

Capteurs quantiques pour la recherche de supraconducteurs à haute pression

Antoine Hilberer

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Quantum sensors for

high pressure superconductivity

Capteurs quantiques pour la recherche de supraconducteurs à haute pression

Thèse de doctorat de l'université Paris-Saclay

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UNIVERSITE PARIS-SACLAY ÉCOLE DOCTORALE Ondes et matière (EDOM)

Titre: Capteurs quantiques pour la recherche de supraconducteurs à haute pression **Mots clés:** haute pression, centres NV, supraconductivité, cellule à enclumes de diamant

Résumé: Lorsqu'une pression statique élevée est appliquée à un matériau, l'arrangement de ses atomes et électrons peut changer radicalement pour permettre une densité plus élevée, ce qui conduit à la création de nouvelles phases ou à la modification des propriétés électroniques et magnétiques des solides. Des pressions de dizaines de kilobars (gigapascals), voire de mégabars, peuvent être atteintes en laboratoire à l'aide de Cellules à Enclumes de Diamant (CED), limitant cependant les échantillons à des tailles infimes. Des études récentes ont affirmé avoir découvert des matériaux, les super-hydrures, étant supraconducteurs jusqu'à des températures proches de la température ambiante dans des conditions de pression extrêmes. Toutefois, la réalisation de mesures fiables des caractéristiques de la supraconductivité sur ces échantillons synthétisés à haute pression est remarquablement difficile, ce qui conduit parfois à des résultats controversés. Dans cette thèse, nous avons choisi de poursuivre le développement d'une nouvelle méthode de magnétométrie optique à haute pression basée

sur l'adaptation d'une technologie quantique mature aux CED : les centres NV du diamant. Nous créons des ensembles de ces centres colorés dans la pointe d'une enclume de diamant, les utilisant comme sondes magnétiques quantiques locales par le biais de leurs propriétés de photoluminescence dépendante du spin. Nous montrons que les centres NV peuvent être utilisés pour cartographier spatialement l'effet Meissner en présence d'un cuprate supraconducteur à haute pression, et mesurons l'évolution de la température critique de l'échantillon avec la pression jusqu'à 31 GPa. Nous étudions ensuite systématiquement les capacités de détection magnétique à haute pression des centres NV, identifiant les contraintes non-hydrostatiques dans l'enclume comme une limitation au-dessus de 40 à 50 GPa. Enfin, nous proposons une stratégie de microstructuration de l'enclume qui lève cette limite et démontre une magnétométrie à centres NV efficace au moins jusqu'à 130 GPa, ouvrant la voie à une future résolution de la controverse sur les super-hydrures par ce nouveau diagnostic.

Title: Quantum sensors for high-pressure superconductivity **Keywords:** high pressure, NV centers, superconductivity, diamond anvil cell

Abstract: When high static pressure is applied to a material, the arrangement of its atoms and electrons can dramatically change to allow higher density, thus leading to the creation of new phases or modifying electronic and magnetic properties of solids. Pressures of tens of kilobars (gigapascals) or even megabars can be achieved in laboratories using Diamond Anvil Cells (DACs), at the expense of working with samples of minute size. Recent studies have claimed to have uncovered materials, super-hydrides, retaining superconductivity close to room temperature under extreme pressure conditions. However, performing reliable measurements of the hallmarks of superconductivity on these samples synthesized at high-pressure is remarkably challenging, sometimes leading to controversial results. In this thesis, we chose to pursue the development of a new high-pressure optical magnetic measurement method based on the adaptation of

a mature quantum technology to the DAC: Nitrogen-Vacancy (NV) centers of diamond. We fabricate ensembles of these color centers inside the tip of a diamond anvil, using them as local quantum magnetic probes based on their spin-dependent photoluminescence properties. We show that NV centers can be used to spatially map the Meissner effect in the presence of a cuprate superconductor at high pressure and record the sample's critical temperature evolution with pressure up to 31 GPa. We then systematically study the NV centers' magnetic sensing capabilities at high pressure, identifying non-hydrostatic anvil stress as a limitation above 40 to 50 GPa. Finally, we propose an anvil micro-structuring strategy lifting this constraint and enabling efficient NV magnetometry at least up to 130 GPa, paving the way toward a future settlement of the super-hydride dispute by this new diagnosis method.

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Résumé en français

Soumettre la matière à des pressions extrêmes la contraint à adopter des états de haute densité en diminuant les distances interatomiques moyennes. Ce faisant, toutes les formes de liaisons et d'interactions entre les atomes peuvent être modifiées, donnant lieu à de nouvelles structures atomiques ou moléculaires, à l'apparition ou à la disparition d'ordres magnétiques, ou à des changements radicaux des propriétés électroniques des matériaux. En utilisant une cellule à en enclumes de diamant (CED), il est aujourd'hui possible de soumettre des échantillons à des pressions statiques allant de la pression atmosphérique jusqu'à quelques centaines de GPa (millions d'atmosphères).

L'un des phénomènes les plus extraordinaires étudiés sous haute pression est la supraconductivité : la capacité d'un matériau à conduire l'électricité sans aucune perte en dessous d'une température critique T_c . La recherche de matériaux ayant des températures critiques toujours plus élevées a connu une révolution en 2015 avec la découverte d'une nouvelle classe de supraconducteurs, appelés "super-hydrures". Ces matériaux à la stœchiométrie inhabituellement importante en hydrogène semblent rester supraconducteurs jusqu'à des températures exceptionnellement élevées (supérieures à 200 K), au prix d'une stabilité uniquement sous des pressions supérieures à 1 Mbar (100 GPa). Ces résultats suscitent une controverse dans la communauté des hautes pressions, car ils démontrent la supraconductivité à ultra-haute pression par des mesures de transport électrique dans des phases mixtes difficilement identifiables, ou sur l'isolation de signatures magnétiques excessivement faibles sur un fond important. Ce domaine est donc actuellement à la recherche de nouvelles techniques expérimentales fiables et compatibles avec ces conditions extrêmes.

Cette thèse porte sur le développement d'une nouvelle méthode de mesure magnétique *in situ* basée sur l'utilisation de la photoluminescence dépendante du spin de défauts luminescents du diamant, les centres NV. La magnétométrie à centres NV est une méthode de métrologie quantique bien établie qui a récemment été adaptée à l'environnement de pression extrême de la CED par implantation des défauts dans la pointe de l'une des enclumes de diamant, dont la transparence permet l'accès optique au volume de l'échantillon. Le but de cette thèse était de démontrer la possibilité d'étendre cette méthode au régime de pression nécessaire à la stabilisation des super-hydrures, au-dessus de 100 GPa.

Le premier chapitre de ce manuscrit est un examen de l'état de l'art de deux domaines de recherche qui interagissent dans cette thèse : la recherche en physique des hautes pressions et la magnétométrie basée sur le centre NV. Nous abordons les spécificités des mesures dans la CED, et les contraintes physiques qui accompagnent son utilisation, nous menant à la controverse actuelle autour des revendications de supraconductivité à température ambiante sous pressions extrêmes. Nous décrivons ensuite les bases de la magnétométrie à centre NV, puis les modifications apportées par les interactions spin-mécaniques à la physique habituelle des centres NV lorsqu'ils sont intégrés dans un environnement sous haute pression. Nous donnons ensuite une revue de la littérature publiée sur l'application de cette méthode aux mesures de comportements magnétiques à haute pression.

Nous décrivons dans le deuxième chapitre des résultats obtenus en utilisant des centres NV implantés dans la tête d'une enclume en diamant pour détecter l'effet Meissner associé à la supraconductivité d'échantillons de cuprate Hg-1223. La mesure de la résonance de spin optiquement détectée (ODMR) des centres NV juste sous la surface de l'enclume indique clairement une réduction locale des champs magnétiques appliqués en présence de l'échantillon supraconducteur. Dans une première série d'expériences, nous avons montré que nous pouvions mesurer la température critique de l'échantillon $T_c = 139 \pm 1 \text{ K}$ sous 1,3 GPa, conformément à la littérature, en mesurant une série de spectres ODMR lorsque la température de l'échantillon varie à travers la transition supraconductrice. Dans un deuxième temps, sur un échantillon différent, nous avons démontré que la magnétométrie NV en large champ peut également fournir des cartes spatialement résolues de l'effet Meissner du supraconducteur, révélant les inhomogénéités de l'échantillon qui seraient inaccessibles à la plupart des autres techniques. En collectant des cartes de l'effet Meissner en fonction de la température, nous avons déterminé une carte de T_c spatialement non uniforme à 3 GPa. Nous avons complété notre étude de cet échantillon en mesurant sa T_c à des pressions de 3, 8, 13 et 31 GPa en mode d'imagerie confocale. Les mesures finales effectuées à 31 GPa ont montré un signal d'ODMR plus faible qui laissait présager d'éventuelles modifications significatives des capacités de détection magnétique des centres NV à cette pression élevée.

Dans le dernier chapitre, nous avons adopté une approche systématique de l'évaluation des performances de détection magnétique des centres NV sous haute pression jusqu'à 70 GPa. Nous montrons que les contraintes non-hydrostatiques appliquées à la pointe de l'enclume accueillant les centres NV détériorent progressivement les signaux ODMR, en affaiblissant la sensibilité initiale des états quantiques aux champs magnétiques statiques et en affectant le contraste de la mesure. Nous confirmons la limite empirique de cette méthode vers 40 à 50 GPa pour des mesures réalistes. En utilisant un modèle simplifié de la contrainte mécanique appliquée à l'extrémité des enclumes en diamant, nous expliquons quantitativement les fréquences de transition observées sous contrainte et champ magnétique.

Notre modélisation donne une estimation de l'anisotropie de la contrainte dans l'enclume, où la contrainte tangentielle ne représente qu'environ 58% de la contrainte appliquée à un échantillon dans la chambre expérimentale. Cette estimation est confirmée par l'analyse quantitative des données de spectroscopie optique de l'émission du centre NV que nous avons enregistrées jusqu'à 80 GPa.

Enfin, nous présentons une stratégie qui nous a permis de surmonter cette limite en étendant la magnétométrie NV bien au-delà de 100 GPa. En micro-usinant la tête de l'enclume, nous avons créé un pilier qui peut accueillir des centres NV dans un environnement localement quasi-hydrostatique au moins jusqu'à 130 GPa. Ces conditions quasi-hydrostatiques locales ont été confirmées indépendamment par des mesures du décalage spectral optique des NV jusqu'à 90 GPa, et par l'apparition d'une signature Raman caractéristique sur le pilier jusqu'à 130 GPa. Dans ces conditions, nous avons montré que les centres NV conservent leurs capacités de détection magnétique même à des pressions extrêmes. Nous avons démontré une amélioration d'un facteur 10³ de la sensibilité magnétique à 70 GPa en utilisant nos enclumes micro-structurées par rapport aux enclumes implantées standard, ainsi que des preuves convaincantes que les centres NV peuvent être utilisés comme capteurs quantiques efficaces jusqu'au régime mégabar. Ce travail ouvre la voie à l'utilisation des centres NV pour sonder la supraconductivité potentielle des super-hydrures.

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List of abbreviations and acronyms

AC	Alternative Current
AFI	Antiferromagnetic Insulator
AFM	Atomic Force Microscope
AIRAPT	International Association for the Advancement of High Pressure Science and Technology
APD	Avalanche Photodiode
ARPES	Angle Resolved Photoemission Spectroscopy
BCS	Bardeen–Cooper–Schrieffer
CCD	Charge Coupled Device
CDW	Charge Density Wave
смоѕ	Complementary Metal Oxide Semiconductor
CVD	Chemical Vapor Deposition
CW	Continuous Wave
DAC	Diamond Anvil Cell
DFT	Density Functional Theory
DM	Dichroic Mirror
ESR	Electron Spin Resonance
EXAFS	Extended X-ray Absorption Fine Structure
FIB	Focussed Ion Beam
НРНТ	High Pressure High Temperature
HTSC	High Temperature Superconductor

- **IPD** Image Plate Detector
- IR Infra-Red
- **ISC** Inter-System Crossing
- **LBCO** Lanthanum Barium Copper Oxide
- LSCO Lanthanum Strontium Copper Oxide
- LTO Longitudinal Transverse Optical
- MO Molecular Orbital
- MPMS Magnetic Properties Measurement System
- MRI Magnetic Resonance Imaging
- MW Microwave
- NCCO Neodimium Cerium Copper Oxide
- **NIST** National Institute of Standards and Technology
- **NMR** Nuclear Magnetic Resonance
- NRFS Nuclear Resonant Forward Scattering
- **NV** Nitrogen-Vacancy
- **ODMR** Optically Detected Magnetic Resonance
- PL Photoluminescence
- PSB Phonon Side-Band
- **PSF** Point Spread Function
- **PTM** Pressure Transmitting Medium
- **SC** Superconducting
- **SDW** Spin Density Wave
- **SNR** Signal-to-Noise Ratio

- **SQUID** Superconducting QUantum Interference Device
- **SRIM** The Stopping and Range of lons in Matter
- **XANES** X-ray Absorption Near Edge Structure
- **XAS** X-ray Absorption Spectroscopy
- **XMCD** X-ray Magnetic Circular Dichroism
- XRD X-Ray Diffraction
- **YBCO** Yttrium Barium Copper Oxide
- **ZPL** Zero-Phonon Line

Introduction

Applying pressure to condensed matter systems forces them into increased density states by lowering average inter-atomic distances. In doing so, all forms of bonds and interactions between atoms can be modified, yielding new atomic or molecular structures, apparition or disappearance of magnetic orders, or stark changes in electronic properties.

These new high-density states studied by high-pressure scientists may seem exotic compared to what we call ambient or atmospheric pressure (1 atm = 1 bar), but actually constitute the conditions exerted on most aggregated matter in the universe. Throughout the cosmos, matter is submitted to a colossal range of pressure conditions, from the vacuum of interstellar space ($\sim 10^{-22}$ atm) to the center of stars (> 10^{11} atm). Already on planet Earth, the volume submitted to atmospheric pressure is limited to the very surface. At the bottom of the Atlantic Ocean, pressure already reaches around 400 atm, or 400 bar. Deeper into the Earth pressure rises to about 500 kbar (50 GPa) at the center of the mantle, and reaches 3.5 Mbar (350 GPa) at the core. In larger astrophysical objects, matter can be submitted to even more extreme conditions, reaching 70 Mbar at the core of Jupiter, for instance (together with temperature likely exceeding 17000 K).

In our earthly laboratories, we have been able to submit samples to static pressures above kilobars for about 100 years. Significant technical progress in the first half of the 20th century lifted record pressures to 200 kbar in the 1950s, using various experimental designs. In 1959, [Weir et al., 1959] laid the foundations of what would become the gold standard to generate high pressure until today: the Diamond Anvil Cell (DAC). They used two diamonds cut into tapered anvils to squeeze their samples to extreme pressures while using the diamonds as transparent windows providing optical access to the sample. Refinements to this device have brought us to modern experiments, where we can reach pressures of 300 - 400 GPa, with a wide variety of diagnoses available to study compressed samples (see [Bassett, 2009]): optical, Raman and infrared spectroscopy, electrical transport, and many synchrotron X-ray based methods (diffraction, absorption, and scattering). The main difficulty is that extreme pressures come at the cost of sample size. Reaching higher pressure takes smaller diamond anvil tips, with samples no larger than $30 \ \mu m$ above 1 Mbar.

One of the most extraordinary phenomena being studied under high pressure is superconductivity. The ability for a material to conduct electricity without any loss has fascinated scientists since the discovery of superconductivity in 1911. Still, its evident potentially revolutionary technological applications have mostly been held back by the need for extremely low temperatures to maintain this quantum macroscopic state. Pressure has played a significant role in the quest to find materials with consistently higher critical temperatures, by stabilizing materials with high critical superconducting temperatures or tuning superconductivity to understand its mechanisms. A recent major example of this synergy is the discovery in 2015 of a new class of superconductors, called 'super-hydrides' [Drozdov et al., 2015], that appear to remain superconducting up to exceptionally high temperatures (above 200 K), at the expense of being stable only under pressures above 1 Mbar (100 GPa). These claims have sparked controversy in the high-pressure community as they epitomize the difficulty of ultra-high-pressure demonstrations of superconductivity through electrical transport measurements of unidentifiable mixed phases or excessively weak magnetic signatures. This field is thus currently in need of new reliable experimental techniques compatible with these extreme conditions.

In 2019, three papers were published back-to-back, establishing the viability of a new potentially decisive measurement technique: high-pressure NV center magnetometry [Lesik et al., 2019, Yip et al., 2019, Hsieh et al., 2019]. They relied on the transfer of a now widespread quantum sensing protocol using luminescent point defects of diamond called Nitrogen-Vacancy (NV) centers to implement *in-situ* magnetic sensing inside the DAC. The versatility of this form of quantum sensing is well-established, having proved its efficiency in various fields of quantum sensing [Balasubramanian et al., 2008, Barry et al., 2016, Gross et al., 2017], quantum computation and quantum communication [Wrachtrup and Jelezko, 2006, Pezzagna and Meijer, 2021]. Taking into account the modifications of the NV centers' quantum states under compression, they can provide efficient optical magnetometers to assess the magnetic behavior of materials compressed in DACs. The work of this thesis focuses on the development of this new sensing technique towards the megabar pressure regime, where it could settle ongoing debates.

Outline of the thesis

Chapter one will be dedicated to reviewing the state-of-the-art of two fields of research interacting in this thesis: high-pressure research and NV center-based magnetometry. First, we will provide a brief overview of the issues high-pressure scientists are concerned with when studying materials under ultra-high static compression. We will discuss the specifics of the most common tool used to achieve pressures up to the megabar regime, the dia-mond anvil cell, and the constraints to physical measurements that come with its use. We will then detail the close links between high-pressure science and superconductivity that have made high-pressure experiments a crucial part of the road to higher critical temperatures in the past decades. This will lead us to the ongoing controversy around claims of near-room-temperature superconductivity under extreme pressures, based on poorly reproducible measurements struggling to provide uncontested proof of superconductivity above 100 GPa.

In this atmosphere where the limits of current measurement techniques are being challenged, we will then describe the basics of NV center magnetometry, a mature magnetic diagnosis technology recently adapted to DACs as a new optical way of detecting magnetic signatures such as the Meissner effect. We will describe the modifications to usual NV center physics when integrated within a high-compression environment and finish by reviewing the published literature on applying this method for high-pressure magnetic behavior measurements.

The second chapter will present results obtained using high-pressure NV magnetometry to detect the Meissner effect associated with Hg-1223 cuprate high-temperature superconductors. After an introduction to this fascinating class of materials, we will describe the experimental setup we designed for high-pressure low-temperature magnetic investigations. We will show the results of two experimental runs where we measured the sample's superconducting critical temperature using NV centers, both in confocal imaging and widefield optical microscopy, at pressures from 1 to 31 GPa. In particular, we show that widefield imaging allows the detection of sample inhomogeneities that are crucial to understanding the mixed phases synthesized at high pressure.

In the last chapter, divided into three sections, we will explore the possibility of extending NV magnetometry to higher pressures. First, we will study the NV centers' sensing capabilities as a function of sample pressure and magnetic field, in the configuration we have used

so far. We will see that modifications of the NV behavior severely degrade magnetic sensitivity above 40 to 50 GPa.

In the next section, we will build a model of the stress exerted on the tip of the pressurized diamond anvil hosting our NV centers, to quantitatively explain the observed changes in the NV spin resonances used for magnetic sensing. This will confirm our hypothesis that it is the non-hydrostatic nature of anvil stress that distorts the defects' symmetry, and degrades their potentiality as efficient magnetic sensors.

Finally, we will present a practical strategy we have devised to overcome the effect of non-hydrostatic stress. We will show NV ESR results obtained on implanted micro-structured diamond anvils on which a micro-pillar carved within the anvil culet can create locally quasi-hydrostatic conditions. We demonstrate that the use of these anvils can enable NV magnetic sensing at least up to 130 GPa, with major sensitivity improvements over the use of standard [100]-cut diamond anvils. The confirmation that NV sensing can be used at pressures in the megabar regime clearly opens the way to subsequent investigations that will attempt to verify the existence of a Meissner effect in super-hydrides.

Chapter 1

State of the art

"Why so hard!" said the charcoal unto the diamond, "are we not near relations?"

FRIEDRICH NIETZSCHE, The Twilight of the Idols, 1888

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1.1 - Introduction

The aim of this first chapter will be to provide a short synthesis of the current state of the art in the fields relevant to this thesis. The topic at hand, NV center magnetometry as a method to probe high-pressure superconductivity, is at the cross-road of various branches of physics that started merging rather recently. First, we will start by introducing some of the stakes in the venerable field of high-pressure physics, one of the most unique areas of condensed matter physics in the extensive set of specialized techniques it requires. Since the 1950s, it has crucially been relying on the diamond anvil cell, an apparatus that exploits the properties of diamond to compress materials to extremely dense states. We will then discuss the tight links of high-pressure with the physics of superconductors, up to some of the most recent results in the field. We will see that the community currently faces challenges that may call for the rise of new experimental methods to provide reliable physical measurements adapted to the constraints of the diamond anvil cell.

Then, we will approach the issue from the quantum technology side, but interestingly still relying on diamonds. We will describe one of the most promising offspring of the second quantum revolution for quantum sensing: Nitrogen-Vacancy centers of diamond and their magnetic field sensing capabilities. We will discuss their mechanisms, and how they may be affected by a highly compressed environment but still provide *in-situ* quantum sensors. Finally, we will give a brief overview of the published literature that started to implement the methods developed in this thesis.

1.2 - High pressure science

1.2.1 - Pressure to explore condensed matter physics

Varying thermodynamic parameters is a fundamental tool to study the properties of matter. Lowering the temperature can have a great variety of effects on materials, some of them very spectacular (superconductivity, superfluidity, Bose-Einstein condensation). When pressure is increased on a substance, a universal behavior emerges: its volume decreases. To do this the arrangement of atoms can dramatically change to allow always denser phases, with properties different from ambient physics. Increasing pressure directly modifies interatomic or inter-molecular distances, yielding both microscopic and macroscopic changes, and providing a uniquely powerful tool to study bonds between atoms. Decade after decade, applying extreme pressure to materials enabled the discovery of an incredible variety of atomic phases and phenomena reaching far beyond the common physics of terrestrial room pressure [Hemley, 2000, Mao et al., 2018].



Figure 1.1: Pressure-temperature phase diagram of hydrogen, extracted from [Guigue, 2019]. Under pressure above 1 million atmospheres (1 Mbar or 100 GPa) hydrogen can adopt multiple crystal structures, which can be insulating, metallic, molecular, or atomic.

Even some of the simplest atomic and molecular systems can exhibit wildly exotic behaviors under high pressure. Water ice, for instance, can assume at least ten different crystal structures between ambient pressure and 100 GPa [Bartels-Rausch et al., 2012]. Many materials undergo dramatic changes in their electronic properties when they are forced into very dense phases. The valence and conduction bands' width often increase under compression until they overlap at the transition to a metallic state (Wilson transition). As an example, iodine becomes metallic following this mechanism around 16 GPa [Riggleman and Drickamer, 1963]. Pure oxygen also becomes a metal when compressed to 96 GPa [Desgreniers et al., 1990, Weck et al., 2009]. Hydrogen, the lightest and most abundant element in the universe, was already predicted to do so under high pressure 80 years ago [Wigner and Huntington, 1935], a phenomenon that has just been observed above 400 GPa [Loubeyre et al., 2020]. Hydrogen also exhibits a fascinatingly complex phase diagram at high density, illustrated in Fig. 1.1. Some other compounds counterintuitively show the opposite behavior, like sodium and lithium [Rousseau et al., 2011] which are room-pressure metals but turn into complex insulators under pressure, probably by interstitial electronic localization. A few materials can even exist in hybrid conductive states, like superionic water [Weck et al., 2022].

These results might seem confined to fundamental physics, but high-pressure science has always been driven by questions from other fields of research and is therefore an intrinsically multidisciplinary domain. The conditions we call high-pressure, in comparison to Earth's atmospheric pressure, are actually realized in many places throughout the universe. In the early days, mineralogists and geoscientists were attracted by the possibility to reproduce the conditions of the Earth's interior (up to about 350 GPa). Nowadays, the limits have been pushed so far that we can probe conditions similar to massive astrophysical objects [Brygoo et al., 2021]. High-pressure chemistry has revolutionized many industrial processes (e.g. Haber-Bosch process for nitrogen-based fertilizers at 10 MPa), and enabled the synthesis of countless new materials. The most famous of those syntheses is probably the creation of 'Man-made diamonds' [Bundy et al., 1955], which has been one of the driving forces pushing the technical limits of high laboratory pressure.

1.2.2 - The Diamond Anvil Cell

The first technical revolution in modern high-pressure science came from the mind of 1946 Nobel prize winner P. W. Bridgman. From 1910 onwards, he consistently came up with new experimental processes (most notably an inventive design for a self-tightening pressure-chamber seal) that took the highest pressure ever obtained from 3 kbar (or 0.3 GPa) to almost 200 kbar (20 GPa) in the late 1940s. Using his unique designs, he routinely studied almost any substance he could get his hands on to pressures at the few gigapascal range in his Harvard laboratory.

The second revolution, most important to us, is the realization by NIST scientists in 1959 that diamond was the ideal material for a high-pressure window [Weir et al., 1959]. They used rare ultrapure type-II natural diamonds to squeeze optically active samples, providing an extremely resilient anvil that was also transparent to very large infrared wavelengths. Note that the authors mention in that seminal paper the use of a 'squeezer' design by no other than Bridgman. The design they coined was later designated as a 'diamond anvil cell' (DAC).

Today, most static compression experiments still rely on modern versions of that initial DAC design [Bassett, 2009]. Diamond really is the material of choice for high-pressure experiments as it can withstand enormous stress, it is transparent from the far infrared to the ultraviolet, and also to X-rays above 10 keV. It is chemically inert, non-magnetic, and can be artificially produced with excellent purity using either chemical vapor deposition (CVD) or



Figure 1.2: (a) Historic design for the very first diamond anvil cell [Weir et al., 1959]. Force was applied using a lever and screw mechanism, and pressure was applied uniaxially to the sample. **(b)** Schematic of a more modern DAC setup, with beveled anvils and a metallic gasket delimiting the experimental chamber.

high-pressure high-temperature (HPHT) methods. The DAC device comprises two tapered diamonds, the 'anvils' which are typically millimeters in size, with opposing tips (or 'culets'). The two gems are placed in seats that are bored in the center to provide optical access on the revolution axis through the whole device. A gasket with a central hole smaller than the diamonds' tips is placed between the two anvils to confine the sample to be squeezed while preventing the diamonds from touching each other. This hole radially delimits a chamber in which the sample of interest is loaded together with a pressure-transmitting medium (PTM). Using this design, when the two anvils are driven towards each other by an external mechanism, the gasket hole constricts by plastic deformation to provide radial pressure almost equal to the diamonds' uniaxial pressure. Consequently, the sample immersed in the soft PTM is squeezed in conditions close to hydrostaticity. The size ratio between the diamonds' tables (where the force is applied) and their culets concentrates the force to transform a few bars at the back into tens or hundreds of kilobars at the tip.

A broad range of pressure regimes can be achieved through the choice of adapted diamonds. In general, using smaller diamond culets yields higher pressures at the expense of sample volume. To give approximate figures, one can reach up to 1 GPa with 1 mm culets, 10 GPa with $600 \mu \text{m}$ culets, 100 GPa (or 1 Mbar) with $200 \mu \text{m}$ culets. This behavior was em-



Figure 1.3: Photograph of the components of a membrane diamond anvil cell. From left to right, we can see the cell cylinder, the metallic gasket, the cell piston, a 1 euro coin for scale and the cell housing containing the toroidal membrane, linked to the capillary tube used to pressurize it.



Figure 1.4: (a) Plot of the empirical law [Ruoff et al., 1990] established for the maximum attainable pressure in a DAC as a function of the anvils culet diameter. The numerical expression is $P_{\text{max}} = 1856 D^{-1/2}$ with P_{max} in GPa and D in μ m · This is analogous to the Hall-Petch law of plastic deformation, or Griffith's criterion for fracture mechanics: the critical stress is proportional to the inverse root of the typical spatial dimension. (b) Schematics showing the different shapes of diamond anvils that can be used for high-pressure experiments. Adapted from [O'Bannon et al., 2018].

pirically modeled to follow a law linking the maximum achievable pressure with the square root of the culet diameter (see Fig.1.4.a, based on [Ruoff et al., 1990, O'Bannon et al., 2018]). Using various anvil designs with successively shallower angles to the culet (called bevels), one can get down to tips around $20 \ \mu m$, then reaching pressures of $300 - 400 \ \text{GPa}$. This limit

was recently improved upon by further machining of the anvil tips to pre-compensate for part of the deformations that the diamonds endure at ultra-high pressure [Dewaele et al., 2018]. These 'toroidal' anvils allow sustained static pressure over 600 GPa, paving the way toward studies in the terapascal regime. All the experiments presented in this manuscript were performed using single bevel Boehler-Almax cut anvils [Boehler and De Hantsetters, 2004].

Some final technical points are worth mentioning :

- The nature of the gasket used in DAC experiments can be varied, but for standard highpressure ones, the material of choice is rhenium metal. Rhenium has been empirically chosen as the substance with the best mechanical characteristics, suited to seal the experimental chamber while deforming to provide quasi-hydrostaticity and prevent the diamonds from bridging (poking through the gasket for direct diamond-diamond contact). Other materials like CuBe alloys or boron-saturated epoxy can be used, but usually don't perform as well at pressures of tens or hundreds of gigapascals. The hole in the gasket is usually drilled by electrical discharge machining or using intense short laser pulses. In the experiments presented here, we used Rhenium gaskets with initial thickness 250 μ m, pre-compressed in the DACs to $10 - 20 \ \mu$ m thickness before machining the holes with a femtosecond laser.
- The mechanism driving the diamonds together varies with cell designs but was generally improved since the original 1959 design (see Fig.1.2.a). Here we will only use membrane DACs [Letoullec et al., 1988]. This system allows to smoothly increase the pressure in the DAC with a pneumatic pump inflating a toroidal membrane behind the piston, which is particularly suited to control the applied pressure for experiments where the temperature is varied. A photograph of the design used in this thesis is shown in Fig. 1.3.
- The pressure transmitting medium (PTM) used to encase the sample can be varied but needs to satisfy some criteria. The PTM must be adapted to each experiment so that its own characteristics (X-ray diffraction peaks or Raman scattering peaks, for instance) do not interfere with the target measurement. It can be fluid or solid, but it must be transparent to keep optical access to the sample, and soft if solid (low bulk modulus) to maintain quasi-hydrostatic conditions in the chamber [Klotz et al., 2009]. Helium is sometimes considered the best PTM, as it only solidifies at 11.5 GPa but is also highly compressible, allowing very large gasket deformation under pressure. It also unfortunately tends to weaken the diamond anvils by diffusing into their microscopic defects.

In very specific cases, the nature of the PTM can be chosen to purposely interact with the sample: some groups use NH_3BH_3 specifically for it to release hydrogen at high pressure to facilitate the synthesis of hydrides. In this thesis, we have used noble gases like argon or neon, as they provide a good compromise between hydrostaticity and compressibility.



