses[46, 44, 28]. When a magnetic field is applied along the NV axis (here $B_{NV} = 1$ mT), the degeneracy between $|m_s = \pm 1\rangle$ is lifted. The two possible transitions from $|m_s = 0\rangle$ to $|m_s = 1\rangle$ and $|m_s = 0\rangle$ to $|m_s = -1\rangle$ can be addressed individually by tuning the driving microwave frequency [47]. If we only consider the higher frequency branch of the ESR, our system becomes equivalent to a two level system where the electron spin is either in the up state $|0\rangle$ or the down -state $|1\rangle$. The pulse sequence used in pulsed ESR measurements is then as follows; A first optical pulse polarizes the spin in the $|m_s = 0\rangle$ level. A microwave π_{pulse} pulse is then applied to swap the population between the bright and dark levels. It is followed by a second laser pulse for spin state read-out. This second

pulse also allows to achieve an efficient polarization of the spin in the $|m_s = 0\rangle$ level for the subsequent π_{pulse} . In such scheme, the ESR linewidth is given by the Fourier Transform of the product of the π_{pulse} rectangular-shaped profile of duration T_π by the inhomogeneous profile of the electron spin characterized by its coherence time T_2^* . This corresponds to the convolution of a sinc function (of width proportional to $1/T_\pi$) with a function whose width is proportional to $1/T_2^*$. If $T_2^* \gg T_\pi$, each resonance in the ESR spectrum can be fitted by sinc functions whose linewidth relates to $1/T_\pi$. By increasing T_π (and hence reducing the microwave intensity), the ESR linewidth becomes sharper, down to reach $1/T_2^*$ when $T_\pi \approx T_2^*$. This protocol allows then to reach the upper bound of the ESR spectral width, optimizing by the way the achieved sensitivity. It requires however the prior knowledge of T_π and T_2^* .

In order to extract the value of T_π for each microwave power, Rabi oscillations of the NV center are carried. The sequence used for such measurement is shown in Figure 1.15((b)). A first laser pulse prepares the NV center in the $|m_s = 0\rangle$ level. A microwave pulse of duration τ is applied and the spin state is read-out by a second laser pulse. The sequence is repeated with increasing values of τ . The result of such sequence is shown in 1.15(d). It shows an oscillation of the photoluminescence signal between the two spin states. A maximum photoluminescence signal is reached when the population is polarized into the $|m_s = 0\rangle$ state while a minimum photoluminescence is observed when the pulse duration allows the preparation of the system into the $|m_s = 1\rangle$ state. The duration of this pulse is known as T_π and is equal to 105 ns in this case with a microwave power of 25 dBm. It corresponds to a rotation of the Bloch vector by an angle π in the Bloch representation of this two level system shown in Figure 1.15(c).

The inhomogeneous dephasing time T_2^* value can also be measured by recording Ramsey Fringes. The sequence used to perform this measurement is presented in Figure 1.16(a) and consists in a first initialization laser pulse that prepares the system in the $|m_s = 0\rangle$ state followed by a $T_{\pi/2}$ microwave pulse that places the two-level system in a quantum superposition state $\frac{|0\rangle+|1\rangle}{\sqrt{2}}$. The system precesses freely for a time τ and a second $T_{\pi/2}$ transfers the bloch vector from the coherence plane to the population axis enabling optical readout using a second laser pulse. This description of the evolution of the spin state in the bloch sphere is schematized in 1.16(c). Ramsay fringes were recorded on a single NV center in a diamond cantilever. They are shown in Figure 1.16(b). The envelope of the fringes decays following a gaussian law [49]. The characteristic decay time of this envelope at $1/e$ yields the value of $T_2^* = 1.824 \mu s$. This value is in agreement with the commonly obtained coherence times in high purity diamond samples.

The knowledge of the T_π pulse duration at different microwave powers and of T_2^* allows us to perform pulsed ESR measurements. The sequence we use is shown in Figure 1.17(a) and consists in an initialization laser pulse of $3\mu s$ duration, followed by a microwave pulse of duration T_π . This sequence is repeated while varying the microwave frequency, and a spectrum of the PL signal as a function of the frequency is recorded. Figure 1.17(b) shows the pulsed ESR spectrum obtained for an microwave_{power} = 24 dBm and corresponding $T_\pi = 105$ ns. The resonance has a FWHM $\Delta f_r^{105 \text{ ns}} = 7.17$ MHz and presents

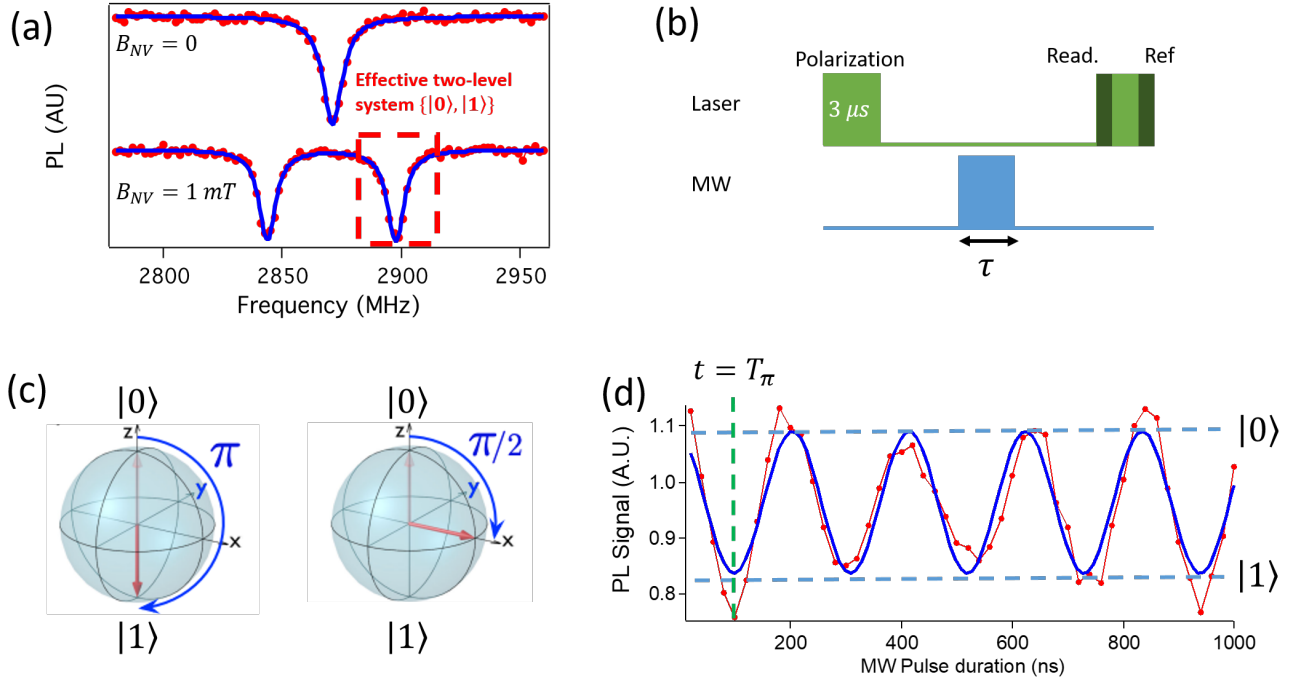


Figure 1.15: Measurement of coherent population oscillations on an NV's single spin (a) ESR spectrum of an NV center at $B_{NV} = 0$ and under $B_{NV} = 1$ mT. For the following, we address the 2 level system indicated by the red dashed square ($|m_s = 0\rangle$ and $|m_s = 1\rangle$). (b) Pulse sequence associated to the Rabi oscillation measurement. (c) Bloch representation of the two level system consisting of $|m_s = 0\rangle = |0\rangle$ and $|m_s = 1\rangle = |1\rangle$ placed respectively in the north and south pole and effect of a microwave pulse of duration T_π and $T_{\pi/2}$ From ref[48]. (d) Rabi oscillations observed on an NV's single spin in a diamond tip under $B_{NV} = 1$ mT; the inferred value of T_π here is 105 ns for an microwave power of 24 dBm.

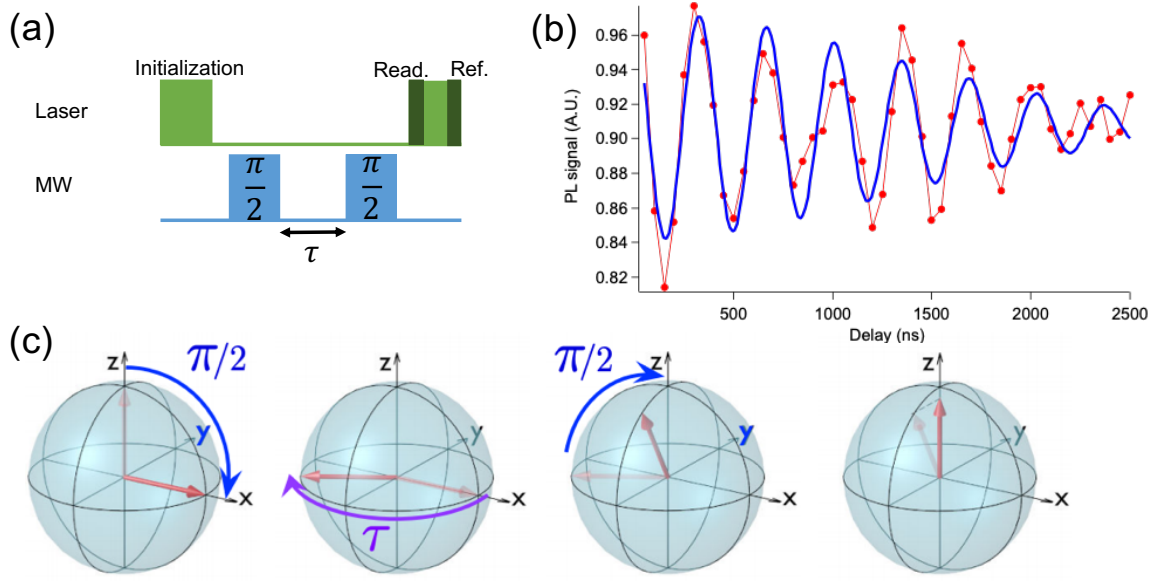


Figure 1.16: Measurement of Ramsey fringes on an NV's single spin (a) Ramsey sequence including a variable delay τ between two microwave pulses of duration $T_\pi/2$, two laser pulses are used to initialize the spin state and for readout. (b) Ramsey fringes observed on a single NV's spin in a diamond cantilever yielding $T_2^* = 1.824 \mu\text{s}$. (c) Representation in the Bloch sphere of the Ramsey fringes sequence, from Ref[48].

a contrast $C_{pulsed}^{105 \text{ ns}} = 22.9\%$ extracted using a Lorentzian profile. Reducing the microwave excitation power extends the T_π duration and suppresses power broadening caused by microwave excitation [35]. A second resonance spectrum is recorded for an $\text{microwave}_{power} = 0 \text{ dBm}$ and corresponding $T_\pi = 1640 \text{ ns}$; it is shown in Figure 1.17(c). In this spectrum the hyperfine components associated to the ^{14}N nuclear spin are observed resulting in three peaks separated by 2.16 MHz in agreement with literature [36]. Each of these peaks shows a linewidth $\Delta f_r^{1640 \text{ ns}} = 0.22 \text{ MHz}$ and a contrast of 8%. Using pulsed ESR measurement with these three resolved peaks for magnetometry, would lead to an enhancement factor for the sensitivity that can be estimated as follows [36];

$$\eta_{pulsed} \approx \frac{4}{3} \sqrt{3} \frac{h}{g\mu_B} \frac{\Delta f_r}{C \sqrt{R_{pulsed}}} \approx 2.2 \mu\text{T}/\sqrt{Hz} \quad (1.26)$$

We have used here $R_{pulsed} = 10 \text{ Kcounts/s}$. This value is an order of magnitude lower than the one obtained in the CW regime.

Identifying the NV center orientation

Knowledge of the NV orientation in the lab frame is essential when performing magnetic field measurements, since the NV center is affected by the projection of the magnetic field along its quantization axis as introduced in (§1.1.2). We will here denote θ_{NV} and ϕ_{NV} the spherical angles describing the NV orientation in the laboratory frame (x,y,z) defined with respect to the translation axis of the AFM (see

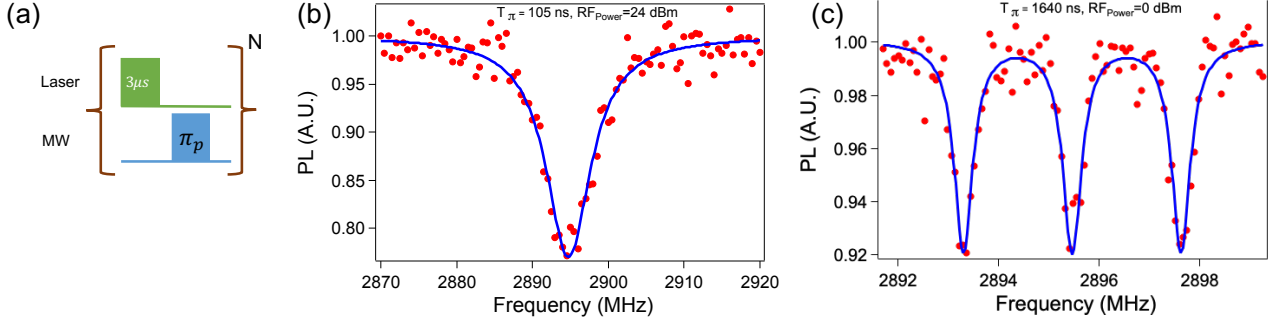


Figure 1.17: Pulsed ESR measurement on a single NV center in a diamond cantilever. (a) Pulsed ESR sequence. π_p indicates a microwave pulse of duration T_π (b) Pulsed ESR measurements on a single NV center in diamond under an external magnetic field $B_{NV} = 1$ mT for $T_\pi = 105$ ns and microwave_{power} = 24 dBm. The linewidth of the resonance is 7.17 MHz and the contrast reaches 22.9 %. (c) Pulsed ESR spectrum for $T_\pi = 1640$ ns and microwave_{power} = 0 dBm. The hyperfine components of the ^{14}N nuclear spin can be resolved, The linewidth of these resonance peaks is of $\Delta f_r^{1640 \text{ ns}} = 0.22$ MHz while showing a contrast of 8 %. In both spectra, dots are data points, and solid blue line is a fit with a lorentzian profile for (a) and a sum of three lorentzians for (c).

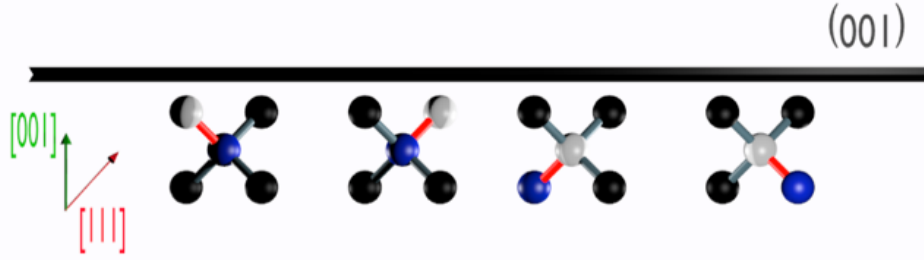


Figure 1.18: Orientations of the NV^- defect in a (001) grown diamond. The N-V bond (red bond) is along the 111 direction, giving 4 possible orientations. The arrows to the left show the growth direction ([001]) and the [111] direction; the black line schematizes the diamond surface, along the (001) plane.

Figure 1.19(a)).

The cantilevers used during the course of this work were fabricated using (001) oriented diamond. As seen in (§1.1.2) the orientation of the NV center is along one of the $\langle 111 \rangle$ set of directions, highlighted in red in Figure 1.18. This limits the θ_{NV} angle to $\approx 125^\circ$ and $\approx 55^\circ$ and the values of ϕ_{NV} to $\approx 0^\circ$ and $\approx 90^\circ$. These angles may slightly vary from a cantilever to another due to tilts in the tip mounting procedure, or when the tip is damaged. Using the vectorial field controlled by the three superconducting coils, it is possible to identify the orientation of the NV center. The procedure relies on rotating the field along the two spherical angles θ and ϕ . A maximum Zeeman splitting is then observed when the magnetic field is along the NV center's orientation.

As a first step, an ESR spectrum is recorded at zero magnetic field in order to obtain the D and

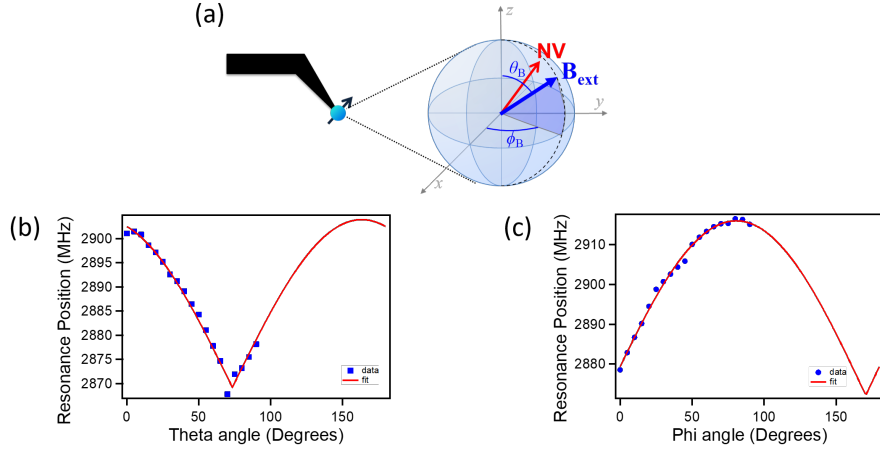


Figure 1.19: Determination of the NV center's orientation using the superconducting coils. (a) Experiment scheme. By controlling the direction of the vectorial magnetic field applied by the superconducting coils, the magnetic field is swept along the two polar angles θ and ϕ . The maximum Zeeman splitting is observed when the magnetic field is along the NV's direction. (b) Determination of the ϕ_{NV} angle. With $B = 1.5 \text{ mT}$ the field is swept along ϕ and an ESR spectrum is recorded in each point. Fitting the curve using a sinusoidal function ($|\cos(\phi)|$) allows the extraction of $\phi_{NV} = 118.6 \pm 1.9^\circ$. (c) Determination of the θ_{NV} angle. With $B = 1.5 \text{ mT}$ the field is swept along θ and an ESR is recorded in each point. Fitting the curve using a sinusoidal function ($|\cos(\theta)|$) allows the extraction of $\theta_{NV} = 80.6 \pm 1.9^\circ$.

E parameters of the NV. One of the frequencies f_+ or f_- is then tracked while varying the magnetic field direction $\mathbf{u}_B$. The amplitude of the magnetic field is fixed to 1.5 mT in order to stay in the low field regime. The projection of the magnetic field along the NV axis here writes as

$$B_{NV} = \mathbf{B} |\cos(\theta_B) \cos(\theta_{NV}) + \sin(\theta_B) \sin(\theta_{NV}) \cos(\phi_B - \phi_{NV})| \quad (1.27)$$

The angles θ_B and ϕ_B denote the polar angles of the magnetic field in the lab frame. Multiple ESR spectra are recorded afterwards while varying in steps θ_B from 0° to 90° while ϕ_B is fixed and vice versa. In a first experiment, θ_B is set to 90° and ϕ_B is swept from 0 to 90° . The evolution of the projection writes then as follows $B_{NV} \propto \cos(\phi_B - \phi_{NV})$, therefore f_+ reaches its maximum value when $\phi_B = \phi_{NV}$ (see Figure 1.19(b)). In a second experiment, ϕ_B is set to ϕ_{NV} , and θ_B is swept from 0 to 90° . In this case $B_{NV} \propto \cos(\theta_B - \theta_{NV})$ and f_+ is maximal for $\theta_B = \theta_{NV}$ (see Figure 1.19(c)). In this particular case, a maximum splitting is observed for $\theta = 118.6^\circ$ and $\phi = 80.6^\circ$. Solid lines are fits using equation (1.27) with θ_{NV} and ϕ_{NV} as free parameters. It should be noted that this measurement only gives the direction of the NV center, since a rotation of 180° of the magnetic field vector does not affect the ESR.

With knowledge of the NV center's orientation let's now measure the flight distance of the NV to estimate the spatial resolution of our probe.

Determination of the probe's spatial resolution

The probe to sample distance d is primordial since it defines the spatial resolution of our sensor. This distance varies from one cantilever to another. In order to extract this tip parameter, one can record the Zeeman splitting map over a uniformly magnetized ferromagnetic wire. In this particular case, stray field is only present at the edges of the stripe. Let's suppose that the stripe consists of an ultrathin magnetic layer of thickness t , which is infinite in (y) direction. The edge's field B^{bd} has an analytical expression [50]:

$$\begin{cases} B_x^{bd}(x, z) = \frac{\mu_0 M_s t}{2\pi} \left(\frac{z}{x^2 + z^2} \right) + O\left(\left(\frac{t}{z}\right)^3\right) \\ B_y^{bd}(x, z) = 0 \\ B_z^{bd}(x, z) = -\frac{\mu_0 M_s t}{2\pi} \left(\frac{x}{x^2 + z^2} \right) + O\left(\left(\frac{t}{z}\right)^3\right) \end{cases} \quad (1.28)$$

It depends on the sample's saturation magnetization M_s , and the distance z , the probe to sample distance. By mapping the Zeeman shift induced by the stray magnetic field produced by the stripe and by fitting the experimental results with previous formula, both M_s and d can be extracted. Such maps of the Zeeman shift are shown on Figure 1.20 (b). These are obtained by scanning the diamond tip over the wire (see Figure 1.20 (a)). In this experiment, the magnetic sample composition is the following : $Ta(5 \text{ nm})|Co_{40}Fe_{40}B_{20}(1 \text{ nm})|MgO(2 \text{ nm})$. The sample is patterned into wires of variable widths ranging from 500 nm to 2.5 μm . It should be noted that this sample was pre-characterized [51] with an $M_s = 9.3 \pm 0.3 \times 10^5 \text{ A/m}$.

Figure 1.20 (b) shows a scan over a 1.5 μm wide wire. The Zeeman splitting corresponding to the higher ESR frequency is plotted as a function of position. As expected, stray field is only observed at the edges of the scanned wire, as confirmed by topographic images shown in Figure 1.20 (c) (black solid lines). The fit of the linecut shown in figure 1.20 (c), is performed using d as a free parameter resulting in a flight distance of $148 \pm 10 \text{ nm}$. This distance can go down to few tens of nanometers for some probes. This experiment was performed at low temperature as a proof of principle for the 4 K operation of the setup. The same experiment was also performed before cooling down the setup (at ambient conditions) and the same tip-sample distance was extracted. This result is not intuitive since when operating at low temperature, the inset containing the scanning apparatus needs to be vacuum pumped. We would have expected this distance to be smaller after pumping and removal of any impurities or layers of contaminant between the diamond probe and the scanned sample.

In the previous experiments, the magnetometer was operated in the weak transverse magnetic field regime. In that case, the quantitative measurement of the stray magnetic field is achieved by retrieving the Zeeman splitting from the optically detected ESR spectrum. In the high magnetic field regime, it is possible to record a qualitative image of the magnetic field distribution. This mode referred to as the quenching mode, will be detailed in the next section. We will in particular detail the model used to simulate the PL quenching maps of the magnetic field arising from a domain wall and then present a proof

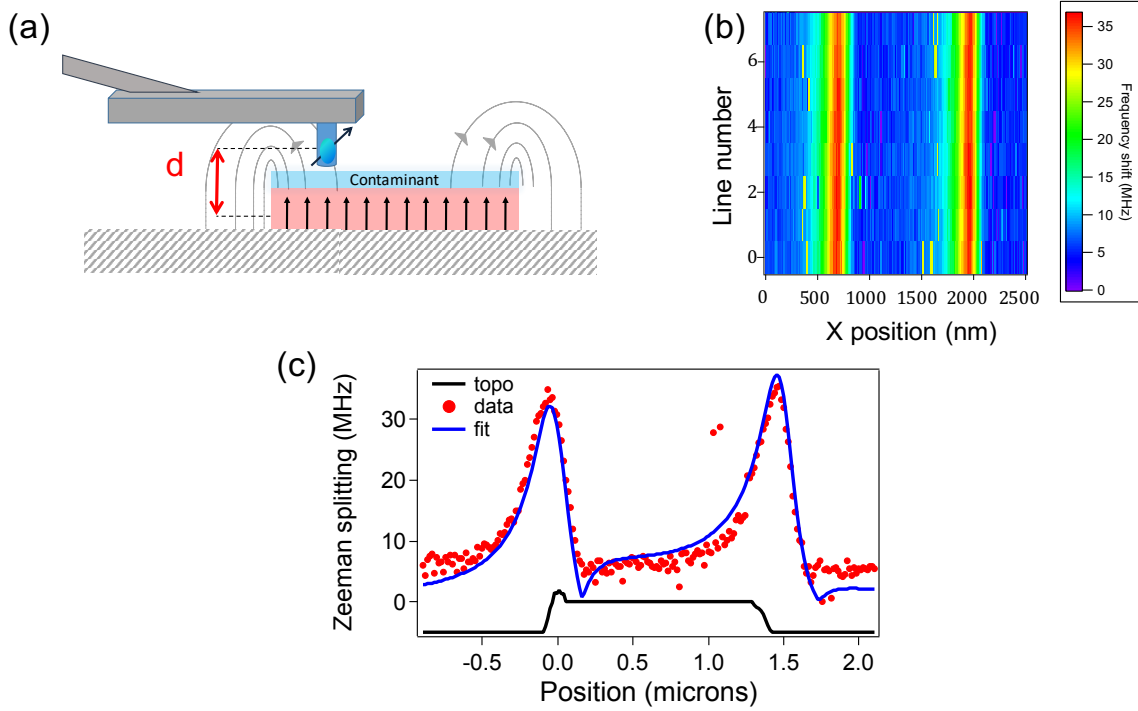


Figure 1.20: Determination of the NV-sample distance. (a) Scheme of the calibration experiment, the diamond cantilever is scanned over a ferromagnetic wire. Stray field is present at the edges of the wire. (b) $2.5 \mu\text{m} \times 100 \text{ nm}$ map of the Zeeman splitting over a portion of the ferromagnetic wire at a temperature of 4 K. In steps of 20 nm in (y) direction multiple lines with an increased time per bin for an increased precision of the frequency shift determination. (c) Line profile fitting. The Zeeman splitting data (red) is fitted (blue) with d as a fit parameter. The topography data is also plotted (black).

of principle experiment in which we image magnetic domains in thin ferromagnetic multilayered material.

1.3.3 PL quenching imaging mode

As discussed in the last paragraph, in the case of a ferromagnetic sample for example, the high off-axis stray fields can cause quenching of the photoluminescence signal (§1.1.4). This reduction of the PL level induced by strong transverse magnetic fields can still be used to give a qualitative image of the observed sample. This technique requires no microwave excitation, and the photoluminescence maps can be recorded in less time than relying on the ESR spectra acquisition, ensuring less piezo drifts during the scan.

