# Conclusion

The work presented in this manuscript is part of an ongoing effort to develop quantum technologies, and NV centers, among many other systems, are a part of this new ecosystem. While the properties of single NV centers have been thoroughly studied in the past 20 years, we showed in this thesis that emerging properties of NV ensemble can still be discovered. These ensemble properties are relevant for the many fields using NV ensembles [1–4]. They also are relevant to explore fundamental aspects [5–7] and for new potential applications [8–10].

At the heart of this manuscript is the notion of cross-relaxation with NV centers. Cross-relaxations are a powerful spectroscopic tool, and NV centers are naturally suited to cross-relaxation studies due to their ability to be optically polarized and read-out, in opposition to their environment.

We have showed how cross-relaxations can be used in a CVD-grown diamond to detect trace amount of other spin impurities, with higher sensitivity than the standard EPR apparatus, and only a fraction of the cost. These observations allowed us to study the temperature dependence of these impurities, and could eventually allow the detection and coherent manipulation of single dark spins through their interaction with an NV bath.

We have then studied the cross-relaxation between NV centers, thanks to the multiple classes of NV and the ability to tune them in and out of resonance. The observation of cross-relaxation between seemingly equivalent spins has led previous researchers to postulate the existence of dark NV centers called fluctuators. We investigated experimentally the predictions of the fluctuator model, in particular the prediction of a stretched exponential profile for the depolarization of the spins, and a broadening of the fluctuators spectra compared to those of regular NV centers. Our observations for the large part comfort the fluctuator model, although we did notice some deviations which could indicate some limitations of the model.

Dipole-dipole interaction within dense ensemble of NV centers ([NV] ¿ ppm) can be responsible for an increase of the depolarization rate by more than a factor of 10. This changes considerably the properties of NV ensemble compared to single NV. Having a better understanding of the fluctuators and of their microscopic origin will be a crucial point in the future development of NV ensemble technologies. The further steps to determine the nature of the fluctuators could include the study of dedicated samples grown with specific concentrations of NV and other defects, as well as the study of nano-diamonds to try to isolate a single fluctuator.

Finally, we investigated the depolarization of NV ensemble at low magnetic field. We identified 4 different contributions to the zero field depolarization which we analyzed both theoretically through the fluctuator model, and experimentally by varying the magnetic field orientation. We concluded that the dominant factor in the zero field depolarization was the degeneracy of the 4 NV classes, followed by the double flips.

The depolarization of NV ensemble in zero field can in itself be used to measure magnetic field. We characterized such a magnetometer and compared it to the state of the art NV magnetometers. We found in particular that the dominant factor in the sensitivity of the magnetometer was the presence of the double flips, and not the classes degeneracy.

The low-field depolarization magnetometer is unique among the NV magnetometers in that is does not require a microwave or a precise orientation of the magnetic field to work, which makes it usable with powdered or polycrystalline samples. Applications of magnetometry with powders include wide-field imaging of uneven surfaces, background free fluorescence microscopy, and microwave-free nano-probe sensing.

# Bibliography

[1] John F Barry et al. "Sensitivity optimization for NV-diamond magnetometry". In: *Reviews of Modern Physics* 92.1 (2020), p. 015004.

[2] James Eills et al. "Spin hyperpolarization in modern magnetic resonance". In: (2022).

[3] Chi-Cheng Fu et al. "Characterization and application of single fluorescent nanodiamonds as cellular biomarkers". In: *Proceedings of the National Academy of Sciences* 104.3 (2007), pp. 727–732.

[4] Maxime Perdriat et al. "Spin-mechanics with nitrogen-vacancy centers and trapped particles". In: *Micromachines* 12.6 (2021), p. 651.

[5] Soonwon Choi et al. "Observation of discrete time-crystalline order in a disordered dipolar many-body system". In: *Nature* 543.7644 (2017), pp. 221–225.

[6] Georg Kucsko et al. "Critical thermalization of a disordered dipolar spin system in diamond". In: *Physical review letters* 121.2 (2018), p. 023601.