Figure 1.5: A useful and practical pressure gauge for high-pressure experiments in a DAC is to use the first-order Raman scattering of light onto the diamond anvils. Diamond exhibits a characteristic sharp Raman scattering line at 1333 cm^{-1} wavenumber, which is progressively displaced to a higher Raman shift with lattice compression. Previous studies, like [Akahama and Kawamura, 2004] from which this figure is extracted, have calibrated the position of the high-energy edge of the Raman signal as a function of sample pressure in a DAC. The edge position is located by taking the minimum of the signal's derivative.

• Finally, the pressure applied to the sample inside the DAC chamber is measured using some sort of *in-situ* gauge. The most accurate one is to place a piece of well-known material, like gold, inside the experimental chamber with the sample of interest. One can then perform X-ray diffraction on this probe and use its calibrated equation of state to retrieve the applied pressure. However, this technique generally requires experiments to be performed at a synchrotron radiation facility. For standard laboratory studies, one can use optical pressure gauges like ruby (Al₂O₃ : Cr) or samarium doped strontium borate (SrB₄O₇ : Sm²⁺). These crystals have clear fluorescence lines that have been precisely calibrated, generally relative to a diffraction gauge [Dorogokupets and

Oganov, 2007, Shen et al., 2020, Datchi et al., 1997]. The third option, which is the one mostly used in this thesis, is to use the diamonds themselves. Diamond has a characteristic narrow Raman scattering response around 1333 cm^{-1} , corresponding to its triply degenerate LTO phonon mode. As this line shifts under pressure, one can use the high-energy edge of the diamond Raman response from the anvil's culet as a pressure gauge (this is illustrated in Fig.1.5). Here again, this shift has been calibrated to pressures above 400 GPa relatively to platinum's equation of state [Akahama and Kawamura, 2010].

1.2.3 - Superconductivity at high pressure

Superconductivity is the first discovered quantum effect manifesting at a macroscopic scale [Combescot, 2022]. In 1911, Kamerlingh Onnes measured that the electric resistivity of mercury metal sharply went to zero when it was cooled below 4 K. In 1933, Meissner and Ochsenfeld realized that a perfectly diamagnetic behavior accompanied this perfectly null resistivity, i.e. perfect exclusion of any static magnetic field from the interior of the superconductor. These two properties are the hallmarks of superconductivity, illustrated in Fig. 1.6. On a microscopic scale, many phenomenological theories tried to describe superconductors. The currently accepted paradigm for their description was created by Bardeen, Cooper, and Schrieffer (BCS) in 1957. The idea is that under sufficiently low temperatures, effective attractive interactions between electrons in some materials can favor new bound states where electrons pair up. Single electrons naturally being fermions, these new socalled Cooper pairs are bosonic and can condense to a gap-protected state below the Fermi level. The superconducting gap protects the condensate from the low energy scatterings responsible for usual electrical resistivity, effectively putting it to zero. We know today that the mechanism for the original electron-electron interactions can vary with materials, but in conventional superconductors we know that it is phonon mediated. The possibility to have material conduct electricity without any dissipation has tremendous potential applications outside of fundamental science and has already participated in constructing our modern world. Superconductors allow the construction of the strongest magnets, used for instance in MRI machines and particle accelerators. Recently massive developments in the field of Josephson-effect-based electronics have propelled superconducting qubits as the current most promising platform for building scalable quantum computers. But industrial applications have always been hindered by the need to cool the devices to very low temperatures to witness this quantum effect. Consequently, one of the main goals of researchers investigating superconductivity has always been to try and find new superconductors with critical

temperatures T_c as high as possible [Rogalla and Kes, 2012]. A simplified timeline of this race to room temperature superconductivity is shown in Fig. 1.7.



Figure 1.6: Hallmarks of superconductivity. (a) The electrical resistance of a superconductor drops to zero below a critical temperature T_c . For a typical metal, this resistance drops with temperature but keeps a finite value even at T = 0 K. (b) When a material becomes superconducting, it spontaneously expells any static magnetic flux from its bulk. This is known as the Meissner effect.



Figure 1.7: Progress of record superconducting critical temperature with years. Two main families of materials drove successive revolutions, cuprates in the 1980s and 1990s, and hydrides since 2015. Both are tightly linked to high-pressure studies. Note that the paper describing the last point of this timeline was retracted during the writing of this thesis.

Applying high-pressure to superconductors is one of the most powerful tools physicists can use to understand them. In the BCS theory, the main physical properties dictating the critical temperature T_c of a superconductor are its electronic density of states at the Fermi energy $N(E_F)$, its characteristic Debye phonon frequency ω_D , and its effective coupling of
electrons and phonons V_{eff} . All of these are directly affected by pressure, as it can modify both the static structure of materials and their vibration properties. For nearly all elemental metallic superconductors, pressure tends to decrease T_c , with the notable exceptions of thallium and rhenium which show non-monotonous behaviors. But in many other compounds, pressure drives materials towards denser and higher symmetry structures that can be superconducting even if their room pressure form isn't. Pressure-induced superconductivity has been recorded in a broad range of materials with extremely diverse compositions, whether elemental (like Sulfur [Kometani et al., 1997], Oxygen [Shimizu et al., 1998], Ytterbium [Song et al., 2018], review in [Shimizu et al., 2005]), or compound (ZrTe₅ [Zhou et al., 2016], GeAs [Liu et al., 2019], MnSe [Hung et al., 2021] and many more).

The first clear revolution in the search for higher T_c happened in 1986, when future Nobel prize winners Bednorz and Müller discovered a superconductor working below 35 K [Bednorz and Müller, 1986], a 50% improvement over the previous highest value of T_c achieved. The class of material they studied, layered copper oxides or cuprates, sparked a surge in record critical temperatures over the next decade. The first one, LBCO (La-Ba-Cu-O), was very quickly found to exhibit a large improvement in T_c when compressed, rising from 35 K at room pressure to 52.5 K under 1.6 GPa [Chu et al., 1987]. Just one year later, it was realized that a form of 'chemical pressure' could be induced by using a smaller Y ion instead of La¹ to emulate lattice compression. This led to the discovery of YBCO, the very first superconductor above liquid nitrogen temperature with $T_c = 93$ K [Wu et al., 1987]. This race culminated in 1994, when [Gao et al., 1994] reported the existence of superconductivity in a mercury-based cuprate up to 165 K at 30 GPa. This record stood for more than 20 years, as the technical limits for higher pressure assessments of superconductivity began to show for the first time. The high-pressure resistivity measurements of [Gao et al., 1994], for instance, were never reproduced, even if broadly accepted. Further details on the physics of cuprate high- T_c superconductors and their pressure-dependent T_c will be given in chapter 2.

The second and most recent revolution in high critical temperature superconductivity (HTSC) is also intimately linked to high-pressure science. In 1968, N.W. Ashcroft predicted that under very high-pressure hydrogen would not only be metallic but could be a conventional BCS superconductor with very high T_{c} , possibly even above room temperature [Ashcroft, 1968]. In the following decades, as experimental studies of extremely dense hydrogen progressed, it became clear that the pressure required to test this prediction was much higher than expected (multiple megabars). However, Ashcroft came back with the idea that chemical pressure applied by impurities in hydrogen-rich materials may be a path

¹Atomic radii 180 pm for Y, 195 pm for La.



Figure 1.8: (a) Under megabar pressure, lanthanum super-hydrides with extremely high hydrogen stoichiometries can be stabilized, like LaH_{10} . These often exhibit clathrate-like structures, where the hydrogen lattice forms cages in which the metallic atoms are inserted in large central sites. Extracted from [Geballe et al., 2018]. (b) Resistance curves as a function of temperature for HTSC hydride LaH_{10} . The inset shows T_c as a function of pressure. Extracted from [Drozdov et al., 2019].

to retain the extraordinary quantum properties of hydrogen to more reachable pressures [Carlsson and Ashcroft, 1983]. In the early 2000s, experimental techniques for transport measurement had improved to the point where probing superconductivity above 200 GPa became conceivable [Eremets, 2003]. In a final stroke of genius, Ashcroft refined his previous idea by postulating that metal hydrides with unusually high hydrogen stoichiometries under pressure might constitute candidate HTSC [Ashcroft, 2004]. At the same time, significant progress in computational random structure searching methods started predicting the stability of these so-called 'super-hydrides'. The current era of high- T_c superconductors dawned in 2015 when [Drozdov et al., 2015] reported superconductivity at 203 K in a new sulfur hydride H₃S, at 200 GPa. This was followed by numerous other claims in materials with clathrate structures even more similar to pure solid hydrogen with rare-earth elements: LaH₁₀ with 250 K at 170 GPa [Drozdov et al., 2019, Somayazulu et al., 2019] (see Fig. 1.8), YH_9 with 243 K at 201 GPa [Kong et al., 2021], CeH_9 phases with 115 K at 95 GPa [Chen et al., 2021], and finally an unknown C - S - H compound with 287 K at 267 GPa [Snider et al., 2020, Smith et al., 2022]. A more detailed review of HTSC hydrides, both theoretical and experimental, can be found in [Flores-Livas et al., 2020].

However, it is important to note that the excitement stirred by the discovery of super-

hydrides is not shared unanimously by the community. Significant critics of those results have been growing, some highlighting inconsistencies in the published results, but mostly revealing the difficulty to reproduce the crucial measurements 'proving' claimed superconductivity in these new compounds. This growing distrust in some of the studies came to a pinnacle on October 6, 2022, when the journal *Nature* decided to retract the article claiming the landmark result of room temperature superconductivity in C - S - H [Snider et al., 2020] over concerns with data processing and analysis [Hand, 2022].

1.2.4 - The challenge of current measurements

Performing physical measurements on high-pressure samples is an integral part of the challenge of high-pressure physics. Smaller diamond anvil tips must be used as experiments go to higher pressure, restricting sample size to a few micrometers above 100 GPa. Moreover, the sample isn't free-standing but instead enclosed in a tightly closed volume defined by the experimental chamber, surrounded by the DAC's mechanically complex and bulky body. Therefore, the most efficient methods are optical, taking advantage of the windows provided by the diamond anvils and their broad transparency. High-pressure scientists routinely use Raman, optical and infrared absorption or reflection spectroscopies to probe compressed samples' electronic or vibrational properties [Mao et al., 2018]. Additionally, tabletop high-pressure techniques are crucially completed by synchrotron light source methods. These massive facilities give access to extremely bright X-ray beams that allow for structure determination using X-ray diffraction (XRD), but also much more complex diagnoses like X-Ray absorption spectroscopy (XAS, completed by EXAFS and XANES) [Pascarelli et al., 2016], magnetic circular dichroism (XMCD) [Mathon et al., 2004], or nuclear resonant forward scattering (NRFS or Mössbauer) [Mitsui et al., 2009, Troyan et al., 2016]. All of these techniques have been successfully adapted to high-pressure experiments, but their practical implementation is challenging.

The main difficulty with hydride superconductors is that they aren't stable at ambient pressure, and thus need to be synthesized *in-situ* in the DAC, by first pressurizing their predecessor compounds (usually around 100 - 250 GPa). A reaction is then usually triggered by laser heating the sample while maintaining high pressure. Reaction products then need to be characterized, ideally through XRD to determine their structure. To then proceed with experiments trying to demonstrate their superconductivity, the method used needs to be able to accommodate all of these synthesis steps. A clear exhibition of the hallmarks of superconductivity on a properly identified high-pressure compound thus turns out to be a real challenge. Very few experimental methods are available, and they can usually be performed

by only a handful of teams worldwide.



1.2.4.1 - Resistivity by transport measurement

Figure 1.9: (a) Schematic of a typical setup for electrical transport measurements within a DAC implementing a fourpoint probe for resistivity measurement. Extracted from [Flores-Livas et al., 2020]. (b) Microphotographs showing different steps in the syntheof sis an alleged C - S - HHTSC by laser heating in a DAC prepared for transport measurements. Extracted from the now retracted [Snider et al., 2020].

The first way to prove superconductivity is to record the drop to zero resistivity under T_c . This method is, however, rendered very difficult by the poor physical contact access to the sample inserted in the DAC. Thin metallic electrical leads are deposited onto the surface of one of the diamond anvils to both contact the sample in the chamber and reach the anvil's slopes to connect to measurement devices (see Fig. 1.9). This can be done manually [Mao and Bell, 1981], with focused ion beam lithography¹ [Rotundu et al., 2013], or by metal sputtering through a mask [Das et al., 1992]. Using this method, the gasket must be covered with an insulating layer if it is metallic so it doesn't short out the deposited electrodes. When pressurizing the whole apparatus, the electrodes must not be ruptured in the highly frictional boundary between the diamond and the plastically deforming gasket. Another difficulty comes from compatibility with the high-pressure synthesis methods required for many high-pressure superconductors. Most hydride superconductors aren't metastable to ambient pressure and are created by overcoming thermodynamical barriers using laser

¹An organometallic gas compound containing the metal to be deposited (platinum for instance) is injected towards the anvil culet. Then, the ion beam is used to locally chemically decompose the gas and perform extremely precise deposition of the metal.

heating under megabar pressure. This means that the synthesized sample's position and contact relative to the electrodes are almost random and poorly reproducible. The laser heating process can also trigger parasitic chemical reactions between the sample and metallic leads, potentially contaminating the material of interest. Extensive XRD characterization of reaction products is then necessary, but is once again hindered by the presence of the electrodes. At megabar pressure, the ratio between the volume of an actual sample and the electrode volume introduced in the chamber is obviously poor. Finally, this two-point or four-point resistivity measurement technique probes the whole volume between the leads. It doesn't allow the resolution of any inhomogeneities in composite synthesized samples, which realistically constitute most experimental efforts.

All these technical challenges make the state-of-the-art transport measurements at megabar pressure poorly reproducible, and very rarely compatible with same-sample structure determination through XRD. Even for some of the accepted results, the obtained resistivity profiles are questioned [Hirsch and Marsiglio, 2021]. Many experts in the field are, for instance, skeptical that the mixed-phase samples synthesized could exhibit such sharp superconducting transitions, almost unaffected by applied magnetic fields, given their inhomogeneous nature. Despite all these interrogations, recent developments using very methodic lithography methods and 4th generation synchrotron facilities have proved that clean signals can indeed be obtained with improved confidence on specific materials like H₃S [Osmond et al., 2022].

1.2.4.2 - Measurement of diamagnetism

The second route to prove high-pressure superconductivity is to measure the sample's sudden perfect diamagnetism. If we exclude the use of synchrotron-based methods, the two main methods for magnetic sensing in DACs that have been used are based on the use of either metallic or superconducting coils.

The first method used to probe the sample's Meissner effect is to detect a change in its AC magnetic susceptibility using a pair of metallic coils (although the Meissner effect is, strictly speaking, the exclusion of DC fields). An AC current is driven into an excitation coil, which induces a current in a secondary pick-up coil. The presence of a sample, or a change in its magnetic susceptibility induced by the superconducting transition, is then detected as a modification of the induced current in the pick-up coil. The magnetic environment of a sample in a DAC is complex, and influenced by the presence of the diamonds and all of the other mechanical elements nearby. To compensate for some of this signal, an additional compensating coil can be used in close proximity to the pickup coil to subtract background signals originating outside the sample [Kim et al., 1994, Debessai et al., 2008] (see Fig. 1.10.a). This is useful when the main pickup coil is wrapped around one of the anvils tips, as close as possible to the gasket. To eliminate the need for this compensation coil, one solution is to dramatically reduce the background by putting the pick-up coil directly inside the experimental chamber of the DAC. This can be done by using a miniature coil that can be inserted inside the gasket hole [Alireza and Julian, 2003], or by integrating the coil inside the anvil itself with diamond encapsulation over micro-fabrication [Jackson et al., 2003] (Fig. 1.10.b). Both of these solutions improve the signals by orders of magnitude thanks to a much better filling factor, but up to now have been limited to studies up to a few gigapascals.



Figure 1.10: (a) Photograph of a DAC prepared for magnetic susceptibility measurements using a pick-up coil around the main anvil in the center, accompanied by a sister compensating coil containing a dummy anvil for background substraction ([Debessai et al., 2008]). (b) Scanning electron microscope image of a 'designer anvil' where a tungsten coil has been micro-fabricated on the culet. In [Jackson et al., 2003], the structure is then encapsulated by a CVD diamond film to protect it under pressure. (c) Schematic cross-section of a miniaturized diamond anvil cell, devised to be used inside of a commercial SQUID machine for magnetic measurements. Extracted from [Marizy et al., 2017].

The second solution is to use the extraordinary sensitivity of superconducting quantum interference devices (SQUIDs). The basis for a SQUID magnetometer is a track of superconducting material with two Josephson junctions placed in parallel. The current within the loop, and the voltage drop at its terminals, is then extremely precisely linked to the magnetic flux through it¹. These are the basis for commercial magnetic properties measurement systems (MPMS) that constitute some of the most useful tools for condensed matter physicists. The

¹It scales as integer multiples of the magnetic flux quantum $\Phi_0 = h/(2e)$ with e the electron charge.

challenge for their adaptation to DACs is that the SQUID loop in these is typically millimeters in diameter, much smaller than standard DAC devices. Using impressive miniaturization steps, a few groups have developed DAC designs with diameters less than 1 cm [Alireza and Lonzarich, 2009, Marizy et al., 2017] (Fig. 1.10.c) that can be integrated in a commercial MPMS. Most attempts have been limited to 40 GPa, but the group of M. Eremets has recently been consistently providing magnetic moment measurements on hydrides upwards of 150 GPa [Drozdov et al., 2015, Minkov et al., 2022]. Once again, only a few groups can approach these kinds of measurements. Additionally, this assessment of the sample's magnetic moment relies heavily on background subtraction procedures, as the signal yields a measurement of the magnetic behavior of the hole mini-DAC, with only a small fraction of it being the sample of interest [Hirsch, 2022]. This means that the signal of interest is actually remarkably small, and claims of superconductivity on this basis could be subject to interpretation.

This section hopefully highlighted some of the fundamental challenges that are currently faced in the field of high-pressure superconductivity. Current methods for detecting potential new superconducting phases in a DAC are severely hindered by the miniaturization efforts needed to get to megabar pressure, either because of poor sample access or simply because of minute sample size. Experimental efforts suffer from poor reproducibility as only a handful of teams have the resources and expertise to test sometimes controversial claims. This context is, however, fertile for the development of new alternative experimental techniques. The following sections will describe how one can use Nitrogen-Vacancy center magnetometry, a well-established technique from modern quantum technologies, as a possible new way of screening potential high-pressure superconductors by *in-situ* detection of the Meissner effect.



Figure 1.11: Photograph comparing a natural diamond stone to a jewelry-cut artificial one. (image credit: *lespierresdejulie.com*).

1.3 - Nitrogen-vacancy centers as in-situ quantum probes

1.3.1 - General properties of the NV center in diamond

In its ideal form under ambient conditions, diamond is a dense cubic arrangement of carbon atoms that forms a strong insulator. It is sometimes described as the most 'extreme' of materials, exhibiting unique physical properties in almost every way imaginable. For instance, it is at the same time the hardest known naturally occurring material (yield strength $\sigma_v = 130 \text{ GPa}$ [Eremets et al., 2005]) and the one with the highest thermal conductivity $(2500 \text{ W/(m \cdot K)})$. Its exceptional mechanical strength gave diamond paramount importance in the world of high-pressure science (as described in the previous section) and industrial applications in cutting tools. This widespread use was largely amplified since the 1960s when industrial processes for the production of artificial diamond reduced the need for naturally sourced stones. A comparison of a raw natural diamond and a gem cut from an artificial diamond is shown in Fig. 1.11. Modern artificial diamond is made either by reproducing its natural thermodynamic forming conditions (high-pressure high-temperature process, HPHT) or by chemical vapor deposition (CVD) of carbon atomic layers onto a substrate. Optically, diamond has a refractive index of 2.4 and a bandgap of 5.5 eV, making it transparent to electromagnetic radiation from the $2-3 \ \mu m$ infrared up to ultraviolet light around 225 nm. This large bandgap allows the existence of a plethora of optically active defects and impurities of diamond that have been studied extensively for decades [Zaitsev, 2001].

The Nitrogen-Vacancy center (denoted NV center for short) is a point defect of diamond that gives diamond very complex and valuable optical properties. Note that an exhaustive review of those properties is available in [Doherty et al., 2013]. We will provide here a short overview condensing the points relevant to its use as a magnetic sensor for high-pressure

studies. The NV center occurs in natural diamonds but can also be engineered into artificial ones. It is constituted of a substitutional nitrogen atom at a carbon lattice site, with an atomic vacancy at an adjacent crystallographic site. Introducing a point defect in the crystal breaks translational symmetry, which means delocalized Bloch states aren't adapted to describe such a local structure. The result is usually localized electronic states that can be addressed separately from the surrounding crystal matrix if they lie within the bandgap of a semiconductor or insulator. This forms within the solid what is sometimes called an 'artificial atom.' In the case of the NV center, the resulting local electronic landscape is comprised of the molecular orbitals (MOs) formed between the nitrogen and carbon dangling bonds from the atoms neighboring the vacancy (schematic in Fig. 1.12.a). One can here apply the linear combination of atomic orbitals technique to the (c_1, c_2, c_3, n) orbitals to form symmetryadapted wavefunctions. The NV defect described previously has C_{3v} point group symmetry, which then yields two A_1 non-degenerate levels (a'_1, a_1) and degenerate E states (e_x, e_y) [Loubser and van Wyk, 1978, Loubser and Van Wyk, 1977, Maze et al., 2011]. The surrounding atoms provide 5 electrons to fill these MOs (Fig. 1.12.b), forming the neutrally charged NV⁰ defect. But the most favorable configuration is this defect capturing an additional electron to form the negatively charged NV⁻ center. As it is the most widely studied charge state of the NV center, and the one relevant to the rest of this manuscript, occurrences of the term 'NV' will always mean NV⁻ in the following unless specified otherwise. Calculations show that the lowest energy a'_1 state is located within the diamond valence band and will thus always be occupied and non-addressable. We can, therefore, fully describe the dynamics of the NV center focussing on the 4 electrons (or equivalently 2 holes) occupying the a_1 and (e_x, e_y) states. Excited states of the defect can then be described using a single-particle picture as the promotion of one electron from the a_1 to the (e_x, e_y) states.

The derivation of the total n-electron wavefunction of the NV center (taking spin multiplicity into account) is beyond the scope of this work, but the resulting observed electronic level structure is described in Fig.1.14. Occupation of the atomic-like orbitals leaves two unpaired electrons, resulting in a spin S = 1 triplet ground state (symmetry ${}^{3}A_{2}$), a triplet excited state (symmetry ${}^{3}E$), and a separate spin singlet S = 0 with two states (${}^{1}E$ and ${}^{1}A_{1}$). All this structure is coupled to the surrounding diamond lattice phonons, broadening these atomic-like levels with vibronic states. These provide a Stokes shift between the photon absorption and emission spectra of the NV center. The NV⁻ center at ambient conditions is characterized by an optical zero-phonon line (ZPL) around 637 nm (or 1.945 eV) with a large phonon side-band (PSB) more than 100 nm wide. According to Franck-Condon principles (Fig. 1.13.a), very strong phonon coupling in the excited electronic state results in a weak



Figure 1.12: (a) Schematic of a Nitrogen-Vacancy center in a diamond unit cell. The defect is constituted of the dangling orbitals from a substitutional nitrogen atom and the three nearest neighbor carbons to an adjacent vacancy. The resulting defect has C_{3v} symmetry, and usually captures an additional electron from the environment (for instance provided by a neighbor donor nitrogen impurity) to form the negatively charged NV⁻ center. Extracted from [Gali, 2019]. (b) Energy diagram and occupation of the resulting molecular orbitals for a NV⁻ center relative to the diamond matrix valence and conduction bands.

ZPL that only accounts for a few percent of the total photon emission at room temperature. The optical transition probability maximum corresponds to an average interaction with 3 to 4 phonons (Huang-Rhys factor S = 3.73 [Davies, 1981, Alkauskas et al., 2014]), yielding an absorption maximum around 560 nm (green-yellow light) and emission maximum near 690 nm (red light). Complete absorption and emission spectra are shown in Fig. 1.13.b. The optical lifetime of the NV excited state is approximately 13 ns. The large spectral separation between the absorption and emission bands is a significant practical advantage of using NV centers. It allows for easy separation of the excitation light and emitted photoluminescence (PL) with a dichroic mirror.

Within the spin-triplet ground and excited states, fine structure states are distinguished by their spin quantum number m_s , indicating spin projection on the N-to-V axis of the center. This intrinsic quantization axis corresponds to the diamond crystal's relevant $\langle 111 \rangle$ equivalent direction. In the NV center, the spin-spin interaction between the two electrons partially lifts the degeneracy between these spin states, creating a splitting D = 2.87 GHz between the ground state $m_s = 0$ and degenerate $m_s = \pm 1$ states. In the excited state, this splitting



Figure 1.13: (a) Energy diagram illustrating the Franck-Condon principle in the case of the NV center. The excited state potential energy surface has a minimum corresponding to a slightly different geometry than the ground state. As a consequence, the most probable optical transitions of the electronic state (depicted as vertical arrows in the Born-Oppenheimer approximation) correspond to wavelengths shifted relative to the zero phonon line (ZPL). These transitions occur into vibronic states, where some energy is then very quickly relaxed non-radiatively. This phenomenon gives rise to a broad phonon side band (PSB) in the NV center emission and absorption spectra. **(b)** Observed NV center optical emission and absorption spectra.

is smaller at $D_e = 1.42$ GHz. Both splittings lie in the microwave part of the electromagnetic spectrum. An important feature of the NV center is the apparent absence of spin-orbit coupling. Contrary to the usual structures found in atomic physics, the spin structure appears then as an intrinsic degree of freedom, independent of the electronic states. The optical transitions conserve the m_s spin state, leading to the selection rules $\Delta m_s = 0$. Other phenomena must then be included to fully describe the NV spin state and its evolution. First, at room temperature, the ground state splitting D is much smaller than the average thermal energy of the system ($k_BT/h \simeq 6$ THz at T = 300 K). For a single NV center, this means that its spin state will randomly fluctuate between the three allowed states in the absence of other perturbations. Accordingly, an ensemble of NV centers will be in a uniform statistical mixture of spin states. Now the real specificity of the NV center over most photoluminescent defects is the existence of other processes enabling detection and control of its spin behavior. Indeed, the S = 0 spin singlet states act as a metastable level that the NV center can reach through non-spin-conserving intersystem crossing (ISC) transitions. The position of these singlet levels is still not exactly known relative to the triplet states. Still, its shelving behavior in the NV photodynamics indicates that it should roughly be between the ground state



Figure 1.14: Diagram of the NV center electronic spin states. The NV center has a triplet ${}^{3}A_{2}$ ground state, and a triplet ${}^{3}E$ excited state. Spin-conserving optical transitions, indicated by green and red arrows, happen between these two manifolds where the electronic states are coupling to the vibronic states of the hosting diamond lattice. These levels are coupled to metastable singlet states ${}^{1}A1$ and ${}^{1}E$ via spin-orbit mediated intersystem crossing (ISC). These states host an additional infrared transition, indicated by the purple arrow. The key point for the usefulness of the NV center as a quantum sensor is that the ISC is spin-dependent, leading to spin polarization by optical pumping in the $m_{s} = 0$ state and spin-dependent photoluminescence of the NV center. Once the electronic spin state has been prepared, one can drive microwave transitions (blue arrows) to coherently manipulate it inside the ${}^{3}A_{2}$ manifold.

and excited state manifolds. We do know, however, that it hosts a radiative transition in the infrared (IR) at 1042 nm with a lifetime around 200 ns and that it couples through spin-orbit mediated ISC to the triplet states. These metastable states offer an alternative non-radiative decay channel (non-radiative in the optical band) for NV centers in their excited state. The crucial point that enables the use of the NV center as a controllable quantum bit is that the decay rates from the excited states to the singlet states are spin-dependent [Goldman et al., 2015]. From photodynamics experiments, it has been measured that the decay rate from the excited states $m_s = \pm 1$ to the singlet state manifold ($k_{\pm 1} = 53$ MHz) is approximatively 6.5 times larger than the one from $m_s = 0$ ($k_0 = 8$ MHz) [Tetienne et al., 2012, Robledo et al., 2011]. The decay rates from the metastable states back to the ground state spin levels are identical. This property is the source of the two most important features of the NV center associated to single-spin optical detection:

Spin-dependent photoluminescence

Once pumped in the $m_s = 0$ excited state, the NV center will essentially decay optically by emitting a red photon, while from the $m_s = \pm 1$ states, it will sometimes decay non-radiatively. The effective decay rate of the NV center in the optical channel is then dependent on its spin state. This translates to a spin-dependent PL intensity. In practice, the difference between the high PL and low PL states (which we will call 'contrast') varies significantly because of experimental factors but can reach up to 30% for a single NV center. This property means that one can optically determine the spin state of an NV center or an ensemble of NV centers by a simple light-intensity measurement. Note that this read-out does not correspond to a projective measurement, that would provide a single-shot detection of the spin state.

Optically induced spin polarization

Under continuous optical pumping of the system, this spin-selective ISC induces depletion of the population in the $m_s = \pm 1$ states and equivalently optical pumping in the $m_s = 0$ state. Once the system is pumped in the $m_s = 0$ state, it will mainly undergo spin-conserving radiative transitions and will remain there. Thus, a NV center that starts in the thermally populated mixed states will progressively statistically polarize to the $m_s = 0$ bright state as it undergoes more and more optical cycles between absorption and emission. One can therefore use a pulse of green light (of appropriate length and intensity depending on the setup) to efficiently prepare the quantum state of NV centers into the $m_s = 0$ spin state. This optically-induced polarization is the

first step in any coherent manipulation scheme applied to the electronic spin of the NV center.

1.3.2 - Optically detected magnetic resonance and magnetometry

The idea behind using the NV center of diamond as a quantum sensor is to use the fact that its quantum states are perturbed by the environment. External perturbations will create slight variations in the initial structure described in the previous section, whether it's applied mechanical stress, temperature, external electric or magnetic fields. We can, therefore, use the NV center as a probe if we can measure this structure. The most straightforward protocol to use the NV center spin properties is continuous-wave optically detected magnetic resonance (CW ODMR). This measurement can quantify the energy difference between the NV center's spin states, usually in the ground state manifold. The experimental scheme is then:

- Constantly illuminate the NV center (or centers) with green laser light, to polarize it into the $m_s = 0$ spin state associated to bright PL ;
- Record the PL intensity that is re-emitted by the NV center using photodetectors, which can be either avalanche photodiodes operated in the photon-counting regime or photodiodes for large ensembles of NV centers;
- Apply an external microwave field, with a varied frequency around the unperturbed splitting of 2.87 GHz, and observe the effect on the recorded PL intensity.

When the frequency of the microwave (MW) field is chosen far from resonance with the spin transition, the system is unperturbed, and the recorded PL intensity is constant. However, when the MW field is resonant with the transition, the NV center can absorb a MW photon to be driven from the $m_s = 0$ state to the dimmer $m_s = \pm 1$ states. This process, called electron spin resonance (ESR), is then detected by a sharp dip in the recorded PL intensity (see Fig.1.15). The lineshape of this dip as a function of frequency is generally Lorentzian corresponding to power broadening by the laser and MW signals [Dréau et al., 2011], but can be Gaussian if the line has a strong inhomogeneous broadening.