Minimization of the free energy in magnetic materials promotes the formation of domains. A domain wall is the region separating two areas of uniform and opposite magnetization. These domain walls can be manipulated by current pulse injection or using an external magnetic field. In the following we will show that these structures that may produce high stray fields (e.g. in ferromagnets) can be

investigated using the quenching technique. We will first introduce a simulation model that allows us to predict the stray field maps from such structures stabilized in ferromagnets. We will afterwards project these field maps along the NV quantization axis while taking into account the quenching effect produced by off-axis fields giving us a glimpse at the expected quenching maps. In the end we will show images of such structures taken by the NV-Magnetometer operated in the quenching regime.

Simulation of the stray field produced by a domain wall and the respective quenching maps.

We simulate here a thin ferromagnetic film of total thickness 2.3 nm with a saturation magnetization $M_s = 1 * 10^6$ A/m and domain wall width $d_{dw} = 33$ nm. The latter is defined as $d_{dw} = \sqrt{A/K_{eff}}$ with A being the exchange constant and $K_{eff} = K_u - \mu_0 M_s^2/2$ the effective magnetic anisotropy, and K_u being the uniaxial anisotropy. These two parameter can be measured experimentally. The sample size used in this simulation is of dimensions $(8 * 10^{-6}, 8 * 10^{-6}, 2.3 * 10^{-9})$ m³, the domain wall is considered as infinite in the y direction, and located at $x = 0$. The normalized spatial magnetization distribution is shown in Figure 1.21(a) where we can distinguish the domain wall position in the top figure with the magnetization being $\neq 0$ in the x direction only at the domain wall location. In the bottom image, we can see that the magnetization is uniform along z but with inverse directions at the left and right of the domain wall position.

We simulate the resulting stray field components at a probe to sample distance $d = 100$ nm (the typical commonly obtained probe-sample distance). The values of B_x , B_y and B_z are shown respectively in Figure 1.21 (b). Details of the calculations are presented in Appendix A. As expected, the stray field is only observed at the domain wall location. These stray field contributions are to be projected along the NV axis in order to obtain the expected maps observed by scanning the NV over the sample. The expression of the field sensed by the NV B_{NV} writes as follows;

$$B_{NV} = B_{perp} + B_{para} = \cos(\theta_{NV})B_z + \sin(\theta_{NV})\cos(\phi_{NV})B_x + \sin(\theta_{NV})\sin(\phi_{NV})B_y \quad (1.29)$$

We use here $\theta_{NV} = 54^\circ$ and $\phi_{NV} = 0^\circ$ as the NV's polar angles. This total field can be divided in two parts, B_{perp} and B_{para} the off-axis and the aligned component with the NV's orientation respectively. The two field maps corresponding to these contributions are plotted in Figure 1.21 (c) where in the upper right corner is a plot of B_{para} , and in the center right is B_{perp} . We can see in this figure that the off axis component reaches values of ≈ 10 mT confirming that the regime of operation of the NV magnetometer, is well in the high field regime. We now use the model presented in (§1.1.4) to finally extract the photoluminescence map which is shown in Figure 1.21(d). In this figure a quenching of the PL rate is observed at the domain wall location, with a quenching contrast going up to 25 %. These simulations prove that the NV-sensor is in measure of detecting such structures using the quenching technique at least qualitatively. Let's illustrate it by imaging domains in a ferromagnet.

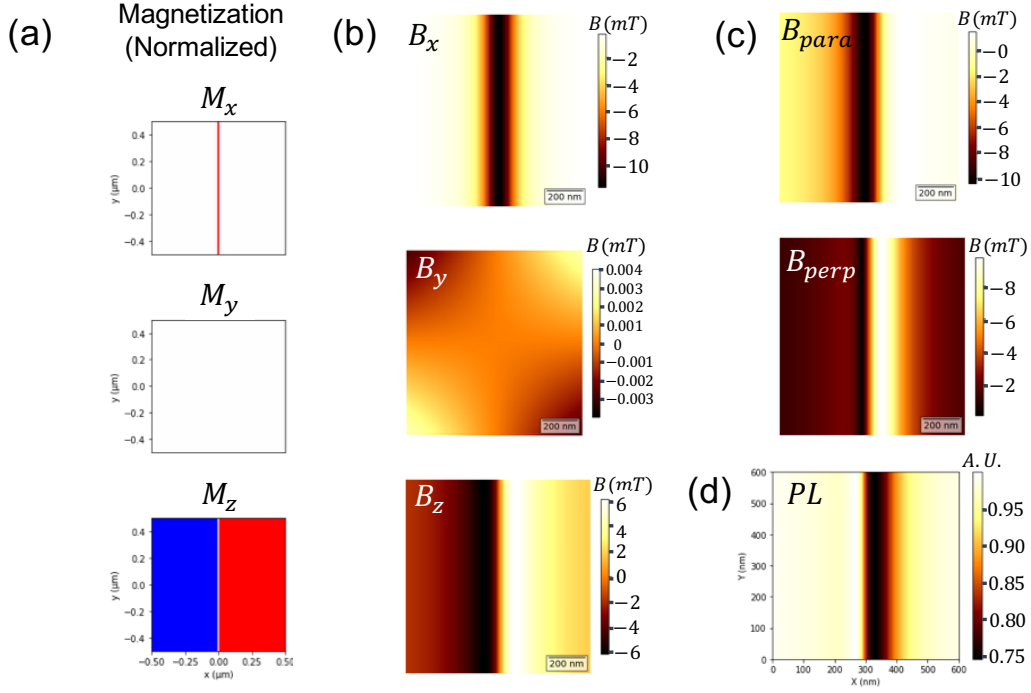


Figure 1.21: Simulation of the quenching map. (a) Normalized magnetization distribution, from bottom to top M_x , M_y and M_z . We consider here that $M_s = 1 \frac{\text{A}}{\text{m}}$ and that the domain wall width is $\delta_{dw} = 33 \text{ nm}$; the total simulated sample is of dimensions $8 \cdot 10^{-6} * 8 \cdot 10^{-6} * 2.3 \cdot 10^{-9} \text{ m}^3$. (b) Simulated maps of x, y and z components of the stray magnetic field produced by the simulated sample at a distance of 100 nm. (c) Simulated maps of B_{para} field in the top right corner, and of B_{perp} field in center right; the NV orientation considered here is $\theta_{NV} = 54^\circ$ and $\phi_{NV} = 0^\circ$. (d) Simulated photoluminescence map for the NV center flying at 100 nm distance above the sample with an NV orientation of $\theta_{NV} = 54^\circ$ and $\phi_{NV} = 0^\circ$.

Quenching image of domain walls in a ferromagnetic material

The sample we used is a multilayer consisting of 5 nm of Ta, 8 nm of Pt and 3 stacks of 0.5 nm of Co and 0.45 nm of Pt ($Ta(5 \text{ nm})|Pt(8 \text{ nm})|(Co(0.6 \text{ nm})|Pt(0.45 \text{ nm}))^3$). It was provided by our collaborators from the Spintronics group in UMR-CNRS-Thales. In this experiment, the NV orientation is given by $\theta_{NV} = 54^\circ$ and $\phi_{NV} = 0^\circ$ and the NV flight distance is $d = 94 \pm 10 \text{ nm}$. The sample is scanned under the diamond cantilever at ambient conditions while recording the photoluminescence signal over an area of $4.166 * 4.166 \mu\text{m}^2$. The recorded scan is shown in Figure 1.22 (a).

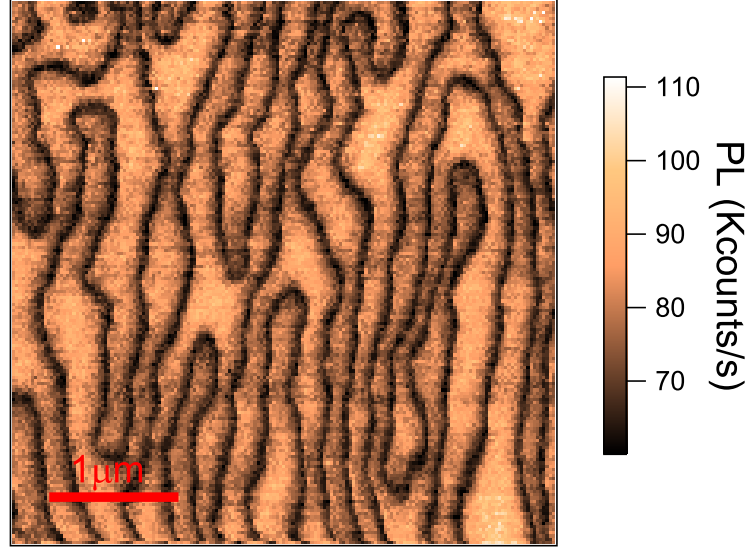


Figure 1.22: Quenching image of domain walls in a $(Ta(5 \text{ nm})|Pt(8 \text{ nm})|(Co(0.6 \text{ nm})|Pt(0.45 \text{ nm}))^3)$ film $4.166 \times 4.166 \text{ } \mu\text{m}^2$ quenching image of the sample, at a flight distance of $94 \pm 10 \text{ nm}$. The observed drops of photoluminescence correspond to domain walls.

Such typical scans require an acquisition time of ≈ 10 minutes in contrast with $\approx 3-4$ hours in the case of a quantitative field map of the same area. As expected, photoluminescence drops are observed at the locations of the domain walls.

We have here an insight on the potential of the PL quenching imaging technique for imaging magnetic structures in ferromagnetic films. In the second chapter of this thesis we will focus mainly on using this technique to image skyrmions in such thin films.

1.4 Conclusion

In this chapter, we have introduced the mechanisms on which relies magnetic field sensing with a single NV center and how this sensitive and local probe can be used to extract stray magnetic field images at both room and low-temperature. The sensitivity can reach values down to few $\mu\text{T}/\sqrt{Hz}$ and the spatial resolution can reach few tens of nanometers. Moreover, this technique is non-invasive.

We discussed the implementation of a NV-scanning magnetometer operating at low temperature. When I joined the lab, the room hosting the set-up was empty and in almost half a year, we were able with the help of L.J. Martinez, the Postdoc I was working with, to run our first experiments at low temperature. In the same section we discussed the procedures we implemented and the specifications of the setup such as the sensitivity in both CW ($\eta_{cw} = 16 \mu\text{T}/\sqrt{Hz}$) and pulsed ESR mode ($\eta_{pulsed} = 2.2 \mu\text{T}/\sqrt{Hz}$). In (§1.3.2) we show a calibration procedure to retrieve the orientation of an

NV center and its flight distance, that fixes the sensor's spatial resolution of about 100 nm. Though the set-up can be operated at cryogenic temperatures, the experiments presented in the following chapters of this thesis were mainly performed at room temperature.

Last, we detailed one of the operating modes of the magnetometer in the high field regime : the quenching mode (§1.3.3). In this operating mode, solely the photoluminescence signal is monitored. When reaching locally high values of off-axis magnetic field, the occurring spin state mixing causes a drop in the detected signal. This drop in the PL signal is exploited to optically map high magnetic field distributions on the PL level : the regions producing higher magnetic fields appears darker in the PL map. We have presented a proof of principle experiment, in which we used this quenching imaging technique to successfully image domain walls in a structure containing ferromagnetic domains.

In the next chapter we will use this technique to explore the nucleation and dynamics of magnetic skyrmions in multiple host materials.

Exploring the physics of skyrmions in ultrathin ferromagnets

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Magnetic skyrmions are topological spin structures with a whirling configuration, which hold great promise for the storage and processing of information at the nanoscale in future memory and logic devices [Fig. 2.1(a)] [52, 53, 54]. As their structure cannot be continuously deformed to a ferromagnetic or other magnetic state, skyrmions are highly robust against material imperfections and thermal fluctuations, a property often coined as *topological protection*. Moreover, skyrmions can be in principle as small as a few nanometers and could thus provide an ultrahigh information storage density. Finally, efficient skyrmion motion through spin transfer torques is predicted at ultralow current densities, which is crucial for applications. These properties make skyrmions highly attractive for information storage and processing at the nanoscale [53, 54].

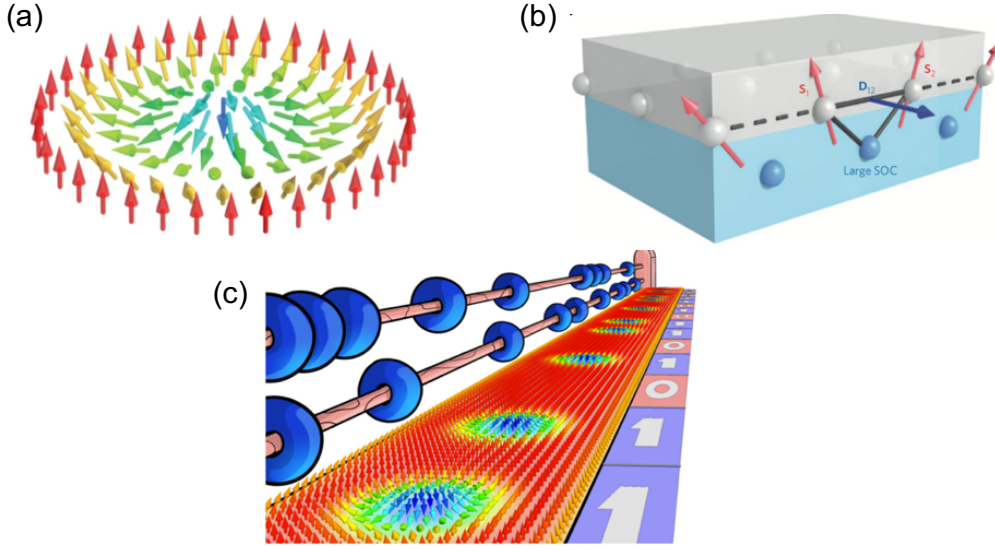


Figure 2.1: Magnetic skyrmions in ultrathin films. (a) Whirling spin texture of a Néel skyrmion with left-handed chirality. (b) Illustration of the DMI arising at the interface between a high spin orbit material (blue) and a magnetic material (grey). From Ref [58]. (c) Schematic of skyrmion racetrack memory, where data is stored by aligning skyrmions similar to beads on an abacus. Adapted from Ref [54]

A skyrmion lattice phase was first detected in 2009 at low temperature and in the presence of large magnetic fields in bulk materials exhibiting broken inversion symmetry [55, 56]. Two years later, magnetic skyrmions were observed in a Fe monolayer deposited on Ir using spin-polarized scanning tunneling microscopy (SP-STM) [1, 57]. In the latter case, skyrmions were promoted by interfacial Dzyaloshinskii-Moriya interaction (DMI), an asymmetric exchange interaction occurring at the interface between a magnetic layer and a heavy metal substrate with large spin-orbit coupling. The interfacial DMI between two neighboring spins $\mathbf{S}_1$ and $\mathbf{S}_2$ induces an effective magnetic field H_{DMI} , which can be expressed as [58]

$$H_{\text{DMI}} = -\mathbf{D}_{12} \cdot (\mathbf{S}_1 \times \mathbf{S}_2) , \quad (2.1)$$

where $\mathbf{D}_{12}$ is the DMI vector, as illustrated in Figure 2.1(b). This interaction, which favors a canted alignment between neighboring spins, promotes the stabilization of chiral domain walls and skyrmions in thin ferromagnets [52].

Driven by the propositions to use magnetic skyrmions for spintronic devices, a concerted research effort rapidly led to the stabilization of skyrmions at room temperature in numerous types of technologically-relevant magnetic materials [59, 60, 61, 62]. Most of these results were obtained in magnetic multilayer stacks lacking inversion symmetry, in which the interfacial DMI promotes chiral spin textures. In recent years, skyrmion diameters ranging from the micrometer scale down to a few tens of nanometers have been observed depending on the balance between the strength of iDMI, magnetic anisotropy and dipolar fields. In addition, deterministic skyrmion nucleation and current-induced motion have also recently been demonstrated, owing to the efficient spin-orbit torques in such magnetic multilayer stacks [63, 64, 65, 66, 67, 68], opening a path towards memory and logic devices where skyrmions

in tracks are used as information carriers [53, 54], as sketched in Figure 2.1(c)].

In this chapter, we use scanning-NV magnetometry to investigate the physics of magnetic skyrmions in ultrathin magnetic layers under ambient conditions. The chapter is divided into three sections. We first investigate the impact of structural disorder and magnetic history on the morphology of skyrmions in an ultrathin magnetic sample relevant for spintronic applications (§ 2.1). We then study the properties of magnetic skyrmions in an Heusler alloy, a class of ferromagnetic materials with an intrinsically low magnetic damping coefficient (§ 2.2). In a last section, we finally demonstrate the stabilization of sub-100 nm skyrmions at zero external magnetic field in an exchange-biased magnetic structure (§ 2.3). We note that all the experiments described in this chapter were performed with a **scanning-NV magnetometer operating in the PL quenching mode**. Indeed, in the vicinity of spin textures in ferromagnets, stray magnetic fields larger than 10 mT are commonly produced. For such fields, quantitative magnetic field imaging cannot be performed with NV-based magnetometry, as discussed in § 1.1.4. We show below that all-optical, PL quenching imaging mode is ideally suited to study the physics of non-collinear spin textures in thin ferromagnets with high spatial resolution.

2.1 Impact of pinning and magnetic history on skyrmion morphology

Current-induced motion of magnetic textures in ultrathin films is the cornerstone of innovative applications in spintronics, such as the racetrack memory [69]. In technologically relevant magnetic materials, structural defects often result in a considerable pinning that limits the propagation velocity. Whereas domain walls experience the entire disorder landscape when propagating along a magnetic track [70, 71], skyrmions are predicted to move in two dimensions while avoiding strong pinning sites [58, 72]. They are therefore expected to display a limited interaction with disorder, leading to a highly efficient motion at low current densities ($10^5 - 10^6$ A/m² for skyrmions compared to $10^9 - 10^{12}$ A/m² for domain walls [72]). Surprisingly, several recent experiments have instead shown that skyrmion dynamics are in fact strongly affected by disorder [59, 73], suggesting that pinning effects have been oversimplified in seminal simulations of skyrmion dynamics [58, 72]. These observations motivated a more precise description of disorder in magnetic materials hosting skyrmions.

Whereas average magnetic parameters of ultrathin films - such as magnetization, anisotropy, Dzyaloshinskii-Moriya interaction or magnetic damping - can be easily measured, the effects of structural disorder remain highly challenging to evaluate and model. In this section, we investigate the impact of disorder on the size and shape of isolated skyrmions using magnetic imaging with a scanning-NV magnetometer operated in the the PL quenching mode. This work was done in close collaboration with A. Hrabec, A. Thiaville and S. Rohart from the Laboratoire de Physique des Solides (LPS, Orsay). The results have been published in I. Gross *et al.* *Phys. Rev. Mat.* **2**, 024406 (2018).

The section is organized as follows. We first briefly describe the sample structure, an ultrathin symmetric ferromagnetic bilayer system with perpendicular magnetic anisotropy, and its preliminary

characterization through magnetic force microscopy (MFM) performed at LPS (§ 2.1.1). We then use NV magnetometry to investigate the morphology of magnetic skyrmions in this symmetric bilayer system (§ 2.1.2). The recorded distributions of skyrmion size and shape reveal the key role of disorder and magnetic history in stabilizing isolated skyrmions. In the last part of this section (§ 2.1.3), we show that micromagnetic simulations including disorder, modeled as a grain to grain thickness fluctuation, allow an accurate description of all experimental observations, opening the way to an in-depth understanding of the skyrmion dynamics in real, disordered media.

2.1.1 Sample structure and characterization with MFM

The structure of the studied sample is sketched in Figure 2.2(a). It consists of two thin ferromagnetic layers, FM=Ni(4Å)\Co(7Å)\Ni(4Å) with a total thickness of $t_0 = 1.5$ nm, which are separated by a 3-nm-thick gold spacer, and sandwiched between two 5-nm-thick Pt layers. The DMI arising at the Pt\FM interfaces, combined with flux-closing dipolar fields, promotes the stabilization of superimposed skyrmions having identical topological charge and opposite chirality in each FM layer, as explained in details in Ref. [63]. The resulting skyrmion pairs are strongly coupled by dipolar fields and behave as magnetic quasiparticles, which are hereafter referred to as skyrmions, for simplicity.

The properties of spin textures in this symmetric magnetic bilayer with perpendicular magnetic anisotropy were first investigated through MFM by our collaborators at LPS [63]. Figure 2.2(b) shows two MFM images recorded for different magnitudes of an out-of-plane magnetic field B_z . At low field ($B_z = 2$ mT), the magnetic texture is characterized by a worm-like demagnetized state. When the magnetic field increases ($B_z = 14$ mT), the magnetic domains are converted into magnetic skyrmions with a typical size of ~ 150 nm.

To investigate the dynamics of such skyrmions under current pulses, the bilayer sample was patterned into $1\ \mu\text{m}$ -wide wires with contact pads at the edges enabling current pulse injection. A serie of MFM images recorded after applying 3-ns long pulses with a current density $J = 3.9 \times 10^{11}$ A/m² is shown in Figure 2.2(c). Isolated skyrmions are moving against the electron flow with a maximum velocity of ~ 60 m/s. The mechanism at the origin of current-induced skyrmion motion will be discussed in details in section § 2.2.4. In addition, the observation of a transverse deflection induced by the Magnus force [63], an effect often referred to as the *skyrmion Hall effect* [73], confirmed the topological charge of chiral magnetic skyrmions.

This symmetric magnetic bilayer system thus enables skyrmion stabilization at room temperature under moderate external magnetic field, with state-of-the art skyrmion motion under current. However, such velocities remain smaller than the one predicted by simulations of skyrmion dynamics [58, 72] and still require large current densities ($J > 10^{11}$ A/m²). Furthermore, a careful inspection of the MFM images shown in Figure 2.2(c) indicates that the skyrmion displacement is not equal from consecutive current pulses, suggesting that skyrmions are moving by hopping between neighboring pinning sites. This observation, which illustrates the important role played by structural defects in the properties of magnetic skyrmion, has motivated an in-depth study of the impact of sample disorder on the size and

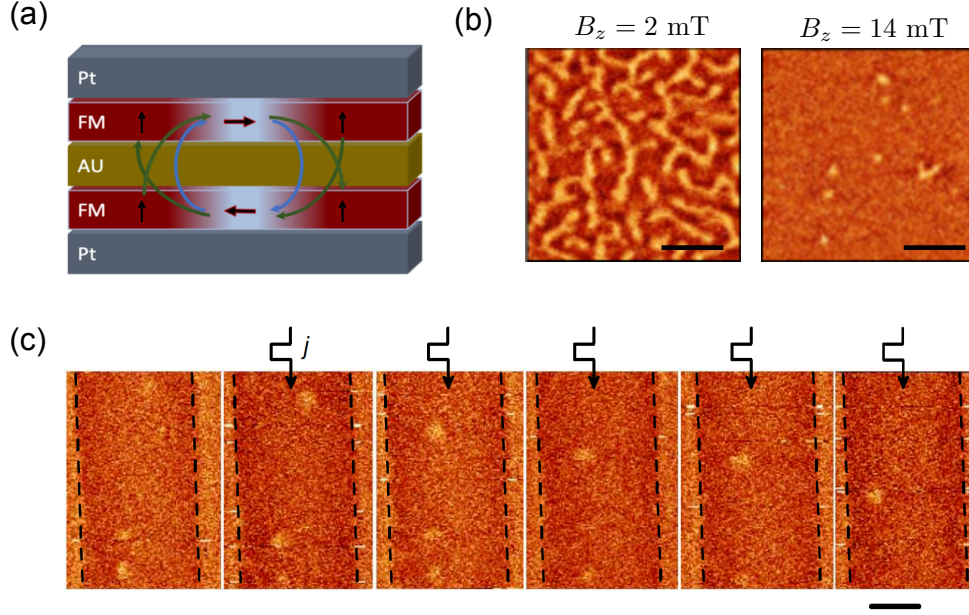


Figure 2.2: Imaging skyrmions in a symmetric bilayer system by MFM. (a) Sketch of the symmetric ferromagnetic bilayer system consisting in a stack of Pt(5nm)\FM\Au(3nm\FM\Pt(5nm), where FM=Ni(4Å)\Co(7Å)\Ni(4Å). The black arrows indicate the magnetization orientation inside the two layers containing a domain wall. The DMI arising at the Pt\FM interfaces combined with flux-closing dipolar fields favor the stabilization of Néel domain walls with opposite chiralities in the two magnetic layers. The blue arrows represent the magnetostatic interaction between the two domain walls, and the green arrows the one arising from the domains on the domain wall. (b) MFM images of the symmetric bilayer system recorded for out-of plane magnetic fields $B_z = 2$ mT (left panel) and $B_z = 14$ mT (right panel). The bright and dark contrast corresponds to repulsive and attractive force respectively. Scale bar, $1 \mu\text{m}$. (c) Series of MFM images recorded after applying 3-ns long pulses with a current density $J = 3.9 \times 10^{11} \text{ A/m}^2$. Experiments are performed with an out-of-plane magnetic field $B_z = 6$ mT. Scale bar, 500 nm . The figures are adapted from Ref. [63].

shape of isolated skyrmions.

2.1.2 Skyrmion morphology imaged by NV magnetometry

Investigating the effect of disorder on the skyrmion properties requires highly precise images of the skyrmion morphology. This cannot be achieved with MFM owing to the intrinsic magnetic nature of the probe, which often induces perturbations of the studied sample and therefore may modify the skyrmion morphology. An illustration of the perturbations induced by MFM will be discussed in (§ 2.3.4). Here, we use scanning-NV magnetometry in *PL quenching mode* to obtain high spatial resolution images of magnetic skyrmions without producing magnetic perturbations on the sample.