[7] Andreas Angerer et al. "Superradiant emission from colour centres in diamond". In: *Nature Physics* 14.12 (2018), pp. 1168–1172.

[8] Rinat Akhmedzhanov et al. "Microwave-free magnetometry based on cross-relaxation resonances in diamond nitrogen-vacancy centers". In: *Physical Review A* 96.1 (2017), p. 013806.

[9] Clément Pellet-Mary et al. "Optical detection of paramagnetic defects in diamond grown by chemical vapor deposition". In: *Physical Review B* 103.10 (2021), p. L100411.

[10] C Pellet-Mary et al. "Spin-Relaxation of Dipolar-Coupled Nitrogen-Vacancy Centers: The role of Double-flip Processes". In: *arXiv preprint arXiv:2207.13899* (2022).

# English Summary

The NV center in diamond is a promising candidate for emerging quantum technologies, including quantum communication, quantum computing and quantum metrology. Thanks to the recent progress in diamond synthesis, samples with high NV center concentration can now be created. This increase in the NV density comes with an increase of the interaction between them, which leads to a rich and complex physics. Numerous applications, such as NMR hyperpolarization, bio-imagery or spin mechanics rely on the use of dense NV ensembles. Understanding and mastering the properties of ensembles of NV centers will be a crucial point in the development of these technologies.

This doctoral thesis focuses on cross-relaxation between dense ensembles of NV centers, as well as on the interaction between NV centers and other diamond paramagnetic impurities. The aim of this work is to better understand the properties of dense NV centers ensembles, and to exploit them for new applications such as the detection of impurities and magnetometry.

In the first part, we will detail the properties of single NV centers and introduce notions regarding dipole-dipole spin coupling and cross-relaxations. We will then show how cross-relaxations can be used to optically detect dark spin resonances, in this case the VH- and War1 defects in CVD-grown diamond. Finally, we will present a study of cross-relaxations between subgroups of NV centers. We will first cover the influence of cross-relaxation on the spin dynamics and discuss its microscopic origin. We will then investigate the role of the magnetic field on cross-relaxations as well as their potential use in low field magnetometry.

# Résumé français

Le centre NV du diamant est un candidat prometteur pour de nombreuses technologies quantiques, que ce soit pour les communications quantiques, le calcul quantique ou la métrologie quantique. Grace aux progrès de synthétisation du diamant, des échantillons contenant une haute concentration en centres NV sont aujourd'hui réalisables. Cette augmentation de la densité de centres NV s'accompagne d'une augmentation des interactions entre ces derniers, ce qui donne lieu à une physique complexe et encore largement inexplorée. De nombreuses applications récentes, telles que l'hyper-polarisation en RMN, la bio-imagerie ou encore la spin-mécanique repose sur des ensembles denses de centres NV. Comprendre et maîtriser les propriétés d'ensemble de ces derniers est un point crucial pour l'établissement de ces technologies.

Cette thèse étudie les échanges de polarisation, par relaxation croisée, entre des ensembles denses de centres NV, ainsi que les interactions entre les centres NV et d'autres impuretés paramagnétiques présentes dans le diamant. Le but de ces travaux est de mieux comprendre les propriétés des ensembles de centres NV, et d'exploiter certaines de ces propriétés pour de nouvelles applications telles que la détection d'impuretés ou la magnétométrie.

Dans un premier temps, nous détaillerons les propriétés des centres NV et nous introduirons des concepts liés à l'interaction dipolaire entre spins et aux relaxations croisées. Nous verrons ensuite comment les relaxations croisées peuvent être utilisées pour détecter optiquement des résonances de spins qui ne sont pas optiquement actifs, en l'occurrence les défauts VH- et War1 dans des diamants CVD. Enfin nous étudierons les relaxations croisées entre différents sous-groupes de centre NV. Nous verrons d'abord leur influence sur la dynamique du spin et leur origine microscopique, puis nous étudierons leur dépendance avec le champ magnétique et leur potentielle utilisation pour la magnétométrie en champs faible.