When a magnetic field is applied to the NV center, its S = 1 ground state will be modified by the Zeeman effect that lifts the degeneracy between states $m_s = \pm 1$ [Rondin et al., 2014]. The new position of the energy levels can then be computed by diagonalizing the following Hamiltonian for the NV center ground state :

$$\hat{\mathcal{H}}/h = D\hat{S}_z^2 + \frac{g\mu_{\rm B}}{h}\vec{S}\cdot\vec{B}$$
(1.1)

49



Figure 1.15: (a) Schematic of an NV center with the relevant excitations and emissions for ODMR. (b) Energy diagram of the NV center ground state spin levels. The $m_s = \pm 1$ states are separated from the $m_s = 0$ state by a microwave electron spin resonance (ESR) transition. Under an external magnetic field, the darker $m_s = \pm 1$ states degeneracy is lifted by a Zeeman effect, turning the single ESR frequency into two. (c) Recorded ESR spectra for an ensemble of NV centers, with increasing magnetic field in the [100] direction. When recording the defects' PL as a function of microwave drive frequency, we can see a dip appearing when the field is resonant with the ESR frequency. Under a magnetic field, the frequency difference between the two dips can be used to infer the magnetic field projection along the NV axis.

where D = 2.87 GHz is the zero-magnetic field splitting, $\hat{S} = (\hat{S}_x, \hat{S}_y, \hat{S}_z)$ is the dimensionless S = 1 spin operator vector, g = 2.003 the Landé factor for the NV center, $\mu_B = 9.274 \times 10^{-24} \text{ J/T}$ is the Bohr magneton, and $h = 6,626 \times 10^{-34} \text{ J} \cdot \text{s}$ is the Planck constant. The strength of the coupling between the spin and an external static magnetic field will often be presented as a global gyromagnetic factor $\gamma_{\text{NV}} = \frac{g\mu_B}{h} = 28 \text{ MHz/mT}$ in the following sections. Here, the spin operators are defined in the NV basis (x,y,z), where z denotes the direction of the NV quantization axis, y is chosen in a reflection plane of the defect's trigonal C_{3v} symmetry, and x completes the basis. Importantly, at first order in the small field approximation, the resulting eigenfrequencies are only affected by the magnetic fields will not modify the NV ESR frequencies but only change the Hamiltonian eigenvectors at first order. The behavior in a strong off-axis field is the main weakness of the NV center as a magnetic sensor, since the coupling to the \hat{S}_x and \hat{S}_y operators induce spin-state mixing that partially quenches the NV PL and kills the mechanisms for spin-dependent PL [Tetienne et al., 2012].

In an ODMR experiment with an applied magnetic field on a NV center, the observed ESR spectrum consists of two resonance lines, respectively, the $0 \rightarrow -1$ and $0 \rightarrow +1$ transitions (see Fig. 1.15.c). These two resonances are separated in frequency by a splitting

 $\Delta \simeq \Delta_B = 2\gamma_{\rm NV}B_{\rm NV}$ where $B_{\rm NV}$ is the magnetic field projection of the NV axis. Given this known and well-calibrated behavior, one can use an optical measurement of this ESR spectrum to infer the local magnetic field at the NV center's location.

1.3.3 - Working with an ensemble of NV centers

An additional feature of using NV centers as an atomic-like magnetometer is that the protocol described above enables the measurement of a particular magnetic field projection along a spatial direction derived from the diamond crystal axes. But the symmetry of diamond allows for four different orientations of NV centers with quantization axes along [111], $[\bar{1}11]$, $[1\bar{1}1]$ or $[11\bar{1}]$. When the NV centers are created in a single-crystal diamond, they are usually randomly aligned with one of these directions¹. This means that using an ensemble of NV centers instead of a single one, it is possible to simultaneously measure up to four independent projections of a given vector magnetic field [Lai et al., 2009]. ESR spectra recorded on ensembles of NV centers in monocrystalline diamond typically show up to eight resonance lines, two per NV possible orientation (Fig. 1.17). Using these simultaneous projections, it is possible to reconstruct the full applied vector magnetic field, with only sign indeterminacy [Chipaux et al., 2015]. Figure 1.16 shows exact numerical calculations of the expected ESR resonance frequencies observed under ambient conditions for an ensemble of NV centers, submitted to an increasing magnetic field in three different spatial directions.

Using a single NV center gives an atomic-size magnetic field sensor that can be brought extremely close to a sample, allowing the combination of this method with atomic-force microscopy (AFM) techniques for nanometer spatial resolution [Balasubramanian et al., 2008, Taylor et al., 2008, Degen, 2008]. This is a fantastic tool to explore magnetic phenomena at the smallest possible scale, where almost no other technique can compete. However, if one doesn't need such extreme spatial resolution, using an ensemble of NV centers instead of a single NV center has many advantages. Working with ensembles provides vector sensing capabilities (described previously), improved sensitivity, and lifts the need for mechanical stability that AFM imposes. The gain in sensitivity is directly linked to the optical nature of this method. The number of NV centers within the optically probed spot can be massively increased from a single center before the average excitation rate per center drops for a given input optical power. This is due to the orders of magnitude difference in the scale of optically possible resolutions (a few hundreds of nanometers) compared to a quantum object like a NV center (a few angströms). Using many NV centers for the probe is equivalent to

¹It is however possible to obtain ensembles of NV centers with preferential orientation for specific applications if they are introduced directly during diamond CVD growth.



Figure 1.16: Calculations of the expected ESR frequencies of an ensemble of NV centers for increasing magnetic field amplitude associated to different spatial directions, relative to the diamond crystal. The NV centers are aligned along the four (111) directions of the lattice. Observed transitions can overlap in preferred symmetry configurations, yielding from two to eight apparent lines.

performing multiple measurements simultaneously, logically improving the signal-to-noise ratio (SNR). The sensitivity of a magnetic field measurement using NV centers in a CW ODMR scheme reads [Dréau et al., 2011, Barry et al., 2020]:

$$\eta_B \approx \frac{\mathcal{P}_F}{\gamma_{\rm NV}} \frac{\Delta \nu}{\mathcal{C}\sqrt{\mathcal{R}}} \tag{1.2}$$

where $\mathcal{P}_{\mathcal{F}} = 4/3\sqrt{3} \simeq 0.77$ for a Lorentzian line, $\gamma_{\rm NV}$ is the NV gyromagnetic factor, $\Delta \nu$ is the ESR linewidth, C is the observed ODMR contrast and \mathcal{R} is the photon-detection rate which is proportional to the number of optically active centers. This sensitivity, expressed in $T/\sqrt{\rm Hz}$, gives the smallest detectable field variation in 1 s integration time with a SNR equal to unity at the photon shotnoise limit. Most single-NV scanning probe experiments combine 10 - 100 nm spatial resolution with sensitivity around $10 \text{ nT}/\sqrt{\rm Hz}$ [Maze et al., 2008, Grinolds et al., 2011]. But on the other hand, using a large ensemble of NV centers, sensitivities reaching 1 pT/ $\sqrt{\rm Hz}$ have been reported [Wolf et al., 2015].

In the NV-ensemble regime, magnetic field measurements are usually done around a functioning point with a small applied magnetic field so that ESR lines start already separated. Then, one records their shift under interaction with the magnetic field produced by the sample magnetization. By choosing the orientation of the applied bias magnetic field, we can adapt the measurement :

- If we align the magnetic bias field is aligned with the [100]-axis of the diamond, all NV center orientations will feel the same field projection. The result is an ESR spectrum with only two dips, since the resonances from all the NV orientations overlap. This maximizes contrast, as the observed dip in PL will be the sum of the signals from all four orientations (Fig 1.16 a). However, in this configuration, the slope of ESR lines with magnetic field is slightly reduced by a geometric factor to $\gamma_{\rm NV}/\sqrt{3}$. Additionally, this field direction has a significant off-axis component for all NV orientations. This affects the linearity of the field behavior and can be problematic if the bias field is too large by introducing parasitic PL quenching and loss of contrast [Tetienne et al., 2012].
- If the bias field is aligned with the [111]-axis of the diamond, it will be perfectly aligned along a single NV orientation. The other three NV groups are misaligned, with equivalent projections. We thus have an ODMR spectrum with four apparent resonances (Fig 1.16 b). The aligned NV centers feel no off-axis field and then show perfectly linear behavior at slope $\gamma_{\rm NV}$ with increasing field. Their eigenstates stay well defined in the magnetic states basis ($|m_s = 0\rangle$, $|m_s = +1\rangle$, $|m_s = -1\rangle$), allowing ODMR up to extremely high magnetic field value (up to 4.2 T in [Fortman et al., 2020]).
- If the bias field is aligned in an arbitrary direction with no particular symmetries, e.g. the [412] direction, then we are in the most general case. All four possible NV orientations feel different magnetic field projections, and we have an ODMR spectrum with eight apparent dips (Fig. 1.16.c). Here, all NV groups feel various amounts of off-axis field, but in the weak field regime resolution of the eight lines allows for full vector magnetic field reconstruction [Chipaux et al., 2015].



Figure 1.17: Typical ODMR spectrum that can be recorded on an ensemble of NV centers in a single-crystal diamond. The four pairs of peaks correspond to the four possible orientations for the NV centers, each seeing a different projection of the arbitrary magnetic field applied here. From [Hamlin and Zhou, 2019].

1.4 - High-pressure NV center behavior

1.4.1 - Spin-stress coupling

Under mechanical stress (or equivalent strain), the lattice of a diamond crystal will be deformed. This perturbation will affect hosted point defects such as NV centers. To perform efficient magnetometry using NV centers at high pressure, we need to understand these effects and how they affect the capability of magnetic field sensing. Theoretical work in describing stress effects on crystal defects was already partially provided in the 1960s by [Hughes and Runciman, 1967], but experimental studies on the NV center were pioneered by [Doherty et al., 2014]. Surprisingly, most of the results could be well explained by the fully analytical results obtained almost 50 years before. The notations used in the following description are inspired by more recent works such as [Teissier et al., 2014], [Barson et al., 2017], [Broadway et al., 2019], and [Barfuss et al., 2019]. Recent extensive ab-initio results can be found in [Udvarhelyi et al., 2018]. We choose to build a model Hamiltonian based on stress here, as it is the most common way to describe the compression state of samples in high-pressure experiments. In this section, we will use the stress tensor $\overline{\sigma}$, defined as

[Landau and Lifshitz, 1986]:

$$\overline{\overline{\sigma}} = \begin{pmatrix} \sigma_{XX} & \sigma_{XY} & \sigma_{XZ} \\ \sigma_{YX} & \sigma_{YY} & \sigma_{YZ} \\ \sigma_{ZX} & \sigma_{ZY} & \sigma_{ZZ} \end{pmatrix}$$
(1.3)

where (X,Y,Z) is the basis for the diamond crystal lattice. This tensor has nine components but needs to be symmetric, which reduces it to six independent components. To reflect this, we will use Voigt notation $\overline{\sigma} = (\sigma_{XX}, \sigma_{YY}, \sigma_{ZZ}, \sigma_{YZ}, \sigma_{XZ}, \sigma_{XY})$. The three first same-index terms are normal stresses, while the others are shear stresses. We will assume the convention that positive stress is compressive. How this tensor couples to the NV center Hamiltonian can then be derived from group theory looking at the effects of mechanical deformation perturbations on the C_{3v} trigonal symmetry of the unperturbed NV center [Hughes and Runciman, 1967]. The natural way of describing the effect of a perturbation on the crystal defect is to separate it into components transforming like the irreducible representations of the defect point group. Including the spin-mechanical interaction, the Hamiltonian for the NV center ground state thus reads [Barson et al., 2017]:

$$\begin{aligned} \hat{\mathcal{H}}/h &= (D + M_Z) \, \hat{S}_z^2 + \gamma_{\rm NV} \vec{\hat{S}} \cdot \vec{B} \\ &- M_X \left(\hat{S}_x^2 - \hat{S}_y^2 \right) \\ &+ M_Y \left(\hat{S}_x \hat{S}_y + \hat{S}_y \hat{S}_x \right) \end{aligned} \tag{1.4}$$

where (M_X, M_Y, M_Z) are the components of an effective field, \vec{M} , resulting from stress. It is a reduction of $\overline{\sigma}$ whose components are obtained as symmetry-adapted linear combinations of the six components of the stress tensor. Those components are :

$$M_X = b_s \left(2\sigma_{ZZ} - \sigma_{XX} - \sigma_{YY} \right) + c_s \left(2\sigma_{XY} - \sigma_{YZ} - \sigma_{ZX} \right)$$

$$M_Y = \sqrt{3} \left[b_s \left(\sigma_{XX} - \sigma_{YY} \right) + c_s \left(\sigma_{YZ} - \sigma_{ZX} \right) \right]$$

$$M_Z = a_{s,1} \left(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ} \right) + 2a_{s,2} \left(\sigma_{YZ} + \sigma_{ZX} + \sigma_{XY} \right)$$

(1.5)

where $a_{s,1} = 4.86 \text{ MHz/GPa}$, $a_{s,2} = -3.7 \text{ MHz/GPa}$, $b_s = -2.3 \text{ MHz/GPa}$ and $c_s = 3.5 \text{ MHz/GPa}$ are spin-stress susceptibility parameters (values from [Barson et al., 2017]). Note that the expressions in eq. 1.5 are valid for a [111] oriented NV center, with $\overline{\sigma}$ expressed in the diamond natural frame (X,Y,Z) where Z is the [100] direction. To compute the values of the effective \vec{M} field for the other three NV orientations in the crystal, one can simply use the same expression after applying to $\overline{\sigma}$ the rotation needed to go from [111] to [$\overline{1}$ 11], [$\overline{1}$ 1] or [$11\overline{1}$]. As expected from the way it was constructed this Hamiltonian shows terms that can be interpreted as different physical phenomena. In the spirit of what is usually done in continuum mechanics, we can differentiate between hydrostatic and non-hydrostatic (or deviatoric) stress.



Figure 1.18: Energy diagram showing the effect of stress and magnetic field on the NV center spin states. Hydrostatic pressure increases the *D* splitting by an amount δ . Non-hydrostatic stress distorts the defect's symmetry, lifting the degeneracy of upper spin states and creating a splitting Δ_{σ} . Additionally, applying a magnetic field will further increase this splitting to the observed value $\Delta = \sqrt{\Delta_{\sigma}^2 + \Delta_B^2}$.

- Hydrostatic stress on the diamond lattice happens when compression is applied isotropically to the material. Its effect is quantified here by M_Z . Hydrostatic pressure P is expressed as a diagonal stress tensor with all identical components, $\overline{\sigma} = (P, P, P, 0, 0, 0)$. Under hydrostatic stress, the symmetry of the NV center is preserved (M_Z couples only to \hat{S}_z^2 , which conserves m_s as a good quantum number to describe the defect). The stress effect is then equivalent to an apparent reduction of the lattice parameter. Consequently, the spin-spin interaction is enhanced, and the D parameter is increased by adding a factor $\delta = M_Z$. This hydrostatic shift of the ESR spectrum center has been measured to be around 15 MHz/GPa up to 60 GPa for diamond placed directly in the chamber of a DAC [Doherty et al., 2014]. For NV centers implanted in the culet of a diamond anvil, the apparent value of this effect relative to the pressure in the experimental chamber is closer to 10 MHz/GPa [Toraille, 2019]. This difference will be extensively discussed in chapter 3.
- Non-hydrostatic stress happens when the compression is not isotropic. Its effect is

modeled by the M_X and M_Y terms in eq. 1.5. When different normal stresses are applied to separate principal directions, shear-stress components are usually created through the non-linear nature of stress-strain relations (the stiffness tensor of the material has non-diagonal elements). Deviatoric stress will distort the NV center hosted by the diamond lattice, potentially breaking its symmetry. In this sense, it acts similar to an electric field, which distorts the NV orbitals [Dolde et al., 2011]. This symmetry breaking changes the eigenstates of the NV hamiltonian, which move away from the $m_s = 0, \pm 1$ state basis, since M_X and M_Y couple to functions of \hat{S}_x and \hat{S}_y which do not commute with \hat{S}_z . Regarding the eigenfrequencies, non-hydrostatic stress then lifts the degeneracy between the $m_s = \pm 1$ states, like a magnetic field, and the associated new eigenstates are mixed states of $m_s = +1$ and $m_s = -1$. It results in an ESR splitting $\Delta_\sigma = 2\sqrt{M_X^2 + M_Y^2}$ even in the absence of an external magnetic field. This splitting was measured to be steadily increasing with sample pressure at 2.3 MHz/GPa for NV centers in the culet of a diamond anvil [Toraille, 2019], where the stress is partly non-hydrostatic. Again, this effect will be discussed in chapter 3.

To summarize, applying first-order perturbation theory to the Hamiltonian in eq.1.4 that takes into account both mechanical stress and magnetic field yields ESR transition frequencies :

$$\nu_{\pm} = D + \delta \pm \frac{\Delta}{2} \tag{1.6}$$

with

$$\begin{cases} \delta = M_Z \\ \Delta = \sqrt{\Delta_\sigma^2 + \Delta_B^2} = 2\sqrt{M_X^2 + M_Y^2 + \left(\frac{g\mu_B}{h}B_{\rm NV}\right)^2} \end{cases}$$
(1.7)

These equations show that in a high-stress regime the dependence of the NV center ESR with the applied magnetic field is significantly modified (see Fig. 1.18). This effect needs to be accounted for to allow quantitative magnetic field assessment, and it also raises the question of a potential pressure limit for NV magnetic sensing. This is still an open question, but the results of this thesis hopefully will advance this question. Note that a manuscript appeared on pre-publication servers in 2022, claiming observation of NV center ODMR in hydrostatic conditions up to 146 GPa [Dai et al., 2022]. The experiment was realized by integrating NV-doped nanodiamonds in a DAC. Although the paper hasn't appeared in a peer-reviewed journal yet, it would be the first occurrence of NV centers being used above the megabar. This result corroborates the idea that the current practical pressure limit might be due to the amount of non-hydrostatic stress applied to the diamond point defects. This topic will be the focus of chapter 3.

However, this dependence to stress fields also means that in a controlled magnetic field environment, the NV center can be used as an extremely accurate complete stress-tensor sensor [Broadway et al., 2019]. Once again, the use of an ensemble of NV centers provides multiple 'projections' of the stress tensor, disclosing its whole nature and not only an average pressure or a single component of the stress tensor. Recent work by [Ho et al., 2020] has shown that this dependence can be used to assess pressure inhomogeneities in a DAC's PTM, although this has already been investigated by measuring the fluorescence of ruby micro-crystals [Klotz et al., 2009]. We will use this method in chapter 3 to better understand the stress at the tip of a pressurized diamond anvil.

For the sake of completeness, one should mention here that a few other published papers have started to investigate coherent spin manipulation schemes with NV centers, to gain more insight into their high-pressure physics and additional sensing capabilities. In [Shang et al., 2019] the authors demonstrated Rabi oscillations, spin relaxation and spin dephasing measurements for an ensemble of NV centers up to 32.8 GPa. More recently, the same group exhibited hyperpolarization and coherent control of ¹⁴N nuclear spins up to 16 GPa [Shang et al., 2022]. This demonstrates that the use of pulse-sequence measurement schemes and nuclear spins as quantum resources, well established at ambient conditions, can be envisioned in a DAC.

1.4.2 - Pressure dependence of the NV photoluminescence

When considering the high-pressure behavior of NV centers, we have focussed so far on the fine structure spin manifold of the ${}^{3}A_{2}$ ground state. It is of course the main focus of this text since it provides the basis for NV-based magnetometry. Still, we shouldn't forget that the experimental realization of these experiments relies on the optical excitation of the NV defects, which involves transitions to the ${}^{3}E$ excited states. Distortions of the diamond lattice induced by stress of any nature also affect the NV center's optical transitions. An extensive review of the high-pressure spectroscopy efforts on the NV center can be found in [Vindolet, 2021].

The optical behavior of an NV center under compressive stress is theoretically described in analogy with the spin-state behavior. The group theoretical approach developed in [Hughes and Runciman, 1967] can be applied to the optical transition between the ground state of A symmetry and the excited state of E symmetry. The NV center ZPL increases in energy under hydrostatic stress (see Fig. 1.19.a), and deviatoric stresses further split it into two components. These effects have also been proposed as a fully optical method to measure stress using NV centers [Grazioso et al., 2013]. However, liquid nitrogen temperature is needed for the ZPL linewidth to be fine enough for efficient sensing.

Regarding ODMR-based sensing, the pressure-induced optical shift of the NV center leads to an experimental challenge. As the pressure increases, the NV centers' emission spectrum shifts towards shorter wavelengths, possibly exiting the spectral filters used at ambient pressure, and the absorption spectrum is also shifted. This means that the green lasers used to pump the NV centers at ambient pressure efficiently will lose efficiency as the experiment proceeds, then requiring the use of alternative shorter wavelength laser excitation.

The displaced and split ZPL energy $E_{\rm ZPL}$ of the NV⁻ with mechanical stress can be expressed as :

$$E_{\rm ZPL} = E_{\rm ZPL}^0 + \delta_o \pm \frac{\Delta_o}{2} \tag{1.8}$$

where $E_{\text{ZPL}}^0 = 1.945 \text{ eV}$ is the ambient condition ZPL energy, and $\delta_o = \gamma_o$, $\Delta_o = 2\sqrt{\alpha_o^2 + \beta_o^2}$ are defined through expressions similar to eq. 1.5 :

$$\alpha_{o} = b_{o} \left(2\sigma_{ZZ} - \sigma_{XX} - \sigma_{YY} \right) + c_{o} \left(2\sigma_{XY} - \sigma_{YZ} - \sigma_{ZX} \right)$$

$$\beta_{o} = \sqrt{3} \left[b_{o} \left(\sigma_{XX} - \sigma_{YY} \right) + c_{o} \left(\sigma_{YZ} - \sigma_{ZX} \right) \right]$$

$$\gamma_{o} = a_{o,1} \left(\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ} \right) + 2a_{o,2} \left(\sigma_{YZ} + \sigma_{ZX} + \sigma_{XY} \right).$$

(1.9)

Here the $a_{o,1}$, $a_{o,2}$, b_o and c_o parameters are spin optical susceptibilities. Their values were computed and measured by [Davies and Hamer, 1976] to be $a_{o,1} = 1.47 \text{ meV/GPa}$, $a_{o,2} = -3.85 \text{ meV/GPa}$, $b_o = 1.04 \text{ meV/GPa}$ and $c_o = 1.69 \text{ meV/GPa}$ up to 2 GPa. Recent results extended these measurements to about 50 GPa under hydrostatic conditions [Kobayashi and Nisida, 1993, Doherty et al., 2014, Lyapin et al., 2018], agreeing on a total shift close to 5.6 meV/GPa or equivalently -1.8 nm/GPa.

As in the case of the spin transitions described in the previous section, results are significantly different when these measurements are performed on NV centers implanted in the culet of a diamond anvil. [Vindolet, 2021] performed spectroscopy experiments on NV centers in the exact same implantation conditions as the one used in this work, and reported a shift with sample pressure of 2.73 meV/GPa or -0.88 nm/GPa, recorded up to 40 GPa. This result falls just in between the slopes measured for hydrostatic pressure and uniaxial stress (see Fig.1.19.b), which supports the idea that the stress landscape in the anvil culet is significantly deviatoric.



Figure 1.19: (a) Optical spectra recorded at 2.5 and 38 GPa for NV centers implanted in the culet of a diamond anvil. We see a shift towards shorter wavelengths. Red arrow indicate the NV ZPL, black arrow indicates the diamond Raman. **(b)** Comparison of the NV ZPL energy evolution with pressure, in different experimental conditions. The results of [Doherty et al., 2014, Kobayashi and Nisida, 1993, Lyapin et al., 2018, Davies and Hamer, 1976] are obtained in hydrostatic conditions, [Davies and Hamer, 1976] in uniaxial stress and [Vindolet, 2021] (Exp n°1 and n°2) using NV centers implanted in the surface of an anvil culet. [Romanova, 2019] is a DFT calculation performed with hydrostatic conditions. Figures from [Vindolet, 2021].

1.5 - Experimental realizations of high-pressure NV magnetometry

First implementations of NV centers of diamond as *in-situ* magnetic quantum sensors in the context of high-pressure DAC experiments originally appeared in 2019, in three independent papers published back-to-back [Lesik et al., 2019, Hsieh et al., 2019, Yip et al., 2019] (note that [Lesik et al., 2019] was published by our group). The idea is to use the NV centers' magnetic field sensing capabilities by bringing them in close proximity to a sample pressurized in a DAC. These three papers demonstrated three different technical approaches, and various proof-of-principle experiments that immediately established the method as useful for high-pressure science. They were shortly followed by work from [Shang et al., 2019]. A year later, the work from our group was completed by [Toraille et al., 2020], where compatibility with synchrotron-based techniques like XRD was demonstrated. Table 1.1 summarizes a comparison of the published papers exhibiting NV center sensing in the context of high-pressure diamond anvil cells, at the time this manuscript was written (during October 2022).

First, the three original studies differed in the implementation chosen to integrate NV centers in the DAC. [Yip et al., 2019] dispersed commercially available diamond particles (nano



Figure 1.20: (a) Schematic of the NV-enabled DAC in [Hsieh et al., 2019]. (b) Zoom on a cross-section of the sample chamber of the DAC. The gasket, realized in a copper-beryllium thin foil, holds a sample and a ruby pressure gauge. NV centers are implanted in the culet of one of the anvils, about 50nm under the surface. (c) Top view showing the position of the platinum foil used as a wire antenna for microwave excitation. The foil is deposited onto the anvil so that when the DAC is closed it passes micrometers away from the diamond culet edge, over the first diamond bevel. Extracted from the supplementary materials of [Hsieh et al., 2019]. (d) Confocal microscope image of the experiment in [Shang et al., 2019]. We can see the circular outline of the gasket hole, with the samples in the center. Here the NV centers are hosted in luminescent nanodiamonds that have been deposited on the culet of an anvil. We also see the outline of a ruby bead that is extremely bright compared to the NV-doped nanodiamonds. This very high contrast in luminescence can be problematic when imaging the NV centers, providing some parasitic background.

Paper	NV implementation	Collection	MW delivery	Max. pressure	Systems investigated
[Lesik et al. 2010]	${\cal N}^+$ implantation into ultrapure anvil	Widefield	Customized MW gasket	30 GPa	Fe $\alpha - \epsilon$ magnetic transition
[Lesik et al., 2015]					MgB_2 superconducting transition
	$^{12}C^+$ implantation into anvil	Confocal	$\operatorname{Pt}\nolimits$ wire next to gasket hole	22 GPa	P-T magnetic phase diagram of Gd
[Hsieh et al., 2019]					Fe $\alpha - \epsilon$ magnetic transition
					Culet stress in (111) anvil
[Vip of al. 2010]	Doped nanodiamonds	Confocal	Micro coil with sample	3 GPa	Superconducting transition of
[rip et al., 2019]					$BaFe_2(As_{0.59}P_{0.41})_2$
[Shang et al., 2019]	Doped nanodiamonds	Confocal	Pt wire next to gasket hole	33 GPa	$\rm Nd_2Fe_{14}B$ magnetic phase transition
Toraillo et al. 20201	${\cal N}^+$ implantation into ultrapure anvil	Widefield	Customized MW gasket	30 GPa	Fe $\alpha - \epsilon$ magnetic transition
[Toralle et al., 2020]					Same-sample synchrotron XRD

Table 1.1: Comparison of published realizations of NV center magnetometry at high pressure in diamond anvil cells.

or microdiamonds) highly doped with NV centers on the surface of one of the anvils (see Fig. 1.20.d). Some particles were trapped in the experimental chamber at random positions with the sample of interest, providing discrete points for local magnetic field assessment. This method is easy to implement since it requires the deposition of a diamond particle solution droplet on an anvil's culet. The downside is that the exact position of the sensors is obviously random, and one might need to perform multiple measurements to obtain a satisfying configuration. Moreover, even if the microdiamonds happen to be monocrystalline (which they aren't necessarily, depending on the process used for their synthesis [Chang et al., 2018]), their orientation upon deposition will also be random. For any vector magnetic field information to be reconstructed, one needs extensive measurements to determine each particle's 3D orientation first.

Another solution to integrate NV centers into the DAC was chosen by [Lesik et al., 2019] and [Hsieh et al., 2019]. Inspired by efforts in the engineering of NV centers [Toyli et al., 2010, Pezzagna et al., 2010b, Spinicelli et al., 2011, Lesik et al., 2013], the authors of these papers chose to use ion implantation directly into the culet surface of anvils to create large ensembles of NV centers (see Fig. 1.20.b). This method can generate high local NV center densities and takes advantage of the single-crystal nature of diamond anvils. Implanted NV centers will adopt only the four allowed orientations possible within the diamond bulk lattice they are put in. This means that if the anvil surface crystallographic plane is known (usually (100), but also (110) or (111)), the orientation of all artificially created NV centers can be computed in the laboratory frame. [Lesik et al., 2019] used ultra-pure llas anvil targets and implanted N^+ ions with 30 keV energy to create a shallow layer of NV centers, around 5 nm thick and 20 nm into the surface. [Hsieh et al., 2019] opted for ${}^{12}C^+$ implantation with similar parameters into Ib anvils already containing traces of nitrogen. This method offers an effective way of creating large addressable ensembles of NV centers without touching the DAC's sample volume, but usually submits the defects to the largely non-hydrostatic stress field inside the anvils. This will be extensively discussed in chapter 3.

Another point differentiating high-pressure NV magnetometry experiments is the optical setup used to excite and collect NV photoluminescence. Most investigations to date have used a standard confocal fluorescence-type microscope to image the NV centers in the DAC. This well-known, standard microscopy setup uses a sensitive point-like detector, like a single photon avalanche diode (SPAD), to count photons within a carefully selected sample volume delimited by the point-spread-function (PSF) of the used optics. This point is then scanned while counting to construct an image of the desired area. The confocal part is a pinhole placed at a lens focal point to spatially select the light reaching the detector. This is a very precise imaging method (down to 250 nm lateral resolution and 500 nm depth of field), but in the DAC environment its capabilities are limited by the need to use low numerical aperture objectives with long working distance to look through the millimeter-thick anvils. Due to diamond's high refractive index, the image quality is usually further degraded by aberrations. All experimental reports of NV-enabled DAC measurements used a confocal setup, except [Lesik et al., 2019] and [Toraille et al., 2020]. In those two papers, our group chose to use the other imaging method for NV magnetometry: widefield microscopy [Scholten et al., 2021]. Here, the optical setup is similar, except that no pinhole is used, and an image of the NV layer is directly formed onto a camera sensor with a lens. This method allows for imaging without scanning, making it much faster to record a high-resolution image using the multiplexing advantage of the camera (usually a CCD or CMOS sensor). The standard depth of field is significantly larger than for a confocal microscope due to the lack of spatial filtering, but in a DAC with the constraints mentioned before one can still achieve comparable spatial resolution. This can be a significant advantage in an environment where the acquisition time can be limited, during allocated synchrotron beamtime for instance (see Fig. 1.21).