As discussed in §1.3.1, a single NV defect located at the apex of a nanopillar in a diamond scanning-probe unit is integrated into a tuning-fork-based atomic force microscope (AFM) and scanned in close proximity of the symmetric magnetic bilayer structure. At each point of the scan, the confocal optical microscope placed above the tip is used to monitor the magnetic-field-dependent PL signal of the NV

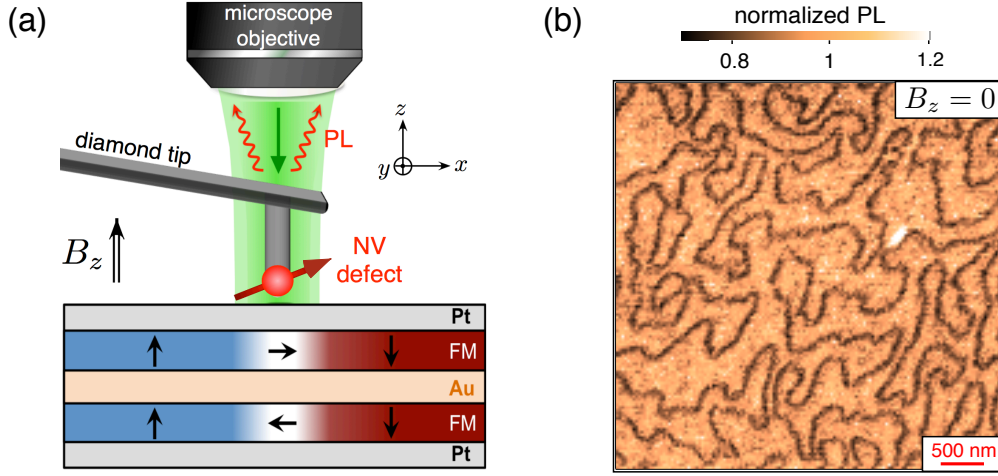


Figure 2.3: Principle of the experiment. (a) Magnetic imaging of the symmetric bilayer system is performed with a scanning-NV magnetometer operating in the PL quenching mode under ambient conditions. A out-of-plane magnetic field B_z is applied by a coil placed below the sample. (b) Typical PL quenching image recorded in zero external field ($B_z = 0$).

defect under green laser illumination, as sketched in Figure 2.3(a). For all the experiments described in this section, the NV defect is flying at a distance $d_{\text{NV}} \sim 50$ nm from the sample surface. This parameter, which sets the spatial resolution of magnetic imaging, is measured through the calibration procedure described in (§ 1.3.2). A typical PL quenching image recorded at zero field above the magnetic bilayer sample is shown in Figure 2.3(b). Sharp dark areas with a contrast greater than $\sim 20\%$ reveal regions of high stray magnetic fields, which correspond to domain walls organized in a worm-like structure. Although very similar images can be obtained with MFM [see Fig. 2.2(b)], the key advantage of NV-based magnetometry is here the absence of magnetic back-action on the sample, which provides unambiguous field measurements.

Starting from a worm-like magnetization structure, isolated skyrmions are obtained by applying an external magnetic field B_z perpendicular to the sample surface [Fig. 2.4]. This field is produced by a calibrated coil placed below the microscope. This configuration also sets a limit for the maximum magnetic field applied, and the duration of the pulses, since current running through the coils causes heating of the piezo-electric scanners therefore inducing scanning drifts. For $B_z = 3$ mT, one domain type starts to shrink but skyrmions are not yet formed, as illustrated by Figure 2.4(b). In the next step, a 10-s magnetic field pulse of larger amplitude is applied in order to release domain walls from pinning sites. The magnetic field image is subsequently recorded at $B_z = 3$ mT. As shown in Figure 2.4(c), a field pulse of 7 mT considerably compresses the magnetic domains, while after a 10 mT pulse the wormy domain structure completely collapses, leading to the formation of isolated skyrmions [Fig. 2.4(d)]. In this experiment, the characteristic skyrmion size remains much larger than the NV-to-sample distance (~ 50 nm). As a result, domain walls from opposite sides of the skyrmion can be easily resolved, leading

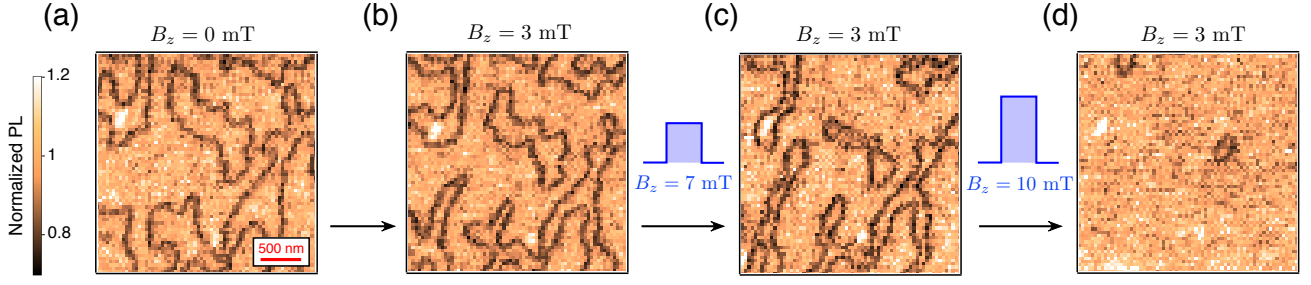


Figure 2.4: Nucleation of isolated skyrmions by applying an external out-of-plane magnetic field. (a) PL quenching images recorded at zero field and (b) $B_z = 3$ mT. (c,d) Images recorded at $B_z = 3$ mT after applying a 10-s field pulse of (c) 7 mT and (d) 10 mT. The bright PL spots correspond to dusts on the sample which serve as position references.

to a dark ring in the PL quenching image. As mentioned above, the skyrmionic nature of such magnetic bubbles was proved by the detection of the skyrmion Hall effect in a previous study conducted by our collaborators at LPS [63].

Magnetic skyrmions were extensively imaged over the sample in order to obtain their size and shape distributions. Whereas perfectly circular skyrmions would be expected owing to the in-plane symmetry of the magnetic energy, we observe significant distortions of the magnetic texture, as illustrated in Figure 2.5(a). These distortions are not related to the NV-center orientation and are introduced neither by the probe nor by the scanning procedure since it has no magnetic back-action on the sample. The characteristic skyrmion size is inferred by measuring the area $\mathcal{S}$ enclosed by the dark ring observed in the PL images. The effective diameter d_s is then defined as $d_s = 2\sqrt{\mathcal{S}/\pi}$, corresponding to a conversion of the distorted skyrmion geometry into a perfectly rounded shape. Measurement of 27 isolated skyrmions leads to $d_s = 268 \pm 63$ nm [see Fig. 2.5(b)]. We note that such a diameter is two times larger than the one inferred from MFM measurements shown in Figure 2.2(b), where a magnetic field of 14 mT was continuously applied.

In the next paragraph, we will show that these observations can be well explained by pinning effects induced by structural disorder in the sample.

2.1.3 Simulation of disorder and magnetic history effects

Micromagnetic simulations including disorder were carried out by S. Rohart from LPS using the MuMax3 code [74].

The sample was modeled as two magnetic layers, each $t_0 = 1.5$ nm thick, with a 3 nm thick spacer. Magnetic parameters extracted from previous measurements were used [63]: interfacial magnetic anisotropy $K_s = 0.75$ mJ.m⁻², saturation magnetization $M_s = 0.85$ MA.m⁻¹, exchange constant $A = 12$ pJ.m⁻¹ and interfacial DMI constant $D_s = \pm 0.3$ pJ.m⁻¹ with a negative (resp. positive) sign in the bottom (resp. top) FM layer. Disorder was included by a random fluctuation of the FM layer thickness t between columnar grains arranged in a Voronoi fashion [75, 76, 77, 78]. The average lateral grain size was

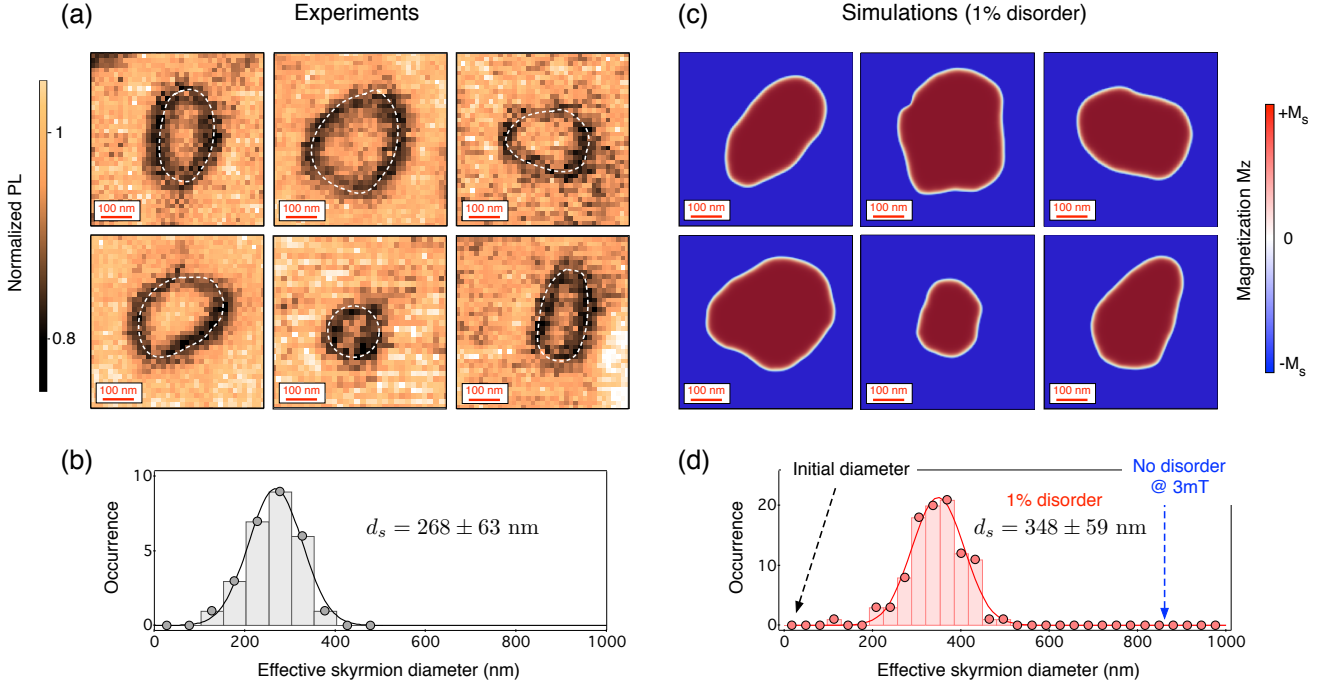


Figure 2.5: Impact of structural disorder on the skyrmion morphology. (a) PL quenching images recorded above several isolated skyrmions at various position in the sample. These experiments are performed at $B_z = 3$ mT after applying a field pulse of 10 mT. The white dashed contours indicate the PL quenching ring from which the skyrmion area $\mathcal{S}$ is extracted. (b) Histogram of the effective skyrmion diameter d_s extracted from measurements over a set of 27 skyrmions. The solid line is a fit with a Gaussian distribution. (c) Typical micro-magnetic simulations of the skyrmion spin texture by including thickness fluctuations with a relative amplitude of 1%. (d) Histogram of the effective skyrmion diameter obtained for a large number of randomly picked disorder configurations. The blue dashed arrow indicates the skyrmion diameter for a disorder-free sample (860 nm) and the black dashed arrow shows the initial skyrmion size in the simulation (40 nm) before expansion in a 3 mT field.

fixed to 15 nm, as observed by high-resolution atomic force microscopy (AFM) imaging [see Fig. 2.7(a)], and the thickness variation between grains was assumed to follow a normal distribution. Since the micromagnetic code requires a computational cell with a constant thickness t_0 over the whole sample, the saturation magnetization was varied from grain to grain as $M_s t / t_0$. Averaged over the thickness, the uniaxial anisotropy K_u and the effective DMI constant D are also directly modified in each grain, *i.e.* $K_u = K_s / t$ and $D = D_s / t$.

In a disorder-free medium, magnetic simulations lead to circular skyrmions with a diameter $d_0 = 860$ nm under a 3 mT magnetic field, which is much larger than the experimental observation. However, we stress that NV-magnetometry measurements are performed after applying a 10-mT field pulse, which means that skyrmions are imaged after a compression of their diameter, followed by relaxation in a constant field of 3 mT. To account for such a magnetic history, circular skyrmions with an initial diameter $d_i = 40$ nm, corresponding to the skyrmion size for a 10-mT field in a disorder-free medium, were first generated and then relaxed in a 3-mT field while including disorder. Figure 2.5(c) shows typical results of the simulation for thickness fluctuations with a relative amplitude of 1%. The

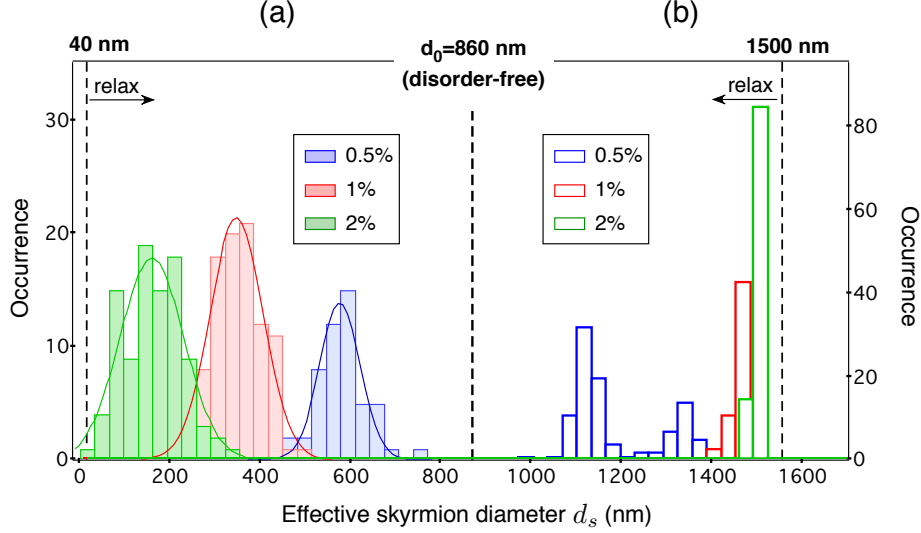


Figure 2.6: Simulations of the effective skyrmion size distribution obtained for different strengths of disorder after relaxation in a 3 mT field while starting with a skyrmion diameter of (a) $d_i = 40$ nm and (b) $d_i = 1500$ nm. The black dashed line in the middle indicates the simulated skyrmion diameter for a disorder-free sample (860 nm).

calculated skyrmion morphology is similar to that observed in the experiments, revealing the role of disorder and magnetic history in the stabilization of isolated skyrmions. Statistics over a large number of randomly sorted disorder distributions leads to an effective skyrmion diameter $d_s^{[1\%]} = 348 \pm 59$ nm [see Fig. 2.5(d)]. A similar analysis performed for disorder amplitudes of 2% and 0.5% thickness fluctuations leads to $d_s^{[2\%]} = 136 \pm 55$ nm and $d_s^{[0.5\%]} = 577 \pm 44$ nm, respectively, as shown in Figure 2.6(a).

It is striking to note that the impact of disorder on the skyrmion morphology is very strong, even for the relatively small thickness fluctuations considered. The key parameter fixing the skyrmion size is the domain wall energy σ , which involves all magnetic parameters [79]. For a single magnetic layer, the domain wall energy is given by

$$\sigma = 4\sqrt{AK_{\text{eff}}} - \pi D, \quad (2.2)$$

with $K_{\text{eff}} = K_u - \frac{1}{2}\mu_0 M_s^2$ the effective magnetic anisotropy. Media adapted for skyrmion stabilization are generally optimized to display a low effective anisotropy in order to decrease the domain wall energy to few mJ.m^{-2} . As a result, tiny fluctuations of any micromagnetic parameter are converted into large relative fluctuations of the effective anisotropy and domain wall energy. As an example, 1% thickness fluctuations lead to about 30% fluctuations in effective anisotropy and domain wall energy in our sample. Such large fluctuations explain the observed strong impact on the skyrmion spin texture.

To further illustrate how the skyrmion size depends on disorder and magnetic field history, the skyrmion relaxation was simulated under the same 3 mT magnetic field while starting from a large skyrmion with a diameter $d_i = 1500$ -nm. The resulting skyrmion size distribution is shown in Figure 2.6(b) for various amplitudes of the thickness fluctuations. We now observe that the skyrmion

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size is larger than the one expected in a disorder-free sample. Such a measurement procedure was not accessible experimentally, since round 1500-nm diameter skyrmions could not be stabilized before the application of the 3 mT magnetic field. However, a qualitative comparison can be made by comparing the first two images in Figure 2.4, where the $1400 \times 500 \text{ nm}^2$ domain at the center in zero field relaxes under 3 mT into a $1200 \times 400 \text{ nm}^2$ domain.

Although illustrative, these micromagnetic simulations were performed at zero temperature, *i.e.* without including the effects of thermal fluctuations. As a result, a direct comparison between simulations and experiments does not allow extracting quantitative informations about thickness fluctuations in the sample. Since thermal agitation helps to overcome energy barriers induced by pinning sites, the actual thickness fluctuations in the sample are most likely larger than 1%. Micromagnetic simulations can be performed at finite temperature using an additional fluctuating field [74, 80] but cannot accurately include all its impact if the temperature is too large [81, 82]. Therefore, we have also simulated the relaxation process at 100 K, and found an agreement with the experiments for a thickness fluctuation of about 5 %, as illustrated in Figure 2.7(a). The actual thickness fluctuations in the sample were inferred by high resolution AFM measurements. The AFM image shown in Figure 2.7(b) allows the extraction of the grain size distribution. The sample exhibits an average grain size of 13.6 nm with a full-width at half maximum (FWHM) of 7 nm. The average roughness is 1.54 nm, which corresponds to about 7 % of the total thickness (magnetic layer and non magnetic layer thickness). This value is in fair agreement with the one inferred from the micromagnetic simulations performed at 100 K.

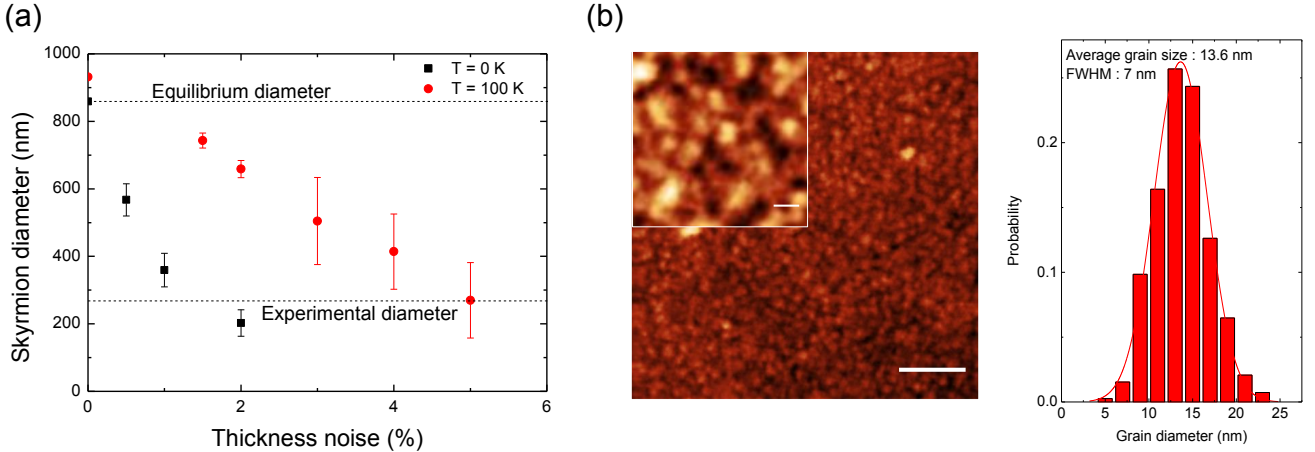


Figure 2.7: (a) Variation of the simulated skyrmion size versus the thickness disorder for 0 K (black) and 100 K (red). The dotted lines correspond to the 0 K equilibrium size and the experimental size. (b) AFM image of the symmetric bilayer sample showing the grain size (scale bar 100 nm). The inset is a zoom (scale bar 15 nm). The right panel shows the grain size distribution with an average grain size of 13.6 nm.

2.1.4 Conclusion

In this section, scanning-NV magnetometry was used to investigate the impact of disorder and magnetic history on the morphology of skyrmions in an ultrathin magnetic sample relevant for spintronic applications. A simple model of disorder based on thickness fluctuations provided a good description of the obtained results. Besides opening the way to a detailed understanding of the dynamics of skyrmions in real, disordered media, this work also highlighted for the first time the potential of NV magnetometry in PL quenching mode to study ferromagnetic textures with high spatial resolution under ambient conditions.

2.2 Skyrmion dynamics in a Co-based Heusler alloy

As discussed above, stacks of ultrathin magnetic layers commonly exhibit structural defects forming pinning sites, which trap skyrmions, impact their morphology and/or prevent their efficient current-induced manipulation. Reducing the defect's density is a long-term scientific endeavor challenging all the community working on magnetic multilayer heterostructures. In this context, a large variety of host materials are currently being explored with the aim of optimizing the properties of skyrmions for spintronic applications.

In this section, we investigate the possibility to improve current-induced skyrmion dynamics by using an Heusler alloy, a class of ferromagnetic materials with an intrinsically low magnetic damping coefficient [83, 84]. Although a skyrmion phase was recently identified at low temperature in some Heusler alloys, such as Mn_2CoAl and Mn_2RhSn , by detecting a topological Hall effect [85, 86, 87], the stabilization of magnetic skyrmions under ambient conditions has remained elusive to date and the potential of Heusler alloys for efficient current-induced skyrmion motion still needs to be explored. In the following, we study the properties of magnetic skyrmions stabilized in a single ultrathin layer of the Heusler alloy Co_2FeAl (CFA) under ambient conditions. This work was pursued in collaboration with

- M. S. Gabor from the Center for Superconductivity, Spintronics and Surface Science at the Technical University of Cluj- Napoca (Romania);
- M. Belmeguenai from the Laboratoire des Sciences des Procédés et des Matériaux (LSPM, Villetaneuse);
- A. Hrabec, A. Thiaville and S. Rohart from the Laboratoire de Physique des Solides (LPS, Orsay).

The results have been published in W. Akhtar *et al.* *Phys. Rev. Appl.* **11**, 034066 (2019).

The section is organized as follows. After a brief description of the CFA sample and the macroscopic characterization of its magnetic parameters (§ 2.2.1), we demonstrate room-temperature stabilization of magnetic skyrmions with diameters in the range of 100 nm in a single ultrathin layer of CFA under moderate magnetic fields (§ 2.2.2). We then investigate current-induced skyrmion nucleation by spin-orbit torque (§ 2.2.3) and show that its efficiency can be significantly improved using tilted magnetic

fields, an effect which is not specific to Heusler alloys and could be advantageous for future skyrmion-based devices. Finally, current-induced skyrmion motion is addressed (§ 2.2.4), showing that pinning effects still limit skyrmion velocity, even in a host material with low magnetic damping.

2.2.1 Sample structure and characterization of the magnetic parameters

The sample used in this study is a multilayer stack deposited by magnetron sputtering on a thermally oxidized silicon wafer in the team of M. S. Gabor (Cluj-Napoca, Romania) [88]. As sketched in Figure 2.8(a), it consists of a CFA layer with thickness $t = 1.6$ nm sandwiched between 3 nm of Pt and 1.8 nm of MgO. Prior to the growth of this Pt(3)\CFA(1.6)\MgO(1.8) heterostructure, a 2-nm-thick Ta buffer layer was deposited on the silicon substrate. A capping layer of Ta was also added to prevent oxidation of the stack. Hysteresis loops recorded with a vibrating sample magnetometer (VSM) indicate a uniaxial perpendicular magnetic anisotropy of the CFA layer $K_u = 8.9 \times 10^5$ J/m³ and a saturation magnetization $M_s = 1.14 \times 10^6$ A/m. In this sample, the effective magnetic anisotropy is therefore low, $K_{\text{eff}} = K_u - \frac{1}{2}\mu_0 M_s^2 \sim 70$ kJ/m³, which induces a low domain wall energy [see Eq. (2.2)] and therefore favors skyrmion stabilization through dipolar effects [89, 90].

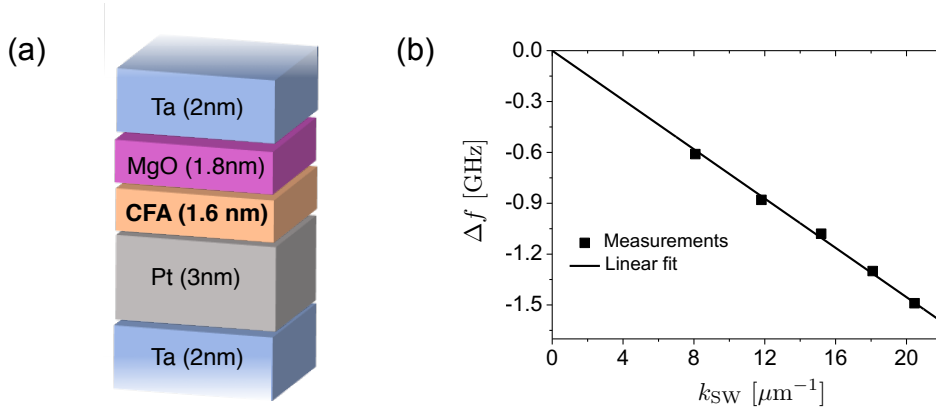


Figure 2.8: Sample structure and characterization. (a) Sketch of the CFA-based multilayer stack deposited by magnetron sputtering on a thermally oxidized silicon wafer. (b) Wave vector (k_{SW}) dependence of frequency shift Δf between the Stokes and anti-Stokes peaks in Brillouin light scattering spectroscopy.

The strength of interfacial DMI, which is another key parameter for stabilizing skyrmions, was determined by monitoring the non-reciprocal propagation of spin waves with Brillouin light scattering spectroscopy (BLS) in the Damon-Eshbach geometry [91, 92, 93]. These measurements were performed by the team of M. Belmeguenai at LSPM (Villetaneuse). Here the sample magnetization is saturated in the film plane by an external magnetic field and spin waves (SW) propagating along the direction perpendicular to this field are probed by a laser with a well-defined wavevector k_{SW} . The DMI induces a frequency shift Δf between the Stokes (SW creation) and anti-Stokes (SW annihilation) modes propagating with opposite wavevectors. This frequency shift can be expressed as [92]

$$\Delta f(k_{\text{SW}}) = \frac{2\gamma k_{\text{SW}} D}{\pi M_s}, \quad (2.3)$$

where γ is the gyromagnetic ratio and D the effective DMI strength. Figure 2.8(b) shows the evolution of Δf with k_{SW} for the CFA-based heterostructure. A linear fit of the experimental data leads to an effective DMI constant $D = -0.70 \pm 0.06 \text{ mJ/m}^2$. Such a negative value of the D parameter promotes the stabilization of Néel skyrmions with a left-handed chirality [92]. Finally a damping parameter $\alpha \sim 0.02$ was inferred from the width of the peaks in BLS measurements.

Once characterized, the multilayer stack was patterned into $1\text{-}\mu\text{m}$ -wide magnetic wires by using a combination of e-beam lithography and ion milling. Ti/Au electrical contact pads were then deposited for applying current pulses into the magnetic wires.

2.2.2 Stabilization of isolated skyrmions by an external magnetic field

Magnetic imaging was performed with scanning-NV magnetometry operating in the PL quenching mode under ambient conditions. The scanning-diamond tip is here characterized by a NV-to-sample distance $d_{\text{NV}} \sim 80 \text{ nm}$. Compared to the experiments described in the previous section (§ 2.1), a permanent magnet placed on a three-axis translation stage was included in the experimental setup in order to apply a static magnetic field B_{NV} along the NV defect quantization axis $\mathbf{u}_{\text{NV}}$. This axis was precisely identified through the procedure described in § 1.3.2, leading to polar angles $(\theta \sim 45^\circ, \phi \sim 4^\circ)$ in the (x, y, z) sample reference frame, as illustrated in Figure 2.9(a). With our permanent magnet, a maximum magnetic field amplitude B_{NV} in the range of 15 mT can be obtained.