Another technical point differentiating the studies listed in table 1.1 is the solution chosen to bring the microwave excitation into the DAC. This is one of the main challenges of implementing NV spin control in high-pressure experiments. For experiments above 10 GPa, the best gasket material is rhenium metal, which can sometimes be substituted for CuBe, which is also metallic. Using these, an oscillating magnetic flux through the gasket hole will induce eddy currents in the gasket edge that will compensate for this flux due to Lenz's law. Consequently, the resulting microwave field created in the sample volume by a loop antenna outside the DAC, for example, is turned to almost zero at the culet surface. This issue was already approached by nuclear magnetic resonance (NMR) specialists trying to study compressed materials [Lee et al., 1992, Pravica and Silvera, 1998, Meier, 2018], but no consensus on a superior technique ever emerged. Within the papers considered here, three approaches were attempted.[Shang et al., 2019] used a micro-coil inside the sample volume,



Figure 1.21: Schematic of the experimental setup used in [Toraille et al., 2020] to perform NVbased magnetic measurement and XRD measurement in a DAC. It shows a typical widefield microscopy setup for imaging NV centers, with a dichroic mirror (DM), a spectral filter (F), and a CMOS sensor. This is all put on a sliding optical breadboard, to which the excitation laser is brought by an optical fiber. The whole setup (grey part with dashed outline) can thus be moved out of the DAC axis to leave room for the synchrotron X-ray beam. The X-ray diffraction patterns are collected onto an image plate detector (IPD).

in a setup very close to the pick-up coil reported in [Alireza and Julian, 2003]. This solution dramatically limits possible sample size reduction, therefore limiting attainable pressures to $\simeq 3 \,\mathrm{GPa}$ here. Alternatively, [Hsieh et al., 2019] and [Yip et al., 2019] took the option of bringing a linear wire antenna as close as possible to the gasket hole by squeezing a plat-inum wire between the gasket and the anvil (see Fig. 1.20.c). This most likely creates an Oersted-type field configuration where the MW field component normal to the hole is highly screened but still significant within the sample chamber, and where the MW tangential components are maintained. In all cases, this technique relies heavily on the integrity of the wire, which is squeezed similarly to electrodes in high-pressure transport measurements. The reported experiments using this technique reached a pressure limit of $\simeq 30 \,\mathrm{GPa}$. Our group implemented another approach to the MW excitation problem. It consists of an additional machining step of the gasket, to operate a topology change turning the gasket itself into an inductive microwave flux concentrator called a Lenz lens [Jouda et al., 2017]. The details of this setup will be explained in chapter 2. This not only allows the microwave flux to penetrate the sample volume, but it also focuses it inside of that volume by creating an effective

antenna which is the hole perimeter. Using this MW delivery technique, we reported results up to 30 GPa in [Toraille et al., 2020], but further improvement since allowed us to reach pressures significantly above the megabar, as shown in chapter 3.

Finally, all of these papers show the versatility of the technique by probing various physical phenomena. In [Lesik et al., 2019, Hsieh et al., 2019, Toraille et al., 2020], NV centers were tested on the well-known magnetic phase transition of iron which is a classic of high-pressure magnetic investigations [Bassett and Huang, 1987, Dewaele and Nataf, 2022]. Around 20 GPa at room temperature, iron undergoes a structural change from a body-centered-cubic α phase to a hexagonal close-packed ϵ phase, which is accompanied by the loss of its common ferromagnetism. [Toraille, 2019] further demonstrated that NV magnetometry could be performed in parallel to XRD to investigate structural and magnetic properties on the same sample. In [Hsieh et al., 2019, Shang et al., 2019], high-pressure NV sensing was used to assess the magnetic pressure-temperature phase diagram of other ferromagnets: elemental Gd and Nd₂Fe₁₄B. Last but not least, [Yip et al., 2019] and [Lesik et al., 2019] also presented the first test detections of high-pressure Meissner effect using NV centers. The method is here to use NV centers in close proximity to a superconductor to detect the local magnetic field change that happens when the material transitions. Both papers investigated superconductors with low $T_{c_{\ell}}$ MgB₂ and BaFe₂(As_{0.59}P_{0.41})₂ and were able to measure their critical temperatures at respective pressures of 7 GPa and 3 GPa (Fig. 1.22). In chapter 2 of this thesis, we will describe our effort to apply this method to measure the critical temperature of a HTSC cuprate up to 31 GPa.



Figure 1.22: (a)(b) Extracted from [Yip et al., 2019]. (a) Recorded NV ESR splitting when crossing the superconducting transition of $BaFe_2(As_{0.59}P_{0.41})_2$ at multiple pressures. We clearly see the screening of the applied bias magnetic field (7 mT) due to the Meissner effect. (b) Phase diagram for the superconducting phase of $BaFe_2(As_{0.59}P_{0.41})_2$ up to 30 kbar (3 GPa). The micro-coil used for MW excitation also allowed AC susceptibility measurements in the same pressure range. (c)(d) Extracted from [Lesik et al., 2019]. (c) Widefield map of the NV ODMR splitting around a MgB_2 sample at 7 GPa, recorded at increasing temperatures across the superconducting transition. We see a clear diminution of the 1.8 mT magnetic field applied which is perfectly correlated with the spatial position of the sample. (red square in the top left-hand corner micrograph). (d) Extracted critical temperature curve from the images shown in (c). The inferred value of $T_c \simeq 30$ K was in perfect agreement with previous measurements (see for instance [Buzea and Yamashita, 2001]).

1.6 - Conclusion

In this first chapter, we provided a review of the state-of-the-art in the two main areas of interest for this thesis: research into high-pressure superconductivity and quantum magne-tometry using Nitrogen-Vacancy centers of diamond.

We saw that studying materials under high pressure constitutes an important branch of condensed matter physics, as it provides a crucial tuning parameter to explore the structural and electronic properties of solids. The phenomenon of superconductivity, in particular, has been tightly linked to high-pressure studies, most notably in the search for higher critical temperatures. However, the most common tool to generate extreme conditions of pressure, the Diamond Anvil Cell (DAC), introduces major constraints on the set of experimental measurements that can be performed on high-pressure samples. The community nowadays faces important challenges in the reliability and reproducibility of experiments trying to study or demonstrate high-pressure superconductivity above a few tens of gigapascals, a situation that calls for the development of new high-pressure experimental magnetic diagnoses.

We then discussed how certain color centers of diamond, called Nitrogen-Vacancy (NV) centers, can be used as quantum optical probes of local magnetic fields. In the past 15 years, they have been extensively used as versatile and robust sensitive magnetometers in a wide variety of conditions, the most recent one being high pressure. It has been shown that NV centers can be integrated within a DAC to provide optical *in-situ* sensing of magnetic properties under high stress, for samples such as ferromagnets or superconductors. Their use as a new way of directly detecting high-pressure superconductivity through the Meissner effect provides a novel pathway to test controversial claims of ultra-high-temperature superconductivity in super-hydrides.

This logically brings us to the work described in this thesis, where we performed further tests of high-pressure NV magnetometry on a high-temperature superconductor, before understanding the limits of this method toward the megabar pressure regime and attempting to circumvent them.

Chapter 2

Measurement of superconducting transition temperatures up to 31 GPa

Thus the mercury at 4.2K has entered a new state, which, owing to its particular electrical properties, can be called the state of superconductivity.

Heike Kamerlingh Onnes, Nobel Lecture, December $11^{\rm th}, 1913$

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2.1 - Introduction

As described in the previous chapter, measuring the properties of known or potential superconductors under high hydrostatic pressure is an important branch of contemporary condensed matter physics. It is however a real challenge to perform reliable and reproducible measurements exhibiting the hallmarks of superconductivity on the minuscule and hardly accessible samples compressed inside a DAC. This challenge is even rendered harder by the extreme pressures necessary to stabilize some of the state-of-the-art best superconductors (more than 100 GPa for most super-hydrides for instance). As described in the previous chapter, NV center-based magnetometry provides a novel method for the *in-situ* detection of the Meissner effect in a DAC. The method has been used in different experimental conditions to detect the superconducting transition of low- T_c superconductors, up to 3 GPa for BaFe₂(As_{0.59}P_{0.41})₂ in [Yip et al., 2019], and at 7 GPa for MgB₂ in [Lesik et al., 2019].

In this chapter, we describe preliminary results on the extension of this method to higher pressure, on a high- T_c superconductor. After providing background information on the chosen test-bed, mercury-bearing cuprate Hg-1223, we will describe our current experimental platform allowing high-pressure low-temperature NV magnetometry. Then, we will detail the results obtained during two separate experimental runs, that demonstrated our capability to detect superconductivity up to 31 GPa. We will present results obtained both in a confocal microscope setup for accurate point measurements, but also widefield cartographies that revealed a spatially inhomogeneous behavior.

2.2 - Cuprate high-temperature superconductor

2.2.1 - Atomic structure

The term 'cuprate' usually designates a family of materials made of copper oxide layers and other metals. Their crystal structure is derived from perovskite structures (the most common example of a perovskite being $CaTiO_3$ with space group *Pbnm*). In general, perovskites have chemical composition RMO_3 , where R is a rare earth element, M is a transition metal, and O is oxygen. In this structure, a cubic lattice of rare earth cations hosts oxygen octahedra with a metal ion at their center. In cuprates in particular, one can add layers inside of that structure to obtain layered perovskites showing tetragonal symmetry where *n* planar CuO structures clearly appear. In this framework, the standard perovskite then corresponds to the $n \to \infty$ case.


Figure 2.1: (a) Schematic of the general structure of cuprates. They are layered materials comprised of quasi-2D copper oxide layers, with intermediate layers acting as charge reservoirs. Superconductivity in these materials is believed to be closely linked to the existence and possible interactions between CuO planes. Picture adapted from *ucdavis.edu*. (b) Crystal unit cell for the most common family of cuprates. Cuprates are often given names in the formalism M12(n-1)n, where M is a metal element and n is the number of CuO planes in a given possible structure's unit cell. When $n \ge 3$, structures host inequivalent CuO layers: outer planes (OP) in contact with the charge reservoirs, and inner planes (IP) sheltered in the middle. These planes with the same composition but different coordinations can be differentiated in element-specific experiments such as nuclear magnetic resonance. Adapted from [Mukuda et al., 2012].

A crucial part of the physics of these materials is the important Jahn-Teller distortions of the CuO₆ octahedra elongating the *c* axis, which imply very different behaviors for electronic orbitals of the 'in-plane' oxygens compared to the 'apical' ones (out of plane). Cuprates are an exciting category of materials, as copper oxide is the only known oxide with an electronic band intercepting the Fermi level. In a theoretical view, cuprates are made of CuO planes sandwiched between rare earth oxide ionic salt blocks that act as charge reservoirs (Fig. 2.1.a). Many different compounds can be made following this scheme, generally using R = Ba, La, Tl, Bi, Nd, Y, and superconductors have been found in almost all of these subfamilies. Combining Ba with another element proved particularly useful historically, with the discovery of $YBa_2Cu_3O_{6+\delta}$ in 1987 being quickly followed by a zoo of isostructural compounds, all with T_c above 90 K using La, Nd, Sm, Eu, Gd, Ho, Er, and Lu instead of Y [Hor et al., 1987].

2.2.2 - Doping properties

Another key point of cuprates physics is their capacity to accept charge carrier doping. By substituting part of their rare earth ions with others with different electronic structures, one can effectively dope CuO planes with either holes or electrons. Here are two examples:

- Hole doping in LSCO: $La_2CuO_4 \rightarrow La_{2-x}Sr_xCuO_4$ by substituting some Sr^{2+} onto La^{3+} sites (takes away one electron per copper atom)
- Electron doping in NCCO : $Nd_2CuO_4 \rightarrow Nd_{2-x}Ce_xCuO_4$ substituting some Ce^{4+} on Nd^{3+} sites (adds one electron per copper atom)

One can also obtain carrier doping without rare earth substitution by oxygen doping the material after or during synthesis (with a high-oxygen partial pressure atmosphere). That way, we can get materials like the one of interest for this chapter: $HgBa_2Ca_2Cu_3O_{8+\delta}$ (Hg-1223).

The behavior of cuprates is then heavily modified by doping, with a particularly rich phase diagram (see Fig. 2.2). Doping percentage is generally denoted p. Note that electron doping is usually more difficult than hole doping, probably because of Coulomb repulsion: the only cuprates known to accept electron doping are those without apical oxygens. Very few materials can be doped both ways.

The main feature of cuprates outside the high-temperature superconductivity (HTSC) phase is the existence of a so-called 'pseudogap' phase: cuprates transform from antiferromagnetic Mott insulators to metals under progressive hole doping, but with an intermediate hybrid regime in the under-doped region (below the optimal doping for superconductiv-



Figure 2.2: Generic phase diagrams for cuprate superconductors. **(a)** Phase diagram showing usual cuprate phases with temperature and doping both with electrons and holes. The doping ranges where some common cuprates have been investigated are shown. Hole doping rapidly kills antiferromagnetic insulator (AFI) behavior, giving rise to the pseudogap and superconducting (SC) phases. In the less studied electron doping regime, the antiferromagnetic phase is more robust, while the domain for superconductivity is reduced. No pseudogap phase has been demonstrated in electron-doped systems. Extracted from [Peets et al., 2007]. **(b)** Generic phase diagram for hole-doped cuprates with temperature and doping. Cuprates exhibit a very rich phase diagram resulting from multiple competing phenomena. They have been proven to host antiferromagnetic behavior, charge density wave (CDW) or spin density wave (SDW) orders, superconductivity, and the pseudogap phase. The name 'strange metal' denotes a conductive phase where resistivity shows a linear dependence with temperature. Extracted from [Mark et al., 2022].

ity). The low-energy excitation deficit in the pseudogap phase has been demonstrated using nearly all spectroscopy techniques, first in NMR experiments, then using neutron scattering, Raman, ARPES, giving many insights into this peculiar state of matter.

2.2.3 - Surprising superconductivity

Cuprates are a very diverse category of HTSC that gained massive interest from 1986 onwards with the discovery of LBCO and mostly YBCO, the very first superconductor with T_c above nitrogen boiling. This discovery was a real surprise at the time, as these exceptionally high critical temperatures went against the most commonly accepted pathways to improving T_c . Cuprates were the first significant class of superconductors to deviate from the standard BCS theory [Bardeen et al., 1957], which explains superconductivity by the formation of electron-electron pairs through a phonon-mediated coupling. From this, one can derive an equation estimating T_c from other physical parameters :

$$k_B T_c = 1.13\hbar\omega_D e^{-\frac{1}{VN(\varepsilon_F)}} \tag{2.1}$$

where ω_D is the material Debye phonon frequency, V the electron-phonon coupling strength, and $N(\varepsilon_F)$ the electronic density of states at the Fermi level. From this equation, three strategies can be envisioned to look for high T_c materials :

- increase ω_D : use light elements (could be the origin of the unusually high T_c in hydrides, containing mostly H).
- increase *V*: this coupling is strong close to lattice instabilities at structural transitions, or in the proximity of charge density wave (CDW) order, for instance.
- increase $N(\varepsilon_F)$: use transition metals.

Another rule of thumb is that magnetic orders dramatically kill superconductivity. Cuprates, however, generally don't involve light elements and don't have a high density of states as they usually only have one band crossing the Fermi level. Moreover, they are typically insulators under ambient conditions and strong antiferromagnets (with $T_{\text{Neel}} \sim 300 - 500 \text{ K}$). These elements would rather tend to make cuprates stray away from HTSC.

The discovery of their robust SC phases actually relied on Bednorz and Muller's intuition that octahedral distortions would enhance electron-phonon coupling. In the end, many experimental studies later proved that the mechanisms for superconductivity in cuprates were strongly non-BCS, then opening the field of 'unconventional' superconductivity (compared to 'conventional' superconductors explained by BCS theory). Estimates of T_c from eq. 2.1 therefore aren't really relevant in the case of cuprates. Doping the cuprates actually kills long-range magnetic order while keeping weak magnetic correlations, which could act as the seed of electron pairing.

From the fundamentals of their structure with their CuO planes, one can easily imagine that cuprates would be highly anisotropic materials. In their pseudogap phase, angleresolved photoemission spectroscopy (ARPES) experiments have shown that they exhibit a peculiar dichotomy between nodal ((π , π) direction in reciprocal space) and anti-nodal ((0, π) direction) regions of the Fermi surface [Kaminski et al., 2005]. The density of states on the Fermi surface appears to be non-uniform, with preferential directions along the Cu – O axes. This directionality also extends clearly into the SC phase.

One of the reasons identified as the origin of these anisotropies is the particular symmetry of the wave function of the SC Cooper electron pairs. BCS theory predicts an orbital part of the wave function of zero angular momentum l = 0, even and without a sign change, and especially isotropic over the whole Fermi surface. This type of conventional pairing is generally referred to as 's-wave.' This symmetry is well verified by most simple metallic superconductors and probably by hydrides. It gives rise to a SC phase without noticeable anisotropies, having an isotropic SC gap. Cuprates clearly show different behavior. The formation of SC pairs of angular momentum $l \neq 0$ allows different pairing symmetries, particularly the so-called 'd-wave' symmetry. This was demonstrated in cuprate HTSC using SQUIDs [Wollman et al., 1993], and phase-sensitive Josephson junctions [Van Harlingen, 1995]. We then have a gap function changing sign by vanishing on the 'diagonal' of the Brillouin zone ($\Gamma - (\pi, \pi)$ direction), giving a gap amplitude depending on the Fermi angle θ (defined on the figure 2.3). The gap thus appears to have the form $\Delta_k = \Delta_0(k_x^2 - k_y^2)$ (see [Hashimoto et al., 2014] for ARPES evidence on Bi2212 for instance).

Undoped cuprates generally aren't superconductors but gain a SC phase when they are hole-doped (electron-doped ones can also show superconductivity, but with much lower T_c and at very precise doping, see Fig. 2.2). Their critical temperature rises with increasing doping before decreasing and vanishing, giving rise to the famous 'superconducting dome' specific to cuprate superconductors. This parabolic boundary for the SC phase shows a maximum at given optimal doping, generally, around p = 0.16 where T_c is maximum, that could coincide with a zero-temperature quantum critical point [Sachdev, 2010]. This nonmonotonous behavior of T_c with doping is another element making cuprates strongly nonconventional superconductors, with incredibly rich physics arising from multiple competing forms of order.



Figure 2.3: (a) Schematic of the first Brillouin zone in the CuO plane for a typical cuprate. The green line is the Fermi surface. The Fermi angle θ is defined to quantitatively distinguish nodal and anti-nodal points of the Fermi surface. **(b)** Measurement of the anisotropic SC gap in overdoped Bi2212 from ARPES measurements, as a function of the Fermi angle. We clearly see the gap vanishing at the nodal points of the Fermi surface, indicating its d-wave symmetry. Extracted from [Hashimoto et al., 2014], together with (a). **(c)** ARPES measurement of the density of states at different points of the Fermi surface in the pseudogap phase of Bi2212. Here too, we see clear anisotropy, with the antinodal (A) points showing a deficit of coherent quasiparticles compared to the nodal region (N). Extracted from [Kaminski et al., 2005].

2.2.4 - High-pressure studies of \mathbf{T}_{c} in Hg-1223

High-pressure investigations of cuprates have been instrumental in improving their properties, first through the foreshadowing of chemical pressure improving T_c through atomic substitutions, and then most directly by improving it at fixed composition and doping. [Mark et al., 2022] provides a recent review of these contributions of high-pressure to our understanding of cuprates. In general, pressure appears to have a similar effect to doping on the SC critical temperature because compressing the material can change carrier density in the CuO planes responsible for superconductivity. As shown in Fig. 2.4, most cuprates exhibit an initial rise in T_c with pressure, reaching an optimum before decreasing. However, cuprates are very diverse, and multiple exceptions to this behavior have been reported. The most notable one is probably Bi-bearing ones, where [Chen et al., 2010, Deng et al., 2019] reported a second surge in T_c around 20 to 30 GPa, without apparent signs of saturation in the pressure ranges that they were able to test. As detailing the entire literature relevant to cuprates under high pressure would be pointless, we will focus, in the rest of this section, on the particular compound that will be of interest in this manuscript.

To test the capabilities of NV-center magnetometry as a high-pressure probe of superconductivity, we decided to focus on the material that held the record highest T_c until the recent discovery of hydrides. Hg-1223 is a mercury-based cuprate discovered in 1993 [Schilling



Figure 2.4: Review of superconducting temperature variation with pressure in the most investigated HTSC cuprates. Pressure usually draws a T_c dome, like doping, but sometimes a second increase of T_c has been It has been postushown. lated that competing electronic orders in the different copper oxide planes might play a role, but the exact mechanisms for this are still unknown. Almost all experiments were limited to a maximum pressure of about 50 GPa. From [Mark et al., 2022].



Figure 2.5: Atomic structure of mercury-based cuprates Hg-1201 and Hg-1223. By adding calcium into Hg-1201, a new structure with three parallel CuO planes is stabilized, leading to the ambient pressure T_c record holder Hg-1223. Extracted from [Auvray et al., 2021].

et al., 1993], in its three copper oxide planes variant, with chemical composition $HgBa_2Ca_2Cu_3O_{8+\delta}$. Its tetragonal structure [Cantoni et al., 1993] is shown in Fig. 2.5. Adding Ca to the previously discovered Hg-1201 compound was the key element to synthesizing a superconductor with $T_c = 133 \text{ K}$ instead of 92 K, most likely by forcing the formation of outer CuO planes protecting the central one. Already a record at the time, T_c was still increased under hydrostatic pressure. [Nuñez-Regueiro et al., 1993, Chu et al., 1993] quickly demonstrated that pressurizing the material could increase T_c up to 157 K for 23.5 GPa, or 153 K at 15 GPa depending on exact doping. Our reference measurement will be [Gao et al., 1994], which provided a study comparing different mercury-bearing cuprates at optimal doping up to 45 GPa, and recording $T_c = 164$ K at 31 GPa (Fig. 2.6). This result was never reproduced since, probably due to the difficulty of high-pressure transport measurements on these samples. Layered cuprates are ceramic materials that can be synthesized as monocrystals at ambient pressure. However, maintaining sample integrity at high pressure while keeping in contact with deposited electrodes above a few tens of gigapascals is challenging. Note that a couple of high-pressure papers have come back to this material since, from slightly different angles. [Monteverde et al., 2005] showed that fluorination could still marginally further improve T_c by a few kelvins, while [Yamamoto et al., 2015] provided a thorough analysis of doping and pressure dependence of T_c up to 12 GPa.

This establishes Hg-1223 as a state-of-the-art cuprate superconductor, with literature

covering its T_c behavior under hydrostatic pressure up to 45 GPa. This particular compound still holds the record for T_c at ambient pressure, allowing experiments investigating it to be cooled only with liquid nitrogen, and giving a great benchmarking platform for NV-magnetometry as it can be synthesized with excellent reproducibility.



Figure 2.6: Resistive measurements of the pressure variation of T_c for the mercury-based cuprate superconductors. The material studied in this chapter, Hg-1223, was shown to exhibit superconductivity up to $T_c = 164$ K at 31 GPa. Extracted from [Gao et al., 1994].

2.3 - Experimental setup for NV measurement of superconducting \mathbf{T}_{c}

We will now describe the experimental setup that we have used to obtain the results presented in the rest of this chapter. Let us remind the reader that the aim here is to use NV centers of diamond to detect the magnetic field variation associated with a sample entering its SC state at high pressure. Taking all the successive elements of that protocol, we see that an experimental apparatus operating all these tasks must combine high-pressure generation, low temperature, microwave delivery, NV center creation, and optical microscopy. All those elements will be described here and are shown in Fig. 2.7.



Figure 2.7: Photograph of the high-pressure low-temperature NV magnetometry experiment in our lab, with different elements highlighted. The red-shaded part is the cryostat, holding the cooled diamond anvil cell. The blue-shaded area around it is the vector electromagnet coil system used to set a given bias magnetic field of arbitrary direction. The green-shaded part is the custom confocal/widefield fluorescence microscope arm imaging the inside of the cryostat. At its sample end is the microscope objective, in the yellow-shaded area. This arm is connected to the laser source and detection part in the orange-shaded area via optical fibers. Finally, the purple-shaded area is comprised of the dewar and transfer stick used to circulate cryogenic fluid (either nitrogen or helium) into the cryostat.

2.3.1 - Hybrid confocal/widefield microscope

The optical setup used for the following experiments was explicitly designed to allow both of the most common NV center imaging techniques, confocal microscopy and widefield microscopy, with high-pressure, low-temperature samples. It allows for easy switching between both modes by adding or removing a dichroic mirror in front of the final microscope objective, together with one collimating lens. The excitation light source was a Coherent Verdi CW single-mode laser, with 532 nm wavelength. We used a Mitutoyo 10x 0.28NA long working-distance microscope objective at the other end of the chain. This choice of a microscope objective with a relatively low numerical aperture is necessary to image the inside of the DAC since the crowding of the DAC prevents the lens from being closer than a



Figure 2.8: Schematic of the optical setup for high-pressure low-temperature NV magnetometry. The dichroic mirror (DM) before the microscope objective can be removed to go from widefield imaging on the camera to confocal imaging. The green line indicates the excitation laser light, while red dotted lines show the path of collected NV PL.

few centimeters to the sample. It is made even more critical by the integration of the DAC in the cryostat used in our experiments, which adds a window between the DAC and the microscope objective, as shown in Fig. 2.8.

2.3.1.1 - Confocal imaging mode

The main optical elements of the confocal microscope are connected inside a cage system, which can be moved on a 3-axes micrometer screw system (see the picture in Fig. 2.7). This allows us to adapt the microscope to the modifications of the DAC holder position inside the cryostat that are induced by the change in temperature. Excitation light is brought to the movable cage using a single-mode optical fiber. It is then reflected by a long-pass dichroic mirror to allow later separation from the collected NV PL. With the sample being fixed, the scanning part of the confocal microscope is operated using a 2-axes steering mirror optically conjugated with the objective entrance back-aperture. This is done using a pair of lenses in a 2f - 2f setup. These lenses allow the laser beam angle reflecting off the mirror, relative to the horizontal optical axis, to be reproduced at the objective entrance. This is a standard fast scanning method in the XY image plane of the microscope objective (up to several thou-

sand Hertz sampling, much faster than piezoelectric actuators), with the added benefit of providing a large field of view. The extent of XY images is limited only by the maximum incidence angle at the objective back-aperture, which can be rather large using an appropriate relay lenses pair. The optical system was designed to collect images scanning a $600 ext{x} 600 ext{ } \mu ext{m}^2$ area on our setup. Precise focussing along the optical axis is achieved through a piezo ring mount for the microscope objective. The same objective lens is used to collect the excited NV centers' PL, which naturally follows the exact inverse path the green excitation laser does (up to minor chromatism of the optics). Upon reaching the dichroic mirror, it is however transmitted and focussed into a collection single-mode optical fiber, acting as our spatial filter for the confocal microscope [Gu and Sheppard, 1993]. This allows collected light to be brought to a separate detection part of the setup on the optical table without re-alignment, even if the microscope cage is moved. At the output of this fiber, light can be sent to an avalanche photodiode operated in the photon counting regime (Excelitas SPCM-AQRH) through spectral filters, or to a spectrograph (Andor Shamrock 303-i) with a flipping mirror. Typical filters used to isolate NV PL from background and remaining excitation light were band-pass filters with 75 nm width centered around 697 nm wavelength (Semrock FF01-697/75). The spectrograph was primarily used for pressure monitoring by recording diamond Raman spectra. All microscope elements described here were controlled and synchronized by a computer running the open source Qudi software [Binder et al., 2017] and National Instrument interface cards. With this customized confocal microscope design, we achieved a resolution at the sample through the cryostat window and the thick diamonds around 500 nm in the XY plane, 20 µm axially. For results presented using this imaging mode, the usual protocol was to capture a sample image (total imaging time around 3 seconds), and then the NV center PL was recorded at a single point while multiple ESR microwave scans were compiled.

Note that a complementary imaging mode is also accessible using our confocal microscope: laser reflection imaging. If we remove the spectral filter in front of the APD detector and therefore use extremely low laser power to protect it, we can detect the laser light reflected by the sample. This provides alternative images that are sensitive to surface topography, as the slightest change in surface roughness or angle relative to the incident beam will affect the reflection intensity collected by the confocal microscope. An example of such an image can be found in Fig. 2.10. This can be extremely useful in situations where a sample or diamond microstructure might not be discernable in PL image contrast.

2.3.1.2 - Widefield imaging mode

This experimental setup can be easily adapted as a widefield fluorescence imaging microscope. A small USB CMOS camera was also attached to the cage system (iDS UI-3240CP-NIR-GL Rev.2), with a spectral filter placed in front of it. A removable short-pass dichroic mirror can be placed just before the objective lens to redirect the collected light to the camera instead of the confocal detection. To use it, the initially collimated excitation laser beam is kept fixed in all the optics, and a new lens is added along its path to focus it onto the objective back aperture. Doing this widens the laser spot in the image plane, allowing illumination of a broad sample area up to $100 \ \mu m x 100 \ \mu m$. We can then collect direct PL images of a large sample target area on the camera. As discussed briefly in chapter 1 section 1.5, using widefield microscopy enables fast mapping of large areas, with a multiplex advantage in the acquisition time. The achieved resolution is comparable with our confocal setup results here since the low numerical aperture objective and diamond windows prevented us from achieving optimal performance in the confocal mode. To record widefield NV magnetic images, the protocol is to capture one picture of the NV PL per scanned MW frequency. We thus obtain a 3D data volume, containing PL images in one plane and one ESR spectra per pixel in the transverse direction. Further data processing (numerically fitting each individual spectrum) can then yield a map of the magnetic field recorded at each pixel [Chipaux et al., 2015, Scholten et al., 2021].

2.3.2 - Cryostat and coil system

To cool our samples down to their SC transition temperature, we used a custom cryogenicfluid circulation cryostat designed specifically for DACs by our collaborators at CEA. It is a simple vacuum chamber with two windows for optical access, into which an arm holding the DAC is lowered. At the end of this arm is a copper block thermal mass where a DAC can be pressure-fitted. Cryogenic fluid, liquid helium or nitrogen, can then be injected from the top and circulated inside the block to cool it down. The evaporated cryogenic fluid is then extracted through the outer jacket of the transfer line going from the dewar to the cryostat and discarded. Good thermal contact between the block and DAC housing ensures the thermalization of the sample inside the cryostat. Temperature is read using thermocouples connected to the outside *via* a dedicated port on the top lid. We would typically use two thermocouples, one on the cold copper block and one directly inside the DAC, as close as possible to the sample (in contact with the diamond anvil seat). The cryostat top lid also bears a port for the capillary tube used to apply the pressure inside the DAC. Sample pressure can thus be changed *in-situ*, as long as the fluid used in the membrane circuit doesn't condense at the current temperature. Cooling a DAC sample down to a steady 77 K using liquid nitrogen typically takes 90 minutes. When the nitrogen flow is stopped, the system slowly heats back up to room temperature over around 4 hours if left untouched. This duration can be strongly reduced by driving a resistive heating circuit inside the copper block.



Figure 2.9: Schematics for the custom DAC cryostat, with dimensions indicated in mm. Cryogenic coolant is injected from the top, circulating down to the sample holder copper block fitting the DAC, suspended inside a vacuum chamber with optical windows. Front view on the left, side cross-section in the center, and close-up view of the DAC in front of the window on the far-right.