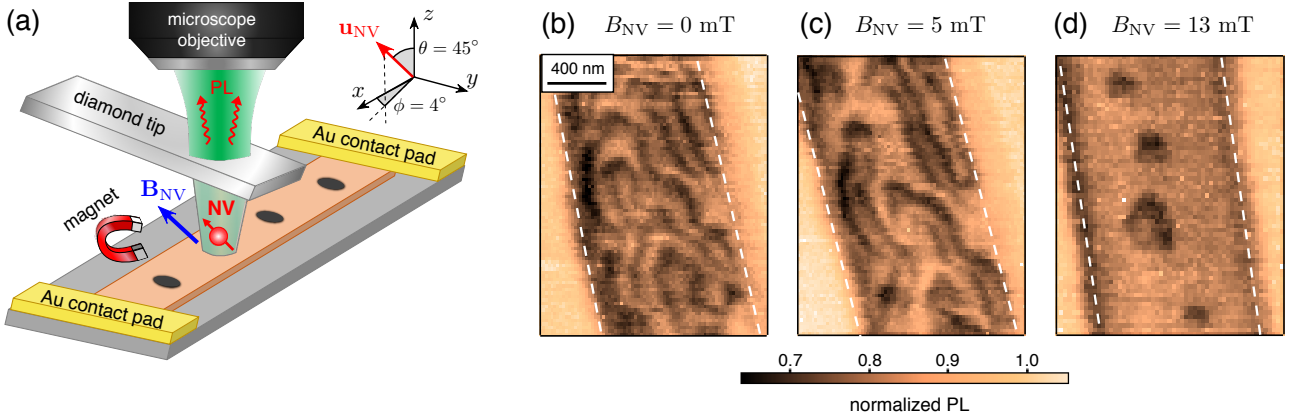


Figure 2.9: Imaging magnetic skyrmions in a single ultrathin layer of CFA under ambient conditions. (a) Magnetic imaging of the Pt(3)/CFA/MgO multilayer stack is performed with scanning-NV magnetometry operating in the PL quenching mode. A permanent magnet is used to apply a static magnetic field B_{NV} along the NV quantization axis $\mathbf{u}_{\text{NV}}$. The Au contact pads are used for current injection. (b-d) PL quenching image recorded at zero field (b), $B_{\text{NV}} = 5 \text{ mT}$ (c) and $B_{\text{NV}} = 13 \text{ mT}$ (d) above the same area of the sample.

Figure 2.9(b) shows a typical PL quenching image recorded at zero field above a $1\text{-}\mu\text{m}$ -wide wire of the Pt/CFA/MgO stack. Dark PL contours indicate high stray field areas, which correspond to a network of domain walls organized in a worm-like structure. Nucleation of isolated skyrmions was first achieved by applying a static magnetic field. When applying an external field larger than few mT, we stress that

its orientation must be along the NV defect quantization axis in order to avoid parasitic PL quenching effects. A precise alignment of the external magnetic field was obtained by monitoring the Zeeman shift of the ESR frequencies of the NV defect with the magnetic sample placed few microns away. Any misalignment of the magnetic field causes dissymmetry in the position of the ESR dips with respect to the zero-field splitting parameter D (see § 1.1.4). By applying an external magnetic field $B_{\text{NV}} = 5$ mT, the magnetic domains start to shrink, and for $B_{\text{NV}} = 13$ mT the worm-like domain structure fully collapses into isolated skyrmions, with a minimum diameter in the range of 100 nm. The variation in shape and size of the resulting skyrmions is attributed to pinning effects arising from structural disorder in the sample, as discussed in the previous section. This experiment corresponds to the first detection of magnetic skyrmions in an ultrathin layer of a Heusler alloy under ambient conditions.

2.2.3 Current-induced skyrmion nucleation

We now investigate skyrmion nucleation induced by short current pulses injected into the magnetic wire. As shown in Figure 2.10(a), the experiments start with a fully saturated wire and a magnetic field $B_{\text{NV}} = 13$ mT applied along the NV quantization axis. *We stress that this corresponds to an external in-plane field component $B_x \approx 9$ mT applied along the $+\mathbf{e}_x$ direction.*

A bunch of three 30-ns pulses with a current density $J = 6 \times 10^{11}$ A/m² was first applied along the $-\mathbf{e}_x$ direction. In these conditions, skyrmions are not nucleated in the magnetic wire [see Fig. 2.10(b)]. By simply reversing the current direction to $+\mathbf{e}_x$, *i.e.* along the in-plane magnetic field B_x , skyrmion nucleation becomes highly efficient, as illustrated in Figure 2.10(c). Such an asymmetric nucleation process with the current polarity cannot be explained solely by a thermal activation through Joule heating [65]. The main driving force of the nucleation process is here attributed to the spin orbit torque resulting from the spin Hall effect (SHE) in the Pt layer, as explained below.

When an electrical current flows into the heavy metal (Pt) of the magnetic heterostructure, the SHE leads to a spin accumulation at the Pt/CFA interface, which results in a damping-like torque associated with an effective magnetic field [94];

$$\mathbf{H}_{\text{SHE}} = \frac{\hbar\theta_H}{2e\mu_0 M_s t} (\mathbf{e}_z \times \mathbf{J}) \times \mathbf{m} , \quad (2.4)$$

where $\mathbf{m}$ is the sample magnetization and θ_H denotes the spin Hall angle, which is positive for Pt. The perpendicular magnetization component m_z leads to a SHE field along $\pm\mathbf{e}_x$, with a sign fixed by the current direction. This effective field induces a slight tilt of the magnetization but does not favor magnetization reversal for a particular current polarity [95]. However, in our experiments the in-plane component of the external magnetic field B_x breaks the symmetry by producing an in-plane magnetization component m_x , which modifies the effect of the SHE-induced torque and promotes a switching directionality, as previously invoked in the context of magnetization reversal in thin magnetic nanodots [95]. More precisely, the m_x component leads to an effective SHE field perpendicular to the sample surface, which can switch the magnetization and assist skyrmion nucleation. In our case, the

in-plane component of the external field being along $+\mathbf{e}_x$, m_x is positive, and H_{SHE} has a component along $-\mathbf{e}_z$ (resp. $+\mathbf{e}_z$) when the current is applied along $+\mathbf{e}_x$ (resp. $-\mathbf{e}_x$). Starting from a saturated state with $m_z > 0$, skyrmion nucleation is therefore expected to be more efficient for a current applied along $+\mathbf{e}_x$, in agreement with the experimental observation.

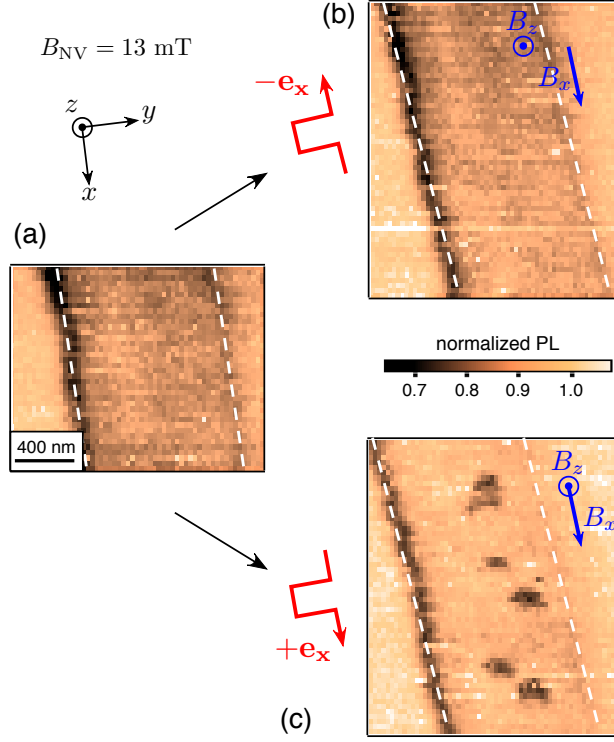


Figure 2.10: Current-induced skyrmion nucleation. (a) PL quenching image recorded over a saturated magnetic wire. (b-c) The same wire is imaged after applying a bunch of three 30-ns current pulses with $J = 6 \times 10^{11} \text{ A/m}^2$ (b) along the $-\mathbf{e}_x$ direction and (c) along the $+\mathbf{e}_x$ direction. These experiments are performed with an external magnetic field $B_{\text{NV}} = 13 \text{ mT}$, which correspond to an in-plane field component $B_x \approx 9 \text{ mT}$ (see blue arrows).

Micromagnetic simulation of the current-induced skyrmion nucleation process

This qualitative interpretation was confirmed by micromagnetic simulations of the nucleation process, which were performed by S. Rohart (LPS, Orsay) using the MuMax3 code [74]. Magnetic parameters extracted from preliminary characterization of the sample were used (see § 2.2.1). In addition, thickness fluctuations of the magnetic layer with a relative amplitude of 2 % were included in the simulation following the procedure described in § 2.1.3. Such a structural disorder provides a network of nucleation centers in the sample. A magnetic field $B_z = 9 \text{ mT}$ was always applied perpendicular to the sample surface and the nucleation process was simulated by applying a single 2-ns long current pulse. The initial state was chosen to be uniform along the perpendicular field direction, so that nucleated skyrmion cores

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are opposite to this field. The skyrmion density was extracted from the simulated magnetization maps, while varying (i) the current density J , (ii) its polarity and (iii) the amplitude of the in-plane magnetic field component B_x . As an example, a magnetization map simulated for $J = 1.75 \times 10^{11}$ A/m² applied along $+\mathbf{e}_x$ and $B_x = 9$ mT is shown in the inset of Figure 2.11(a). Here a typical skyrmion density of about 3 per μm^2 is obtained. We note that these simulations do not intend to quantitatively reproduce the experimental observations because we lack an accurate description of several key parameters of the experiment, such as the pinning landscape induced by structural disorder or thermal activation.

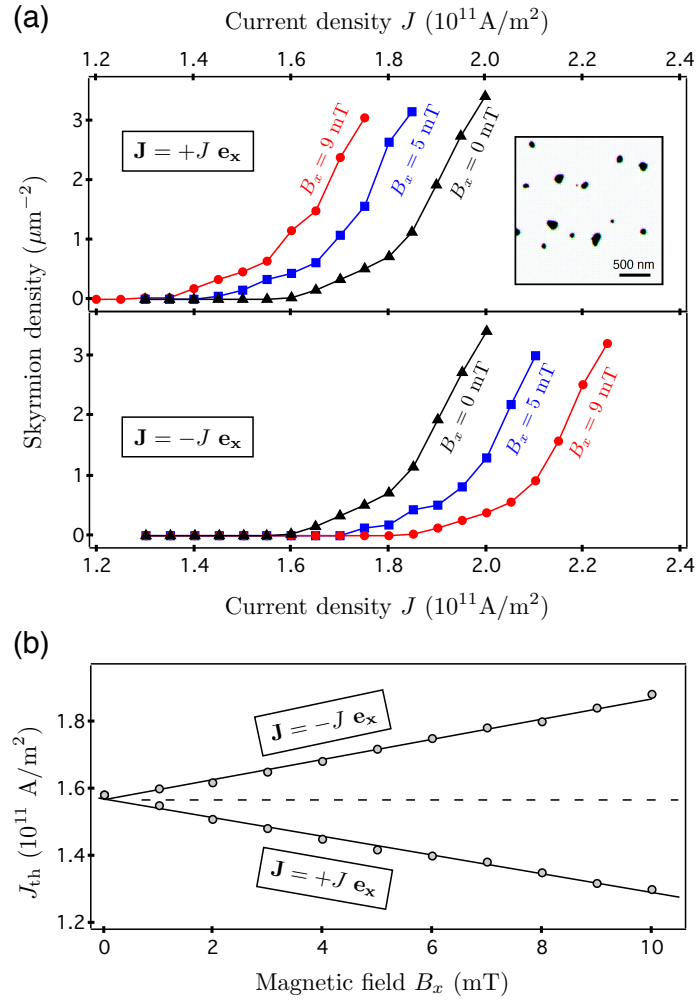


Figure 2.11: Simulations of the skyrmion nucleation process. (a) Variation of the nucleated skyrmion density as a function of the current density and polarity, for three values of the in-plane magnetic field B_x . The inset shows a typical simulated magnetization map obtained for $B_x = 9$ mT and $J = 1.75 \times 10^{11}$ A/m² applied along $+\mathbf{e}_x$. (a) Current threshold for skyrmion nucleation, J_{th} , as a function of B_x for the two different current polarities.

Simulations of the nucleated skyrmion density as a function of the current density are shown in Figure 2.11(a). Without in-plane magnetic field, skyrmion nucleation is obtained above a current

threshold $J_{\text{th}} \approx 1.6 \times 10^{11} \text{ A/m}^2$, independently of the current polarity. This nucleation threshold is found to be tuned by an in-plane magnetic field. More precisely, J_{th} decreases when the current is applied along the in-plane field direction ($+\mathbf{e}_x$), and increases when the current direction is reversed. As discussed earlier, this effect is expected from the symmetry of the SHE-induced torque. This is further illustrated by Figure 2.11(b) showing the evolution of J_{th} as a function of the in-plane magnetic field. For $B_x = 10 \text{ mT}$, the nucleation threshold decreases (resp. increases) by $\approx 20\%$ when the current is applied along $+\mathbf{e}_x$ (resp. $-\mathbf{e}_x$). This effect leads to an asymmetric nucleation efficiency with the current polarity, as observed in our experiments. Although recent reports in the literature have also invoked SHE-induced torque as a driving force to explain deterministic skyrmion nucleation [64, 66], our work demonstrates that its efficiency can be significantly improved by applying an additional in-plane magnetic field.

2.2.4 Current-induced skyrmion motion

Once the microwires are filled with isolated skyrmions, we then studied their current-induced motion. To this end, PL quenching images were recorded after applying subsequent single current pulses with a magnetic field $B_{\text{NV}} = 13 \text{ mT}$ applied along the NV axis. In order to avoid nucleation or annihilation of skyrmions by Joule heating and SHE-induced torque, the current density was decreased to study their dynamics.

Figure 2.12(a-c) shows the initial magnetic configuration of a microwire and those observed after applying single 30-ns current pulses along the $+\mathbf{e}_x$ direction with a current density $J = 3 \times 10^{11} \text{ A/m}^2$. Although most of the magnetic textures remain pinned in the wire, current-induced motion can be observed for one skyrmion. Importantly, the motion is found against the electron flow. This observation was confirmed in another wire in which the current polarity was reversed, as shown in Figure 2.12(d-f).

These observations suggests that the SHE is the principal source of current-induced skyrmion motion. Indeed, when an electric current passes through the Pt layer, the spin accumulation induced by the SHE at the Pt/CFA interface produces a force $\mathbf{F}_{\text{SHE}}$ acting on a skyrmion, which can be expressed as [63]

$$\mathbf{F}_{\text{SHE}} = \pm \frac{\hbar}{2e} \pi \theta_H b \mathbf{e}_z \times (\mathbf{e}_z \times \mathbf{J}) , \quad (2.5)$$

where θ_H is the spin Hall angle, which is positive for Pt, and b is a skyrmion characteristic length. The sign of the force is set by the chirality, as specified by the $\pm$ symbol in Eq. (2.5), where the negative (resp. positive) sign stands for a left-handed (resp. right-handed) chirality of the magnetic skyrmion. In our experiments, Néel type skyrmions with a left-handed chirality are expected owing to the negative value of the DMI constant measured by Brillouin light scattering spectroscopy (see § 2.2.1) [52, 96]. For a current applied along the $+\mathbf{e}_x$ direction, $\mathbf{F}_{\text{SHE}}$ is therefore expected along $+\mathbf{e}_x$, *i.e.* opposite to the electron flow, as experimentally observed.

We note that skyrmion displacements are not equal for successive current pulses owing to pinning effects. The motion is thus in the hopping regime, which prevents a clear observation of the skyrmion

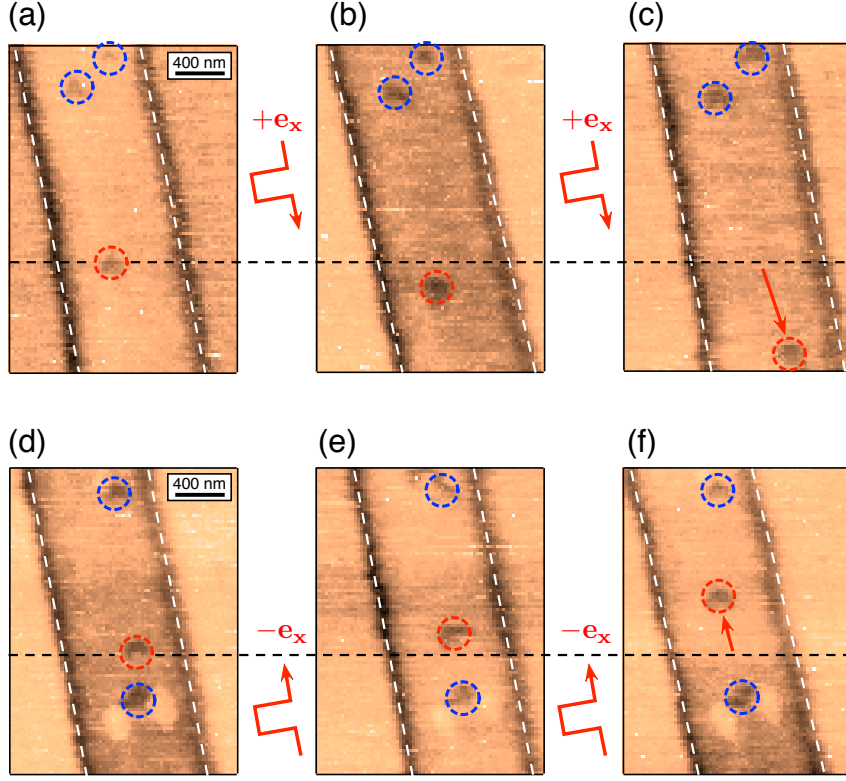


Figure 2.12: Current-induced skyrmion motion. (a-c) Series of PL quenching images recorded above a magnetic wire after applying subsequent 30-ns pulses with a current density $J = 3 \times 10^{11}$ A/m² along the $+\mathbf{e}_x$ direction. (d-e) Same experiments performed on another wire while reversing the current polarity and using 15-ns pulses with $J = 4.5 \times 10^{11}$ A/m². All images are recorded with a magnetic field $B_{\text{NV}} = 13$ mT applied along the NV axis.

Hall effect [73]. Nevertheless, based on the data shown in Figure 2.12, we can estimate a velocity in the range of ≈ 10 m/s. It is worth mentioning that motion at higher current density could not be studied owing to parasitic skyrmion nucleation or annihilation effects. Although thin layers of CFA exhibit a low damping parameter, our observations indicate that skyrmion dynamics remain limited by strong pinning effects in this material.

2.2.5 Conclusion

In this section, we have used scanning-NV magnetometry to image current-induced nucleation and dynamics of magnetic skyrmions in a Co-based Heusler alloy at room temperature. Skyrmion nucleation was found to be asymmetric with the current polarity. This asymmetry is attributed to the SHE-induced spin orbit torque in the presence of an in-plane magnetic field, which is further corroborated by micromagnetic simulations. This effect suggests a path towards efficient, deterministic generation of skyrmions via spin-orbit torques, which will be advantageous for future skyrmion-based devices. Current-induced skyrmion motion in our experiments remains limited by strong pinning effect, pointing out the key role of sample defects in skyrmion dynamics even in materials with intrinsically low magnetic

damping.

2.3 Room temperature skyrmions at zero field in exchange-biased ultrathin films

In the previous sections, the nucleation of isolated skyrmion was always assisted by applying an external magnetic field. To realize skyrmion-based spintronic devices, small-sized skyrmions must be stabilized at ambient conditions and *zero external field*. This challenging task can be pursued by using confined geometries [61, 97, 98], metastable skyrmion textures induced by pinning effects [99, 100], frustration of exchange interaction in ultrathin ferromagnets [101], or ferrimagnetic materials close to the magnetization compensation [102]. Another promising strategy consists in designing magnetic heterostructures in which interlayer exchange coupling acts as an effective internal magnetic field B_{int} , therefore suppressing the need for an external magnetic field [103, 104]. In this section, we follow this approach by exploiting exchange bias occurring at the interface between a ferromagnetic material and an antiferromagnet (see Fig. 2.13). This effect, which is commonly considered as a mean to pin the magnetization of a ferromagnetic material, is extensively used in magnetic hard drive technologies. It can be described by an internal magnetic field B_{int} produced at the ferromagnet/antiferromagnet interface, which results in a global shift of the ferromagnet's hysteresis loop, as illustrated in Figure 2.13(b).

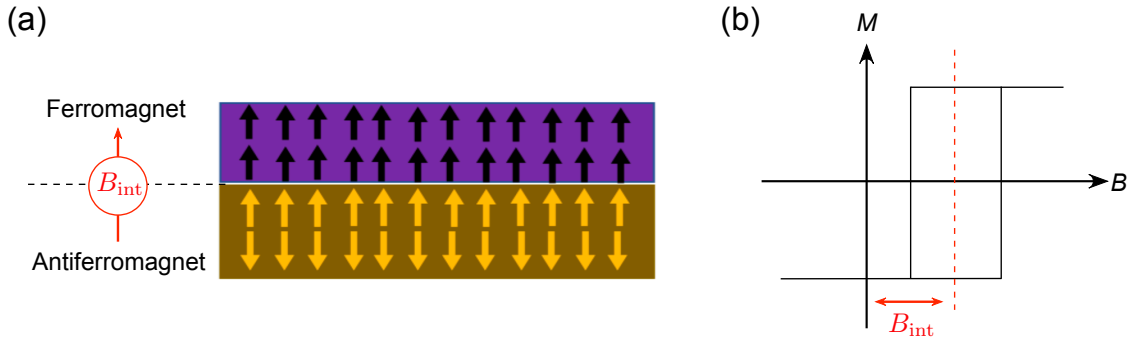


Figure 2.13: Sketch of exchange bias interaction effect(a) At a ferromagnet/antiferromagnet interface, the exchange bias interaction pins the magnetization of a ferromagnetic material by an internal effective magnetic field B_{int} . (b) Sketch of the hysteresis loop for an exchange-biased ferromagnet.

The first observation of skyrmion in an exchange-biased magnetic structure was reported by G. Yu *et al.* [104]. Using a Ta\CoFeB\IrMn multilayer stack, the stabilization of micrometer-sized skyrmions was achieved at zero field. In this section, we demonstrate that magnetic skyrmions with a mean diameter around 60 nm can be stabilized at room temperature and zero external magnetic field in an exchange-biased Pt\Co\NiFe\IrMn multilayer stack. Compared to previous studies, this result thus corresponds to a reduction in skyrmion diameter by one-order of magnitude. This is achieved through an advanced optimization of the multilayer stack composition in order to balance the different magnetic energies controlling the skyrmion size and stability [89, 90]. This work has been done in close

collaboration with the team of O. Boulle at CEA Spintec (Grenoble). The results are published in K. G. Rana *et al.* *Phys. Rev. Appl.* **13**, 044079 (2020).

In the following, we start by describing the optimization of the exchange-biased multilayer stack (§ 2.3.1). We then show magnetic images recorded by scanning-NV magnetometry (§ 2.3.2). A comparison between experimental results and simulations of PL quenching images enables to conclude that zero-field skyrmions with a mean diameter around 60 nm are stabilized in the optimized exchange-biased multilayer stack. We then show that skyrmions stabilized by exchange bias are robust against moderate external magnetic field perturbations, in the tens of mT range, which is an important feature for applications as memory devices (§ 2.3.3). To close the section, we finally compare magnetic images recorded with NV magnetometry and MFM (§ 2.3.4).

2.3.1 Optimization of exchange-biased multilayer stacks

The growth of the exchange-biased sample and its preliminary magnetic characterization was performed by the team of O. Boulle at CEA Spintec.

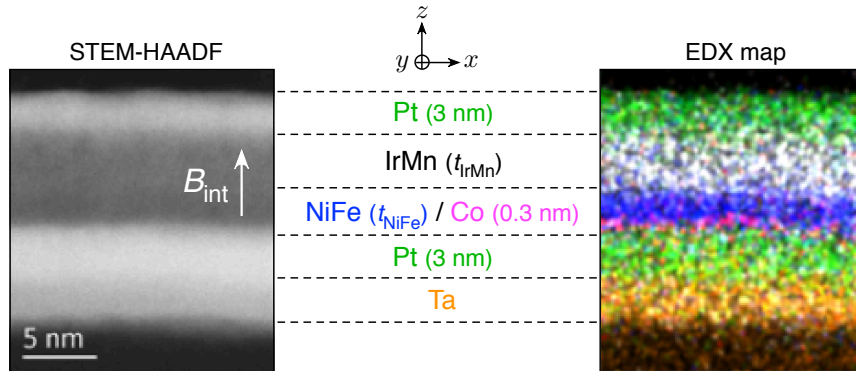


Figure 2.14: Structure of the exchange-biased sample. Central panel: Schematic structure of the exchange-biased multilayer stack. Left panel: Scanning transmission electron microscopy image of a cross-section of the sample obtained in a high-angle annular dark-field imaging (STEM-HAADF) mode. Right panel: energy-dispersive X-ray (EDX) elemental map. The white arrow indicates the direction of the internal exchange bias field B_{int} across the NiFe/IrMn interface.

The sample consists of a Ta/Pt(3)/Co(0.3)/Ni₈₀Fe₂₀(t_{NiFe})/Ir₂₀Mn₈₀(t_{IrMn})/Pt(3) multilayer stack (unit in nm) deposited by magnetron sputtering on a 100 mm diameter Si substrate [see Fig. 2.14]. Here the Pt/Co interface was chosen because it yields perpendicular magnetic anisotropy combined with a sizable interfacial DMI [91, 92], which is a key ingredient for stabilizing skyrmions. Furthermore, this interface provides large spin orbit torques for efficient current induced skyrmion motion [98]. The use of a NiFe thin film offers (i) a large exchange bias at the interface with the antiferromagnetic IrMn layer and (ii) a lower spontaneous magnetization compared to cobalt, so that small-sized skyrmions are expected owing to a reduced dipolar energy [89, 90]. To induce exchange bias, the samples were annealed at 200°C for 2 minutes under a large out-of-plane magnetic field $B_z = 570$ mT. Element-resolved scanning

transmission electron microscopy of the sample was performed by the team of R. E. Dunin-Borkowski at the Peter Grünberg Institute in Jülich (Germany). The image of a cross-section of the sample reveals sharp interfaces with negligible intermixing [see Fig. 2.14].

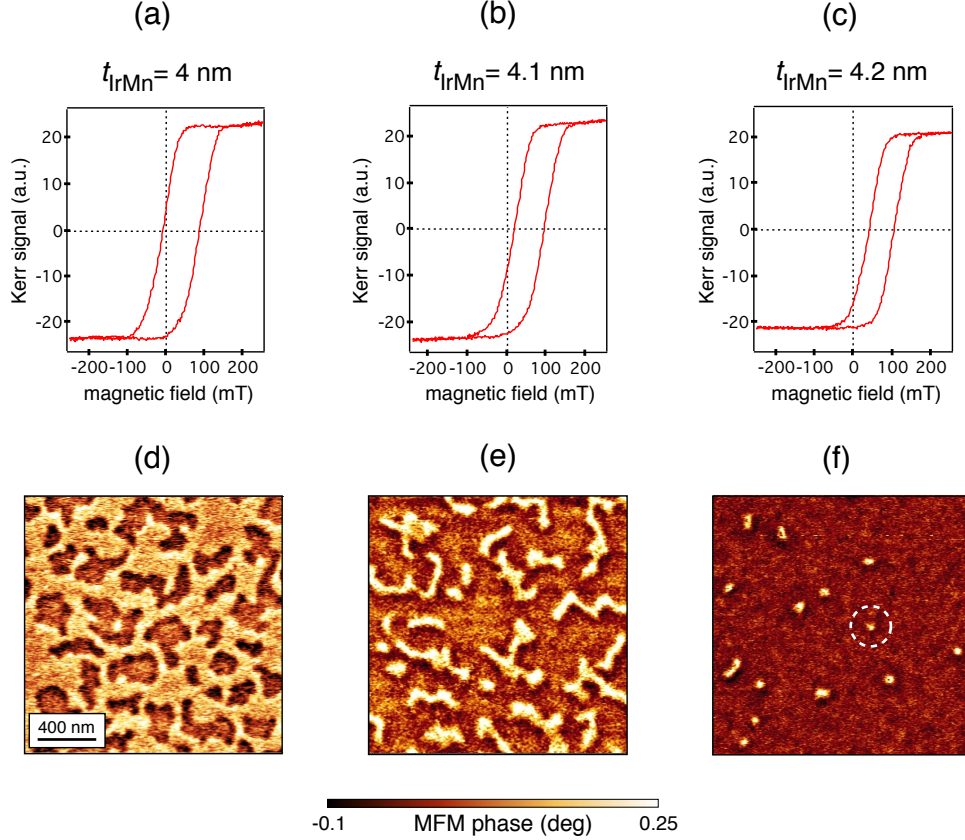


Figure 2.15: Optimization of the multilayer stack composition. (a-c) Magneto-optical Kerr rotation recorded as a function of a magnetic field applied perpendicularly to the film plane for various IrMn thicknesses, (a) $t_{\text{IrMn}} = 4$ nm, (b) $t_{\text{IrMn}} = 4.1$ nm and (c) $t_{\text{IrMn}} = 4.2$ nm. For these experiments, the NiFe thickness is $t_{\text{NiFe}} = 2.1$ nm. (d-f) Corresponding magnetic force microscopy (MFM) images recorded at zero external magnetic field. The smallest skyrmion is marked with the white dashed circle in (f). It is characterized by a full width at half maximum $w_{\text{MFM}} \sim 35$ nm.

An important parameter controlling the skyrmion size and stability is the NiFe film thickness, t_{NiFe} , since the main skyrmion energy terms, namely the magnetic anisotropy, DMI and dipolar fields, are strongly dependent on the thickness of the ferromagnetic layer [61]. Similarly, the exchange bias and magnetic anisotropy are highly sensitive to the IrMn film thickness t_{IrMn} [104]. In order to find the optimal sample composition stabilizing zero-field skyrmions, gradients of NiFe and IrMn thicknesses were deposited along the x and y axis of the 100-mm wafer, respectively, using off-axis deposition. Systematic hysteresis loop mapping was then carried out at CEA Spintec using magneto-optical Kerr effect supplemented by MFM.

Optimal sample composition stabilizing zero-field skyrmions was achieved for a NiFe thickness

around $t_{\text{NiFe}} = 2.1$ nm, close to the out-of-plane to in-plane transition of the magnetization, and an IrMn thickness around $t_{\text{IrMn}} = 4.2$ nm. Typical magnetic hysteresis loops recorded for different thicknesses of the IrMn layer are shown in Figure 2.15(a-c). The observation of slanted hysteresis loops suggests the existence of multidomain states. In addition, these measurements indicate that the effective exchange bias field B_{int} , characterized by the overall shift of the hysteresis loop, increases with the IrMn film thickness. MFM images recorded at zero external magnetic field for different IrMn thicknesses, *i.e.* for different exchange bias fields B_{int} , are shown in Figure 2.15(d-f). For $t_{\text{IrMn}} = 4$ nm, the small exchange bias field combined with a large coercivity of the ferromagnetic layer leads to a multidomain state, with a nearly equal density of up- and down-magnetized domains [Fig. 2.15(d)]. As the IrMn thickness is slightly increased to $t_{\text{IrMn}} = 4.1$ nm, down-magnetized domains start to shrink and few skyrmions can be observed [Fig. 2.15(e)]. Further increase in IrMn thickness ($t_{\text{IrMn}} = 4.2$ nm) leads to the stabilization of well-isolated skyrmions in the ferromagnetic layer [Fig. 2.15(f)]. The smaller skyrmions exhibit a full width at half maximum down to ~ 35 nm in the MFM image. However, as already mentioned in § 2.1.1, MFM often induces perturbations of the studied sample and therefore may modify the skyrmion size. A striking illustration of this effect will be discussed in § 2.3.4. This motivates a systematic study of the skyrmion size through non-invasive, magnetic imaging with scanning-NV magnetometry.

In the following, we will focus on the optimized Pt\Co(0.3)\NiFe(2.1)\IrMn(4.2) multilayer stack. Vibrating sample magnetometry was used to infer its effective saturation magnetization $M_s = 720$ kA/m and uniaxial perpendicular magnetic anisotropy $K_u = 350$ kJ/m³. The strength of interfacial DMI was determined by monitoring the non-reciprocal propagation of spin waves with Brillouin light scattering (BLS) spectroscopy (see § 2.2.1), yielding $D = -0.4$ mJ/m². The negative value of the D parameter promotes the stabilization of Néel skyrmions with a left-handed chirality in the exchange-biased ferromagnetic film.

2.3.2 Magnetic imaging with NV magnetometry

NV magnetometry was performed with a scanning-diamond tip characterized by (i) a probe-to-sample distance $d_{\text{NV}} = 65 \pm 9$ nm and (ii) a quantization axis defined by the polar angle ($\theta \sim 54^\circ, \phi \sim 4^\circ$) in the (x, y, z) sample reference frame. These parameters were extracted through the calibration procedures described in § 1.3.2.

Figure 2.16(a) shows a typical PL quenching image recorded at zero field above the optimized exchange-biased multilayer stack. Dark PL spots result from the stray field produced by isolated magnetic skyrmions. This observation confirms unambiguously the zero-field stability of skyrmions in the exchange-biased stack under ambient conditions. The full-width at half maximum w and the contrast $\mathcal{C}$ of the dark PL spots were inferred by fitting line profiles with a Gaussian function for a set of 51 isolated skyrmions [see Fig. 2.16(b)]. The resulting statistics are shown in Figure 2.16(c-d). Data fitting with a normal distribution leads to a mean value of the width $\bar{w} = 66 \pm 1$ nm, with a standard deviation $\sigma_w = 20 \pm 2$ nm [see Fig. 2.16(c)]. For the PL quenching contrast, which is linked to the stray field amplitude, a mean value $\bar{\mathcal{C}} = 23 \pm 1\%$ is obtained with a standard deviation $\sigma_{\mathcal{C}} = 6 \pm 1\%$ [see Fig. 2.16(d)].

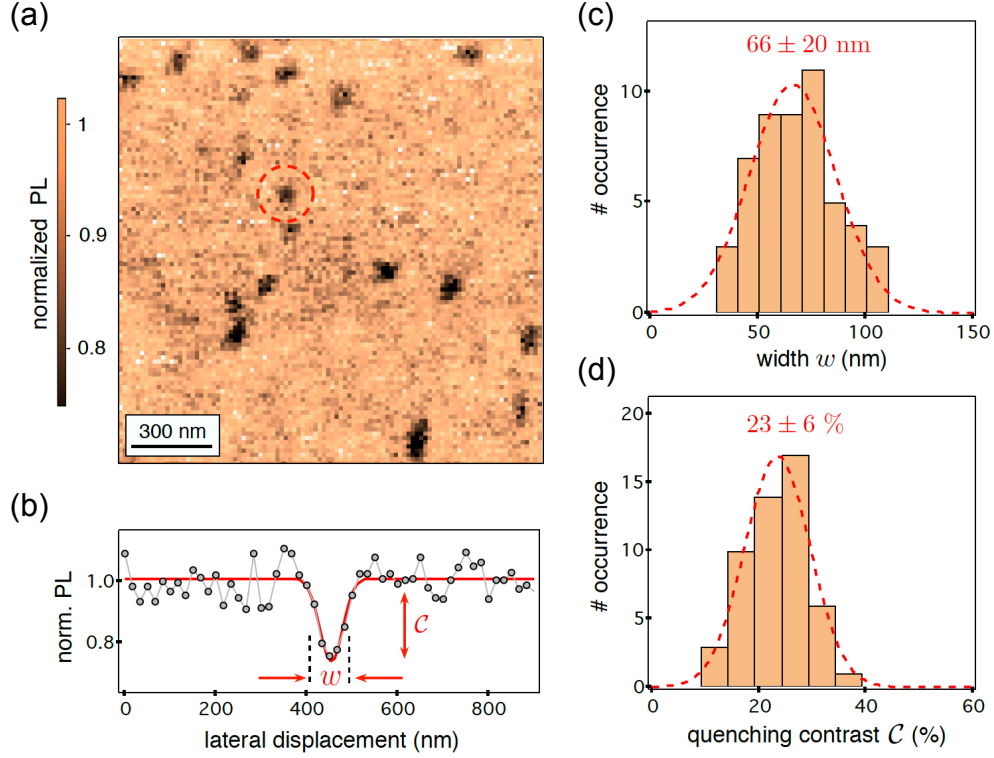


Figure 2.16: Imaging the exchange-biased multilayer stack with NV magnetometry. (a) PL quenching image recorded above the optimized exchange-biased multilayer stack at room temperature and zero external magnetic field. (b) Line profile across the skyrmion marked with the dashed circle in (a). The profile is taken along the fast scan direction (horizontal) and the red solid line is a Gaussian fit, leading to a full width at half maximum $w = 58 \pm 8$ nm and a PL quenching contrast $C = 27 \pm 2\%$. (c,d) Statistical distributions of (c) the width w and (d) the quenching contrast C , inferred from measurements over a set of 51 isolated skyrmions. The dashed solid lines are data fitting with normal distributions. The values written on top of the histograms correspond to the mean value $\pm$ standard deviation of the distributions.

Simulation of PL quenching images

In order to extract informations on the actual skyrmion size from these experimental results, simulations of the PL quenching image were performed for various skyrmion diameters d_{sk} . The details of the simulation procedure are given in Appendix. The skyrmion profile was simply modeled by a 360° Néel domain wall with a left-handed chirality [105] and a characteristic domain wall width $\sqrt{A/K_{\text{eff}}}$, where A is the exchange constant and $K_{\text{eff}} = K_u - \mu_0 M_s^2/2$ denotes the effective magnetic anisotropy. The exchange constant was fixed to $A = 6$ pJ/m, a value in line with measurements in permalloy ultrathin films [93]. The stray field distribution was first calculated at the flying distance of the NV sensor $d_{\text{NV}} \sim 65$ nm for different skyrmion diameters d_{sk} . The resulting PL quenching images were then simulated by using the model of magnetic-field-dependent photodynamics of the NV defect introduced in § 1.1.4. Typical simulations of PL quenching images are shown in Figure 2.17. Note that the slight asymmetric shape of the simulated images results from the orientation of the NV defect quantization axis. A fair agreement with experimental results is obtained for $d_{\text{sk}} = 60$ nm, both for the measured

mean values of the width and PL quenching contrast. We can thus conclude that skyrmions with diameters around 60 nm are stabilized at zero field in our optimized exchange-biased sample, corresponding to a reduction of skyrmion diameter by one order of magnitude compared to previous reports [104].

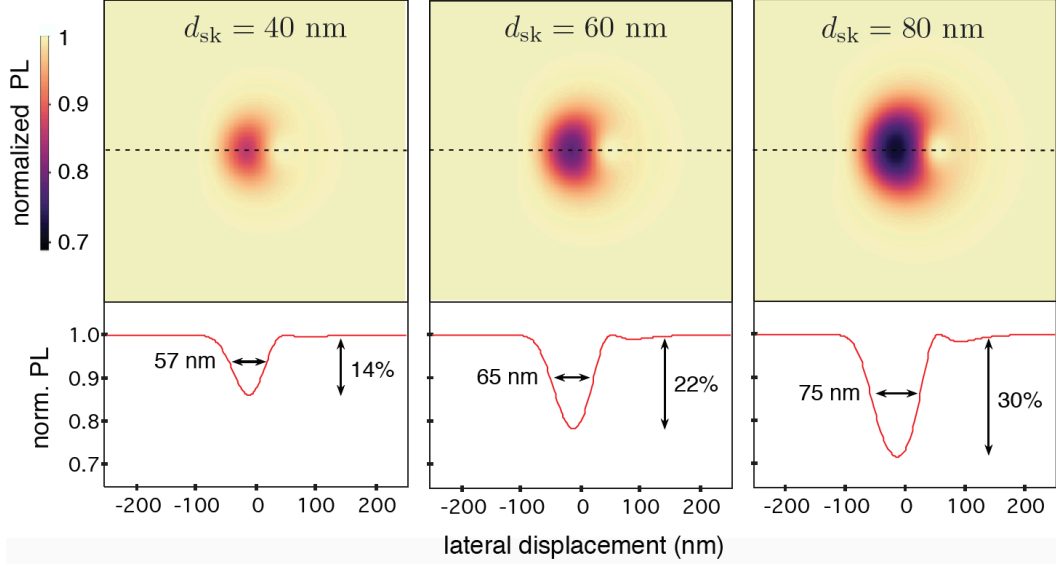


Figure 2.17: Simulations of the PL quenching image. The simulation was performed for skyrmions with diameters $d_{\text{sk}} = 40$ nm, 60 nm and 80 nm (from left to right). Line profiles taken across the skyrmions (black dashed lines) are displayed below the PL maps, indicating the width and the quenching contrast. The best agreement with experimental results is obtained for $d_{\text{sk}} = 60$ nm.

Discussion

We note that smaller skyrmions, down to ~ 10 nm diameter, have been recently observed at zero field in ferrimagnetic thin films close to the magnetization compensation at room temperature. However, such skyrmions were found as metastable states, with lifetimes limited to few hours [102]. More generally, stable, sub-100 nm skyrmions have been obtained at room temperature by using multiple repetitions of magnetic multilayers, in which the thermal stability is enhanced by the large sample thickness [54, 97]. Nevertheless, skyrmion stabilization always requires to apply external magnetic fields in such multilayer stacks. Our results therefore demonstrate the potential of exchange-biased multilayer stacks to stabilize small-sized skyrmions at zero external magnetic field in ultrathin magnetic films. In such samples, exchange bias might enhance the skyrmion stability, a behavior already pointed out for the magnetic moment of magnetic nanoparticles [106, 107] or nanomagnets in MRAM cells [108].

2.3.3 Stability against external magnetic perturbations

In order to characterize the impact of external magnetic field perturbations on the skyrmion stability, magnetic imaging was performed before and after the application of a few-seconds pulse of an

out-of-plane magnetic field B_z . These experiments are similar to the one reported in § 2.1.2, where we explored the impact of pinning and magnetic history on the skyrmion morphology in a symmetric bilayer magnetic system. However, the amplitude of the field pulses is limited to $B_z = 10 - 15$ mT in the scanning-NV magnetometry setup. In order to probe the stability of exchange-biased skyrmions to larger fields, the experiments were performed by MFM at CEA Spintec. In such setup, magnetic field pulses with amplitudes up to 200 mT can be achieved.

In these experiments, positive (resp. negative) magnetic field pulses result in a dilatation (resp. compression) of the skyrmion diameter, followed by relaxation at zero-field. As an example, Figure 2.18(a)-(c) show MFM images recorded before [Fig. 2.18(a)] and after the application of a field pulse of either -12 mT [Fig. 2.18(b)] or $+12$ mT [Fig. 2.18(c)]. For such field amplitudes, the skyrmion pattern is not modified. This observation indicates that the skyrmion size is mainly governed by exchange bias rather than magnetic history and pinning effects, in contrast with the results obtained in § 2.1.2 for a symmetric magnetic bilayer system.

The impact of larger fields was analyzed by measuring variations of the skyrmion density. As shown in Figure 2.18(g), the skyrmion density is little affected by field pulses with amplitudes lying between -12 and $+40$ mT. For larger fields, a different behavior is observed depending on the pulse polarity. While the skyrmion density drops for negative field pulses below -20 mT, only small variations are observed for positive magnetic fields up to $+200$ mT. This observation can be understood by considering the hysteresis loop of the exchange-biased stack [see inset in Fig. 2.18(g)]. Negative magnetic fields tend to make skyrmion smaller and thus more unstable, possibly leading to their annihilation, which results in an overall reduction of the skyrmion density. Conversely, positive magnetic fields tend to enlarge magnetic skyrmions, thus increasing their stability, or leading to the nucleation of new skyrmions. An example of skyrmion patterns recorded at zero magnetic field before and after applying a large magnetic field pulse of -200 mT are shown in Figure. 2.18(d-e). A significant decrease of the skyrmion density is observed together with a reversed MFM contrast, in qualitative agreement with the lower Kerr signal evidenced in the hysteresis loop [see inset in Fig. 2.18(g)]. However, most skyrmions of the initial state can be recovered at zero field after saturation by applying a large positive magnetic field pulse of $+200$ mT [Fig. 2.18(f)], which indicates a strong return-point memory of the sample [109]. The magnetic skyrmions are therefore imprinted in the material, most likely at pinning sites induced by thickness variations in the multilayer stack. If an external magnetic field perturbs the domain structure, the information can be recovered after the application of a large magnetic field pulse.

2.3.4 Comparing magnetic images recorded with MFM and NV magnetometry

To close this section, we give an illustration of the perturbations induced by MFM on the skyrmion morphology.

As a first experiment, the magnetization of the MFM tip was aligned parallel to the skyrmion core magnetization. In this case, the MFM images look very similar to the one recorded with scanning-NV

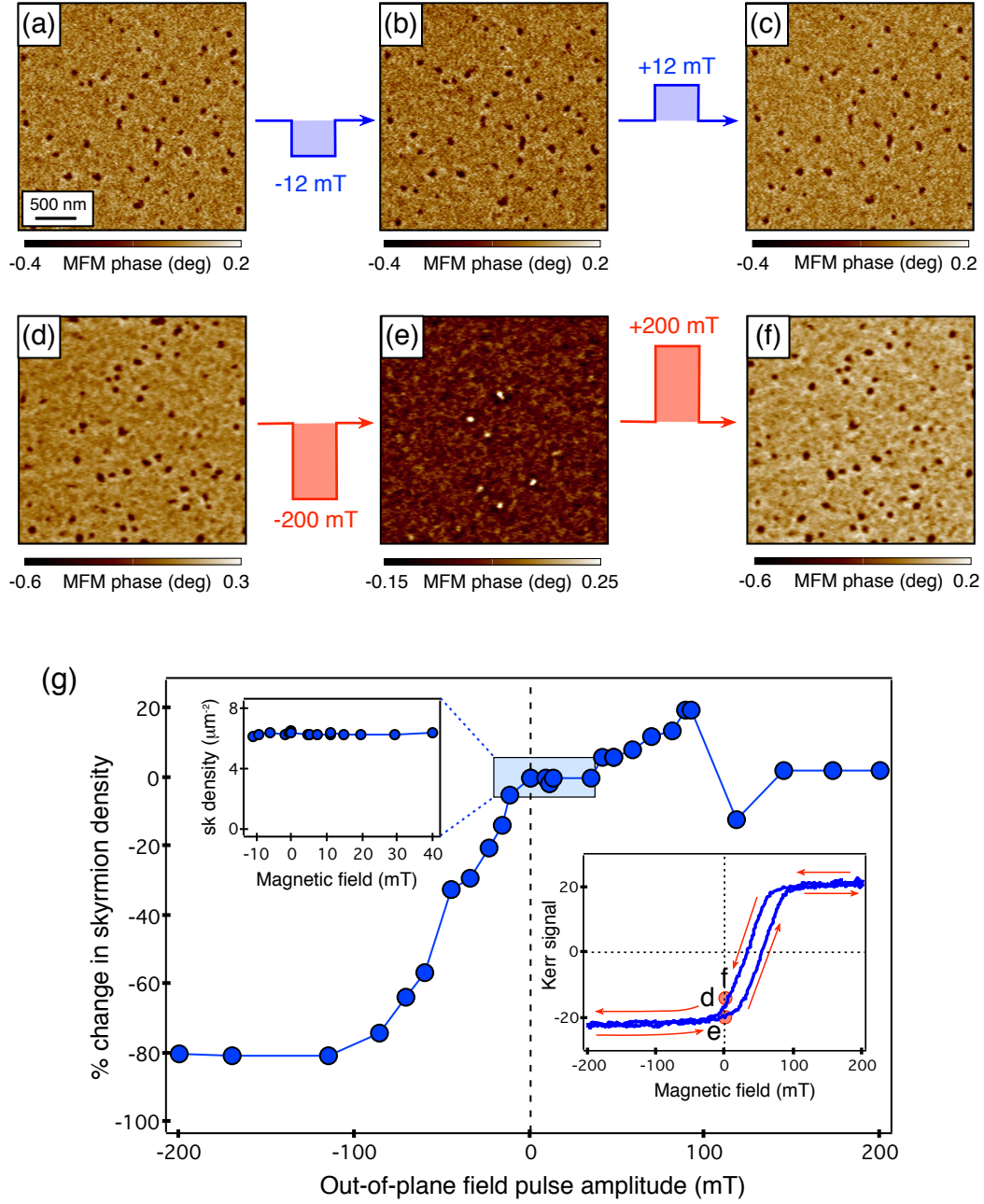


Figure 2.18: Stability against external magnetic field perturbations. (a)-(c) MFM images recorded at zero external magnetic field before (a) and after applying a few-seconds out-of-plane field pulse of (b) -12 mT and (c) $+12$ mT. (d-f) Same experiment before (d) and after applying a field pulse of (e) -200 mT and (f) $+200$ mT. (g) Percent change in skyrmion density as a function of the magnetic field pulse amplitude. The top left inset is a zoom on weak magnetic field amplitudes. The bottom right inset is the hysteresis loop of the exchange-biased multilayer stack measured by recording the magneto-optical Kerr rotation as a function of out-of-plane magnetic field. The letters (d,e,f) refer to the MFM images.

magnetometry, both in terms of skyrmion size and density [see Fig. 2.19(a)]. A statistical analysis over a set of 139 isolated skyrmions results in a skyrmion size distribution with a mean value $\bar{w} = 55 \pm 1$ nm and a standard deviation $\sigma_w = 13 \pm 1$ nm [see Fig. 2.19(b)]. Interestingly, the measured size distribution depends on the tip magnetization orientation. Indeed, when the tip magnetization is reversed, *i.e.* aligned antiparallel to the skyrmion core magnetization, the mean value of the skyrmion size distribution drops to $\bar{w} = 42 \pm 10$ nm [see Fig. 2.19(c,d)]. This observation reveals a sizable perturbation of the skyrmion spin texture by the stray field generated by the MFM tip. While scanning, the local gradient of magnetic field leads to a deformation of the domain walls towards or away from the tip depending on its magnetization orientation, resulting in an apparent increase or decrease of the skyrmion size. Averaging over the two magnetization orientations leads a skyrmion diameter around 50 nm, a value slightly smaller than the one inferred from NV magnetometry.

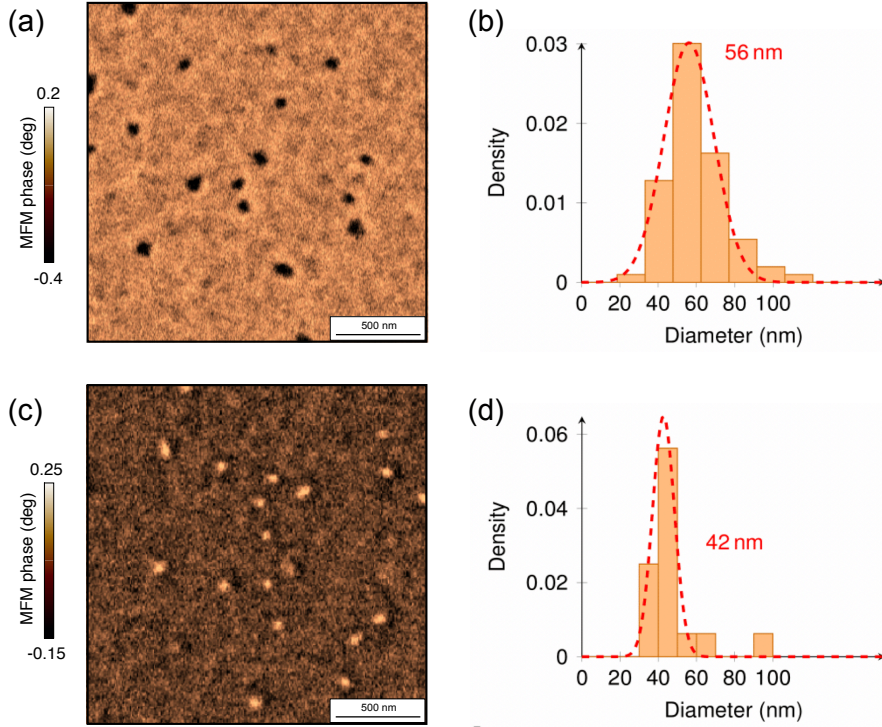


Figure 2.19: Skyrmion size distributions inferred from MFM measurements. (a) MFM image recorded above the exchange-biased multilayer stack with a tip magnetization aligned parallel to the skyrmion core magnetization. (b) Statistical distribution of skyrmion diameters inferred from MFM measurements over a set of 139 skyrmions. (c) MFM image recorded with a the tip magnetization anti-parallel to the skyrmion core magnetization. (d) Statistical distribution of diameters inferred from MFM measurements over a set of 16 skyrmions.