This cryostat is used with a custom coil system that allows us to apply a magnetic field on the DAC. It consists of three orthogonal coil pairs in Helmholtz configuration, wrapped around a heatsink tightly fitting the cryostat around the sample volume. These coils are connected to a three-channel 10 A current generator from Rohde & Schwarz. They allow the application of a 10 mT magnetic field in any vector direction with homogeneity of $\pm 0.05\%$ within a millimeter-sized volume at the center of the system. This is particularly useful for NV center experiments as it allows tuning the frequency of ESR lines to any configuration desired for experiments.

2.3.3 - NV engineering using ion implantation

The method we used to bring NV centers to the DAC was ion implantation using a focused ion beam (FIB). Our team developed a specialized FIB column, in collaboration with Orsay Physics, that is optimized for the implantation of nitrogen ions into diamond. A schematic view of the elements in the FIB column is shown in Fig. 2.10.a, with a picture of the complete machine in 2.10b. First, a microwave cavity creates a dense N_2^+ plasma from high purity N_2 gas. Then, a mass-selective Wien filter allows cleaning of impurities and selection of only the $^{15}N_2^+$ isotope for implantation. Then the ion beam is accelerated and collimated by a series of electrostatic lenses before being focused on the sample. We typically performed implantation with ion current between 1 and 3 pA, and energy 30 kV. With these parameters, we achieve fast implantation with an estimated 100 nm lateral resolution, which is much smaller than our optical resolution. By implanting around 10^{14} N/cm² and annealing for 8 hours at 800 °C, we achieve a standard yield of 10^{-2} [Pezzagna et al., 2010a] to obtain approximately 10^4 NV/ μ m². These are dispersed in a layer with 5 to 8 nm thickness, centered at a depth of 20 nm under the anvil surface as estimated by Monte Carlo SRIM simulations.

The FIB's excellent spatial resolution, coupled with its scanning electron microscopy (SEM) capabilities allows for very versatile implantation patterns. Depending on the use intended for the diamond, it can implant single NV centers at low current, all the way up to extremely high surface density. At high density, we can choose between arrays of spots down to 1 μ m diameter for easy microscope repositioning, or quasi-uniform sheets for cartography (see example in Fig. 2.10.d). If necessary our FIB can even deliver doses above the diamond damage threshold to do micro-milling of the surface, or to create graphite markers or tracks [Uzan-Saguy et al., 1995].

2.3.4 - Microwave delivery

As discussed in section 1.5, a major challenge in the adaptation of NV magnetometry to high-pressure DAC experiments is to create a microwave (MW) field strong enough at the NV centers' location to drive ESR transitions. The solution we have developed in our group is to keep working with rhenium gaskets, as they are the best choice to reach up to megabar pressures, but modifying them to create the MW excitation. Inspired in part by the NMR experiments of [Pravica and Silvera, 1998, Meier et al., 2017], the solution to screening currents in the metallic gasket that was first introduced in [Lesik et al., 2019] is to change the gasket topology by micro-machining, as illustrated in Fig. 2.11.c and d. We use a loop of copper wire fixed onto the gasket around the anvil tip to produce a MW field perpendicular to the diamond's surface. The issue comes from the fact that the sample chamber constitutes



Figure 2.10: (a) Cross-section schematic of a typical focussed ion beam column from Orsay Physics. **(b)** Picture of the implantation FIB machine in our lab, with annotated parts. **(c)** Confocal laser reflection image of the culet of a $300 \ \mu\text{m}$ anvil after implantation and annealing. The surface state of the diamond looks unaffected. The observable gradient is due to a slight tilt of the anvil, and the inhomogeneities are due to dust particles. **(d)** Confocal PL image of the same anvil. We clearly see the implanted NV center pattern, showing both a uniform densely implanted area and an array of $2 \ \mu\text{m}$ spots with $10 \ \mu\text{m}$ spacing. Some of the dust visible in (c) is also fluorescent in the NV band, resulting in some inhomogeneities here too.

a hole in the metallic gasket, around which screening currents can be induced if a magnetic flux is passed through. By drilling a slit through the gasket that opens the hole all the way to the gasket edge, this hole disappears. This change in geometry actually does more: it effectively turns the gasket itself into an electromagnetic 'Lenz lens', by redirecting induced currents so that they rotate around the chamber in the same direction as the original current in the wire. However, the diameter of this new current loop is much smaller yielding a much-improved flux (the wire loop diameter is $\sim 1 \text{ mm}$ but the hole diameter is $\sim 100 \text{ }\mu\text{m}$), which

eventually leads to much improved ODMR contrast.

The downside of this method is obviously that the cutting of this slit into the gasket introduces a weak point into the DAC apparatus. The slit breaks the revolution symmetry of the DAC around its optical axis and provides a direction over which the gasket strength is reduced. To minimize these effects and still achieve high pressure, several improvements were implemented step by step. First, the slit is cut using the same femtosecond pulsed laser that is commonly used by our collaborators at CEA to drill gasket holes in rhenium. It allows accurate and reproducible machining of the structure, with excellent reproducibility. Additionally, the slit cannot be left empty upon compression of the now open chamber. An empty slit would either open, which would allow the PTM and sample to escape, or close which would restore electrical contact of the slit sides and defeat its purpose. It must thus be filled with an insulating material that can be forced into the fine slit and matches rhenium's mechanical properties as closely as possible. In our experiments, we used various types of epoxy glue, into which we dispersed a very high concentration of elemental boron particles to increase mechanical stiffness. This also prevents the glue from developing macroscopic cracks at low temperature.

The last improvement was to take into account the 3-dimensional topography of the gasket by testing different slit geometries. In reality, the gasket is not compressed evenly across its surface. The slit going from the hole in the center to the gasket edge spans thin areas that are under strong stress and deformation at the culet, variable thickness areas where rhenium is heavily displaced on the slopes of the anvil, and finally, a large thick region where the diamonds don't touch the gasket. This means that the deformations the slit undergoes under compression are non-uniform along the slit. Here again, different slit geometries were tested (straight, spiral, angles, variable width ...), and we progressively converged to the design shown in Fig. 2.11.a and b. It comprises a 10 μ m wide slit from the hole to the center of the first anvil bevel, a quarter-circle turn on this bevel, and finally a straight part 30 – 50 μ m wide to the edge. Using refinements of this design, we achieved efficient MW delivery into the DAC without instability up to 40 GPa at low temperature (this chapter, limited because of the NV centers and not because of the MW antenna), and above 100 GPa at room temperature without signs of failure (see chapter 3).



Figure 2.11: (a) 3D rendering of one of our typical gasket microwave resonator designs, here shown on a $300 \ \mu\text{m}$ anvil. We can see the machined slit going from the central gasket hole to the gasket edge. The copper wire loop is laid on the gasket to fit around the top anvil closing the DAC. (b) Microphotograph of a machined gasket, following the design shown in figure (a). The top right corner show scratches used as an orientation mark during manipulation of the gasket. (c) and (d) Schematic of the effect of the slit cut into the metallic gasket. In the untouched gasket of (c), using a wire loop above the hole induces eddy currents that perfectly compensate for the MW field created by the loop. In this configuration, the MW field (indicated by the red-shaded areas) created in the sample region is zero. However, if we drill a slit into the gasket, the induced currents now can't rotate freely around the hole. To complete a loop, they are redirected around the hole boundary in a direction that matches the original current in the wire loop. As a consequence, the induced current around the hole now acts as a lens focusing the MW field from the wire loop into the sample region.

2.4 - Experimental run 1

Using the setup described in the previous section, we performed experiments where we tried to measure the Meissner effect of a mercury-based cuprate using NV center magnetometry at high pressure. The cuprate samples used were micro-crystals synthesized by Dorothée Colson and Anne Forget (CEA), with the protocol described in [Loret et al., 2017]. The batch of crystals was prepared to obtain Hg-1223 samples with nearly-optimal doping to achieve the highest T_c possible. According to [Gao et al., 1994], the T_c should start at $T_c = 133$ K, and then rise to a maximum 164 K at 30 GPa.

Two separate runs were performed, using two different samples. Even if the first run didn't achieve pressure above 2 GPa, both runs are described below as this experiment proved to be extremely informative.

The following results will in general be presented in terms of directly extracted ESR splitting for a given bias magnetic field value applied along the anvil axis. This configuration provides a direct view of the local magnetic field mapped by the NV center layer. The exact description of the intricate relationships between ESR splitting, magnetic fields, mechanical stress and experimental setup will be the main focus of the following chapter. The mapping of ESR splitting to magnetic field values is not shown in this chapter, as it is not necessary to simply extract the value of T_c , which was our main goal here.

The first experimental run was conducted using (100)-cut 300 μ m culet anvils, compressing a rhenium gasket with a 100 μ m diameter hole, for a 50x40x15 μ m sample micro-crystal. The cell was loaded with neon as the PTM, and the anvil was implanted with a uniform layer of NV centers. An optical microscope image, a white-light transmission image and a confocal PL scan of the cell after loading are shown in Fig. 2.12. The sample is almost invisible in the PL and laser reflection images, which indicates that it interacts very little with the diamond surface. This could indicate poor contact between the sample and the diamond anvil. A possible explanation could be that the solidification front of the PTM upon pressurizing the cell lifted the sample from the surface, effectively suspending it in the PTM. After loading, we recorded NV ESR spectra with central frequency 2.883 GHz and a non-hydrostatic splitting of 19 MHz. These values are compatible with a sample pressure of 1.3 GPa since previous calibrations established a shift of 10 MHz/GPa, and here we measured $\delta = 13$ MHz compared to ambient pressure D = 2.87 GHz. No other pressure gauge was used here as diamond Raman scattering is too inaccurate below a few gigapascals, and we didn't want to introduce a fluorescent marker in the chamber that could hinder our PL measurements. The ESR spectra recorded were essentially identical all over the sample and its surrounding area within the gasket hole (3 MHz variability at most).



Figure 2.12: (a) Optical microscope image of sample 1 after loading in a DAC. The outer circle is the culet edge ($300 \ \mu m$ in diameter), and the central hole and gasket slit are visible. The micro-crystal sample of Hg-1223 is visible as the opaque shape within the gasket hole. **(b)** White light transmission image of the cell loaded with sample 1. The sample is opaque, its outline is clearly visible. **(c)** Confocal PL image of the NV centers above the only visible part of sample 1 in the DAC. The low visibility of the sample could be due to its being suspended in the PTM, not directly at the interface of the anvil tip hosting the NV layer. The gasket edge appears on the left side as a very bright area where the NV PL is reflected by the metallic gasket.

2.4.1 - Magnetic field exclusion from the superconductor

We then cooled the DAC and sample to liquid nitrogen temperature (77 K), well below the estimated T_c of 133 K. The sample was cooled in the absence of external magnetic field, as the so-called 'zero-field cooling' protocol should be the one allowing the most important Meissner effect. Field cooling (i.e. cooling the sample with an applied magnetic field) of samples can indeed allow flux trapping inside type II superconductors like our cuprate which then reduces the intensity of the Meissner effect. At 77 K, we applied a 1.5 mT magnetic field in the [100] direction and then proceeded to record ESR spectra pointing the microscope at two different spots inside the cell, one directly above the SC sample and one far from it ($\sim 20 \ \mu m$ away). Results are shown in Fig. 2.13 and clearly show the expected Meissner effect. The reference point outside the sample shows an ESR splitting of 54.0 ± 0.7 MHz, compatible with the value of the applied fields and an additionally measured strain splitting of 19 MHz. Over the superconductor, however, the apparent splitting was only 30.0 ± 0.8 MHz, a 44% reduction. We note here that above the superconductor the contrast of the ESR lines is slightly reduced, from 4.4% and 4.5% to 3.1% and 3.3%. This reduction could have multiple causes as ODMR contrast depends on many experimental parameters, but it could indicate partial screening of the MW excitation by the superconductor itself.





2.4.2 - Quantitative magnetic field screening

While at 80 K, we also recorded ESR spectra for increasing magnetic fields. The idea was to measure if the screening of the applied field by the superconductor would weaken at larger fields, which would indicate flux penetrating the sample. Extracted results are shown in Fig. 2.14. As the applied field is increased from 0 to 10 mT, we quickly observe the ESR splitting increasing linearly as expected in the weak field regime, but with different slopes above and away from the superconductor. The slope above the sample is smaller, confirming the screening of the applied magnetic field. To extract a quantitative value for this screening, we can model the expected behavior for this experiment using eq. 1.7. Under both anisotropic stress and magnetic field, we expect the ESR splitting of NV centers to behave as:

$$\Delta = \sqrt{\Delta_{\sigma}^{2} + \Delta_{B}^{2}} = \sqrt{\Delta_{\sigma}^{2} + (2\gamma_{\rm NV}B_{\rm NV})^{2}}$$
(2.2)

Here, we know that the bias magnetic field we applied was aligned with the diamond [100] axis so that all NV centers exhibit the same ESR frequencies. In this configuration, the magnetic field projection along the NV axis includes a geometric $\sqrt{3}$ factor giving $B_{\rm NV} = \|\vec{B}\|/\sqrt{3}$. If we now assume that the superconductor reduces the local magnetic field at the NV centers (without field rotation) by a fraction ϵ , we can model the results in Fig. 2.14 with the equation:

$$\Delta = \sqrt{\Delta_{\sigma}^{2} + \left[2\gamma_{\rm NV}\frac{(1-\epsilon)}{\sqrt{3}}\|\vec{B}\|\right]^{2}}$$
(2.3)

with anisotropic stress splitting Δ_{σ} and screening fraction ϵ as the only free parameters. Fitting this to our results, we obtain the following best-fit parameters:

	Δ_{σ}	ϵ
Reference	$16.8 \pm 0.6 \text{ MHz}$	-0.028 ± 0.002
SC sample	$17.7 \pm 1.8 \text{ MHz}$	0.456 ± 0.010

Table 2.1: Best-fit parameters for NV center ESR behavior as a function of magnetic field over SC sample 1, compared to a reference outside the sample. Data are shown in Fig. 2.14.

This clearly shows the Meissner effect: the screening fraction ϵ is essentially zero at the reference (a small underestimation of the applied field norm may explain the apparent slight negative value), but the field is reduced by around 46% for NV centers close to the superconductor. Furthermore, we see that the model exposed in eq.2.3 fits the data with excellent agreement all the way to 10 mT. This seems to indicate that the magnetic field at the NV center's location is still linearly increasing with the applied field: the screening fraction stays

constant, which indicates that no flux is progressively penetrating the sample. This would indicate that the sample stays in its full Meissner screening state at least up to 10 mT. Such behavior is reasonable for a high-temperature superconductor. The NV centers being local probes outside the sample, the measured value of the Meissner screening at the NV centers cannot be predicted as it depends heavily on experimental geometric factors like the sample shape and the distance to the sensors. However, the magnitude of the effect demonstrated here shows that if the field is still screened by more than 45% at the NVs, the field screening fraction should be much higher within the sample, possibly 100%, as the theory would suggest.



Figure 2.14: Measurement of the NV center ESR splitting with increasing magnetic field over the SC sample and away from it (reference). The magnetic field is applied in the diamond [100] direction, at 80 K and 1.3 GPa. The presented fit was done with the model in eq. 2.3. Best-fit parameters are in table 2.1.

2.4.3 - Confocal measurement of $\mathbf{T}_{\mathbf{c}}$

Even if they can't allow measurement of the exact magnetic screening amplitude inside the sample volume, the NV centers still allowed us to measure without doubt the existence of the Meissner screening inside our sample. The next step towards our goal of measuring the T_c variation with pressure was then to attempt a measurement of the material's superconducting critical temperature. This possibility was already shown by [Lesik et al., 2019] and [Yip et al., 2019] but was never attempted on a high T_c material. The protocol for this measurement is straightforward. The sample was first zero-field cooled to 80 K, well below its estimated T_c to ensure superconductivity. Then we continuously recorded ESR spectra on the same spot over the sample as it was allowed to warm up slowly. At the critical temperature, we should record the disappearance of the Meissner screening effect, which should lead to the ESR spectra over the sample becoming similar to the reference spectra away from it. This type of measurement was performed upon heating the sample rather than cooling, as is often the case in the literature, as heating naturally happens smoothly as the sample slowly thermalizes when active cooling is stopped. Our cryogenic equipment isn't well suited for temperature stabilization while cooling and has proved much more mechanically stable upon slow heating.

(a.u.)

Normalized PL intensity



Figure 2.15: Colormap of observed ESR spectra over SC sample 1 taken across its SC transition. Spectra were taken at 1.3 GPa, with 1 K temperature resolution and 1 mW laser power. We see the splitting of ESR lines, indicative of the magnetic field at the NV centers, abruptly go from a Meissner screened regime to a normal regime when the sample is heated.

The results of the measurements are compiled in Fig. 2.15. We show here a colormap compiling ESR spectra recorded at 1 K intervals over the SC transition, at 1.3 GPa for 1 mW laser power and 1.5 mT bias magnetic field in the [100] direction. This was done over 120 minutes to allow sample thermalization. We clearly see the transition happening in our sample. Below 118 K, the recorded ESR spectra all show a splitting around 30 MHz, exactly as in the static 80 K results shown previously. Then, between 118 K and 124 K, the apparent splitting reflecting the magnetic field at the NV centers suddenly increases back to an average of 54 MHz. This marks the end of the transition, with the sample now in its normal state where it doesn't screen the magnetic field.

The apparent value for T_c was here extracted to be 124 ± 1 K (transition onset, transition middle point at 121 ± 1 K). This value may seem surprising, as the ambient T_c for the crystal batch from which the sample was extracted was measured at 134 K (SQUID measurement reproduced as the grey curve of Fig. 2.16). However, we quickly realized that the laser power

used to probe the NV centers at low temperatures could be sufficient to heat our sample. The key point is that the temperature reading shown in all results reproduced here comes from a thermocouple placed inside the DAC that cannot instantly reflect the temperature of a micrometer-sized sample in the experimental chamber. In the case of very localized heating, like with a focused laser beam, a sustained temperature gradient appears between the sample and the temperature probe. This can explain the first-try apparently low T_c : as the experiment proceeds, the sample is constantly being heated by the laser beam without enough dissipation into its environment, offsetting its exact temperature compared to our readout. This is usually mitigated in DAC experiments if the sample of interest has good contact with the extremely high thermal conductivity diamonds. However, from confocal images of this particular experiment, we have already established that diamond-sample contact seemed poor.



Figure 2.16: NV center ESR splitting recorded over SC sample 1 as a function of temperature, for excitation laser powers from 0.5 to 2.5 mW at pressure 1.3 GPa. The apparent SC transition of the sample is shifted due to local heating from the laser. Dotted lines are fitted to the data using a step function model. The grey line represents the T_c measurement performed by SQUID magnetization measurement on the bulk of the micro-crystal batch where sample 1 originated (relevant units on the right-side axis). This independent measurement was performed at room pressure by collaborators at CEA.

To test this hypothesis, we proceeded to record multiple T_c measurements using different laser powers. Results are shown in Fig. 2.16 and 2.17. The observed behavior is consistent with the previous analysis. As laser power used to excite the NV centers increases, we record a clear linear shift of the apparent T_c of -14.4 ± 0.6 K/mW. The apparent transmission of the second sec

sition width also appears to increase by 3.1 ± 0.5 K/mW, which is consistent with the local heating picture. As local heating is increased with laser power, temperature gradients within the sample may grow and affect the observed critical transition width. If we use these linear heating behaviors to extrapolate the observed transition at a null laser power, we get an estimated onset $T_c = 139 \pm 1$ K and transition width 0.9 ± 0.9 K at 1.3 GPa. This value for T_c appears to be perfectly in line with the measurement of [Gao et al., 1994] at 140 K, which was reproduced in Fig. 2.6.



Figure 2.17: (a) Apparent measured Tc for sample 1 as a function of NV excitation laser power. Using a linear fit, we retrieve a slope of -14.4 ± 0.6 K/mW and an extrapolated $T_c = 139 \pm 1$ K at null laser power. (b) Apparent measured SC transition width for sample 1 as a function of NV excitation laser power. A linear fit gives a slope of 3.1 ± 0.5 K/mW and an extrapolated width of 0.9 ± 0.9 K at null laser power.

The widefield imaging mode of our setup proved inefficient for this experimental run, most probably because of the same heating effects. To perform widefield sensing we need to illuminate the NV centers with enough power so that we can detect PL with our camera, which has much lower sensitivity than the APD used in confocal mode. When doing so, the ESR splitting maps we recorded appeared totally uniform, even at low recorded temperatures. Our interpretation of this result is that, with this particular sample proven to be very sensitive to local heating, the laser power needed to record widefield ESR maps was large enough to constantly heat the sample into its normal state under our full cooling capabilities (when the recorded temperature of the DAC was otherwise 80 K). We will show in the next section that this limitation indeed is highly sample-dependent, and not general.

Unfortunately, this promising first experimental run was stopped when we tried to in-

crease the pressure inside the DAC. As we increased the pressure, the gasket slit suddenly was destabilized and opened, allowing both the sample and PTM to leak from the chamber. Even if we couldn't raise the pressure above 1.3 GPa, this experimental run was still valuable. It constituted an informative test run on the measurement of critical temperature with NV centers at high pressure and revealed the importance of parasitic heating due to laser excitation.

2.5 - Experimental run 2

The second experimental run presented was performed in conditions almost perfectly similar to the first one. We still used (100)-cut 300 μ m culet anvils implanted with a uniform layer of NV centers, neon as a PTM, a rhenium gasket with a 100 μ m diameter hole and a MW-enabling slit of our design. This time, however, the sample was obtained by carefully splitting a larger micro-crystal from the same batch as sample 1. Most crystals yielded from the synthesis steps were far too large to fit inside our DAC, and the sample dimensions we were looking for were too small to be efficiently selected using a sieve. We thus resorted to fracturing a larger crystal to obtain a suitable sample. Cuprates are ceramic-like materials that easily cleave along their crystallographic axes. This step was carried out by simply compressing a 350 μ m crystal uniaxially between two millimeter-culet sapphire anvils under an optical microscope.

Confocal images of sample 2 once loaded into the DAC are shown in Fig. 2.18. Initial pressure after loading was 3 GPa, according to the calibrated ESR central frequency. We immediately noticed that the sample surface appeared much clearer than for sample 1. The contact between the sample and diamond anvil culet was probably improved compared to the previous experiment. This can be seen by the multiple and intricate interference patterns that appear under the sample in the reflection images of the coherent laser light, formed by small cavities with a thickness of the order of the laser wavelength between the flat diamond and the rough surface of the sample. Even in the PL image, the NV PL intensity is not uniform over the sample, but a bright line indicates one edge of the sample being pressed against the diamond surface.

Taking into account the small shift of ESR lines with temperature (7 MHz at 77 K according to [Chen et al., 2011]), sample pressure rose to 3.3 GPa upon cooling down to 80 K. As we cooled the sample down to liquid nitrogen temperature, we recorded the presence of a very significant Meissner effect, like in the previous experimental run 1. However, it appeared very clear from our quick confocal assessment that the intensity of the effect seemed highly



Figure 2.18: (a) and (b) Confocal laser reflection images of our second cuprate sample loaded into a DAC. The extremely bright region is where the metallic reflective gasket is compressed against the anvil culet. We see the dimmer central hole, with the start of the slit in the top right corner of (b). The sample appears as a rectangle in the center, with intricate interference fringes appearing under it. This indicates close contact of the sample with the diamond and that the sample surface wasn't flat. **(c)** Confocal PL image with the same field of view as in (b). Here again, the reflective gasket increases the amount of NV PL collected over it, giving a dimmer region in the central hole where the NV centers are above the chamber. One edge of the sample could be pressed against the diamond surface, making the bright line visible.

non-uniform over the sample. This motivated us to complete the software work we had started to make use of the widefield imaging capabilities of our optical setup. With the contact between the sample and diamond looking better, it seemed plausible that laser heating effects would be mitigated here, enabling widefield sensing with our setup. This method should in theory be the perfect tool to exhibit fast imaging of sample inhomogeneities and possibly direct mapping of a spatially heterogeneous T_c which has never been demonstrated at high pressure.

2.5.1 - Sample inhomogeneity revealed by widefield magnetic imaging

We started by recording an image of the magnetic field reduction at the location of the NV center layer when the sample temperature was deep within the SC domain. We stabilized the DAC and sample to a temperature of 80 K, and proceeded to record an ODMR widefield image under 1.5 mT magnetic field. This is done by illuminating a wide area in the cell with the laser and recording images of the PL intensity when scanning the microwave excitation frequency. Typical acquisition parameters consist of 75 frequencies tested, with 160 ms exposure per frame and the signal for each MW frequency being averaged over 5 recorded images. This amounts to a total acquisition time of around 1 min for a complete map of ODMR spectra. This time was chosen to provide the best compromise of signal-to-noise ratio and total integration to be eventually compatible with data collection while heating the sample for performing the T_c measurement.



Figure 2.19: Extracted widefield maps of the ESR splitting over sample 2 at 3 GPa. **(a)** Map recorded at a temperature of 150 K, under 1.5 mT bias magnetic field in the diamond [100]-axis. Splitting is almost uniform over the sample and its surroundings, indicating that the magnetic field fully penetrates the sample which is in its normal state. Variations of a few megahertz may arise from inhomogeneous splitting du to non-hydrostatic stress. **(b)** Map recorded at 80 K in the same magnetic field condition, after zero-field cooling and turning the magnetic field back on. We see a clear reduction of the splitting, and thus magnetic field, over the sample. This effect is however not uniform over the sample, with some parts of it not being not SC at all.

A typical image is shown in Fig. 2.19, in comparison with the signal recorded for $T > T_c$ at T = 150 K. This is the end result after processing all the data to extract the observed spatial variation of the ESR splitting. For this experiment, we were able to show the existence

of the Meissner effect over our sample and to demonstrate that its apparent intensity was inhomogeneous. The ESR splitting Δ (which is proportional to the magnetic field) is homogeneous all over the experimental chamber, except in large areas inside a rectangle shape delimited by the sample boundaries. On average, the reduction of the ESR splitting Δ was 27% over the areas of the sample exhibiting any effect, but above one corner of the sample Δ was reduced by as much as 48% at the NV centers, which is of the same order as the 44% reduction observed in experimental run 1. Some areas over the sample didn't show any field reduction, which we attribute to parts of the sample being in a non-superconducting state. This points to the sample being inhomogeneous in its composition, or local doping. Our current interpretation is that it could be due to this particular sample that consisted of a micro-crystal originating in the cracking of a larger initial crystal. The high uniaxial stress briefly applied to the original crystal could have induced degradation of the sample leading to only some regions being superconducting. It could also be that the doping of the cuprate, which highly influences the superconducting properties, was inhomogeneous. To optimize their T_c the cuprate crystals are oxygenated after synthesis, by putting them under an oxygen flow atmosphere for a duration of days or months [Loret et al., 2017]. This forces additional oxygen to penetrate the crystal bulk from the outside in, which could lead to slightly uneven doping of the crystal center compared to its surface. By cracking a large micro-crystal, we cannot exclude that the specific sample we retrieved for the experiment came from a sub-optimal doping pocket. This hypothesis is compatible with some of the results shown in the rest of this chapter, namely that the observed T_c for this micro-crystal sample was significantly lower than initially expected from both the bulk measurement and the previous run.

2.5.2 - Sample edge effects

Upon further inspection of this initial mapping of the magnetic field within the SC phase, we noted additional information that will be investigated in subsequent work. We interpreted some of the signals as other consequences of the field exclusion from the SC bulk, complementary to the previous results.

First, we noticed a significant anti-correlation between maps of the observed ESR splitting and OMDR linewidths. A map of the observed average linewidth is shown in Fig. 2.20.a. Investigating the apparent ODMR linewidth is interesting since it can provide us with information about ESR line displacements happening without the resolution of individual overlapping lines. In the configuration of a magnetic field applied in the [100] direction, we should observe two ESR lines with a splitting representative of the field's projection on the NV axes,



Figure 2.20: (a) Extracted widefield map of the average ESR linewidth over sample 2 at 3 GPa and 80 K, in the SC domain of pressure and temperature. We observe an increase of ESR linewidth over the edges of the areas exhibiting Meissner field screening (see map in Fig. 2.19). This effect could be interpreted as an effect of local field rotation due to magnetic flux exclusion in parts of the sample. (b) Simulations of the field rotation effect on the measured ESR linewidth, with all NV orientations exhibiting 20 MHz linewidths. In the [100] bias magnetic field configuration, the observed ESR spectrum is composed of two peaks consisting of four perfectly overlapping lineshapes only if the field is perfectly aligned. When we introduce a slight misalignment angle θ , which could be induced by the Meissner effect of the superconductor, we then lift the degeneracy of ESR frequencies associated with different NV orientations. When fitted with the expected lineshapes of two Lorentzian lines, the total ESR spectrum yields an apparent linewidth increase with θ . (c) Simulation of the apparent fitted ESR linewidth variation as a function of misalignment angle θ relative to the true diamond [100] direction.

equal for all four orientations (see Fig. 2.13). We thus numerically fit the data with the expected two lines, which is much less computationally expensive than fitting the data with eight lines. However, the observed ODMR contrast is due to the superposition of four overlapping lines per PL dip, one associated to each NV orientation. These lines are at the same MW frequency if the bias magnetic field is exactly aligned along the [100] axis. The apparent linewidth resulting from a fit with two lines thus results from the overlap of four sub-lines, and is minimal as they perfectly concur. Now, in the event of a small perturbation of the magnetic field orientation, the exact frequency of those four sub-lines should slowly diverge, but we may not resolve this division if their movement is smaller than the observed linewidth. The total resulting line could however be distorted, going from a Lorentzian to a set of Lorentzian functions slightly shifted, while still being fitted within our data processing as a single line of broader width. Small deviation of the bias field orientation compared to the perfect [100] axis can therefore introduce variations of observed and extracted ESR linewidth, even without detectable displacement of the line's barycenter. A numerical simulation of this effect is shown in Fig. 2.20.b and c.



Figure 2.21: Same widefield extracted map of ESR splitting over sample 2 as in Fig. 2.19.b, at 3 GPa, 80 K and 1.5 mT bias field. It is here shown in a colorbar normalized by the value of the uniform ESR splitting when the sample is not SC (48 MHz). We see that in addition to the field reduction over the SC parts of the sample, a halo of slightly increased magnetic field is present at the sample edges. This is due to flux conservation forcing the field excluded from the SC regions to concentrate around it.

This effect could provide an explanation for the observed anti-correlation between ESR

linewidth and areas exhibiting a significant Meissner effect. As the applied [100] bias field is locally distorted by the presence of the superconductor parts, field lines necessarily rotate slightly to turn around the sample. If NV centers are present where this rotation occurs, this deviation from perfect [100] field alignment could widen the observed ESR linewidth around the edges of SC sample parts.

We also note that, in the SC state, the measured ESR splitting can also be slightly increased around the sample. As shown in Fig. 2.21, a halo where the magnetic field at the NV centers is actually increased by up to 10% appears when the sample is SC. Here again, this could be explained by the field exclusion from the SC bulk. As the bias magnetic field is screened from the inside of the material, conservation of magnetic flux forces magnetic field lines to 'bunch' at the sample edges where they are distorted, locally increasing the field amplitude compared to the normal state. This effect was also reported by [Yip et al., 2019], by the ESR splitting in nanodiamonds that were in close proximity the SC sample's edge.