The stray field generated locally by the MFM tip therefore modifies the skyrmion spin texture during the observation. While this perturbation is generally seen as an issue, we note that it can also be exploited to modify spin textures in a controlled way. For instance, recent experimental works have demonstrated the controlled nucleation of magnetic skyrmions in ultrathin films by using the stray field of a MFM tip [8, 110, 111, 112]. However, this technique must be used with great caution in order to

2. Exploring the physics of skyrmions in ultrathin ferromagnets

avoid experimental artefacts. As an illustration, Figure 2.20 shows a MFM image recorded with a tip magnetization aligned antiparallel to the skyrmion core and a lowered scanning height, such that the tip-sample interaction is enhanced. In such experimental conditions, a reversed MFM contrast is observed at the skyrmion center. Such a magnetic image could be interpreted by considering the stabilization of a double core spin textures also called *skyrmonium*. This exotic spin structures have already been described in the past by several authors [113, 114, 115, 116]. While skyrmions are characterized by a continuous spin rotation by 2π along the skyrmion diameter, *skyrmonium* spin textures correspond to a continuous rotation by 4π . By fitting a line profiles across the spin texture with the sum of two Gaussian functions, a full width at half maximum $w_i = 14 \pm 1$ nm is obtained for the inner core. Surprisingly, this value is beyond the spatial resolution of the MFM apparatus, pointing out that the reverse contrast at the skyrmion center is here an artefact. It results from a magnetization reversal at the very apex of the MFM tip, which is induced by the stray field produced by the sample. Such a field is maximal above the skyrmion center. When the field decreases, the magnetic grains of the MFM tip are switched back to their initial configuration through exchange coupling with the upper part of the tip. This effect explains the reversed contrast in the MFM image shown in Figure 2.20.

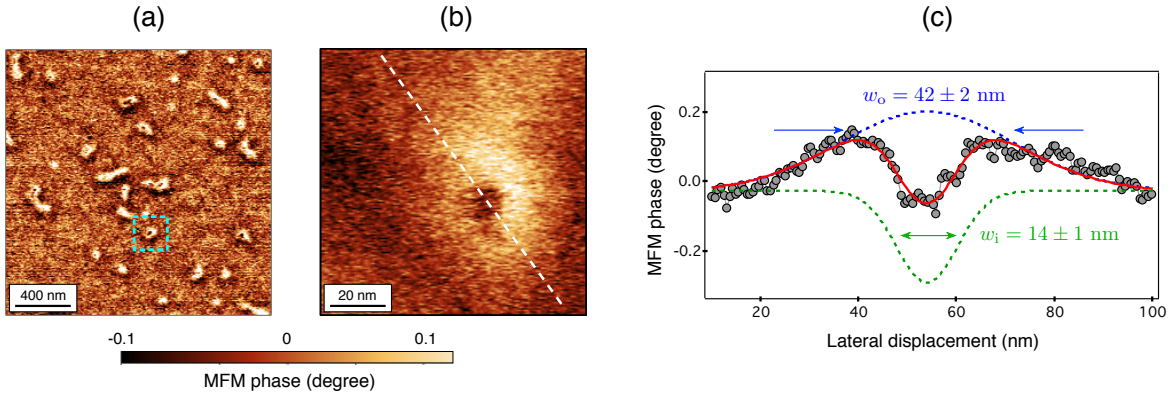


Figure 2.20: Experimental artifacts in MFM images. (a) Typical MFM image showing a reversed contrast at the center of skyrmions. (b) Zoom on the region indicated with a dashed square in (a). (c) Line profile along the white dashed line in (b). The red solid line is data fitting with a sum of two Gaussian functions. The blue and green dashed curves are the outer core and inner core resulting from the Gaussian fit, respectively.

The experiments described in this paragraph illustrate the need of non-invasive magnetic microscopy techniques, such as NV magnetometry, for studying the magnetic order in ultrathin magnetic materials.

2.3.5 Conclusion

To summarize, we have shown that magnetic skyrmions with diameters around 60 nm can be stabilized at room temperature and zero magnetic field in an optimized exchange-biased Pt\Co\NiFe\IrMn multilayer stack. In such samples, exchange bias provides an immunity of the skyrmion spin texture

to moderate external magnetic field perturbations, in the tens of mT range, which is an important feature for applications as memory devices. These results establish exchange-biased multilayer stacks as a promising platform towards the effective realization of memory and logic devices based on the manipulation of magnetic skyrmions.

2.4 Outlook

In this chapter, we have examined the physics on magnetic skyrmions in ultrathin magnetic layers using a non-invasive, scanning-NV magnetometer operated in PL quenching mode under ambient conditions.

We first examined the impact of structural disorder and magnetic history on the morphology of skyrmions in a symmetric bilayer system, opening the way to an in-depth understanding of skyrmion dynamics in real, disordered media. In the quest to find a host ferromagnetic material providing efficient current-induced skyrmion dynamics, we then explored the possibility to use Heusler alloys, a class of ferromagnetic materials with an intrinsically low magnetic damping coefficient. We demonstrated (i) the first stabilization of magnetic skyrmions in a single ultrathin layer of Co_2FeAl and (ii) an efficient current-induced nucleation process mediated by the SHE-induced spin torque, which is not specific to Heusler alloys and could be advantageous for future skyrmion-based devices. However, current-induced skyrmion motion experiments revealed that pinning effects still limit skyrmion velocity, even in a host material with low magnetic damping. In the last part of this chapter, we finally demonstrated the stabilization of 60 nm skyrmions at zero external magnetic field in an optimized exchange-biased multilayer stack. Compared to previous studies [104], this result corresponds to a reduction of skyrmion diameter by one-order of magnitude. The next challenge will be to investigate the skyrmion dynamic properties under current pulses in such exchange-biased multilayer stack in order to qualify if exchange bias could enable to mitigate pinning effects.

To close this chapter, we note that despite many impressive results recently reported in the literature [53, 54], ferromagnetic skyrmions suffer from at least three limitations in view of applications:

- First, strong dipolar interactions inherent to ferromagnetic materials prevent the stabilization of ferromagnetic skyrmions with very small size [90, 102];
- Second, besides pinning effect, current-induced skyrmion motion along a track is disturbed by a transverse deflection resulting from the Magnus force, a phenomenon coined as skyrmion-Hall effect, which is a direct consequence of topology [73];
- Third, large current densities are still required to move efficiently ferromagnetic skyrmion and their velocity hardly exceeds a few tens of meters per second [53, 54].

In principle, all these limitations can be circumvented by working with **skyrmions in antiferromagnetic materials** [117]. Indeed, vanishing dipolar fields in AF materials promise the stabilization

of sub-10 nm skyrmions at room temperature and zero applied magnetic field [90]. A first experimental illustration of this key advantage was recently reported by using a ferrimagnetic material close to the magnetization compensation. In such conditions, skyrmion down to ~ 10 nm diameter could be stabilized at zero field [102]. Furthermore, antiferromagnetic skyrmions are predicted to move in straight lines owing to the compensation between the Magnus force from the two spin sublattices of the antiferromagnet [ref]. Finally, theoretical simulations indicate that antiferromagnetic skyrmions should move orders of magnitude faster than their ferromagnetic counterpart and could be driven with much lower current densities. Antiferromagnetic skyrmions have been recently observed in synthetic antiferromagnets [118]. One of the next challenge will be to investigate the properties of these topological spin textures with a scanning-NV magnetometer.

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NV-based magnetometry is currently developed along two main architectures. The first one relies on functionalized AFM probes hosting single NV centers which are scanned above the sample of interest. This architecture was at the core of the two previous chapters. Though it provides an ultimate spatial resolution down to few tens nanometers, it requires relatively long acquisition times, higher than few tens ms per pixel. A second architecture relies on diamond chips put in contact with the probed sample and hosting near-surface NV centers. These latter are probed optically in a wide-field configuration, enabling fast images acquisition yet with a spatial resolution bounded by the diffraction limit

to few hundreds nm. In the last years, this architecture has been used in several groundbreaking applications in various fields of research. For instance, in nuclear magnetic resonance (NMR) spectroscopy, it enabled to resolve chemical-shift spectra from molecules [119]. Another example relates to condensed matter physics, enabling the investigation of the drastic modifications of some material properties when exposed to high pressures [120].

This chapter deals with the performances optimization of this second architecture for fast and wide-field magnetic imaging. In a first section, we will recall its operation principle and the related requirement specifications to boost its performances (§3.1). These include the control over the orientation of the NV centers, their density and in-depth localization. In a second section, we will introduce the various approaches currently pursued to produce quantum-graded diamonds hosting NV centers and will focus on the most favourable one, that is Chemical Vapour Deposition (CVD) growth (§3.2). The strategies that have been implemented up to now to control the NV centers orientation during CVD growth, will be summarized. In a third section, I will detail our results on the tailoring of the NV centers orientation by tuning the CVD chamber temperature on a (113)-oriented diamond substrate (§3.3). Last, we will apply this tuning parameter to localize in-depth dense and preferentially-oriented NV centers, thanks to the temperature-dependent incorporation of NV defects during the CVD growth (§3.4).

All the investigated samples were grown by O. Brinza, A. Tallaire and J. Achard at the Laboratoire des Sciences des Procédés et des Matériaux in Villeteuse. The results presented in this chapter have been published in S. Chouaieb *et al.* *Diamond and Related Materials* **96**, 85 (2019).

3.1 Magnetic imaging with an ensemble of NV defects

In this section we will introduce the main principles behind wide-field magnetic imaging with NV centers. We will then discuss the key requirements to boost the performance of such architecture, in particular the sensitivity.

3.1.1 Principle of operation of wide-field NV-based magnetic imaging

A scheme of a wide-field configuration experiment is shown in Figure 3.1. In such imaging configuration, the central element is the diamond probe, that consists of either a dispersion of nanodiamonds on the probed sample or a diamond substrate holding a thin layer of NV centers close to the surface and put in contact with the magnetic sample of interest. These NV centers are optically excited and detected in a wide-field configuration. Optical excitation of the NV centers is usually achieved using a green laser set to wide-field illumination by focusing the laser onto the back-focal plane of the objective. Note that in order to avoid any heating or damage due to the high power laser beam, total internal reflection excitation is also adopted : the excitation laser is injected with an appropriate angle in the diamond slab and is propagated to the field of view by total internal reflections at the faces of the diamond crystal [121]. The two-dimensional photoluminescence produced by the NV defects is collected

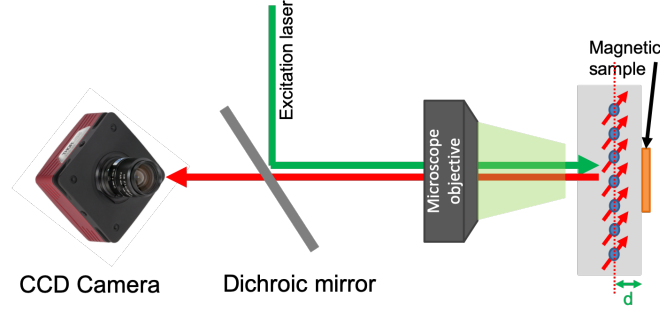


Figure 3.1: Wide-field measurement configuration. The magnetic sample is commonly deposited directly on a diamond substrate which contains a highly doped thin layer of NV centers near its surface. Magnetic imaging is achieved by optically exciting the NV centers ensemble by a green laser set to wide-field illumination, and by optically recording the ESR spectra onto a CCD camera, by sweeping the microwaves (MW) and simultaneously detecting the entire field of view.

by the same microscope objective and projected onto a CCD camera. A microwave (MW) antenna is placed in the vicinity of the diamond chip, in order to deliver the microwave magnetic field used to induce the magnetic resonances of the NV centers. The magnetic field images are then retrieved by recording the ESR spectra on each pixel of the camera. The acquisition of these ESR spectra usually relies on a multiplexed data acquisition of a large field of view : the frequency of the microwave source is swept around the NV centers spin resonance frequency and for each microwave frequency, a complete image of the photoluminescence (PL) of NV centers, is recorded. All the PL images are then processed to extract, for each pixel, the ESR spectra, the induced Zeeman shift and thus the stray magnetic field amplitude. In such experiments, the usual field of view is about $100 * 100 \mu m^2$. This simple experimental implementation comes with the price of a reduced spatial resolution compared to the case of single scanning NV center, it is in fact limited by diffraction to the hundreds of nanometers range [122].

Such imaging architecture has been first implemented in Refs. [123, 22]. In Ref. [123], a layer of NV centers was created by ion implantation into an ultrapure [100] diamond slab. This ensemble was then used to image the magnetic field distribution emanating from gold microwires carrying current that were deposited directly on top of the diamond as shown in Figure 3.2(a). Taking advantage of the 4 projections of the magnetic field along the 4 orientations of NV's in the ensemble, vectorial reconstruction of the magnetic field was achieved through an analysis of the multiplexed ESR spectra recorded on each pixel individually. In this experiment, the imager achieved a sensitivity down to $20 \text{ nT}/\sqrt{Hz}$ and a spatial resolution of about 250 nm. In Ref. [22], the diamond chip consisted of a (110) diamond crystal doped with a high concentration of NV defects. It was applied to image the stray magnetic field produced by permalloy $Ni_{0.8}Fe_{0.2}$ squares patterned on top of the diamond substrate. In these experiments (see Fig. 3.2(b) and (c)), the spatial resolution was about $\approx 300 \text{ nm}$ and the sensitivity reached $10 \mu T/\sqrt{Hz}$. This technique was further employed in the following years for multiple applications in various areas. It enabled the mapping of the magnetic field produced by magnetotactic bacteria [19], the characterization of ferromagnetic mineral samples that were saturated by ancient magnetic fields [20] or the imaging of

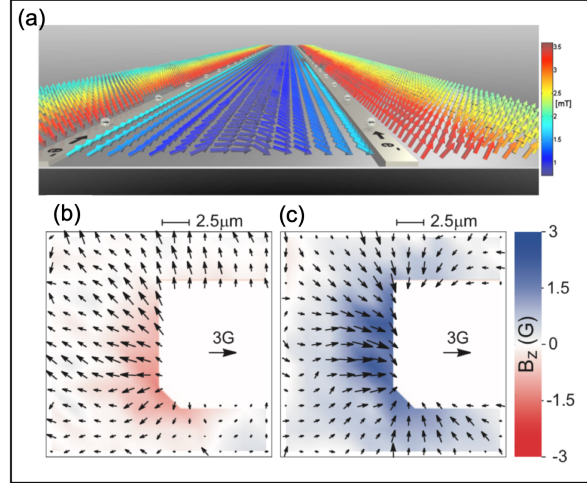


Figure 3.2: Proof of principle experiments of wide-field magnetic imaging with NV centers. (a) Magnetic field produced by two gold microwires carrying 75 mA of DC current. From [123]. (b-c) Magnetic field reconstruction map from a permalloy disk with negative (b) and positive (c) magnetization with respect to the external applied magnetic field. From [22]

current flow in graphene [21], to name a few.

3.1.2 Requirements specifications for wide-field NV-based magnetometry

Among the specifications around the performances of any magnetic imagers, two of them will be here considered : the spatial resolution and the sensitivity. In wide-field NV-based imaging configurations, the spatial resolution is diffraction-limited, with a lower bound around few hundreds nm. Regarding the sensitivity, let's recall here the expression of the measurement sensitivity for the case of a single NV center η , defined in the first chapter.

$$\eta \approx \frac{h}{g\mu_B} \frac{\Delta f_r}{C\sqrt{R}} \quad (3.1)$$

Here C is the contrast of the optically-detected ESR spectrum, R is the number of detected photons per second and Δf_r denotes the linewidth of the detected resonance peak whose ultimate limit equals $\approx 1/T_2^*$ with T_2^* being the inhomogeneous spin dephasing time of the NV center [124]. The contrast is an intrinsic property of the NV defect. The collection rate R can be improved by relying on photonic structures. The spin dephasing time can be optimized by relying on diamond crystals with an extremely low content of impurities [124]. Another strategy to further improve the sensitivity relies on increasing the number of sensing spins N_{spin} . Indeed, for an ensemble of NV defects, the sensitivity scales as [124];

$$\eta_e \propto \frac{h}{g\mu_B} \frac{1}{C_e \sqrt{R N_{spin} T_2^*}} \quad (3.2)$$

Where C_e is the ESR contrast for an ensemble of NV defects Yet, increasing the density of the NV defects, brings many challenges for material scientists. These challenges include [125]:

- **Maximizing the spin coherent time T_2^***

The spin dephasing time is mainly limited by the magnetic interactions with a bath of paramagnetic impurities both inside the diamond matrix and on its surface. From this point of view, the use of bulk crystals [47] is more favourable than the use of nanodiamonds [126, 127]. In the case of bulk diamond, a key challenge is to produce diamond crystals with an extremely low density of paramagnetic impurities.

- **Enhancing the density of NV defects**

The creation of negatively charged NV defects in diamond usually leads to the creation of other N-based impurities, such as the neutral luminescent NV^0 defects. The luminescence produced by such optically-active N-based impurities may impair the signal-to-noise ratio when optically detecting the ESR spectra. In addition, the increased fraction of incorporated N content, may lead to a higher contribution of the electron spin bath of nitrogen impurities (P1 center) and of the ^{14}N nuclear spin bath, degrading by the way the spin coherence. The associated challenges here relates to the enhancement of the N to NV conversion ratio and to the control of the NV's charge states.

- **Spatially localizing in depth the NV defects**

The stray magnetic field produced by the sample of interest, produces a magnetic field gradient inside the diamond matrix. As such, it is of prime importance to precisely position all NV centers in-depth near the diamond surface, in order to precisely control the distance between the NV's spins and the magnetic sample. This requires to create thin layers doped with NV defects, usually referred to as delta-doped layers, close to the diamond surface.

- **Controlling the NVs orientation**

In standard (001) oriented diamond, the NV defect's orientation is equally distributed along the four equivalent directions. Since the NV spin measures the projection of the stray magnetic field along its quantization axis, the use of NV ensembles leads to four distinct projections of the magnetic field. The recorded ESR spectra on NV defects ensemble, will then feature eight ESR peaks as shown in Figure 3.3(b), unlike ESR spectra recorded on single NVs that features solely two peaks [see Fig. 3.3(a)]. For each peak, only a quarter of the spins are contributing to the detected signal and the others produce background photoluminescence. The ESR contrasts are therefore affected with an order of magnitude reduction [124] as shown in Figure 3.3. This translates into a decreased sensitivity. Yet, this effect could be avoided if one could promote a preferential orientation of the NV defects during their creation.

Some of the strategies developed to address these challenges, will be described in the next section. We will thereafter mainly focus on the control of the NVs orientation and their in-depth localization within delta-doped layers.

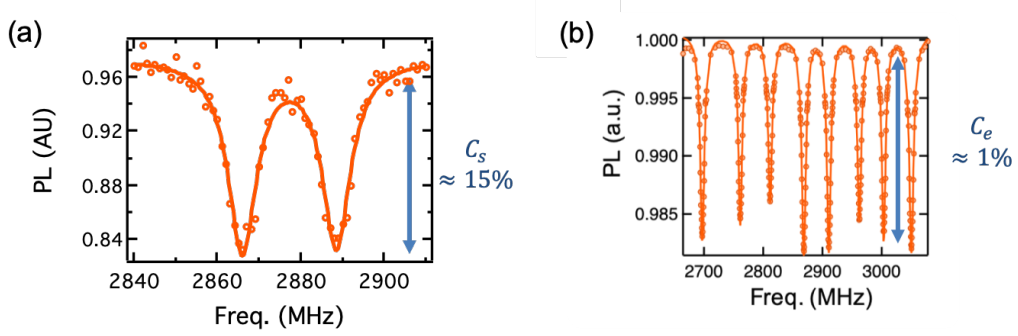


Figure 3.3: ESR spectra in the presence of a magnetic field. (a) Measured on a single NV center. (b) Measured on an ensemble of NV defects in a standard (001) oriented diamond with a contract C_e of about 1%. From [128]

3.2 State-of-the-art in the control of the NV orientation

In this section, we will first give a short summary of the various strategies implemented to grow ultra-pure diamond crystals and incorporate NV centers. We will afterwards present the different techniques that have been developed for controlling the NV centers orientation, by use of non-classical growth orientations.

3.2.1 Creation of localized in-depth layers of NV defects with long dephasing times

Diamond growth is usually done by High-Pressure-High-Temperature (HPHT) or Chemical Vapour Deposition (CVD) techniques. In view of quantum-enabled applications, the purity of HPHT diamond keeps limited and pure diamond films homoepitaxially grown by CVD on HPHT substrates, are usually preferred [129, 130].

Plasma assisted Chemical vapor deposition (CVD) is indeed a technique that produces diamond sample with extremely high purities. Growth is achieved over a diamond seed (a HPHT substrate for instance) placed in the growth chamber. This chamber is filled with carbon-containing gas (mixture of hydrogen and methane) and heated at a temperature in the range of 700 to 1100 °C (see Fig. 3.4(a)). Activation of the gas is performed by applying a microwave field into the resonant cavity reactor (see Fig. 3.4(b)). The microwave beam causes the gas molecules to break down and the carbon to precipitate out of the plasma cloud; the carbon atoms then diffuse towards the colder, flat diamond seed plates and deposit onto the seed crystal. High microwave powers are preferred for achieving high growth rates and a low content of structural defects, while low microwave powers enable a better nm-scale control on the thicknesses of the created layers and on the precise positioning of the dopants or colour centers. An asset of CVD growth lies in its ability (i) to prepare isotopically enriched layers, enabling to reduce the contribution of the ^{13}C nuclear spin bath and hence enabling the creation of NV defects with enhanced spin coherence times and (ii) to engineer stacked layers doped with various impurities.

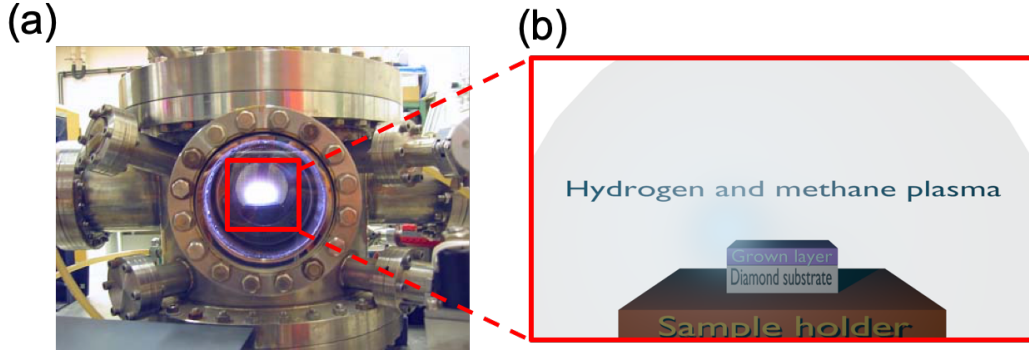


Figure 3.4: Chemical Vapour Deposition for diamond film growth. (a) Photography of the plasma enhanced chemical vapor deposition chamber from the Laboratoire des Sciences des Procédés et des Matériaux in Villetaneuse. (b) Scheme of the growth of a diamond sample in a CVD chamber : a diamond seed is incorporated in the chamber filled with a H_2 and CH_4 gas mixture.

Incorporation of the NV defects in such CVD-grown diamond films, can be done in two main ways. A first way consists of implanting in the diamond crystal nitrogen ions or N-content molecules, creating vacancies (possibly simultaneously with the N impurities introduction) and then annealing the sample at high temperature (in the 800-1000 °C range) to promote the recombination of the vacancies with the nitrogen atoms. While implantation enables relatively accurate in-depth localization of the NV centers [131], the major constraint of implantation lies in the usually low coherence time of the created defects, probably due to the creation of unwanted paramagnetic defects during the implantation process [132, 133]. Moreover, the required surface proximity of the delta-doped layer is only achieved at low energy implantation, which translates into a low conversion yield. Highest coherence times are obtained on defects that are created by in situ doping of the diamond film during growth. N doping during CVD growth can indeed be carried out by adding into the plasma another precursor gas containing N atoms (such as N_2). This technique enables to create NV centers with long coherence times in a wide range of densities (from single NVs to tens ppb). Stacks of NV center doped layers can also be grown, by either turning on and off the N-content precursor gas flow [130], or modifying the substrate temperature with increased NV concentrations at lower temperature [134], or by mechanically quickly displacing the substrate in and out of the plasma region [135]. Yet, whether they are ex situ or in situ created, the NV centers exist along four equiprobable orientations in standard (100)-oriented diamond crystals (see figure 3.5-(a)). In the next section, we will discuss the strategies that have been developed to control the NVs' orientation.

3.2.2 Dependence of the NV orientation on the orientation of the growth substrate

In order to control the NV orientation, all strategies up to now relied on growth on diamond substrates with non-classical orientations.

First demonstration of preferential orientation has been obtained by CVD growth on (110)-oriented

substrates [136, 137]. This particular configuration yields a near 100% preferential orientation, however along two directions and not only one as requested : the $[111]$ and $[\bar{1}\bar{1}1]$ directions (see figure 3.5-(b)). These results were supported by quantum-mechanical simulations suggesting that the NV defect energy formation is minimized for orientations closest to the CVD growth direction, while in-plane NV orientations are highly improbable [138]. This also explains why preferential NV alignment is not observed in conventional diamond samples grown by CVD on (100)-oriented substrates, because the angle between the NV axis and the growth direction is identical for the four NV defect orientations (see figure 3.5-(a)). These predictions were further confirmed by the observation of a perfect alignment of NV defects along the $[111]$ direction in diamond samples grown on (111)-oriented substrates [139, 140, 141], for which there is just one type of the bond pointing towards the $[111]$ direction of the lattice (see figure 3.5-(c)). Such a geometry seems ideal because it also leads to an optimized collection efficiency of the NV defect emission. Yet, high quality growth on (111)-diamond crystals is hard to reach due to impurities incorporation and higher strain parameter [142, 140, 139], in particular for diamond layers thicknesses larger than 10 μm .

An alternative to the (110)- and (111)-oriented layer is the (113)-oriented diamond growth. Preferential orientation was indeed also observed in this configuration, with a proportion of 74 % of the NV's aligned along the direction closest to the growth direction (111) [143] (see Fig. Figure 3.5(d)). Despite a less pronounced preferential orientation compared to the (111) case, growth on (113)-oriented diamond features various important advantages. First, the quality of the diamond layer is improved leading to smooth surfaces and less strain. Second, the diamond layers can be grown faster and thicker. Third, doping of nitrogen at high content is easier compared to the (111) case and can be tuned with the growth temperature, as we will show in the next section.

3.3 Tuning the preferential orientation with the temperature of CVD growth

In this section, we will show that control over the crystalline orientation of NV defects in diamond can be achieved by tuning the temperature of chemical vapor deposition (CVD) growth on a (113)-oriented diamond substrate, leading to preferential alignment of the NV defects along the $[111]$ axis. In a first part, we will describe the samples under study. In a second part, the experimental methods we used to retrieve the NV orientations, will be detailed. These include measurements of the ESR spectra and of the polarization-dependent PL intensity diagrams. In a last part, we will analyze the statistics of the NVs orientation as a function of the growth temperature.