2.5.3 - Widefield measurement of $\mathrm{T_{c}}$

As we could clearly detect the Meissner effect of sample 2 in widefield imaging, we then repeated the experiment while varying the temperature to retrieve the value of T_c . We recorded ESR images as described above upon heating the sample from 80 to 145 K. This yields a data set where we now have PL information as a function of MW frequency for each image pixel, recorded for 53 different temperatures across T_c . The local critical temperature can then be assessed at each pixel by fitting the data as a function of temperature with a step-function model. Here again, as for the ESR splitting deep in the SC phase, the values are inhomogeneous over the sample surface. T_c curves extracted at different points of the image are shown in Fig. 2.22. The spatially varying intensity of the field screening is again visible, including the slight increase of the ESr splitting in the outer regions of the sample. Note here that the parasitic heating effects due to laser power were neglected. In the widefield mode, and with a sample in close contact with the diamond anvils, the excitation laser power is spread over a greatly increased surface (approximately $40x25 \ \mu m^2$ compared to $1x1 \ \mu m^2$ in confocal), leading to negligible effects on apparent T_c . This will be confirmed by the comparison with confocal measurements in the following subsection. We, therefore, present results for a single laser power, without the need for the extrapolation to null laser excitation power.

A full map of extracted T_c at 3 GPa is shown in Fig. 2.23 (together with the estimated errors) for the region that exhibited Meissner screening. Over this restricted area, the average was $T_c = 125.7$ K, with standard deviation 7.6 K. This value was lower than expected for the optimal doping of HG-1223. Note that we recorded an estimated 139 K in experimental run



Figure 2.22: (a) Same widefield extracted map of ESR splitting over sample 2 as in Fig. 2.19. The colored and numbered dots indicate the pixels at which T_c curves have been extracted in (b). (b) Variation of ESR splitting with temperature at 5 different pixels over sample 2. Dotted lines are step-function fits used to determine T_c , and the corresponding values of T_c are indicated by the corresponding colored vertical lines.

1, which was in line with the literature. Values of T_c spatially varying around a lower value is however compatible with the previously discussed hypothesis that the sample probably exhibited uneven sub-optimal doping. This could also be corroborated by the much wider transition width: the recorded SC transitions had a width of 10.6 K on average over the area masked in Fig. 2.23. If we consider that heating had a minimal effect on transition width this time (as it had on apparent T_c value), this is large compared to the 1 K width measured on sample 1. The recorded onset drops of the splitting were also much less sharp compared to experiment 1, which added to the poor precision of T_c evaluations. The reason for this was not fully determined, as further confocal results showed that it didn't appear to be because of the sample. Our current best hypothesis is that the widefield method of recording ESR spectra might be more sensitive to mechanical vibrations and drift of the sample, leading to slightly spatially averaged signals smoothing the apparent T_c curve.

Even if the particular sample used was apparently not an optimally doped Hg-1223 cuprate micro-crystal, these results still provided a compelling testing ground to establish that wide-field NV magnetometry can reveal inhomogeneities in the SC properties, which is actually expected for many high-pressure SC, especially hydrides. This technique will then strongly benefit from simultaneous XRD measurements realized on a synchrotron beamline (like in [Osmond et al., 2022] for instance) in order to correlate these inhomogeneities with structurally mixed phases.



Figure 2.23: (a) Widefield extracted map of the SC T_c over sample 2 at 3 GPa. The image has been masked to show only the pixels exhibiting significant SC field exclusion ($\Delta_{80K} < \Delta_{150K}$). Over this selected area, the average was $T_c = 125.7$ K, with standard deviation 7.6 K. (b) Extracted map of the estimated error in the determined T_c .

2.5.4 - Additionnal widefield results to $13\ \mathrm{GPa}$

We recorded widefield ESR images of this sample at two additional successive pressure steps, 8 GPa and 13 GPa. Data was recorded in the same configuration, applying a 1.5 mT bias magnetic field in the [100] direction. The extracted ESR maps are shown in Fig. 2.24. When increasing the pressure, the ESR splitting started to show variations correlated with the presence of the sample, even in the normal phase above T_c . As it can be seen in Fig. 2.24.a. for instance, some areas of the sample exhibited an excess splitting of 5 to 10 MHz compared to the uniform values away from the sample. This can be interpreted as a locally increased non-hydrostatic split-ting on parts of the anvil culet where the sample is pressed into the diamond surface. At 8 and 13 GPa, the amplitude of the SC field screening at low temperature remained essentially identical compared to 3 GPa, reaching 35 to 40% locally. However, the average ESR contrast decreased significantly (from 5-10% to 1-3% going from 3 to 13 GPa), leading to a reduced signal-to-noise ratio. In some areas, the quality of data was too poor to accurately determine the ESR splitting through the data fitting procedure previously described, leading to unphysical results in small parts of the reconstructed images.

Even if those widefield results were encouraging for the imaging of inhomogeneities inside our particular sample, determination of the sample's critical temperature was costly in data post-processing, requiring over an hour of computation time for a trial fit of all the spectra from a 150x150 pixels image. It proved to be less accurate than the confocal measurements. For the last part of this experimental run, we therefore focused on showing that T_c determination could be done using the optical confocal method, at pressures up to



Figure 2.24: Extracted widefield maps of ESR splitting over sample 2 at pressures of 8 and 13 GPa. (a) Map recorded at 8 GPa and 150 K, under 1.5 mT bias magnetic field in the diamond [100]-axis. Variations of a few megahertz are most likely from inhomogeneous non-hydrostatic splitting upon compression. (b) Map recorded at 8 GPa and 80 K in the same magnetic field conditions, after zero-field cooling and turning the magnetic field back on. (c) Map recorded at 13 GPa and 150 K in the same magnetic field condition as (a). (d) Map recorded at 13 GPa and 80 K in the same magnetic field condition as (b). Areas with sharp boundaries are regions where the signal was too weak to be properly fitted by the global data processing procedure. Values obtained in these regions are unphysical.
31 GPa.

2.5.5 - Confocal T_c measurements for pressures up to 31 GPa

The confocal method of recording T_c with the NV centers at a single sample point was used to record the results presented in this last section. We chose a single spot above the part of the sample that exhibited the largest field screening, and wrote software into our data acquisition procedure to periodically make a fast image scan to reposition the measurement point, compensating for thermal drifts upon heating the DAC in the cryostat. In total, we measured ESR spectra over the SC transition at four different pressure points (3, 8, 13 and 31 GPa), and for two or three different values of excitation laser power to extrapolate out heating effects. Results are compiled in Fig. 2.25 and 2.26.

The resulting T_c curves were generally sharper than those obtained with the widefield method. The splitting plateau above T_c abruptly drops below a certain temperature, clearly indicating the onset temperature for superconductivity. Over 10 to 20 K, the splitting reaches a low plateau once the sample has fully transitioned. In this temperature regime, the measured ESR splitting exhibits some variability that is mostly due to larger errors as the contrast is decreased over the sample when it is SC. For this particular sample, laser heating effects indeed appeared to be greatly reduced compared to experiment one. In these better conditions, the apparent value of T_c only shifted by -0.42 to -0.62 K/mW depending on the pressure. Still, we performed extrapolation to zero laser power to retrieve T_c values of 125.9 ± 1.0 K, 131.6 ± 1.0 K, 127.4 ± 1.0 K and 141.7 ± 1.0 K at 3, 8, 13 and 31 GPa respectively for the sample part with the strongest screening effect. Points at 3,8 and 31 GPaconfirmed the monotonous increase in T_c with pressure that had been reported by resistive measurements in the literature (see Fig. 2.26.b), albeit with a downshifted initial T_c due to a probably sub-optimal sample doping, as explained above. The values recorded at 13 GPawere surprising, as they don't follow this trend. It could be due to a faulty repositioning of the measurement point over the sample that yielded a measurement performed on a different portion of the inhomogeneous sample.

An important remark to be made here is that the measurement of T_c at 31 GPa has been performed using an increased bias magnetic field of 8 mT. The reason is that we were unable to record any variation of ESR splitting over the sample using only 1.5 mT. At this pressure, the ESR spectra appeared highly asymmetrical in contrast, with the low-frequency branch being essentially undetectable without applying a high enough magnetic field. When we increased the applied magnetic field, we retrieved the two usual ESR lines in the [100] field configuration. However, the line's sensitivity to magnetic field variations appeared greatly di-



Figure 2.25: Confocal measurements of ESR splitting variation with temperature over sample 2 relative to a reference point away from the sample, at different laser powers and pressures. (a) is for 1.5 mT bias field and 3 GPa. (b) is for 1.5 mT bias field and 8 GPa. (c) is for 1.5 mT bias field and 13 GPa. (d) is for 8 mT bias field and 31 GPa. Since transitions appeared to be sharp at the onset but asymmetric at low T, the dotted lines are piecewise linear fits used to determine the onset T_c . Fit results are compiled in Fig. 2.26.



Figure 2.26: (a) Apparent laser power dependence of the measured T_c over sample 2. Linear fits yielded zero laser power T_c values 125.9 ± 1.0 K, 131.6 ± 1.0 K, 127.4 ± 1.0 K and 141.7 ± 1.0 K at 3, 8, 13 and 31 GPa respectively. Fitted laser heating slopes were -0.47 K/mW, -0.46 K/mW, -0.63 K/mW and -0.42 K/mW respectively. (b) Comparison of our measurements of T_c over the best part of our sample with previous studies from [Chu et al., 1993, Gao et al., 1994]. The general trend of T_c increasing with pressure is reproduced, except that our sample probably was not optimally doped, then leading to smaller values of T_c .

minished. Recall from eq. 2.2 that the contributions to ESR splitting from non-hydrostatic stress Δ_{σ} and magnetic field Δ_B do not add linearly, but in a root-of-squared-sum fashion. At 31 GPa, Δ_{σ} reached 115 MHz which means that the total splitting's sensitivity to variations of Δ_B was reduced. Even with 8 mT bias magnetic field, the effect of the superconductor on the NV center's resonances was much reduced compared to lower pressure (20% reduction in the SC phase, against 40 to 60% previously). This effect severely limits the ability of NV centers to make accurate quantitative measurements of local magnetic fields in the experimental configuration used up to now, and will be discussed at length in the next chapter.

2.6 - Conclusion

In this chapter, we described results using NV centers implanted in the culet of a diamond anvil to detect the Meissner effect associated with the superconductivity of Hg-1223 cuprate samples. We detailed the setup we built to detect the photoluminescence (PL) of the diamond defects inside a low-temperature DAC using a customized microscope easily converted from confocal optical imaging to widefield microscopy. Using a slit-gasket design to allow efficient microwave excitation inside the DAC, we measured ODMR of NV centers in a layer just under the diamond anvil's surface, clearly indicating a local reduction of applied magnetic fields in the presence of a SC sample.

In the first experimental run, we showed that we could measure the sample's SC critical temperature $T_c = 139 \pm 1$ K under 1.3 GPa, consistent with the literature, by measuring a series of ESR spectra as the sample temperature was varied across the SC transition. We showed that a parasitic heating effect from the NV excitation laser needed to be accounted for to accurately determine T_c .

In a second run on a different sample, we demonstrated that widefield NV magnetometry can additionally provide spatially resolved maps of the superconductor's Meissner effect, revealing sample inhomogeneities that would be inaccessible to most other techniques. We performed a measurement of the sample's Meissner screening with varying temperatures using the widefield imaging mode, effectively yielding the measurement of a map of spatially non-uniform T_c at 3 GPa. We completed our study of this sample by measuring its T_c at pressures of 3, 8, 13 and 31 GPa in the confocal imaging mode. The inhomogeneous sample showed lower T_c than expected, which we attribute to this particular sample being unevenly doped. These experiments will be reproduced in the near future, hopefully making quantitative measurements on a better sample above 50 GPa.

The final measurements performed at 31 GPa sample pressure exhibited a weaker ODMR Meissner signal that hinted at possible significant modifications of the NV center magnetic sensing behavior at this elevated pressure. In the next chapter, we will systematically investigate this to see if compression really imposes a limit on the efficacy of NV centers at high pressure.

Chapter 3

Extension of NV magnetometry to megabar pressure using anvil micro-structuring for stress engineering

God made the bulk, the surface was invented by the devil.

WOLFGANG PAULI

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3.1 - Introduction

At the end of the previous chapter, we demonstrated that we could successfully use NV centers implanted into the culet of a diamond anvil to record local variations of magnetic fields created by a superconductor up to 31 GPa. However, it became apparent that the sensitivity of the measurement decreased significantly with increased pressure, first because ODMR contrast appeared to be reduced compared to ambient pressure but also because the ESR lines' displacement with magnetic fields was altered. This situation naturally raises the question of the robustness of the NV-based magnetic field measurement method at higher pressure. Are there any intrinsic limitations to the pressure under which NV ODMR can be used efficiently in this manner? And if such a limit exists, can it be overcome?

In this chapter, we will start by reporting a systematic exploration of the effect of pressure on the NV centers' sensing capabilities by recording NV ESR spectra with varying magnetic fields from 10 GPa to 70 GPa. We will then model the stress applied to the tip of a pressurized diamond anvil and describe how it may affect implanted NV centers. Then, we will identify that the non-hydrostatic stress imposed on the tip of a pressurized anvil currently sets a practical limit to the implementation of high-pressure magnetometry as realized in chapter 2 around 40 - 50 GPa.

Finally, we will propose and demonstrate a circumventing strategy that allows us to push NV sensing well beyond this limit, above the megabar (100 GPa). By micro-machining a pillar onto the diamond anvil surface, we engineer the stress landscape inside the tip of the NV-implanted anvil to locally force hydrostaticity. We provide multiple pieces of evidence proving that we managed to create locally quasi-hydrostatic conditions, able to host functioning NV centers up to unprecedented pressures. Using this method, the influence of an applied magnetic field on the NV states remains identical until the highest tested pressure of 130 GPa. This limit was due to the breaking of the diamond anvil, and not to any detrimental behavior of the NV center itself. This paves the way for applying this new diagnosis to superconductors in the megabar regime, notably super-hydrides, which are currently the subject of fierce controversy.

3.2 - Experimental limits of NV centers implanted in a diamond anvil

3.2.1 - Experimental setup

To systematically test the possibility and effectiveness of NV center-based magnetometry at multiple tens of gigapascals pressures, we performed a series of experiments on a modified version of the optical setup described in chapter 2. For this iteration of the investigation, we used a NV-implanted DAC loaded with no sample outside of the pressure-transmitting medium filling the chamber of the DAC. The goal was to record simple ODMR spectra of the NV centers implanted in one of the anvil culets, for various applied magnetic fields and under increasing pressure to test the behavior of the NV centers in the absence of a sample perturbation. The updated version of the experimental setup is shown in Fig. 3.1. The cryostat was removed to leave the DAC at ambient temperature but still in the middle of our custom coil system that allows us to apply any vector magnetic field on the DAC and the NV centers. The results shown in this chapter almost exclusively used the confocal imaging capabilities of our setup. The main addition to the previous design is the possibility of using an alternative laser source for the optical excitation of the NV centers. We connected to our optical cage the output fiber of an additional 4-laser combiner box (Hübner C-FLEX), consisting of four diode lasers with respective wavelengths 405, 457, 488 and 515 nm. Compared to the usual excitation at 532 nm wavelength, these shorter wavelengths were chosen to test the compensation of the NV center optical spectrum shifting at high pressure. As the NV absorption spectrum shifts toward blue wavelengths with increasing pressure, the efficiency of the 532 nm laser at exciting NV center PL decreases but can be compensated for by using excitation lasers with higher energy instead.

Since we were aiming to go as high in pressure as possible, we chose to work this time with single bevel anvils, with 150 μ m final culet. This design can, in principle, reach a maximum pressure of about 150 GPa. We fitted them with a rhenium gasket into which our custom microwave slit had been cut, with adapted dimensions. The anvil was here implanted in our usual conditions, but with an array of spots pattern of NV centers. This pattern allows easy microscope repositioning to measure the behavior of NV centers always at the same position within the diamond tip. The cell was loaded with argon as the PTM, acting as the sole sample here. A confocal scan of the loaded cell is shown in Fig. 3.1.

The protocol we followed for these measurements consisted of three steps:



Figure 3.1: (a) Schematic of the optical setup used to test NV ODMR at room temperature and pressure above the megabar. The basis is the same as the setup shown in 2.8, but the cryostat has been removed. We added a second fibered laser source that combined four independant diode lasers with wavelength 515, 488, 457 and 405 nm. These shorter wavelengths are necessary to efficiently excite NV centers at high pressure as their optical spectrum shifts with stress. **(b)** Confocal PL scan of the culet of the DAC used to test the limits of ODMR on a standard diamond anvil implanted with NV centers. It is a single bevel $150 \mu m$ culet anvil, implanted with an array of NV center dots. As usual, the gasket hole is visible as the central dimmer part where the anvil isn't pressed against the reflective metallic gasket. Experiments were carried out on the NV spot closest to the gasket hole center.

- We measured the pressure applied to the sample chamber by recording a diamond Raman spectrum of the anvil tip at the NV center spot closest to the gasket hole center.
- We measured ODMR spectra at this NV center spot for applied magnetic fields between 0 and 10 mT, with the field direction aligned first with the diamond's [100] and then [111] axes. This was done to provide one configuration close to the experimental considerations shown, for instance, in the previous chapter, and one where the field is perfectly aligned with one NV orientation to factor out the effects of off-axis magnetic fields if necessary. The excitation laser wavelength, laser power, and microwave power were chosen to maximize contrast while limiting the power broadening of the ESR lines [Dréau et al., 2011].
- We then increased the pressure while monitoring the Raman spectrum to achieve the next pressure step and repeated the measurement protocol.

3.2.2 - ESR up to $70 \ \mathrm{GPa}$

The typical results we achieved will be presented here in a colormap fashion to capture the evolution of NV center ESR lines under applied magnetic fields. Colormaps of ESR signal collected at the starting pressure 9.6 ± 0.46 GPa are shown in Fig. 3.2. These maps show the displacement of the ESR frequencies with the applied magnetic field due to the Zeeman effect on the NV center spin. Under 9.6 GPa sample pressure, we see that the NV ESR is already slightly modified by stress, as expected.



Figure 3.2: (a) Colormap compiling ESR spectra recorded on implanted NV centers at 9.6 GPa sample pressure, with varying magnetic field amplitude oriented in the diamond's [100] axis. Spectra were recorded with 1 min integration time, with 25 dBm microwave power. (b) Colormap compiling ESR spectra recorded in the same conditions with the magnetic field oriented in one of the diamond's $\langle 111 \rangle$ axes.

The ODMR spectrum appears with a central frequency of 2.96 GHz, corresponding to a $\delta = 90$ MHz shift compared to ambient pressure D = 2.87 GHz. It also already exhibits a slight degeneracy lift due to non-hydrostatic stress $\Delta_{\sigma} = 24$ MHz even for an applied magnetic field of null amplitude. The observed contrast is sufficient to locate the resonance frequencies (more than 10% PL dip without magnetic field). It is, however, already clear that the contrast has become asymmetric, especially under zero magnetic field. The initial contrast of the high-frequency branch was here 12%, while the low-frequency branch contrast was only 4%. When we applied a magnetic field in the [100] direction, this asymmetry was reduced to 14% and 10% contrast for fields above 1 mT. This effect is also visible on the

apparent ODMR linewidths, with the low-frequency branch width going from 5 to 12 MHz width between 0 and 1 mT, while the high-frequency branch holds a steady 22 MHz width.

The expected symmetries of the ESR resonance lines for different orientations of the applied magnetic field are conserved. In the [100] direction, all four NV orientations experience the same magnetic field projection, and ESR frequencies appear degenerate with only two branches. The lines' displacement with the magnetic field deviates slightly from linearity because of the off-axis field component in this configuration. On the other hand, in the [111] direction, we see the aligned NV orientation separating from the other three equivalent orientations, corresponding to the linearly shifting pair of lines with the largest splitting.

We then recorded series of ODMR spectra in these configurations for sample pressures going from 9.6 GPa to 69.8 GPa. The corresponding diamond Raman spectra for the [100] data are shown in Fig. 3.3. The [100] and [111] field orientation series results are presented in the colormap plots of Fig. 3.4 and 3.5.



Figure 3.3: Reference diamond Raman spectra recorded at the central NV measurement spot, used as sample pressure measurements in the standard ODMR test experiment. The bottom panel shows the signal derivative used to locate the high-energy diamond edge according to the standard method of [Akahama and Kawamura, 2004]. Spectra are consistent with sample pressures of 9.60 ± 0.46 GPa, 20.31 ± 0.47 GPa, 30.39 ± 0.49 GPa, 40.77 ± 0.50 GPa, 50.92 ± 0.51 GPa, 61.85 ± 0.53 GPa, and 69.83 ± 0.54 GPa. All Raman spectra exhibit a slight spectral modulation that we attribute to a poor anti-reflection coating of one of our optics, possibly the camera window used in the spectrograph. This parasitic modulation, however, didn't disturb the location of the Raman edges used to determine the pressure.



Figure 3.4: Colormaps of the ODMR data recorded as a function of pressure and magnetic field in the [100] direction, up to sample pressure 69.8 GPa. All the data were recorded with 1 min integration per spectrum under 532 nm laser illumination, except the last two pressure points with low contrast that required 20 min per spectrum using 488 nm laser illumination. This laser source was much more efficient than the green laser which almost didn't yield any NV PL at these pressures. Respective MW powers used are, in order of increasing pressure, 25, 25, 23, 30, 35, 33, and $35 \, dBm$.

A detailed extraction of all the interesting parameters is complex at this point. We can immediately see that the NV centers' behavior is heavily modified compared to the room pressure physics described previously. Attempting to fit this vast dataset without any prior information or modeling would be extremely costly, inefficient, and inaccurate, so we will first make some general remarks, that we will then try to explain with the model developed in the following section.

- First, we see that the trend in the consequences of stress on the NV centers' ESR frequencies is preserved to 70 GPa sample pressure. The whole spectrum is shifted to higher frequencies with increasing pressure, as expected from applying some hydrostatic stress. From D = 2.87 GHz at atmospheric pressure, the center of the observed ESR spectra reaches 3.54 GHz at 69.8 GPa, for a total shift of $\delta = 670$ MHz. We also continue to record the increase of the zero-magnetic field splitting Δ_{σ} due to nonhydrostatic stress, reaching 265 MHz at 69.8 GPa.
- Confirming what was hinted at the end of chapter 2, a visible direct consequence of the



Figure 3.5: Colormaps of the ODMR data recorded as a function of pressure and magnetic field applied in the [111] direction, up to sample pressure 70.4 GPa. All the data were recorded with 1 min integration per spectrum, except the last three pressure points with low contrast that required 20 min per spectrum. We used 532 nm laser illumination up to 40 GPa, and switched to 488 nm wavelength after. Respective MW powers used are, in order of increasing pressure, 30, 25, 30, 30, 33, 35, and 35 dBm.

increase of non-hydrostatic stress splitting Δ_{σ} according to eq. 2.2 is the weakening of the displacement rate of the ESR lines with magnetic field amplitude when pressure is increased. At each pressure point, the initial value of the ESR lines' slope with applied magnetic field becomes smaller and smaller, requiring an increasing magnetic field amplitude to retrieve the quasi-linear behavior once the effect of non-hydrostatic stress becomes dominated by the Zeeman effect.

- The contrast asymmetry between the high-frequency and low-frequency branches previously described for the 9.6 GPa measurement is worsened by increasing the pressure. The low-frequency branch contrast consistently weakens with increasing pressure up to 40.8 GPa, before reappearing at higher pressure with a positive contrast ESR line when off-axis magnetic field is applied (never observed for the NV orientation aligned with the magnetic field). This effect of ODMR contrast inversion has never been reported in observations of NV center photodynamics before, which confirms that stress has an unprecedented impact on the physics of these NV centers.
- Finally, the overall ODMR contrast amplitude we observed in our experiments gener-

ally decreased with increasing sample pressure. We tried to compensate for this effect by gradually increasing the excitation MW power we used to enable the detection of ODMR at pressure as high as we could. Still, the ODMR signal became essentially impossible to record within a reasonable acquisition time above 70 GPa (despite increasing the applied MW power from $25 \, dBm$ at $9.6 \, GPa$ to $35 \, dBm$ at $69.8 \, GPa$). A possible explanation for this apparent signal weakening could be the gradual degradation of the MW delivery due to gasket deformation that may occur at high pressure. However, this hypothesis was excluded by the simple observation that we retrieved the full amplitude of contrast upon lowering the pressure once the experiment was terminated. Gasket deformations happening at these pressures are almost entirely plastic and irreversible, so it would be highly unlikely for a degraded gasket antenna to improve back to its initial state upon pressure lowering. This indicates that the overall OMDR contrast weakening we observed is intrinsically linked to physical changes in the mechanisms allowing the electronic spin dependence of the NV PL.

3.2.3 - Optical ZPL shift

In addition to ODMR data, we also conducted a study of the optical spectrum of the NV center at ambient temperature under sample pressure from 15.1 GPa to 77.6 GPa. This experiment was performed using the exact diamond anvils described previously, except they were loaded into a separate cell with a standard rhenium gasket. There was no need to use microwaves to record the evolution of the NV center's optical spectrum, so we chose not to use our MW slit design here. Additionally, spectroscopy of NV centers in a cell without any sample is wildly inaccurate. As depicted in Fig. 3.6.a, the issue is that our NV centers implanted into the anvil tip are close to an optical cavity with significant finesse. Facing each other at a distance fixed by the gasket thickness (typically $\sim 10 - 20 \ \mu m$), the two diamond anvil surfaces are so well aligned to be parallel that they constitute an optical cavity containing the pressure transmitting medium (PTM). As the NV centers are excited, the emitted PL has multiple interferences with itself within the cavity, resulting in a Fabry-Perot modulated spectrum. This spectrally modulated transmission or reflection of the DAC sample cavity is usually not a problem for the spectroscopy of spectrally narrow objects. It can even be used to measure the cavity thickness [Schifferle et al., 2022]. The NV centers, however, emit in a spectral range more than 100 nm wide and thus exhibit distorted spectra if nothing special is done.

To circumvent this issue, we used a thin piece of gold foil as a reflecting screen deposited on the surface of the implanted anvil (see Fig. 3.6). This opaque layer prevents NV PL from



Figure 3.6: (a) Schematic of cavity effects on spectroscopic measurements in a DAC. The two diamond anvils are aligned to be perfectly parallel. Therefore, the experimental chamber constitutes an optical cavity where light is reflected and therefore interferes with itself. This Fabry-Perot-type cavity filled with the PTM has spectrally modulated transmission and reflection, hindering spectroscopic measurements of luminescent centers with broad emission spectra, like the NV center. To perform optical spectroscopy of the NV center, we deposited a thin piece of gold foil on the anvil surface upon loading the DAC so that the NV PL is redirected towards the collecting microscope objective without interfering with the cavity. **(b)** Confocal PL scan of the implanted anvil culet used in the spectroscopy experiment, with the gold foil piece increasing signal in a central area. The two circled NV spots are the ones where the spectra shown in (c) were recorded. **(c)** Optical spectra recorded on implanted NV centers at 45 GPa sample pressure. Spot 2 is located below the 'naked' optical cavity constituted by the experimental chamber, and thus exhibits spectral modulation. Spot 1 is located below the gold foil, and thus shows a normal NV and diamond Raman spectrum, with signal collection improved by the reflective gold foil.

interacting with the optical cavity. It also improves the collected signal as it reflects both the excitation laser and PL initially emitted away from the collection optics.

Using this specially prepared cell, we recorded the shift of the NV center optical spectrum towards shorter wavelengths with increasing stress up to 77.6 GPa. These results are shown in Fig. 3.7. The apparent peak for the ZPL was fitted with a single Lorentzian line on top of a quadratic background locally modeling the phonon sideband. We observed a total shift of the ZPL central energy of 186 meV at 77.6 GPa (ZPL at 581.8 nm), with no apparent splitting of the line. By fitting the data with a simple linear model, we report here a lineshift with pressure of -0.64 ± 0.01 nm/GPa, or 2.21 ± 0.02 meV/GPa. The value of the observed shift is relatively close to the 2.73 meV/GPa measurement of [Vindolet, 2021] in the exact same experimental conditions up to 40 GPa. Note that if we fit our data with only the points below 40 GPa, the shift is 2.55 ± 0.04 meV/GPa, indicating that the pressure dependance of the ZPL energy deviates from linearity (more on this in section 3.4.6). To see if this measurement can confirm our ESR determination of the stress at the anvil tip, we will again need a more complete model of the stress state exerted on the tip of a pressurized anvil hosting NV centers.



Figure 3.7: (a) Example optical spectra recorded on implanted NV centers at sample pressures from ambient to 78 GPa. **(b)** Fitted position of the NV center ZPL for implanted centers as a function of sample pressure. A linear fit gives a slope of $-0.642 \pm 0.006 \text{ nm/GPa}$. Data was acquired using 532 nm laser excitation up to 65 GPa, 491 nm above. **(c)** Converted results giving the measured NV ZPL energy as a function of sample pressure. A linear fit gives a slope of $2.21 \pm 0.02 \text{ meV/GPa}$.

3.3 - Non-hydrostatic stress environment at a diamond anvil tip

3.3.1 - General considerations

To try and make sense of those observations in ODMR and optical spectroscopy of the implanted NV centers, we will need an attempt to reduce the number of variables of our problem by taking informed guesses regarding the stress exerted on the diamond anvils in a DAC. The critical concept here will be that in our configuration, the NV centers are located within the surface of the diamond anvil. The DAC was originally designed to maximize the hydrostaticity of the pressure applied to a sample in the experimental chamber using a plastically deforming metallic gasket and a rather soft PTM. The diamond anvils constitute the main intermediate element transforming the uniaxial stress provided by the external loading mechanism into quasi-hydrostatic stress in the sample chamber. Predicting the exact distribution of stresses inside a diamond anvil is a highly ambitious task, even for state-ofthe-art finite element modeling, as it results from competing effects of elastic deformation, plastic deformation, and friction, all happening at length scales from the millimeter to the micrometer on at least three different materials: the diamond, the rhenium, and the PTM. It is also highly dependent on experimental factors such as diamond anvil shapes or gasket thickness, which can vary greatly. A few studies have taken a practical approach to this issue, trying to assess the stress distribution at the anvil tips using Raman spectroscopy [Hanfland and Syassen, 1985] or X-ray diffraction and absorption [Hemley et al., 1997, Eremets et al., 2005]. This has proven paramount in understanding anvil deformations under ultra-high pressure, trying to improve on the practical pressure limit of the standard DAC design [Li et al., 2018] and leading to optimized designs that allowed researchers to achieve pressure above 400 GPa [Dewaele et al., 2018]. However, the limited amount of information we can gather through these methods has brought little quantitative information about the complete distribution of the stress tensor inside the diamond anvils. In this section, we will try to make simple hypotheses about the stress applied at the tip of the anvils, designing a toy model able to account for our observations.

We can start with simple symmetry considerations associated with the DAC geometry. For simplicity, we will use the standard reference frame where the Z axis designates the optical axis of the DAC, and the orthogonal XY plane is parallel to the anvils' surfaces. In a (100)-cut anvil, this frame can also designate the crystal lattice frame. We will here consider the stress at the point with the highest symmetry: the center of an anvil's surface. At this

specific point in space within the diamond, we can make the following reasoning:

• The DAC exhibits a clear revolution axis along the *Z* direction, which means that the *X* and *Y* directions should be indistinguishable. This already simplifies the possible total stress tensor from eq. 1.3 to the form

$$\overline{\overline{\sigma}} = \begin{pmatrix} \sigma_{\parallel} & \sigma_{XY} & \sigma_{XZ} \\ \sigma_{YX} & \sigma_{\parallel} & \sigma_{YZ} \\ \sigma_{ZX} & \sigma_{ZY} & \sigma_{\perp} \end{pmatrix}$$

where σ_{\parallel} denotes the stress in the directions tangential to the surface and σ_{\perp} the stress normal to it.

• An important piece of information is provided by calibrated pressure gauges such as fluorescent ruby, or the diamond Raman edge to estimate the stress inside the sample chamber, which is in contact with our surface of interest. In this particular volume, we will consider the stress tensor to be hydrostatic with an average pressure of *P*. We can then apply continuity of normal stress at the PTM-to-diamond surface interface to estimate that we should have $\sigma_{\perp} = P$. This brings us to:

$$\overline{\overline{\sigma}} = \begin{pmatrix} \sigma_{\parallel} & \sigma_{XY} & \sigma_{XZ} \\ \sigma_{YX} & \sigma_{\parallel} & \sigma_{YZ} \\ \sigma_{ZX} & \sigma_{ZY} & P \end{pmatrix}$$

• We will consider that all shear stresses are negligible compared to the uniaxial and hydrostatic components. This is a strong hypothesis, but it greatly simplifies the problem while maintaining an excellent agreement with the data, as shown later. We then yield:

$$\overline{\overline{\sigma}} = \begin{pmatrix} \sigma_{\parallel} & 0 & 0 \\ 0 & \sigma_{\parallel} & 0 \\ 0 & 0 & P \end{pmatrix}$$

• Finally, we will consider that tangential stress will be modified as the load onto the cell is increased. This simply means that σ_{\parallel} is actually not independent of the sample pressure P inside the PTM. As the most simple functional form describing this, we chose to approximate $\sigma_{\parallel}(P) = \alpha P$, α being an adimensional parameter encompassing

the stress anisotropy in the anvil tip. This yields the hypothesis for the stress tensor:

$$\overline{\overline{\sigma}} = \begin{pmatrix} \alpha P & 0 & 0 \\ 0 & \alpha P & 0 \\ 0 & 0 & P \end{pmatrix}$$

Under those assumptions, the amplitude of the α parameter relative to unity determines if the average stress at the anvil tip is higher or lower than inside the sample chamber:

$$\sigma_{average} = (\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ})/3 = P(2\alpha + 1)/3.$$
(3.1)

To estimate this, we can turn either to the sparse literature ([Hanfland and Syassen, 1985, Ruoff et al., 1991] for instance), or try to get a physical intuition. Fig. 3.8 schematically describes the situation. When uniaxial pressure is applied on the back face of the anvil to press it against the gasket and opposing anvil, it first plastically deforms the metallic gasket until the gasket bulk modulus reaches that of diamond. Then its natural response, once the gasket cannot be deformed anymore, is to elastically deform to continue transmitting the applied force to the tip. Due to the sloped shape of the anvil, the force applied along the Z axis to the diamond seat is partially converted into radial XY components pressing towards the anvil center. At the tip, the resulting stress is generally compressive, with XY components of the same order as the axial Z components. If this were the only effect playing a role, the stress tensor at the anvil tip would likely be close to hydrostaticity.

However, a second effect is specifically responsible for a reduction of tangential stress. The previously described distortion of the anvil tends to bend the anvil culet so that the gasket thickness gets smaller at the culet edges than at the center. This so-called 'cupping' effect is well documented in the high-pressure community ([Li et al., 2018, Schifferle et al., 2022]) as it constitutes a limiting factor when trying to achieve multi-megabar pressures. At our pressure scale of a few tens of gigapascals, the effect is small, but the anvils can nonetheless be elastically deformed by as much as a few micrometers. Our experiments revealed this cupping from the onset of interference rings in laser reflection images, indicating an experimental chamber optical cavity of spatially varying thickness (see Fig. 3.9). This cupping of the anvil surface creates surface tension at the diamond culet, which can be seen as tangential tensile stress competing with the previously described compression. Overall, this participates in weakening the compressive stress happening in the plane of the diamond anvil surface, exactly where our NV centers are located.

These elements suggest that the α parameter is smaller than unity. In this case, the



Figure 3.8: Schematics of diamond anvil stress and deformation (a) & (b) before compression, (c) & (d) at high pressure. (a) Schematic cross-section of the initial position of a diamond anvil in a DAC, pressed by the diamond seat against the gasket and sample chamber. (b) Close-up cross-section of the anvil tips and experimental chamber, before pressurization or at very low pressure. The two anvils are aligned to be parallel for uniform compression of the gasket and pressure transmitting medium (PTM). (c) Schematic cross-section now at high pressure. The uniaxial force applied to the anvil back face through the diamond seat is transmitted through the anvil (black arrows), and partially redirected by the anvil's tapered shape. In this geometry, the total anvil will slightly deform (initial position shown with dotted outline), generating areas of high-strain low-stress at the back and low-strain high-stress at the tip. (d) The anvil deformation at high pressure induces a 'cupping' effect that results in the diamond surfaces bending. The gasket and sample cavity thickness is not spatially uniform anymore. The resulting stress in the diamond anvil tip is mostly compressive, with components both in the DAC axis and radial directions. The bending of the anvil surfaces results in significant surface tension that partially compensates for compressive stress in tangential directions to the anvil surface. Overall, this results in an anisotropic stress distribution in the anvil culet surface, where the stress is lower in the tangential directions than in the normal direction. Blue arrows signify compressive stress, red arrows tensile stress due to surface tension.



Figure 3.9: (a) Confocal image recorded on the 532 nm laser reflection of a pressurized DAC at 34 GPa with no sample inside the PTM. Within the sample chamber, we observe interference rings characteristic of a cavity of varying thickness, with the radial symmetry of cupping. Bright or dark fringes constitute lines of equal cavity thickness. **(b)** Confocal laser reflection image of the same DAC with pressure lowered to room conditions. We see that the interference pattern visible at high-pressure disappeared, indicating that the anvils returned to their original geometry. The high-pressure deformation was thus elastic in this regime.

resulting stress at the diamond anvil tip center where we have implanted NV centers of diamond should be compressive overall, with anisotropies reducing stress in the directions perpendicular to the surface. This is all summed up in our approximate form for the stress tensor:

$$\overline{\overline{\sigma}} = \begin{pmatrix} \alpha P & 0 & 0 \\ 0 & \alpha P & 0 \\ 0 & 0 & P \end{pmatrix} \quad , \quad 0 < \alpha \le 1.$$
(3.2)

In this approximation, we can rewrite the components of the effective \vec{M} field describing the effect of stress in the NV center Hamiltonian in eq. 1.4 as:

$$M_X = 2bP(1-\alpha)$$
, $M_Y = 0$, $M_Z = a_1P(1+2\alpha)$. (3.3)

Combining this with the approximate expressions for the ESR frequencies in eq. 1.7, we see that the value of α indeed quantifies the effect of non-hydrostatic stress. If $\alpha = 1$, the stress tensor is fully hydrostatic, and the only impact of stress is to increase M_Z , which simply adds to the average ESR frequency D = 2.87 GHz. However, when $\alpha < 1$, this shift of the central frequency with P is reduced, and a zero magnetic field splitting $\Delta_{\sigma} = 2M_X$ appears.

3.3.2 - Data modeling and processing

Now that we have a quantitative toy model for the stress applied to the diamond anvil tip hosting the NV centers under high pressure, we can compare it to the data. To this end, the full NV center ground state Hamiltonian of eq. 1.4 can be numerically diagonalized, within the stress approximation given by eq. 3.2. This diagonalization mainly yields the ground state's eigenenergies, which can be converted into predicted ESR frequency values for a given set of model parameters (α , P) and magnetic field \vec{B} . In this particular experiment, \vec{B} is a control parameter, as it can be varied using our coil system. For a given set of ESR measurements where the applied magnetic field values and direction are known, the remaining free parameters are (α , P) with a good guess at P coming from Raman measurements of the pressure inside the PTM.

The fitting software was designed to make use of all the information contained in the colormaps corresponding to a certain series of magnetic field values at a given pressure (Fig. 3.2 or 3.4 for instance). Instead of fitting individual ESR spectra with a sum of Lorentzian lines with free parameters, we performed physically informed fits of the whole colormap. We used a function generating a simulated full colormap Image(α , P, $\{B_i\}$, \vec{b} , $\{C_n, w_n\}$) where $\{B_i\}$ are the set of experimentally tested magnetic field values in orientation \vec{b} (normalized orientation vector), and the only true fitting parameters are $(\alpha, P, \{C_n, w_n\})$ where $\{C_n, w_n\}$ are the set of contrast-width lineshape parameters for each apparent ESR line. The position and displacement of ESR lines were thus restricted to comply with physical solutions of the NV ground state Hamiltonian, while lineshapes were left as free parameters. An example of a synthetic physically informed colormap can be seen as the best-fit result of Fig. 3.10.

Using this procedure, we demonstrated that our simplified stress model could closely fit the position of the ESR lines in all our experimental data with great success. The resulting best-fits are shown in Fig. 3.11 and 3.12.

Extracted values for the best-fit parameters are shown in Fig. 3.13. We thus extended the measurements of ESR behavior for implanted NV centers up to 70 GPa sample pressure (previously 35 GPa in [Toraille, 2019]), recording a central frequency shift δ of 9.56 ± 0.14 MHz/GPa and a non-hydrostatic splitting Δ_{σ} of 3.74 ± 0.11 MHz/GPa. Our simplified stress model allowed us to accurately reproduce the ESR lines' frequencies by converging at every pressure point to an estimated sample pressure within a few percent of the real value measured by diamond Raman spectroscopy, and almost constant values of the α anisotropy parameter, on average $\alpha = 0.58$. This value confirms the anisotropy estimation found in [Ruoff et al., 1991] ($\alpha = 0.61$). Note that the estimated fitting error on the value of α at each pressure



Figure 3.10: Example output of our physically informed ESR colormap fitting routine. We designed a fitting software able to generate synthetic colormaps modeling our data with the magnetic field variation of ESR line positions by numerically solving the NV ground-state Hamiltonian. The procedure directly fits the total data colormap for a given magnetic field orientation, the only free parameters being the ODMR linewidth, contrast, and the stress model parameters *P* and α .

point never exceeded 0.005.

The first physically-informed colormap fitting procedure described above captured the displacements of ESR frequencies by fitting lines of constant contrast and width to our data. However, some additional information can be gained by this time extracting these contrast and width values for each individual ESR spectrum. This was not done in the first step, as it would introduce many fitting parameters, dramatically reducing its effectiveness at locating line positions. However, with the line positions now already extracted, we were able to perform a second round of in-depth data processing where we extracted the observed evolutions of ODMR contrast and linewidth with both pressure and magnetic field amplitude. The detail of all this additional extracted information is not shown in this thesis, but some derived results will be discussed here.



Figure 3.11: Colormaps of the dependence of the ESR eigenfrequencies with sample pressure and magnetic field applied in the [100]-axis presented in Fig. 3.4, now with fitting results displayed as the green dashed lines. Extracted fitting parameters P and α are shown in Fig. 3.13.

3.3.3 - Pressure dependence on the sensitivity of NV magnetic sensing

The main goal of our systematic study of NV center ESR with DAC sample pressure and magnetic field was to evaluate the effect of stress on the NV centers' sensing capabilities at high pressure. Now that we have extracted most of the information in the ESR colormaps, we can directly compute estimations of the magnetic field sensitivities we could achieve. In section 1.3.3, we briefly evoked the usual definition used to assess NV center magnetic field sensitivity, as described in [Dréau et al., 2011] or [Barry et al., 2020]. This can be concisely written as:

$$\eta_B \approx \frac{\mathcal{P}_F}{\gamma_{\rm NV}} \frac{\Delta \nu}{\mathcal{C}\sqrt{\mathcal{R}}}$$
(3.4)

where η_B is the sensitivity, $\mathcal{P}_{\mathcal{F}} = 4/3\sqrt{3} \simeq 0.77$ for a Lorentzian line, $\gamma_{\rm NV}$ is the NV gyromagnetic factor, $\Delta \nu$ is the ESR linewidth, \mathcal{C} is the observed ODMR contrast and \mathcal{R} is the photon-detection rate. This definition is, however, not well adapted to reflect the capabilities of high-pressure experiments, where we have seen that the physics of the NV center is heavily modified. Our experiments showed that non-hydrostatic stress significantly hinders ESR lines' displacement with the applied magnetic field through an apparent increasing



Figure 3.12: Colormaps of the dependence of the ESR eigenfrequencies with sample pressure and magnetic field applied in the [111]-axis presented in Fig. 3.5, now with fitting results displayed as the green dashed lines. Extracted fitting parameters P and α are shown in Fig. 3.13.

 Δ_{σ} . Eq. 3.4 only captures the sensitivity of NV centers in conditions where magnetic field response is linear with the applied magnetic field along the NV axis $B_{\rm NV}$.

In our case, the $\Delta = \sqrt{\Delta_{\sigma}^2 + \Delta_B^2}$ dependence of observed splitting makes this response strongly depending on the value of $B_{\rm NV}$ compared to Δ_{σ} . As $B_{\rm NV}$ increases, the ESR lines' slope with a magnetic field progressively goes from zero to $\gamma_{\rm NV}$ (if the field is aligned with the NV axis). To account for this observation, we propose using an adapted definition of sensitivity reflecting the change in sensing capabilities with the value of the bias magnetic field applied. We will write:

$$\eta\left(\vec{B},P\right) \approx \frac{\mathcal{P}_{\mathcal{F}}}{\gamma\left(\vec{B},P\right)} \frac{\Delta\nu}{\mathcal{C}\sqrt{\mathcal{R}}}$$
(3.5)

where $\eta(\vec{B}, P)$ is the magnetic field and sample pressure-dependent sensitivity to DC fields, and $\gamma(\vec{B}, P)$ is an effective gyromagnetic factor consisting of the slope of the ESR lines at a given magnetic field and pressure. Using this adapted definition and all the measured ESR parameters extracted from the previous measurements, we can now provide a quantitative evaluation of sensing performances for implanted NV centers at high pressure. To be consistent with the high-contrast configuration we would likely use for detecting the Meissner effect, we present in Fig. 3.14 the results we achieved with a bias field oriented in the [100]



Figure 3.13: Extracted values resulting from the standard implanted anvil high-pressure ODMR data fitting. (a) Shifted ESR central frequency $D + \delta$ as a function of sample pressure. a linear fit yields a shift of 9.56 ± 0.14 MHz/GPa. (b) Value of the anisotropic stress ESR splitting Δ_{σ} with increasing sample pressure. Linear fitting yields a slope 3.74 ± 0.11 MHz/GPa. (c) Fitted values of the NV center pressure as a function of pressure inside the PTM, determined from diamond Raman. A linear fit gives an adimensional slope of 0.935 ± 0.013 . This value could be explained by the NV centers not being exactly at the diamond-PTM interface (where normal stress must be continuous), but around 20 nm under the surface. (d) Fitted value of the anisotropy parameter α as a function of sample pressure. After the first value of around 0.65, all pressure points closely converged to an average $\alpha = 0.58$.



Figure 3.14: Estimated magnetic field sensitivity for implanted NV centers with increasing sample pressure and magnetic field in the [100] orientation. The values of the sensitivity are obtained using eq. 3.5 and the high-pressure ODMR colormaps.

diamond direction.

These results essentially reflect the intuition one would have upon examining the highpressure raw data presented previously. At low-bias magnetic fields, the sensitivity is always at its poorest and is improved by increasing the bias field. Working at 3 mT instead of 0 mT generally improves sensitivity by at least an order of magnitude, even two for the highest pressures tests (above 50 GPa). Above 7 mT bias field, the off-axis components start to degrade ODMR contrast, which hinders sensitivity. Overall, NV center magnetic sensitivity is steadily degraded with increasing sample pressure, going from an optimum $5.0 \times 10^{-6} \text{ T}/\sqrt{\text{Hz}}$ at 10 GPa down to $6.1 \times 10^{-4} \text{ T}/\sqrt{\text{Hz}}$ at 70 GPa. This reduction of sensitivity to static magnetic fields by a factor 100 constitutes a clear limitation for applying high-pressure NV center magnetometry above 50 GPa.

3.3.4 - Analysis of optical spectroscopy data

We can test our model of the stress applied to the tip of a diamond anvil hosting NV centers by the comparison to optical spectroscopy data. As already mentioned in section 1.4.2 and confirmed by our measurements, the recorded NV optical emission spectral shift with pressure exhibits a pressure slope about halfway between hydrostatic and fully uniaxial behaviors. Now that we have a model of the anvil stress with an estimate of the α anisotropy parameter from the ESR measurements, we can see if this can quantitatively explain our spectroscopy measurements.

Recall that in close analogy with the theory describing spin-state transitions, the expected modification of the energy E_{ZPL} of the NV zero phonon line under pressure can be described as:

$$E_{\rm ZPL} = E_{\rm ZPL}^0 + \delta_o \pm \frac{\Delta_o}{2}$$
 with $\delta_o = \gamma_o$ and $\Delta_o = 2\sqrt{\alpha_o^2 + \beta_o^2}$ (3.6)

where α_o , β_o and γ_o (defined in eq 1.9) are stress-optical equivalents to the spin-mechanical coupling terms M_X , M_y and M_Z . Using our anisotropic stress model, we retrieve the following:

$$\alpha_o = 2b_o P(1 - \alpha) , \ \beta_o = 0 , \ \gamma_o = a_{1,o} P(1 + 2\alpha).$$
(3.7)

Using the susceptibilities from [Davies and Hamer, 1976] and the diamond Raman estimates of the pressure P, we can use this expression to fit our data and retrieve, using an independent route from the ESR measurements, another estimation of the anisotropy parameter α (supposing α constant with pressure here). The result is shown in Fig. 3.15.

An effect not accounted for in previous studies of implanted centers under pressure is that the defect symmetry lowering due to anisotropic stress imposes new selection rules on NV optical emission. As detailed in [Davies and Hamer, 1976], and in a more modern version in [Rogers et al., 2015], anisotropic stress along the [100]-axis lifts the degeneracy between the NV excited E_x and E_y states yielding two ZPL lines with different polarizations. In our DAC experiments where [100] is also the optical axis, we are confined to the excitation of so-called ' σ -modes' where electric field polarization is perpendicular to the stress axis. In this configuration, the relative intensity of the two dipole emissions becomes very asymmetric. When evaluating the expected line position for $\alpha \sim 0.6$, it becomes clear that the optical line we recorded as 'the' ZPL is actually only one of the two real ZPLs, namely the one with lower energy, the other one being too weak to be detected in our observation configuration. By fitting our data with the lower branch of our model, we converge to a value of our only fitting parameter $\alpha = 0.61$. This is remarkably close both to our estimation of $\alpha = 0.58$ from NV ESR data, and to the literature ($\alpha = 0.61$ in [Ruoff et al., 1991]). The observed small deviations



Figure 3.15: Modeling of the NV ZPL energy shift with pressure based on the group theorybased model of eq. 3.6 and 3.7. The measured ZPL line is consistent with being only the low-frequency branch of a double ZPL split by anisotropic stress. Using this model, we independently retrieve an anisotropic α parameter value close to the ESR estimation and the literature at $\alpha = 0.61$. Deviation from the linear model is visible in this high-pressure regime. The corresponding theoretical expected position for the second ZPL line is shown as a dotted line. It was here undetected due to polarization selection rules imposed by anisotropic stress.

of the data from the linear model exposed in eq. 3.7 could be explained either by α not being constant as pressure is increased or, more probably, by the susceptibilities not being independent of pressure since the values used have been measured only to 2 GPa. This last hypothesis is also linked to the nonlinearity of the equation of state of diamond, an effect that will be discussed in section 3.4.6.

We have thus been able to use our model of anisotropic stress within the anvil tip to quantitatively understand the high-pressure optical shift of implanted NV centers, independently converging to a value of the anisotropy parameter α that is very close to the one inferred from the ESR measurements. To improve these measurements, and possibly resolve finer components of the NV ensemble ZPLs, these experiments would be interesting to repeat at low temperature (T < 10 K).

3.3.5 - The ODMR contrast issue

The analysis of the results presented up to now was focused mainly on the description of the NV center eigenfrequencies in the ground state under stress at the tip of a diamond anvil. By successfully fitting the measurements with great precision, we proved that combining theory from previous studies establishing the NV center spin ground-state Hamiltonian with the stress toy model can accurately predict the ESR line positions, even at high stress. We have shown that the effect of anisotropic stress on the lines' displacement due to the applied magnetic field can alter the NV sensing capabilities, but also that this effect can be mitigated by using a larger bias field to compensate the detrimental influence of non-hydrostatic stress. Consequently, the main problematic modification of the NV center sensing efficiency under high pressure is the heavy altering of the optical contrast that appears in Figs. 3.4 & 3.5.

Giving definite answers to questions about NV center ODMR contrast can already be challenging under ambient conditions as it results from many factors, both due to experimental conditions and also to fundamental aspects of NV centers. Any quantitative claims about the origin of contrast variation with pressure would be highly hypothetical at best at this point. However, we will briefly summarize how ODMR contrast arises in the NV center and how mechanical stress may affect this mechanism in multiple ways.



Figure 3.16: Simplified model of CW ODMR contrast from [Dréau et al., The optical contrast $\mathcal C$ ob-2011]. tained when the microwave field is resonant with the ground state ESR transition is described by driven Rabi oscillations with frequency Ω_{R} , while simultaneous optical cycling and pumping are modeled by Γ_c and Γ_{p} . Intrinsic relaxation of the populations through lattice interactions Γ_1 and inhomogeneous coherence dephasing rate Γ_2^* can be ignored when the optical polarization rate Γ_p is large enough.

As described in chapter 1, the ODMR contrast arises from the NV energy level structure that natively allows both 1) spin-dependent photoluminescence, and 2) optically induced spin polarization. By combining two-level Bloch equation modeling of microwave-induced transitions in the ground state manifold with an approximate rate equation model of the transitions between the ground, excited and singlet states, [Dréau et al., 2011] derived an approximate equation for the observable optical contrast in the unperturbed NV center (see simplified model in Fig. 3.16). This equation was derived to describe the functioning of a single NV center, but the reasoning can be applied to an ensemble of NV centers. This calculation yields:

$$C = \Theta \frac{\Omega_R^2}{\Omega_R^2 + \Gamma_p^\infty \Gamma_c^\infty \left(\frac{s}{1+s}\right)^2}$$
(3.8)

where C is the estimated optical contrast, Θ is a normalizing factor derived from the relative PL intensities in the dark and bright spin states, Ω_R is the driving Rabi frequency at electron spin resonance, Γ_p^{∞} is the optically induced polarization rate into the bright state at optical saturation, Γ_c^{∞} is the saturated rate of optical cycles (approximately the inverse of the excited state lifetime), and finally s is the optical excitation saturation parameter. To understand the complexity of contrast variations under pressure, one needs to realize that pretty much every single one of those terms could be modified under stress in ways that have never been quantified independently. The overall contrast C thus results from the competition of those multiple factors changing under high pressure. More specifically :

• **Optical saturation** s: the optical behavior of the NV center can roughly be considered as a two-level system (with a ground state and an excited state) with a finite lifetime for its upper state. NV optical emission will thus exhibit a standard saturation behavior where no additional average emission can be gained after reaching a cycling rate close to the inverse lifetime. The $s = \mathcal{P}_{opt}/\mathcal{P}_{sat}$ parameter quantifies proximity to this cycling limit in actual experimental conditions. It can be determined by recording PL while increasing laser excitation power \mathcal{P}_{opt} , to measure the limit power \mathcal{P}_{sat} needed to saturate the system. Under high pressure, we have seen that the optical spectrum of the NV center shifts, both in emission and absorption, towards shorter wavelengths. This means that the center's absorption cross-section for a given excitation wavelength will vary with pressure. Consequently, a given laser wavelength's efficiency at exciting the defects will vary with pressure, effectively changing the value of *s* for a given wavelength and power. This effect can be estimated by systematically measuring the NV's saturation curve at each pressure point, with the specific laser used. Such determination is time-consuming but doable.

• Rabi angular frequency $\Omega_{\rm R}$: the standard ODMR contrast is obtained by driving the NV center spin population, polarized into the bright state, towards the darker upper state. The Rabi angular frequency describes the typical coherent oscillation time between those two levels when the transition is excited on resonance at a given electromagnetic field amplitude. Ω_R is thus proportional to the amplitude of the microwave magnetic field used to drive spin transitions. Experimentally, this mostly seems to be dictated by the microwave power used. But the subtlety here is that this Rabi frequency Ω_R actually also quantifies the coupling between the applied microwave field and the quantum system through its magnetic transition dipole moment (see [Kölb] et al., 2019] for instance). This is the quantity that might be problematic at high pressure. The magnetic dipole matrix elements are directly derived from the spin system's eigenstates, by a simple scalar product of the magnetic dipole moment operator $\hat{\vec{\mu}}$ with the lower and upper states of the transition: $\vec{\mu}_{\text{lower,upper}} = \langle \text{upper} | \hat{\vec{\mu}} | \text{lower} \rangle =$ $-2\mu_B \langle upper | \vec{S} | lower \rangle$. We haven't specified here the exact nature of those upper and lower states, as it will vary with pressure and magnetic field. In the usual ambient conditions, these are the magnetic-basis spin states $|lower\rangle = |m_s = 0\rangle$ and $|lower\rangle =$ $|m_s=\pm1
angle$ (eigenvectors of S_z), giving a baseline coupling of the MW field with the defect and a Rabi frequency $\Omega_R = \frac{2\pi}{h} |\vec{B}_{MW} \cdot \vec{\mu}_{lower,upper}|$. Under high non-hydrostatic stress, however, the system dramatically changes, as its symmetry is distorted. Stress terms now dominate the hamiltonian, and the good eigenstates of the system are no longer those described by the magnetic field basis. Anisotropic stress mainly couples to the $\hat{S}_x^2 - \hat{S}_y^2$ operator with strength M_X , pushing the system towards eigenstates $|\pm\rangle = (|m_s = +1\rangle \pm |m_s = -1\rangle)/\sqrt{2}$. These are very different from the original $|m_s = 0\rangle$ and $|m_s = \pm 1\rangle$ eigenstates, as they have zero total angular momentum, and yield new magnetic dipole moments that are orthogonal and linearly polarized. This could partially explain the observed contrast asymmetry observed at low magnetic field and high stress, given that our microwave antenna most likely produces a microwave magnetic field oscillating along the [100]-axis. This orientation drives equivalently the two transitions $|m_s = 0\rangle \leftrightarrow |m_s = +1\rangle$ and $|m_s = 0\rangle \leftrightarrow |m_s = -1\rangle$, but has a very different effect on the transition between $|m_s = 0\rangle \leftrightarrow |+\rangle$ and $|m_s = 0\rangle \leftrightarrow |-\rangle$. Suppose we now add the effect of an applied static magnetic field. In that case, the system's eigenstates will continuously be steered from one base to another, depending on the field's strength and orientation relative to the NV centers. To summarize, we can say that even with an experimental microwave source applying a driving field independent of sample pressure, the NV centers' coupling to this field will be constantly

modified by both stress, on-axis, and off-axis magnetic fields, resulting in part in the complex ODMR contrast variations we have observed. If we suppose that our modeling Hamiltonian of the NV ground-state under pressure is correct (good fit to eigenenergies), this variation could be numerically approximated.

- Saturated rate of optical cycles Γ_c^{∞} : this essentially describes the maximum rate of optical cycles a given NV center can undergo. It is mainly fixed by the NV excited state lifetime. Under pressure, the NV energy levels are displaced, leading for instance to the increase in emission energy. This could also have an impact on the excited state's effective lifetime. This could easily be measured by performing time-resolved PL decay measurements with a short-pulse excitation laser.
- Parameters $\Gamma^\infty_{\mathbf{p}}$ and Θ : these two parameters phenomenologically encompass the strength of the fundamental properties of optical spin polarizability and spin-dependant PL intensity. Physically, they are both directly linked to the intersystem crossing (ISC) mechanism coupling the NV excited states to the singlet metastable manifold. This is where the most significant uncertainty lies at high pressure. The ISC appears through energy-conserving spin-orbit mediated transitions from the ${}^{3}E$ manifold to the vibronic states of the upper metastable ${}^{1}A_{1}$ state [Goldman et al., 2015]. The strength of that coupling will depend on a matrix element of initial and final states, and a wavefunction overlap varying with the ${}^{3}E \longleftrightarrow {}^{1}A_{1}$ energy detuning. Under anisotropic stress, the ${}^{3}E$ excited state structure is yet to be determined but is hardly measurable at room temperature, possibly modifying matrix elements. On the other hand, the exact ${}^{3}E \longleftrightarrow {}^{1}A_{1}$ detuning is not perfectly known at room pressure [Wolf et al., 2022], and the predictions for its evolution with stress are sparse ([Romanova, 2019] for instance) and in desperate need of experimental verification. Depending on the stress orientation relative to the diamond axes, this detuning could be increased or decreased by compression, yielding different results on optical contrast for different diamond cuts. We should mention here that some other groups have taken up this approach by experimenting with (111) cut anvils. Heavy modifications to the ISC rate from the complex excited state structure could also be at the origin of the observed crossover to positive ODMR contrast. Overall, we can say that the strength of the ISC mechanism creating spin-dependent behavior in the NV center should be strongly modified under anisotropic stress, leading to dramatic variations in ODMR contrast.

All of the above parameters could be partially responsible for the complex contrast behaviors we observed. The current understanding of it is illustrated in Fig. 3.17. Disentangling



Figure 3.17: Schematic diagram evaluating the current knowledge of the mechanisms for high-pressure ODMR contrast of the NV center. In this work, we have shown successful modeling of the NV ground state behavior under the conditions of a pressurized diamond anvil. Within the ground state, the specificities of the coupling to the microwave field and its polarization are conceptually known but need to be verified experimentally. The NV center's optical transitions have also been investigated, with measurements of the spectral shift with pressure. Measurements of the excited-state lifetime or the optical dipole degeneracy lift under high stress still remain to be investigated. The excited state structure of the NV center remains unknown under ultra-high stress. It most likely plays a major role in the intersystem crossing (ISC) coupling to the metastable singlet states, which is responsible for optical polarization and spin-dependent PL. The singlet states pressure behavior and detuning to the excited state also remain unexplored.
the respective effect of each mechanism is a challenging task that calls for many more experimental studies of NV centers in the high-stress regime. This task will require combining complementary methods, using for instance time-resolved photodynamics, stronger magnetic fields, low-temperature spectroscopy, photoionization measurements, ... Note that most of the photodynamics of the NV center was determined using single-defect measurements, as in [Beveratos, 2002]. This regime is unfortunately not currently reachable for NV centers in a DAC, due to the limit on the detection numerical aperture.

Within our experiments, we realized that fully explaining the behavior of the ODMR contrast would be far too ambitious a task. We then decided to focus on detecting ESR frequencies and modeling the NV ground-state behavior. We thus used an empirically determined optimal microwave power, optical power, and optical wavelength at each pressure step to maximize contrast within our realistic experimental capabilities.