3.3.1 Description of the samples

The samples under study were grown by O. Brinza, A. Tallaire and J. Achard at the Laboratoire des Sciences des Procédés et des Matériaux in Villetaneuse. They were synthesized by microwave plasma-assisted CVD using optical grade diamond substrates provided by Element 6 which are oriented along

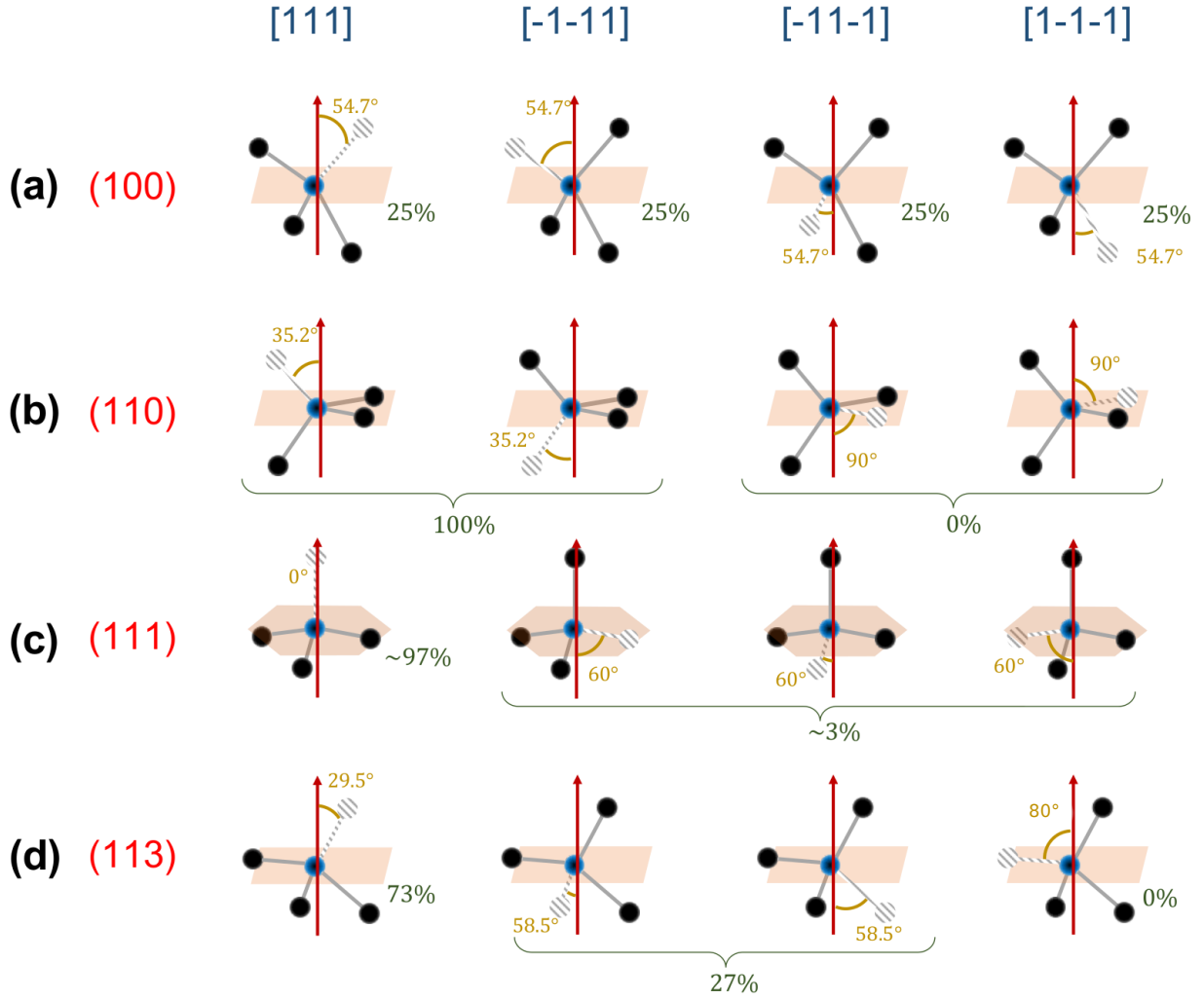


Figure 3.5: Schematic drawing of the possible NV orientations depending on the orientation of diamond sample (a) For a [100] oriented diamond sample. (b) For a [110] oriented diamond sample. (c) For a [111] oriented diamond. (d) For a [113] oriented diamond. Black circles represent the carbon atoms, blue circles the nitrogen atoms and white circles the vacancies. The angles which are indicated in yellow are the ones between the growth direction and the direction of the Nitrogen to vacancy bonds in each case, red arrows represent the growth direction. The statistics of the NV defect orientations are indicated for each crystal orientation according to Refs. [137],[139],[143] respectively for (c) to (d).

the [113] direction. In order to remove surface dislocations commonly induced by polishing, the substrates were first submitted to a H_2/O_2 (98/2) plasma etching directly inside the CVD reactor. Diamond growth was then performed under high power density conditions with a H_2/CH_4 (96/4) gas mixture at a total flow rate of 500 sccm. The growth temperature was modified by tuning the microwave power and the pressure in the CVD chamber. This procedure was facilitated by the fact that (113) CVD growth allows obtaining high quality and smooth films over a wide temperature range.

Two samples have been investigated. Sample A was grown at 1000 °C by using a microwave

power of 3.5 kW and a pressure of 250 mbar, while sample B was grown at 800 °C by decreasing both the microwave power and the pressure to 2.8 kW and 180 mbar, respectively. The in-situ creation of NV defects is done by adding a slight amount of N₂ (about 2 ppm) into the gas phase throughout the entire growth run. The resulting growth rates were in the range of 10 to 20 μm/h depending on the power density conditions. The growth temperature was measured with an accuracy of about ± 30 °C.

3.3.2 Optical discrimination of the NV defects orientation

Unicity of the NV defects

Individual NV defects were optically isolated in these (113)-oriented diamond samples with a scanning confocal microscope operating under green laser excitation at ambient conditions. In a first stage, the unicity of the probed NV defects was experimentally confirmed via photon correlation measurements, as described in chapter 1 (§1.3.2). Optical excitation of the NV color centers is realized with a continuous green laser operating at 532 nm wavelength, focalized through an oil-immersion microscope objective with a numerical aperture of 1.37. In order to perform the raster-scan images of the sample, the microscope objective is mounted on a piezo-electric stage enabling translations within three axes with displacement range of 50 * 50 μm² in transverse and axial direction. The photoluminescence emitted by the NV centers is collected by the same objective, is filtered with a dichroic mirror and bandpass filter centered at 697 nm with 75 nm transmission window, and is detected by a set of two avalanche photodiodes operating in photon counting mode in a Hanbury-Brown and Twiss configuration. The Hanbury Brown and Twiss consists of a beam splitter separating the detected signal into two optical paths, each detected by an avalanche photodiode. The detected signals on each photodiodes are then recorded, in order to build the histogram of the time correlation between two photodetection events, one on each photodiode. Supposing that the probed luminescence arises from a single NV center, solely one photon is emitted per excitation cycle. This photon can be detected on one of the APD or the other, but never on both APDs simultaneously since the photon can not be split into two on the beamsplitter. This translates into a drop in the histogram at null time delay, with a coincidence rate equal to zero. This antibunching effect is illustrated on Figure 3.6-(c) : the number of coincidences goes down to almost zero at null delay, confirming the unicity of the probed defect.

ESR spectrum in the presence of an applied magnetic field

The NV orientation distribution was inferred from electron spin resonance (ESR) spectra recorded for a large set of individual NV defects while applying a static magnetic field B_0 . In the weak magnetic field regime, the ESR frequencies are indeed given by (see section §1.1.3):

$$f_{\pm} = D \pm \frac{g\mu_B}{h} B_{NV} \quad (3.3)$$

where B_{NV} is the projection of the applied magnetic field on the NV defect quantization axis. In our experiments, the orientation of the magnetic field B_0 was chosen so that all four NV defect orientations could be easily distinguished by their ESR resonances, as illustrated in Figure 3.7(a) to (d). In this

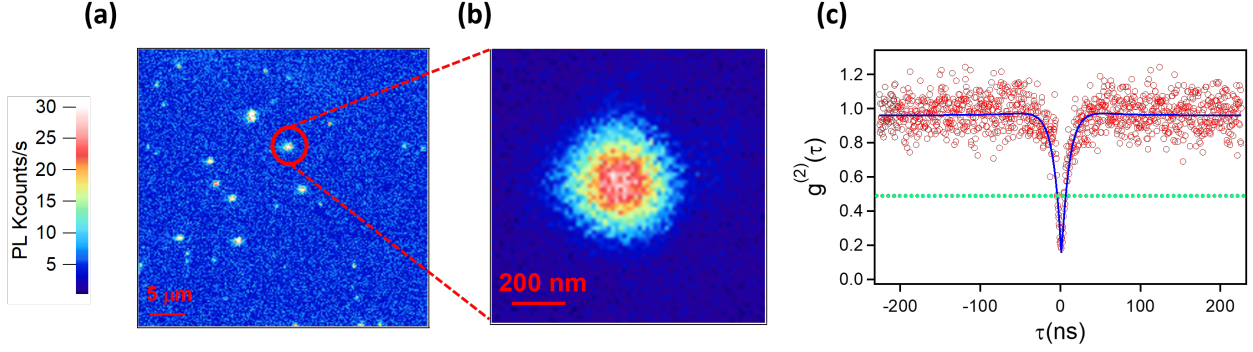


Figure 3.6: Optical isolation of single NV defects. (a) PL scan over a 40*40 μm^2 area on sample A. One can distinguish multiple spots, each corresponding to single or multiple defects. This experiment is carried at an excitation laser power of 76 μW . (b) PL scan over an area of 1*1 μm^2 zoomed on a single spot. The color scale is here identical to the one in (a). (c) $g^{(2)}(\tau)$ function recorded for the NV center in the diamond tip. The green line shows the 0.5 threshold for a single photon source, the blue solid line is a guide to the eye proving that the anti-bunching goes lower than 0.5. Red dots show data points. A Hanbury-Brown and Twiss setup similar to the one presented in §1.3.2 is used. The histogram is normalized as described in Ref [144].

experiment, the microwave excitation to a given zone on the sample is implemented via a copper wire of 25 μm diameter placed directly on the sample surface and connected to the sample holder by two copper stripes. The sample holder is a printed circuit board equipped with two SMA connectors soldered on it, corresponding to the input/output for the current driving the transitions between the spin levels of the NV center. The microwave signal is provided by a synthesizer. The ESR spectra are retrieved by sweeping the microwave frequency and recording the photoluminescence signal from the single NV centers. Four of these spectra, corresponding to four different single NV's orientation and thus featuring different Zeeman splittings, are shown on Figure 3.7. Since the direction of the applied magnetic field is not known in our experiments, the observed Zeeman splitting do not allow to determine the NV defect orientation. In order to assign each ESR spectrum to a specific defect orientation, a complementary measurement has been carried out on a subset of NV centers. This complementary experiment consists in measuring the photoluminescence intensity, while rotating the polarization angle of the linearly-polarized excitation laser. This measurement is described in more details the next section.

Polarization-dependent PL intensity diagrams

The NV center possesses two orthogonal dipoles, which are lying in the plane perpendicular to the NV center axis. The excitation rate of the NV defect is then linked to the projection of these dipoles along the linear laser polarization in the (113) diamond surface plane. Unbalanced excitation of the two dipoles leads to a polarization-dependent PL intensity whose modulation depends on the NV defect orientation. For a laser excitation power much smaller than the saturation power of the optical transition, the NV defect PL intensity can be expressed as [145]:

$$I_{tot} = I_{max} * (1 - \cos^2(\alpha - \phi) \sin^2(\theta)) \quad (3.4)$$

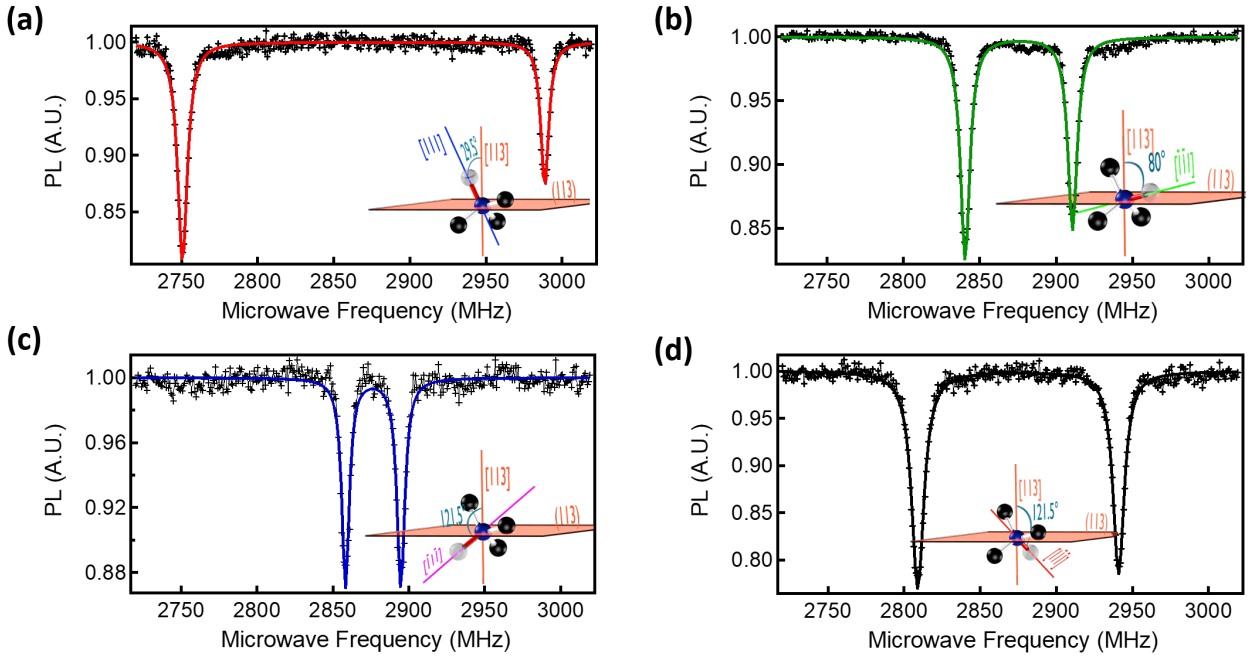


Figure 3.7: Orientation-dependent ESR spectra recorded on different single NV defects in sample B, while applying a static magnetic field B_0 . In these experiments, the ESR spectra were recorded at a low laser power of $60 \mu\text{W}$ in order to minimize saturation effects of the optical transition. The different observed Zeeman shifts could be related to different NVs orientation with $\theta = 30 \pm 2^\circ$ in (a), $\theta = 73 \pm 5^\circ$ in (b), $\theta = 126 \pm 2^\circ$ in (c) and $\theta = 127 \pm 2^\circ$ in (d). The θ angle denotes the polar angle in the (x,y,z) sample reference frame as shown in the insets. The continuous lines are fits assuming a Lorentzian shape of the resonances.

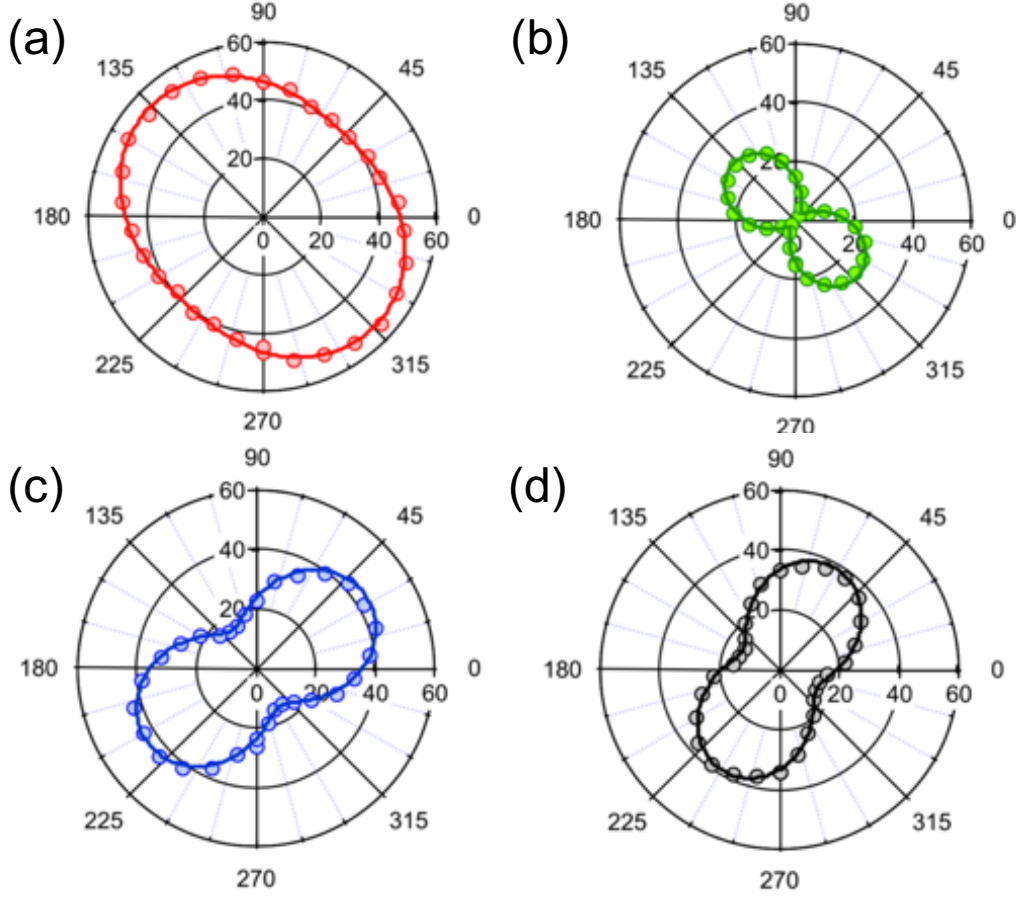


Figure 3.8: Polarization-dependent PL intensity diagrams of single NV centers inside (113)-grown sample B, with four different orientations. The different diagrams could be related to different NVs orientation with $\theta = 30 \pm 2^\circ$ in (a), $\theta = 73 \pm 5^\circ$ in (b), $\theta = 126 \pm 2^\circ$ in (c) and $\theta = 127 \pm 2^\circ$ in (d). Circles are experimental points, while solid lines are fits using equation (3.4) with θ and ϕ as fitting parameters.

In this expression, (θ, ϕ) are the spherical angles defining the NV orientation in the (x,y,z) sample reference frame with the (x,y) plane corresponding to the (113) diamond surface plane, α is the laser polarization angle in the (113) diamond surface plane, which is experimentally modified by rotating a half-wave plate placed on the excitation optical path. I_{max} depends on the collection efficiency of the NV defect emission. From this expression, one can see that a minimum of PL intensity I_{min} is obtained for $\alpha = \phi[\pi]$. Moreover, the contrast of the PL modulation depends on the NV defect polar angle through $I_{min}/I_{max} = \cos^2\theta$. As such, by fitting the measured polarization-dependent intensity diagrams with equation (3.4), one can retrieve the polar angle θ between the NV center axis and the normal to the diamond sample, as well as the azimuthal angle ϕ modulus π , since the detected signal can not distinguish between the two orientations of the N-to-V axis.

Figure 3.8 shows four different polarization-dependent PL intensity diagrams, corresponding to the four different NVs orientation created in sample B. These polarization diagrams were recorded with

Orientation	Family	θ	$\phi[\pi]$
$[111]$	F1	30 ± 2	137 ± 2
$[\bar{1}\bar{1}\bar{1}]$	F2	73 ± 5	137 ± 2
$[\bar{1}1\bar{1}]$	F3	126 ± 2	70 ± 1
$[1\bar{1}\bar{1}]$	F4	127 ± 2	35 ± 2

Table 3.1: Orientation of the probed single NV centers in sample B. The polar θ and azimuthal $\phi[\pi]$ angles deduced from the polarization-dependent PL diagrams, are indicated for each of the four possible NV's orientations.

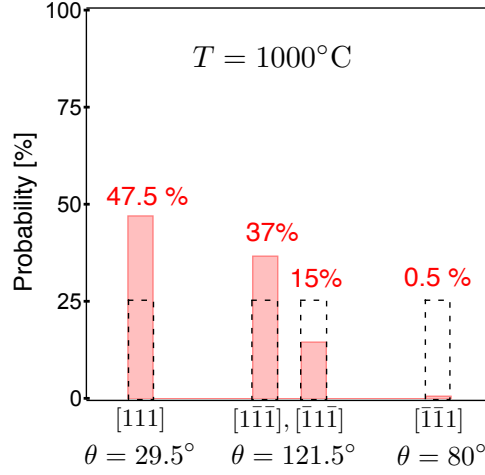


Figure 3.9: Probability distribution of the NV defect orientation sorted by polar angle θ in sample A. Red bars indicate the occurrence probability of each orientation. The black dotted bars indicate the expected distribution for a diamond sample without preferential alignment.

the same magnetic field as that used for ESR measurements. For $[111]$ -oriented NV defects, the polar angle is minimal ($\theta = 30 \pm 2^\circ$), leading to the weakest amplitude of the PL modulation (see Figure 3.8-(a)). Conversely, NV defects with a $[\bar{1}\bar{1}\bar{1}]$ orientation are almost lying in the diamond surface plane ($\theta = 73 \pm 5^\circ$), resulting in a PL modulation with maximal contrast (see Figure 3.8-(b)). For the two other orientations ($[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$) with $\theta = 126 \pm 2^\circ$ and $\theta = 127 \pm 2^\circ$, similar polarization diagrams are observed with a moderate contrast and a global phase shift resulting from different ϕ angles (see Figure 3.8-(c)-(d)). These different NV's orientation are summarized in Table 3.1. This simple method enabled us to link each ESR spectrum to a given NV defect orientation.

3.3.3 Dependence of the preferential orientation on the growth temperature

The analysis of the single NV's orientation distribution, has been carried on two samples grown at two different temperatures : sample A grown at 1000 °C and sample B grown at 800 °C, both on a (113)-oriented diamond substrate. This analysis relied on a large set of individual defects (about 200). The results on the occurrence statistics are summarized in Figures (3.9) and (3.10) for samples A and B respectively.

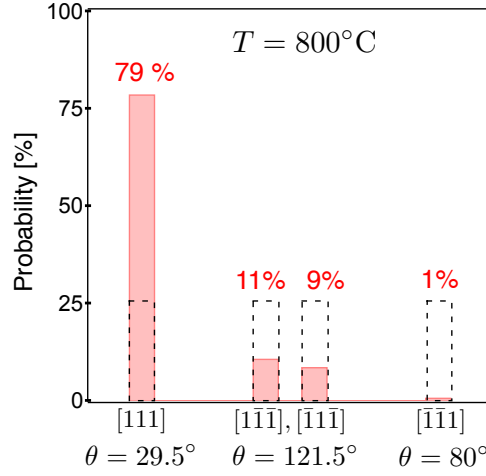


Figure 3.10: Probability distribution of the NV defect orientation sorted by polar angle θ in sample B. Red bars indicate the occurrence probability of each orientation. The black dotted bars indicate the expected distribution for a diamond sample without preferential alignment.

For sample A grown at 1000 °C, $[111]$ -oriented defects are observed with a probability of about 47.5%, while $[1\bar{1}\bar{1}]$ and $[\bar{1}\bar{1}1]$ defects are detected with a probability of 37% and 15% respectively. This distribution reveals a moderate effect on the preferential orientation. Interestingly, defects oriented along the $[\bar{1}\bar{1}1]$ direction, i.e. almost lying in the (113) diamond surface plane, are hardly observed. These results are in agreement with previous studies showing that NV defects are predominantly aligned along the orientation closest to the growth direction, while in-plane orientations are energetically unfavourable. Let's note that the detrimental effect of high temperatures on the NVs orientation control, is not specific to temperature growth.

Conversely, for sample B grown at 800 °C, the degree of preferential orientation along the $[111]$ direction, is significantly enhanced : it reaches a probability of 79 %. Again, defects along the $[\bar{1}\bar{1}1]$ direction are hardly observed, while defects aligned along the $[1\bar{1}\bar{1}]$ and $[\bar{1}11]$ directions, are almost equiprobable with respective probabilities of 11% and 9%. This slightly unbalanced populations of these two latter orientations ($\theta = 121.5^\circ$) could be attributed to a tilt angle of the (113)-oriented diamond substrate. We note that a previous study performed on a (113)-oriented substrate grown at 900°C has shown a preferential alignment of about 73% along the $[111]$ direction [143, 139], this is in agreement with the trend of our experimental findings.

To explain the effect of temperature on the selective incorporation of an orientation, we use a simple thermodynamic model in which we define two thermodynamic activation energies E_1 and E_2 that correspond to the formation of NV's with orientations along the $[111]$ and $([1\bar{1}\bar{1}], [\bar{1}11])$ respectively. The ratio of the obtained populations is therefore given by;

$$\frac{P_{[111]}}{P_{[1\bar{1}\bar{1}],[\bar{1}1\bar{1}]}} = \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (3.5)$$

where k_B is the boltzmann constant, and $\Delta E = E_1 - E_2$. Given the distribution measured in our experiment, this energy difference is in the order of 100 meV. This rough estimation might be usefeful for theoretical models aiming at describing the mechanisms of NV creation in CVD-grown diamond crystals [138]. Its dependence on temperature allows one to manipulate the preferential orientation of the obtained NV centers.

On a recent publication by Ozawa et al.[146], the thermal stability of preferentially oriented NV center ensembles in (111) oriented substrates was studied. The goal of their study was to investigate the effect of high temperature annealing on preferential orientation. Their findings show that high temperature annealing promotes vacancy migration, thus enabling the formation of random NV orientations. This re-orientation can occur at temperatures ranging up to 1050°, for higher annealing temperatures, even NV centers are destroyed and vacancies end up discharged out from the diamond surface. Their study also shows that the alignment is dependent on the growth temperature and that for the case of 111 oriented substrates, 100 % preferential alignment is observed for growth temperatures lower than $\approx 850^\circ$. It should be noted that in our case the diamond samples were not annealed but the NV realignment due to this process remains possible in particular for deeply located ones since they are heated during the whole growth process.

Besides controlling the NV defect orientation, variations of the CVD growth temperature can also be employed to tune the NV defect density in diamond layers and its in-depth localization. This will be the goal of the next section.

3.4 Growth of preferentially-oriented NV centers delta-doped layers by tuning the temperature of CVD growth

We have seen that the growth temperature can be used as a flexible tuning parameter for the preferential orientation of NV centers during CVD growth. It has also been shown that the growth temperature can be used a parameter for controlling the efficiency of the NV defects creation [147]. In the next section, we will combine these effects to create thin doped layers of preferentially-oriented NV centers using CVD growth on (113)-oriented substrates. We will first recall the techniques that can be used to engineer delta-doped layers of NV centers and we will propose a novel strategy based on the tuning of the growth temperature in the CVD chamber, to grow delta-doped layers containing dense and preferentially-orientated NV centers.

3.4.1 Engineering of delta-doped layers of NV centers

As summarized previously, the control of the in-depth localization of the NV centers can be achieved in two ways. A first way makes use of ion implantation. If near-surface (≤ 100 nm depth) delta-doped layers can be incorporated in diamond crystals yet with a relatively low N to NV conversion yield

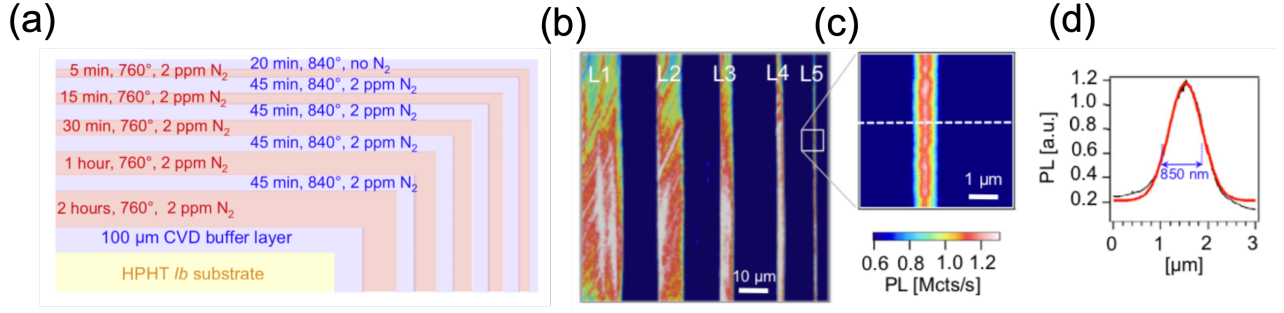


Figure 3.11: Growth of thin NV doped layers by varying the growth temperature, From ref. [147]
 (a) Sketch of the cross-section of the grown diamond : blue layers correspond to layers grown at high temperatures (840°) and red layers correspond to layers grown at lower temperatures (760°). The deposition durations and the N₂ flows are indicated for all high temperature layers. (b) Raster PL scan of the cross section of the diamond sample, revealing layers (L1 to L5) featuring higher PL signals. These layers correspond to the five layers grown at low temperature and incorporating a higher density of NV defects level. (c) Zoomed PL scan on the thinnest layer (L5). (d) Linecut of the PL intensity along the white dashed line in (c); the solid line is a fit by Gaussian function with a FWHM of ≈ 850 nm

(< 1 %), control over the NV orientation is precluded. A second way exploits the control of the CVD growth parameters to localize the NV centers created in situ during growth. These parameters include : the N₂ precursor gas flow, the temperature or the position of the sample holder.

This control over the in-depth localization of the created NV centers during CVD growth, is illustrated on Figure 3.11 [147]. The results were obtained on (100)-oriented substrates during the PhD of M. Lesik [47]. The NV centers are created in situ by adding a slight N₂ precursor gas flow and control over their localization in depth makes use of the tuning of the growth temperature. Indeed, decrease of the growth temperature leads to a more efficient nitrogen incorporation in the diamond layer. This behaviour possibly stems from the high probability for N atoms to remain on the surface without being etched away when the temperature is lower. One advantage of temperature control, is that this parameter can be changed quickly as opposed to the composition of the chamber's gas phase for instance. It enables, by tuning the temperature, to control the in-depth localization of the in situ created NV defects. In this experiment, the sample alternates layers grown at high (840° C) and low (760° C) temperatures. The growth duration of each low temperature layers, is varied, in order to vary the layers thicknesses. A PL raster scan of a cross-section of the sample is shown in Figure 3.11-(b)-(c). It reveals the position and presence of the five low temperatures layers, which features a higher photoluminescence signal due to the higher densities of NV centers. This density is estimated to be about 200 NVs per μm³. The thickness of the thinnest layer is about 850 nm.

In this latter experiment, no control over the NV orientation is observed, since the sample is grown on a (100)-oriented substrate. All four orientations of the NV centers are equiprobable. In order to in addition promote preferential orientation in the delta-doped layers, we extended this work to samples

grown on (113)-oriented substrates. Our results will be detailed in the next section.

3.4.2 Delta doped layers with preferential orientation on (113) oriented substrates

Description of the sample

The sample, referred to as sample C, was again grown by O. Brinza, A.Tallaire and J. Achard at the Laboratoire des Sciences des Procédés et des Matériaux in Villeneuve. In this sample grown on a (113)-oriented diamond substrate, variations of the CVD growth temperature is employed to tune the NV defect density in diamond layers. Fast and abrupt temperature variations are applied during the growth through quick modifications of the microwave power and the pressure in the CVD chamber. As sketched in Fig. 3.12-(a), the resulting sample consists of a stack of alternating layers grown at low and high temperature. Low temperature diamond layers grown at 800 °C, are deposited with an increasingly short deposition time (ranging from 10 to 2 minutes) and are separated by high temperature layers grown at 1000 °C. The typical time required to achieve such a temperature variation was around one minute. A slight amount of N₂ (about 2 ppm) was intentionally added into the gas phase throughout the entire growth run in order to increase the NV density.

Spatial profile and density of the delta-doped layers

The in-depth distribution of the NV centers within the sample was probed optically, by confocal microscopy.

In a first series of experiment, the sample was probed from the sample top surface. Figure 3.12-(a) shows a raster PL scan recorded along the depth of the sample. We observe that the largest PL signal is detected from the diamond layers grown at the lowest temperature, as expected due to the temperature-dependent creation of NV defects during the CVD growth which is promoted at low temperature. This scan along the depth of the sample, do not yet allow to estimate the low temperature layers thicknesses, due to the poor longitudinal spatial resolution of the microscope. In order to assess the spatial profile of the doped layers, a cross-section of the sample was obtained through laser cutting and polishing, and in a second series of experiment, the sample was probed from the cross-section plane. Figure 3.12-(b) shows a PL raster scan obtained in this configuration. It clearly reveals well-defined NV-doped layers with a spatial resolution limited by the lateral resolution of the confocal microscope (of about 350 nm). The thinnest layer, obtained for the shortest deposition time (2 min), features a PL profile with a linewidth (FWHM) in the order of 450 nm. Layers with thicknesses down to few tens of nanometers could be obtained by reducing the growth rate, for example by limiting the amount of methane introduced in the gas phase or by reducing the pressure/microwave power set [148]. Considering the spatial resolution of the microscope, it corresponds to a thickness in the range of 300 nm.

Most of the NVs are mainly created in the negatively-charged state in the doped layers. This is illustrated by the PL spectrum shown in Fig. 3.13. This spectrum features the characteristic NV⁻

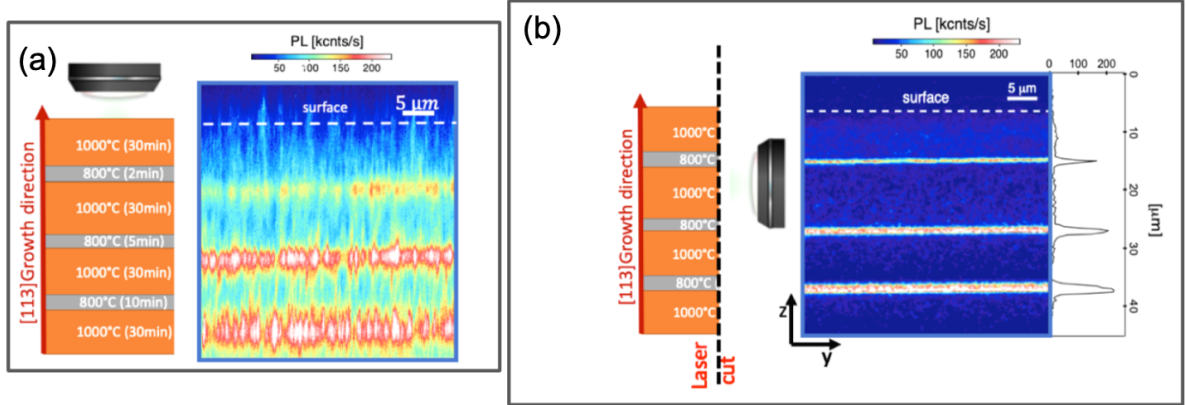


Figure 3.12: Sketch of the sample under study and PL raster scans of the sample along its growth direction. (a) Schematic of sample C and photoluminescence raster scans along the sample depth recorded from the top of the sample surface. In this case the objective axis is along the growth direction. (b) Confocal PL raster scan of a cross-section of sample C obtained after laser cutting. In this case the objective axis is perpendicular to the growth direction. A linecut along the z direction is shown, enabling to retrieve the layers thicknesses.

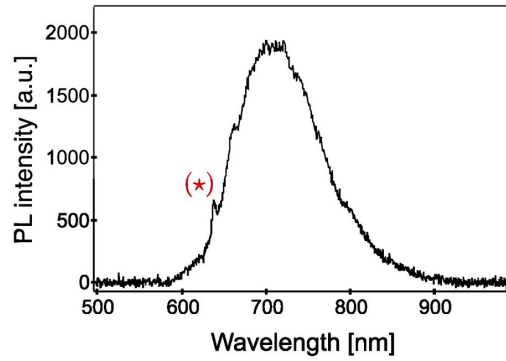


Figure 3.13: PL spectrum of the NV centers. Typical room-temperature photoluminescence spectrum recorded on the NV doped layers on sample C. The star indicates the characteristic zero phonon line of negatively charged NV defects at 637 nm.

center Zero Phonon Line (ZPL) at 637nm. More importantly, it does not exhibit any feature of the characteristic emission of the neutral charge state NV^0 with a zero-phonon line at 575 nm. Such an efficient charge-state stabilization is assigned to a large incorporation of substitutional nitrogen atoms that act as deep electron donors, thus increasing the negatively- charged NV population [149].

The density of NV defects in the doped layers was roughly estimated by normalizing the PL intensity emitted by the doped layers to that measured for a single NV defect (located in the adjacent high temperature layer) with a laser excitation power well below the saturation of the optical transition. The NV density on the doped layer is estimated in the range of 10^{15}cm^{-3} . This density can be further increased by at least one order of magnitude by increasing the N_2 injection rate [148].

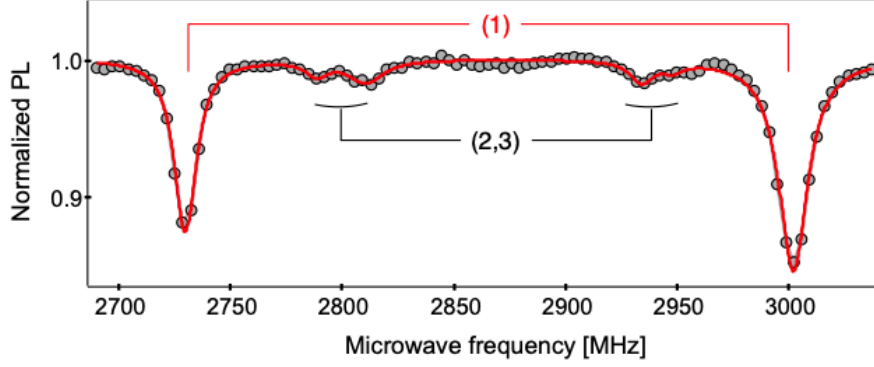


Figure 3.14: ESR spectrum of the NV centers. Typical ESR spectrum measured on the NV doped layers while applying an external magnetic field. The peaks denoted (1) correspond to the defects oriented along the $[111]$ direction; the peaks denoted (2) and (3) correspond to the defects oriented along the $[1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}]$ directions.

Orientation of the NV defects in the delta-doped layers

The orientation of the NV center was investigated by recording the ESR spectrum on the low-temperature layers. Yet, conversely to previous experiments on samples A and B, the ESR spectrum is not recorded on single NVs but on ensemble of NV defects. When a static magnetic field is applied so that it separates all NV defect orientations, the ESR spectrum shall feature 8 peaks, corresponding to the four projections of the magnetic field along the NV axes. The depth of these resonances can then give an insight on the distribution between the different orientations.

Figure 3.14 shows a typical ESR spectrum measured on the NV doped layers. It features three doublets. These could be assigned to three possible orientations : the $[111]$ orientations for peaks (1), and the $[1\bar{1}\bar{1}]$ and $[\bar{1}1\bar{1}]$ orientations for peaks (2) and (3). Again, we do not observe the defects along the $[\bar{1}\bar{1}1]$ direction. Most importantly, the pair of peaks corresponding to the $[111]$ orientation, presents the maximum contrast. This confirms the strong preferential orientation of the NVs along this direction.

Spin coherence time

As we have seen in the first chapter (§1.1.3), the spin coherence time T_2^* represents the loss of coherence of an electronic spin initially prepared in a quantum superposition state. This time can be extended into T_2 using multiple sequences [150, 151] such as the Spin Echo sequence [152]. This pulse sequence eliminates the slowly fluctuating components of the spin bath and is described as follows; a microwave π -pulse is applied halfway through the free precession interval. This π -pulse alters the direction of the spin precession, such that the phase accumulated due to static or slowly varying fields during the second half of the free precession interval cancels the phase accumulated during the first half. As a consequence, the spin rephases, producing a recovered signal termed a spin echo [139]. The decay of this echo signal, due to fields that fluctuate over the course of the measurement sequence, is called

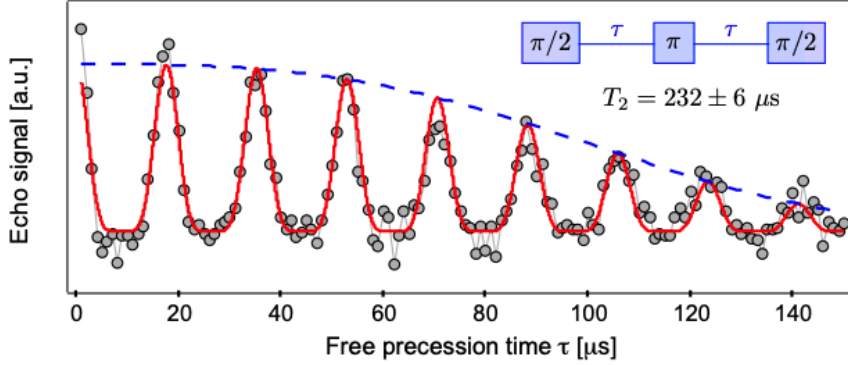


Figure 3.15: Coherence time of the NVs spin. Typical Hahn-echo measured signal on the NV doped layers. The envelope of the spin echo signal indicates a coherence time of $T_2 = 232 \pm 6 \mu s$. Inset : Hahn echo pulse sequence used for the NVs .

the coherence time and is denoted T_2 . In NV ensembles, T_2 can exceed T_2^* by orders of magnitude[124].

In our experiments, we measured the spin coherence time T_2 , using a spin echo sequence as described in the inset of Figure 3.15. A $\pi/2$ -pulse creates a coherent superposition of the $|m_s = 0\rangle$ and $|m_s = -1\rangle$ states. This superposition is then allowed to dephase during a time τ . A π -pulse is then applied to reverse the slow components of the dynamics on the time scale of the free precession interval; it enables to invert the accumulated phase over the second free precession interval τ compared to one accumulated during the first free precession interval. Last a $\pi/2$ -pulse is applied to map the echo signal. The efficiency of the net phase refocusing is dependent on how slow the magnetic field fluctuations are in comparison to the free precession interval.

A typical NV spin decoherence curve is shown in Figure 3.15. It shows the evolution of the amplitude of the echo signal as a function of the free precession time τ . Various contributors to spin decoherence occur in NV centers. The Larmor precession of ^{13}C nuclei is usually the main contributor. When the free precession time τ is a multiple number of ^{13}C Larmor periods, phase contributions from each individual ^{13}C cancel out, giving rise to collapses and revivals of the echo signal. The NV spin coherence T_2 is given by the decay of the envelope of Larmor-resonant peaks in the ^{13}C -induced revivals. In our experiment, this coherence time reaches values of about $T_2 = 232 \pm 6 \mu s$. This value is of the same order of magnitude as for (100) diamonds with same isotopic purity [44, 153]

3.5 Conclusion

In this chapter, we proposed a new direction path for creating delta-doped layers of preferentially oriented NV centers, which are a prerequisite for optimal magnetometry in a wide-field configuration. We take advantage of the flexibility of CVD growth which enables the in situ creation of NV centers with long coherence times. We make use of growth on non-classical diamond orientation, more specifically (113) oriented substrates, to control the orientation of the NV centers. We proposed a novel tuning

3. Optimizing Synthetic Diamond samples for quantum sensing

parameter to promote the incorporation of preferentially oriented NV defects : the growth temperature.

We more specifically showed that by relying on (113) oriented crystals, preferential alignment of NV defects along the [111] axis is improved from 47.5% to 79% when the growth temperature is decreased from 1000 °C to 800 °C. The combination of this effect with temperature-dependent creation efficiency of NV defects allows for the formation of thin diamond layers doped with dense ensembles of aligned NV defects. Importantly, such an engineering is realized while preserving the spin coherence properties of NV defects. These results establish that temperature-dependent CVD growth on (113)-oriented substrates is a promising approach for the design of optimized diamond samples for quantum sensing applications.

This work opens in addition novel paths for improving further the engineering of dense delta-doped layers embedding preferentially oriented NV centers. The first one concerns the NV density. The further decrease of the growth temperatures and the addition of more N₂ into the gas phase, could lead to a higher incorporation of NV centers. The second one concerns the thickness of the delta-doped layer. In our experiments, the thinnest layer was in the range of few hundreds nm. Layers with thicknesses down to few tens of nanometers could be obtained in future by decreasing the diamond growth rate, for example by limiting the amount of methane introduced in the gas phase or by reducing the pressure/microwave power set [148]. This will be facilitated by the wide range of suitable growth conditions provided by the (113) orientation.



Conclusion

The goal of this PhD work was to develop magnetic imaging methods that rely on the single spin of the NV defect. The first part of my PhD was devoted to the development of a scanning NV magnetometer operating at cryogenic temperatures. This experimental setup was presented in the first chapter, along with the fundamentals of the NV defect and how it can be integrated into diamond cantilevers engineered for the use in a scanning configuration. We have also seen at the end of the first chapter with the support of magnetic simulations of domain walls in ferromagnets that these spin structures can be detected in an all-optical, non-perturbative, fast and qualitative technique.

In the second chapter, we have examined the physics on magnetic skyrmions in ultrathin magnetic layers using a non-invasive, scanning-NV magnetometer operated in PL quenching mode under ambient conditions. We first examined the impact of structural disorder and magnetic history on the morphology of skyrmions in a symmetric bilayer system, opening the way to an in-depth understanding of skyrmion dynamics in real, disordered media. In the quest to find a host ferromagnetic material providing efficient current-induced skyrmion dynamics, we then explored the possibility to use Heusler alloys, a class of ferromagnetic materials with an intrinsically low magnetic damping coefficient. We demonstrated (i) the first stabilization of magnetic skyrmions in a single ultrathin layer of Co_2FeAl and (ii) an efficient current-induced nucleation process mediated by the SHE-induced spin torque, which is not specific to Heusler alloys and could be advantageous for future skyrmion-based devices. However, current-induced skyrmion motion experiments revealed that pinning effects still limit skyrmion velocity, even in a host material with low magnetic damping. In the last part of this chapter, we finally demonstrated the stabilization of 60 nm skyrmions at zero external magnetic field in an optimized exchange-biased multilayer stack. Compared to previous studies [104], this result corresponds to a reduction of skyrmion diameter by one-order of magnitude.

In the last chapter of this thesis we shift our focus towards the use of ensembles of NV's for imaging applications with a goal of maximizing their measurement sensitivity. We rely on PE-CVD in the High

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power density regime to engineer diamond samples containing NV centers. We first address the issue of preferential alignment, that directly impacts the signal to noise ratio when performing a measurement with an ensemble of NV centers since in a standard (001) oriented diamond, only a quarter of the NV spins contributes efficiently to the detected signal. We perform a statistical study on two different diamond samples grown by our collaborators at the LSPM over (113) oriented substrates at two different chamber temperatures. We observe that preferential orientation is maintained for the direction closest to the growth direction ([111]) which is in accordance with literature. However, we see that for smaller growth temperatures, preferential orientation is enhanced [154]. We combine this effect with temperature dependent incorporation of NV centers [147] to engineer thin doped layers of preferentially aligned NV centers. We obtain low growth temperature layers containing preferentially aligned NV centers with an expected ratio of with thicknesses down to ≈ 300 nm, densities of 10^{15} cm $^{-3}$ and a coherence time $T_{2e} = 232 \pm 6$ μ s.

A potential application for NV-based magnetometry has emerged in the last years in the recently discovered 2D magnetic atomic crystals [155, 156]. Most of the available 2D materials fabricated by mechanical exfoliation are only operational at low temperatures. Furthermore, the magnetic characterization requires the use of magnetic probes with high spatial resolutions [157]. The NV center in diamond fits in this role perfectly as quantification of the absolute magnetization in 2D-CrI $_3$ flakes has recently been performed using the NV center in a scanning configuration [18]. A wide array of materials based on these magnets remains to be investigated.

At last, we have devoted most of the work performed during this thesis to the measurement of magnetic fields using the NV center. This defect however has also been proven to be an effective temperature [33], electric field [158] and pressure [159] with high sensitivities and nano-scale spatial resolution. One could think in the near future of the NV center as a multi-functional sensor, that can be integrated in scanning configurations or employed in arrays.

A

Appendix A : Simulating magnetometry images through magnetization discretization

A.1 Simulating stray field from a magnetization pattern

The procedure we use in order to simulate the NV magnetometry images consist of three steps;

1. Discretizing the magnetization distribution $\mathbf{M}_{x,y,z}$ of the magnetic structure.
2. Calculating the stray field emanating from the magnetization pattern at the flight distance d of the NV center.
3. Projecting the magnetic field along the NV direction, in order to obtain the Zeeman splitting, or to apply the Photoluminescence quenching model described in §1.1.4

A.2 Discretizing the magnetization distribution

The first step aims at discretizing the magnetization distribution $\mathbf{M}_{x,y,z}$ in an ensemble of uniformly magnetized parallelepipeds. Therefore we define an ensemble of N cells $\{i\}_{1..N}$, where i is of dimensions $2a_i \times 2b_i \times 2c_i$ and of magnetization $\mathbf{M}_i$ centered in (x_i, y_i, z_i) . Depending on the desired precision, one can use a small mesh parameter and use a dedicated software to calculate the steady state of the magnetic structure, or use a decomposition directly from a theoretical model. This is the case for the simulations of the skyrmions using the 360 DW model.

A.3 Calculating the stray field

In order to calculate the stray field, we use the analytical expressions of stray field generated by a uniformly magnetized parallelepiped. We consider a parallelepiped of dimensions $2a \times 2b \times 2c$ of magnetization along the z axis $\mathbf{M} = M_s \mathbf{U}_z$ where M_s is the saturation magnetization of the material. We use the Coulomb approach that describes the magnetization by magnetic charges making which brings us to the case of a uniformly magnetized condensator where the charges are located on both surfaces at $z = \pm c$, with a surface charge density $\pm\sigma_m$, $\sigma_m = \mathbf{M} \cdot \mathbf{U}_z = M_s$. The scalar magnetic potential therefore writes as

$$V(x, y, z) = \frac{1}{4\pi} \left(\int \int_{[-a,a] \times [-b,b]} \frac{\sigma_m dx' dy'}{\sqrt{(x-x')^2 + (y-y')^2 + (z-c)^2}} - \frac{\sigma_m dx' dy'}{\sqrt{(x-x')^2 + (y-y')^2 + (z+c)^2}} \right) \quad (\text{A.1})$$

An analytical solution to magnetization pattern is not always easy to find and the field has to be calculated numerically, as the gradient of the potential we just described;

$$\mathbf{H}_{\text{dipolar}} = -\mathbf{grad}(V) \quad (\text{A.2})$$

We therefore obtain the three components of the magnetic field,

$$\begin{aligned} H_{z,x} &= \frac{1}{8\pi} \ln \left[\prod_{i=\pm 1} \prod_{j=\pm 1} \prod_{k=\pm 1} \left(\frac{(y+jb) - \sqrt{(x+ia)^2 + (y+jb)^2 + (z+kc)^2}}{(y+jb) + \sqrt{(x+ia)^2 + (y+jb)^2 + (z+kc)^2}} \right)^{ijk} \right] \\ H_{z,y} &= \frac{1}{8\pi} \ln \left[\prod_{i=\pm 1} \prod_{j=\pm 1} \prod_{k=\pm 1} \left(\frac{(x+ia) - \sqrt{(x+ia)^2 + (y+jb)^2 + (z+kc)^2}}{(x+ia) + \sqrt{(x+ia)^2 + (y+jb)^2 + (z+kc)^2}} \right)^{ijk} \right] \\ H_{z,z} &= \frac{1}{8\pi} \sum_{i=\pm 1} \sum_{j=\pm 1} \sum_{k=\pm 1} ijk \tan^{-1} \frac{(x+ia) + (y+jb)}{(z+kc) + \sqrt{(x+ia)^2 + (y+jb)^2 + (z+kc)^2}} \end{aligned} \quad (\text{A.3})$$

The field that can be produced from magnetization lying along different directions can be obtained by swapping the variables a, b, c . And the stray magnetic field from the structure is obtained by summing the contributions over the cells of the structure. Since we are interested in describing the magnetic field at the flight distance of the NV d , the sum is evaluated for only one altitude z . We have here a convolution product between the magnetization distribution and the stray field of an elementary cell, which makes the use of the Fourier transform efficient in calculation time.

A.4 Calculating the response of an NV center to the simulated stray field map

Once $\mathbf{B}_{x,y}$, the response of the NV center is calculated by diagonalizing numerically the Hamiltonian that we have seen in 1.1.3,

$$H = hD\hat{S}_Z^2 + hE(\hat{S}_X^2 - \hat{S}_Y^2) + g\mu_B \mathbf{B} \cdot \mathbf{S} \quad (\text{A.4})$$

We recall here that μ_B is the Bohr magneton, $g \approx 2$ is the Landé g-factor, $\hat{S}_X, \hat{S}_Y, \hat{S}_Z$ are the spin operators, h is the Plank constant. The NV quantization axis $\mathbf{u}_{\text{NV}}$ is along the Z direction, D and E are the zero-field splitting parameters.

The ESR frequencies f_+ and f_- are therefore retrieved for each point of the map while taking into account the zero field splitting parameters and the NV orientation.

A.5 Skyrmion description as a 360 domain wall profile

Skyrmion profile is assumed to be analogous to a 360° domain wall [105, 1], the expression of its magnetization therefore writes as;

$$\begin{aligned} M_x &= \pm M_s \sin\left(\frac{\theta x}{\rho}\right) \\ M_y &= \pm M_s \sin\left(\frac{\theta y}{\rho}\right) \\ M_z &= M_s \cos(\theta) \end{aligned} \tag{A.5}$$

where $\rho = \sqrt{x^2 + y^2}$ and $\theta = \arcsin(\tanh(\frac{\rho+d/2}{\Delta_{dw}})) + \arcsin(\tanh(\frac{\rho-d/2}{\Delta_{dw}}))$ where d is the skyrmion diameter and Δ_{dw} is the domain wall width. In our case, the negative DMI value for Pt/Co forces the stabilization of left chirality domain walls.



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