3.4 - Microstructured anvils for NV magnetometry above the megabar

In the previous section, we systematically tested the ODMR of NV centers implanted within the tip of a pressurized diamond anvil to estimate the viability of this method of quantum sensing at a pressure approaching the megabar. We were able to record ESR signals up to 70 GPa but identified a significant degradation of sensitivity. This behavior severely hinders sensing possibilities above 40 to 50 GPa. This section will demonstrate our practical strategy to circumvent this limitation.

3.4.1 - Anvil machining to restore hydrostaticity

The exact mechanism behind the pressure limitations we previously observed is not fully explained, as many pieces of the puzzle still need dedicated investigations (see Fig. 3.17). However, we clearly identified that the loss of sensitivity at high pressure is linked to non-hydrostatic stress within the diamond anvil tip hosting the NV sensors. Anisotropic compression of the defect distorts its conformation and lowers its symmetry to a point where stress-induced splitting in the ground state hinders its sensitivity to an applied magnetic field. This distortion likely modifies the other state manifolds' coupling, giving rise to ODMR contrast. It thus seems like the problematic point for high-pressure NV sensing lies in the non-hydrostaticity of stress imposed onto the implanted diamond defects.

We propose to mitigate these effects by using micro-structuring of the diamond anvil surface to locally engineer a hydrostatic environment for the implanted NV centers. Machining a circular groove into the anvil surface around a small spot should isolate it from the rest of the culet, which is strained at high pressure. The resulting 'pillar' embedded within the anvil culet is then insulated from all stress tangential to the culet surface resulting from the uniaxial applied external pressure and the effects of cupping (see Fig. 3.8), and is immersed into the quasi-hydrostatic PTM allowed to penetrate the trench around it. The pillar, hosting the implanted NV centers, is then submitted to compression from the PTM, just like a sample within the usual experimental chamber. This concept is schematically represented in Fig. 3.18.

To test this idea, we used Gallium FIB milling or femtosecond-laser drilling to machine micropillars on the tip of diamond anvils, before implanting them using the usual parameters on our implantation FIB machine. Further investigation of the detailed effect of the struc-



Figure 3.18: Schematic of the proposed anvil micro-structuring step to create locally hydrostatic conditions for implanted NV centers. By machining a circular groove around a pillar onto the anvil culet, we can isolate a portion of the anvil tip that is then immersed inside the quasi-hydrostatic PTM. The pillar surface is protected from the surface tension arising from the anvil cupping that occurs due to the combined response of the pressure load applied to the anvils, the metallic gasket, and the PTM, as explained in the previous section. The blue arrows signify compressive stress while the red arrows display tensile stress due to surface tension.

ture's dimensions will need to be carried out, but the first shape we tried already showed extremely promising results. As shown in Fig. 3.19, we machined pillars with a 7 μ m flat tip, and a 2 μ m deep groove around the pillars. We then proceeded to repeat the systematic ODMR testing experiments detailed in the previous sections, to explore the NV center behavior in such a modified anvil tip.



Figure 3.19: (a) Scanning electron microscope images of a FIB-machined pillar on the tip of a 100 μ m culet diamond anvil. The pillar is 7 μ m wide, with a 2 μ m deep trench around it. (b) Same pillar imaged with better resolution. The grainy white surface present over most of the surface is a 100 nm thick gold layer deposited on the anvil before machining to avoid surface charging during the FIB milling with Ga⁺ ions.

3.4.2 - Observation of OMDR in suppressed stress anisotropy up to $130 \ {\rm GPa}$

Using these modified microstructured anvils implanted with NV centers, we were able to record ODMR spectra up to 130 GPa with almost identical responses to an applied magnetic field. We performed four experimental runs in total, with perfectly reproducible results. The first two runs were performed at CEA using a setup that couldn't apply control magnetic fields to well-defined directions, but already exhibited significant indications that anisotropic stress was massively reduced for NV centers located on the pillar compared to ones located elsewhere on the diamond anvil tip. The first run reached a pressure of 32 GPa, and the second run 60 GPa. In both cases, the pressure was determined using the fluorescence of a ruby micro-crystal. These runs were performed using a $300 \ \mu m$ culet anvil. Runs 3 and 4 were done on the setup described in the previous sections, using anvils with a $100 \ \mu m$ culet, as shown in Fig. 3.19, in order to reach a much higher pressure. In these two runs, we achieved ODMR measurements at PTM pressures from 20 GPa to 130 GPa. Corresponding diamond Raman spectra used for the pressure determination are shown in Fig. 3.20. Above 130 GPa, an intense parasitic broad luminescence emerged from the diamond anvils, which is usually interpreted as coming from diamond plastic deformations created at the anvil breaking point. This signal became so intense that the NV PL could not be distinguished from this background. We however were able to retrieve both NV PL and ODMR contrast upon lowering of the cell pressure, indicating that the split-gasket microwave antenna was functional during the full run. Upon later microscopic examination of the diamond anvil, we determined that it had cracked in a very typical fashion, totally uncorrelated with the presence of the pillar, which remained perfectly intact. The fracture of the diamond was, therefore, not due to a destabilization of the diamond by the milling of the pillar.

In Fig. 3.21, we show that the obtained ODMR behavior of NV centers is greatly improved on the micropillar compared to standard anvils. Fig. 3.22 shows the colormaps compiling the ESR measurements with increasing PTM pressure and magnetic field applied in the diamond [100] direction, together with the results of the ESR line position fitting procedure described in section 3.3.2. Using this modified anvil design we observed an NV ODMR behavior almost unaffected by pressure up to 130 GPa, almost double the pressure achieved with standard anvils. At 130 GPa, the study was finished by the fracture of the diamond anvil. Extracted quantitative results are shown in Fig. 3.23.

All the extracted parameters confirmed the creation of an almost hydrostatic environment for the NV centers implanted on the pillar. The center of the spectra continuously



Figure 3.20: Reference diamond Raman spectra recorded outside the machined pillar during experimental runs 3 and 4. Spectras are consistent with PTM pressures of 20.31 ± 0.4 GPa, 28.93 ± 0.48 GPa, 40.77 ± 0.50 GPa, 49.89 ± 0.51 GPa, 60.79 ± 0.53 GPa, 73.60 ± 0.54 GPa, 88.43 ± 0.56 GPa, 102.56 ± 0.57 GPa, 114.72 ± 0.58 GPa and 130.74 ± 0.60 GPa.

shifted to higher frequencies with a slope of 13.42 ± 0.14 MHz/GPa, reaching the limits of our microwave equipment graded up to 4 GHz, already above 75 GPa. We still were able to detect the ESR lines with contrast close to 1% up to 130 GPa. This central resonance frequency shift is faster than what was observed on the standard anvil and outside the pillars (9.68 ± 0.8 MHz/GPa on these 'reference' data), and is closer to the ~ 15 MHz/GPa reported in hydrostatic conditions up to 60 GPa in [Doherty et al., 2014].

The most dramatic effect of the pillar was on the apparent ESR splitting at zero magnetic field. On the standard anvil and references outside the pillars, we observed Δ_{σ} increasing by 3.89 ± 0.06 MHz/GPa, while the pillars only exhibited 0.29 ± 0.03 MHz/GPa stress splitting. Consequently, the ESR lines' displacement with the magnetic field was essentially not modified by the stress conditions on the microstructured anvils. In hydrostatic conditions, the symmetry of the NV defect is conserved, and therefore the stress-induced degeneracy lift between spin levels is minimal. These locally improved hydrostatic conditions are clearly indicated by the fitted values of the α parameter: with increasing pressure on the pillars, the anisotropy parameter converges to a value of $\alpha = 0.96$ on average.

Between 0 and 25 GPa, the fitted results indicate a smooth increase of α from 0.6 to the high-pressure value 0.96 on the pillars. This is however most probably due to an omission in

our model. In our calculations, we didn't account for the possibility of the diamond exhibiting a slight ESR splitting at zero pressure. In reality that is often the case in the presence of residual diamond growth stress, or small electric fields due to trapped surface charges. We indeed consistently recorded a zero-field slitting around 6 to 8 MHz at ambient pressure, which isn't modified by the DAC pressure and is rapidly becoming negligible compared to the DAC stress. At weak pressures, this residual splitting is misleadingly interpreted as a non-hydrostatic stress splitting in our model, introducing a bias in the estimation of the α parameter. However, as soon as real stress from the DAC increases and starts to dominate, the predicted α values start to converge to a more sensible value reflecting the real anisotropies inside the DAC.



Figure 3.21: Comparison of ESR spectra recorded on a standard anvil and on a microstructured one. **(a)** ESR spectra recorded at 61.9 GPa on a standard anvil for null magnetic field amplitude and for 6 mT applied in the [100] direction. **(b)** Equivalent ESR spectra recorded at a similar pressure of 60.8 GPa on microstructured anvil. Contrast compared to the standard anvil is greatly improved in amplitude, stays negative and with limited asymmetry. **(c)** Equivalent ESR spectra recorded at a pressure of 130.7 GPa on microstructured anvil. The general ESR behavior is still the same as at 60.8 GPa, but the contrast is decreased due to limitations of our microwave amplifier above 4 GHz.



Figure 3.22: Colormaps of the ESR data recorded on a microstructured diamond anvil as a function of pressure and magnetic field applied in the [100] direction, up to a PTM pressure of 130.7 GPa. All data were recorded with 2 min integration per spectrum using, respectively in order of pressure, 532 nm, 532 nm, 515 nm, 515 nm, 515 nm, 488 nm, 488 nm, 457 nm, 457 nm and 457 nm laser excitation wavelength. The respective microwave powers used are, in order of increasing pressure, 20, 20, 20, 20, 20, 25, 35, 35, 35, and 35 dBm. The decrease of the ODMR contrast observed above 4 GHz is due to the limit of our current microwave source and amplifier.



Figure 3.23: Extracted values resulting from the high-pressure ESR data obtained on standard anvils and the four runs performed on microstructured anvils. **(a)** Shifted ESR central frequency $D + \delta$ as a function of sample pressure. Linear fits yield a shift of 13.42 ± 0.14 MHz/GPa on the micropillar anvil, and 9.68 ± 0.8 MHz/GPa on the combined data of the reference points outside the pillars and the standard anvil. Data from a diamond chip under hydrostatic compression from [Doherty et al., 2014] is reproduced as the green dashed line. **(b)** Value of the anisotropic stress ESR splitting Δ_{σ} with increasing sample pressure. Linear fitting yields a slope of 3.89 ± 0.06 MHz/GPa for the reference points, and only 0.29 ± 0.03 MHz/GPa on the anvils with a pillar. **(c)** Fitted value of the anisotropy parameter α as a function of PTM pressure.



3.4.3 - NV magnetic sensitivity up to the megabar regime

Figure 3.24: Comparison of magnetic field sensitivity at high pressure for NV centers in a standard diamond anvil and in a microstructured one. **(a)** Achieved magnetic field sensitivity for NV centers implanted within the pillar of a microstructured anvil, with increasing sample pressure and magnetic field in the [100] direction, estimated using eq. 3.5. **(b)** Achieved magnetic field sensitivity for NV centers implanted within a standard diamond anvil, with increasing sample pressure and magnetic field in the [100] orientation. **(c)** Calculated magnetic field sensitivity around a bias magnetic field of 1 mT in the [100] direction, for both types of implanted anvils.

We then performed the same second round of fitting as before on our data to additionally extract ESR contrast and linewidth for each individual spectrum. We could then reproduce the estimation of the achieved magnetic field sensitivity on these modified anvils up to 130 GPa sample pressure. The results and comparison to the standard implanted anvil are shown in Fig. 3.24. We demonstrated that by using our microstructured anvils we enabled NV magnetic sensing up to 130 GPa, with a sensitivity never worse than $10^{-3} \text{ T}/\sqrt{\text{Hz}}$. At a bias field of 1 mT in the [100] direction, representative of typical experimental conditions we might use to assess high-pressure superconductivity, we report a 1.5×10^3 improvement in sensitivity at 70 GPa over the standard implanted anvils, and sensitivity down to $2.3 \times 10^{-4} \text{ T}/\sqrt{\text{Hz}}$ up to 130 GPa. Note here that the sensitivity we observed above 75 GPa is very likely significantly underestimated compared to the achievable optimum due to the decrease of the ODMR contrast observed above 4 GHz because of the limits of our current microwave source and amplifier. These results prove the viability of NV center magnetic sensing at least up to 130 GPa, and we are confident that under locally hydrostatic conditions this could be extended to even greater pressures.

3.4.4 - Consistent optical lineshift

To confirm this quasi-hydrostaticity regime induced by the machining of the diamond anvils, we also repeated the optical spectroscopy measurements on the NV center ZPL energy. Using an implanted microstructured anvil with a thin gold layer on the culet, we recorded the NV ZPL wavelength as a function of sample pressure up to 90 GPa (see Fig. 3.25). We report a shift of the NV optical spectrum that is faster on the pillar than on the normal anvils, again as expected. The data exhibited very significant deviation from linearity at high pressure (see section 3.4.6). If we fit our data only up to 40 GPa to compare it to previous studies, we report a quasi-linear shift of $4.86 \pm 0.07 \text{ meV/GPa}$, much closer to the 5.6 meV/GPa reported in the literature for hydrostatic conditions than the previous value of 2.21 meV/GPa observed for the standard implanted anvils. Despite the obvious nonlinear dependence, this measurement on the machined pillar still generally follows the trend expected from the linear stress model in fully hydrostatic conditions with $\alpha = 1$.

3.4.5 - Diamond Raman proof of local hydrostatic regime

During the study of the behavior of those microstructured anvils under pressure, we uncovered a third independent element indicating that we indeed created locally quasihydrostatic conditions at the tip of the micropillar. Under high pressure, we noticed a significant change in the diamond Raman scattering signals collected on the pillar compared to the other parts of the anvil culet or to a standard anvil.

An example of these different Raman responses is given in Fig. 3.26.a at a sample pressure of 92 GPa. Away from the micropillar, the observed Raman response is unchanged compared to a standard anvil, with a 1518 cm^{-1} single high-energy edge high-pressure Raman signal consistent with standard anisotropic strain in pressurized diamond anvils and a PTM pressure of 92 GPa according to the calibration of [Akahama and Kawamura, 2004]. On the pillar, we recorded a strong Raman edge at a lower energy shift indicating lower pres-



Figure 3.25: Optical spectroscopy of NV centers implanted in a microstructured anvil up to 90 GPa. (a) Measured NV ZPL wavelength as a function of PTM pressure. The spectra were recorded using a 488 nm laser source, and the pressure was measured using the fluorescence of a piece of samarium doped strontium borate ($SrB_4O_7 : Sm^{2+}$) deposited inside the DAC chamber. The results previously obtained on NV centers implanted in a standard diamond anvil are included for comparison. (b) NV ZPL energy as a function of pressure. To compare this data to previous studies in hydrostatic conditions, we performed a linear fit of the data up to 40 GPa, yielding a shift of $4.86 \pm 0.07 \text{ meV/GPa}$. The full curve up to 90 GPa exhibits a nonlinear behavior as a function of pressure. We also give here the expected shifts from the group theory-based simple model, combined with our anisotropic α model of the stress at the anvil tip.

sure (1504 cm^{-1} , or 84 GPa) together with the same 92 GPa edge as before. The signal had a lower amplitude and was accompanied by a new Raman peak located at a higher shift of 1549 cm^{-1} . We observed this additional Raman peak from 20 to 130 GPa, only on the pillar, shifting in frequency with pressure at a rate progressively separating it from the standard diamond anvil Raman edge. The evolution is reported in Fig. 3.26.b. This signal is characteristic of the presence of diamond submitted to hydrostatic pressure within the diamond anvil cell [Occelli et al., 2003].

To understand this, we will give a brief description of the mechanism for stressed diamond Raman scattering. The Raman mode observed in our optical spectra is the first-order scattering of the incident single-mode laser due to the interaction with the Brillouin-zonecenter optical phonon mode of diamond. Under ambient pressure and temperature conditions, this mode is triply degenerate due to the cubic symmetry of diamond. The longitudinal and transverse optical phonon branches are then combined into a single 'LTO' mode. Under



Figure 3.26: (a) Comparison of two Raman spectra obtained on a microstructured anvil at a PTM pressure of 92 GPa. Away from the pillar on the anvil culet, the signal is a standard high-pressure DAC diamond Raman edge signal. On the pillar, the frequency of the strongest edge is decreased (probably reflecting stress at the surface of maximum tangential stress, now pushed at the bottom of the pillar deeper into the diamond bulk), but we observe a distinct new Raman feature at a higher Raman shift. This peak is consistent with the presence of diamond under hydrostatic compression at 92 GPa. (b) Measured frequency of this separate Raman peak observed only on the pressurized microstructured anvils, as a function of pressure. For comparison, we reproduce the results of hydrostatic diamond Raman spectroscopy measured in [Occelli et al., 2003], taking into account the correction introduced in the latest AIRAPT calibration [Shen et al., 2020].

uniaxial stress, the cubic symmetry is lowered and the degenerate LTO mode splits into separate branches. For uniaxial stress applied along the [100] crystal axis, the LTO mode splits into a singlet mode and a doublet mode [Venugopalan and Ramdas, 1973]. Under these conditions, one can compute that these singlet and doublet modes exhibit different pressure dependence coefficients. According to the stress-linear model described in [Hanfland and Syassen, 1985], we get:

$$\nu_{S} - \nu_{0} = \Delta \nu_{H} \sigma_{H} + \frac{2}{3} \Delta \nu_{[100]} \sigma_{z}$$

$$\nu_{D} - \nu_{0} = \Delta \nu_{H} \sigma_{H} - \frac{1}{3} \Delta \nu_{[100]} \sigma_{z}$$
(3.9)

where ν_0 is the room pressure mode frequency, ν_S is the singlet mode frequency, ν_D is the doublet mode frequency, $\Delta\nu_H$ is the hydrostatic stress susceptibility, $\Delta\nu_{[100]}$ is the uniaxial frequency splitting, σ_H is the hydrostatic stress component, and σ_z is the pure uniaxial

stress component. The values of the susceptibility and splitting are linked to the diamond crystal's effective spring constants and elastic compliances, and have been measured to $\Delta \nu_H = 3.2 \text{ cm}^{-1}/\text{GPa}$ and $\Delta \nu_{[100]} = 0.73 \text{ cm}^{-1}/\text{GPa}$ [Cerdeira et al., 1972].

In the context of high-pressure DACs, the typical diamond Raman signal used for pressure determination is attributed to the high-energy edge of the singlet mode. The doublet mode is not observable in the back-scattering geometry that is usually implemented for light scattering experiments in DACs, due to the specificities of the polarizability tensor when the diamond symmetry is lowered by uniaxial stress. We previously established that in the diamond anvil tip the local stress tensor can be approximated by $\overline{\sigma} = (\alpha P, \alpha P, P, 0, 0, 0)$. This tensor can be decomposed in order to distinguish hydrostatic and pure uniaxial stress as:

$$\overline{\overline{\sigma}} = \alpha P \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} + (1 - \alpha) P \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$
(3.10)

so that:

$$\sigma_H = \alpha P, \sigma_z = (1 - \alpha) P. \tag{3.11}$$

From the model of the Raman singlet mode, we then obtain:

$$\nu_{S} - \nu_{0} = \alpha P \Delta \nu_{H} + \frac{2}{3} (1 - \alpha) P \Delta \nu_{[100]}$$
(3.12)

$$= P\left[\alpha\Delta\nu_{H} + \frac{2}{3}(1-\alpha)\Delta\nu_{[100]}\right]$$
(3.13)

Overall, this equation corresponds to a linear shift of the Raman singlet mode proportional to PTM pressure P, with a slope between the hydrostatic and pure uniaxial cases that is determined by the value of α . Predictions of this model for the hydrostatic case $\alpha = 1$ and for the standard diamond anvil with the expected $\alpha = 0.6$ are represented in Fig. 3.27.

We see that combining the standard description of stressed diamond Raman scattering with the anisotropic α model for stress in a diamond anvil tip once again yields consistent results. The model predicts a Raman shift of the singlet mode that closely reproduces the empirical diamond anvil tip Raman calibration of [Akahama and Kawamura, 2004] for $\alpha = 0.6$ below 80 GPa. Above this, non-linearities in the measured Raman signal with pressure become too large to be fitted by a first-order expansion in pressure. In the hydrostatic case, the model's agreement with measurements is poorer. The measured Raman mode shift in hydrostatic stress is much more nonlinear with pressure, thus poorly reproduced by the calculation of eq. 3.13 apart from the shift being faster than in the anisotropic case. However, our



Figure 3.27: Diamond anvil Raman signals as a function of PTM pressure. The hydrostatic diamond Raman line is the data of [Occelli et al., 2003] with corrected pressures. We compare the predictions of a first-order perturbation model of diamond Raman combined with our DAC stress model resulting in eq. 3.13. Using $\alpha = 0.6$ we can once again reproduce the observations for a normal anvil up to 80 GPa, shown here as the commonly accepted empirical calibration of [Akahama and Kawamura, 2004]. In the hydrostatic case, however, the nonlinearity with pressure creates a significant deviation from the model with $\alpha = 1$.

data collected for the separating Raman peak present on our pressurized microstructured anvils do not follow the linear model either, but are in good agreement with the reference data for diamond under hydrostatic compression. This constitutes yet another convincing element indicating that our machining of the diamond anvils locally creates hydrostatic conditions at the pillar tip.

3.4.6 - Beyond pressure-linear models

In the pressure range we could reach, we observed deviations of our results from the expected linear models on several occasions. Most of the theoretical descriptions we used to model our data were based on first-order perturbation of the ambient equilibrium state by an external perturbation, corresponding to pressure in our case. However, many properties do not exhibit a linear scaling with pressure. A common way of linearising high-pressure variations of a physical quantity is to realize that many processes are correlated to crystal volume rather than pressure. The crystal volume is linked to the applied hydrostatic pressure by the material's equation of state, one of the most crucial characteristics of compressed materials. This P - V relation is nonlinear and exhibits a kind of saturation curve caused by the fact that materials get harder to compress at higher pressure. It can also be subject to discontinuities which allow high-pressure scientists to identify the occurrence of pressure induced structural phase transitions.

In the case of diamond, a common model for the non-linear equation of state is the 'universal' Vinet equation [Vinet et al., 1987]:

$$P = 3K_0 \left(\frac{1-f}{f^2}\right) \exp\left[\frac{3}{2} \left(K'_0 - 1\right) \left(1 - f\right)\right] \quad \text{with} \quad f = \sqrt[3]{\frac{V}{V_0}}$$
(3.14)

where *P* is pressure, *V* is the crystal volume, V_0 is the crystal room pressure volume, K_0 is the isothermal bulk modulus and K'_0 is the derivative of bulk modulus with respect to pressure. In the following, we will use the latest values that were checked by our colleagues at CEA, $V_0 = 3.417 \text{ cm}^3 \cdot \text{mol}^{-1}$, $K_0 = 443.3 \text{ GPa}$ and $K'_0 = 3.7$. A graphical representation of this nonlinear behavior is shown in Fig. 3.28.



Figure 3.28: Computed values for the Vinet equation of state of diamond (sometimes called 'Rose-Vinet') given by eq. 3.14 [Vinet et al., 1987]. The values for the parameters we used are the latest estimation from XRD data provided by CEA collaborators: $V_0 = 3.417 \text{ cm}^3 \cdot \text{mol}^{-1}$, $K_0 = 443.3 \text{ GPa}$ and $K'_0 = 3.7$.

3.4.6.1 - Optical ZPL shift

A piece of information we recorded that showed an obvious nonlinear pressure dependence was the measurement of the NV optical ZPL, especially on the machined micropillar up to 90 GPa (Fig. 3.25). In Fig. 3.29, we show that this data is however almost perfectly linear when given as a function of the diamond volume. We can then report a linear shift of the NV ZPL with a much better agreement with the data, with respective slopes $-434 \pm 2 \text{ meV}/(\text{cm}^3 \cdot \text{mol}^{-1})$ for the standard implanted anvil and $-769 \pm 4 \text{ meV}/(\text{cm}^3 \cdot \text{mol}^{-1})$ for the micropillar. We note that the nonlinear dependence with pressure is clearest in the conditions closest to hydrostaticity, due to the increased average pressure within the diamond.



Figure 3.29: Dependence of the measured NV ZPL energy with the diamond molar volume inferred by the Vinet equation of state. We see that the previously nonlinear data as a pressure function becomes linear, with a slope of $-434 \pm 2 \text{ meV}/(\text{cm}^3 \cdot \text{mol}^{-1})$ for the standard implanted anvil and $-769 \pm 4 \text{ meV}/(\text{cm}^3 \cdot \text{mol}^{-1})$ for the modified microstructured anvils where the NV centers are in quasi-hydrostatic conditions.

3.4.6.2 - Pillar Raman peak

The effect of increased density at high pressure on the phonon frequencies probed by Raman scattering is usually described by a Grüneisen parameter γ . This parameter quantifies the expected linear relative shift of the phonon frequency with relative crystal volume, through the definition $\ln (\nu/\nu_0) = -\gamma \ln (V/V_0)$. In Fig. 3.30, we apply this treatment to the reference hydrostatic diamond Raman data provided by our CEA collaborators, as well as to the Raman signal recorded on a micropillar. We see that the values on the micropillar are very close to the perfect hydrostatic diamond case, corresponding to Grüneisen parameters $\gamma = 0.950 \pm 0.021$ for the micropillar and $\gamma = 0.985 \pm 0.003$ for the reference hydrostatic case. This confirms that pressure conditions on the machined micropillar are close to hydrostatic-ity.

3.5 - Conclusion

In this final chapter, we took a systematic approach to the evaluation of NV magnetic sensing performances under high pressure up to 70 GPa. We first studied the effect of pressure and magnetic field on the ESR of NV centers implanted in the culet of a standard diamond anvil. With increasing sample pressure, we showed that the non-hydrostatic stress applied to the anvil's tip hosting the NV centers gradually deteriorates ODMR signals, by



Figure 3.30: Comparison of the Raman data recorded for diamond in hydrostatic conditions ([Occelli et al., 2003] with corrected pressures) and for the micropillar. The linear fits correspond to the Grüneisen model often used to describe phonon frequencies with compression. Linear fits in relative logarithmic space give parameters $\gamma = 0.950 \pm 0.021$ for data recorded on a micropillar and $\gamma = 0.985 \pm 0.003$ for the reference hydrostatic case.

weakening the quantum states' initial sensitivity to static magnetic fields and affecting ODMR contrast. At high stress and off-axis magnetic field, we observed a slight revival of ODMR contrast as an increase of NV PL at resonance, which is unprecedented in studies of NV centers. Overall, the loss of ODMR contrast puts a limit to NV magnetic sensing around 40 to 50 GPa, above which sensitivity is greatly reduced.

Using a simplified model of the mechanical stress applied at the tip of the diamond anvils, coupled with our knowledge of the NV ground-state Hamiltonian under compression, we then showed that we could quantitatively explain the observed ESR frequencies under anvil stress and magnetic field. Our modeling gives an estimation of the anisotropy of stress in the anvil, where the tangential stress is only around 58% of the stress applied to a sample in the experimental chamber. This estimation is confirmed by quantitative analysis of optical spectroscopy data we recorded of the NV center ZPL emission up to 80 GPa.

Finally, we presented a strategy that allowed us to overcome this issue to perform NV magnetic sensing well above 100 GPa. By using micro-machining of the diamond anvil tip, we designed a micropillar that can host NV centers in a locally quasi-hydrostatic environment up to at least 130 GPa. These local quasi-hydrostatic conditions have been confirmed independently by measurements of the NV optical spectral shift up to 90 GPa, and by the appearance of a characteristic Raman signature on the pillar up to 130 GPa. In these conditions, we showed that NV centers conserve their magnetic sensing properties with only a shift of

their whole ESR spectrum to higher microwave frequencies. We demonstrated a factor 10^3 improvement in magnetic sensitivity at 70 GPa using our microstructured anvils compared to standard implanted ones, together with convincing evidence that NV centers can be used as efficient quantum sensors well into the megabar regime. This opens the direct possibility to use NV centers to probe the potential superconductivity of super-hydrides.

Conclusion and perspectives

This thesis manuscript has presented our results on developing NV center magnetometry for high-pressure detection of the Meissner effect associated with superconducting samples compressed in DACs.

We expanded on the first published test detections of the Meissner effect by measuring the superconducting T_c of mercury-based cuprate samples up to 31 GPa. We performed measurements in two different optical configurations, confocal and widefield imaging, demonstrating the advantages of each technique. We showed that widefield recording of the NV center ESR could be used to spatially map inhomogeneities in the Meissner signal from an inconsistent sample, both in the amplitude of the observed field exclusion at fixed low temperature and in the reconstruction of a map of non-uniform T_c under 1.3 GPa. In the confocal imaging mode, we recorded ESR signatures of the superconducting transition at pressures 3, 8, 13 and 31 GPa, indicating a modification of the faulty sample's T_c with pressure. These promising results would have, of course, been more impactful had they clearly reproduced or extended previous results on these materials from the literature, but probably deficient doping of the specific sample crystal used prevented us from already reproducing state-ofthe-art results on T_c . These experiments nevertheless provided major technical developments for the practical realization of these measurements in our group, which will hopefully be rewarded in upcoming runs to be performed with new samples. Apart from the goal of extending results to pressures above 50 GPa, we also started to explore the possibility of combining our diagnosis of the Meissner effect and T_c with *in-situ* high-pressure Raman spectroscopy of the superconducting gap, which has been largely developed in the cuprate community [Auvray et al., 2021].

In the last chapter, we detailed a pragmatic effort to understand the limits of the technique that had started to be felt in our last measurements on the cuprates. We provided a thorough study of the combined effects of stress and applied magnetic fields on the magnetic sensing capabilities of NV centers implanted in the culet of a standard diamond anvil. We showed that published spin-stress coupling Hamiltonians for the NV center ground state could successfully reproduce the NV ESR frequencies at least up to 70 GPa when combined with a model of the specific anisotropic stress applied to the anvil tips, converging to estimations of stress anisotropy values $\alpha = 0.58$ confirmed by the literature, optical spectroscopy, and diamond Raman measurements. This model partially explains the apparent progressive loss of ODMR contrast observed with increased pressure, leading to dramatically lowered magnetic sensitivity above 40 to 50 GPa sample pressure.

We then presented a circumventing strategy we implemented to diminish non-hydrostatic stress on the implanted NV centers by micro-structuring the diamond anvil tip. NV centers implanted within a micro-pillar machined from the anvil surface are submitted to muchimproved anisotropy $\alpha = 0.96$, providing an environment where the magnetic field response of their ESR lines is conserved up to at least 130 GPa. We confirmed this diagnosis of quasihydrostaticity again by first extending our measurements of the NV ZPL in these conditions up to 90 GPa, then by recording a Raman signal in close agreement to previous studies of hydrostatically compressed diamond. The experiments we conducted were stopped at 130 GPa because the diamond anvil failed, when NV centers didn't show significant signal degradation. We, however, note that such a substantial extension of the working pressure range of NV magnetometry comes with additional experimental difficulties we hadn't anticipated. The consistent shift of the ESR central frequency beyond 4.5 GHz above 130 GPa became troublesome for our experimental setups designed to work close to 3 GHz. Even more problematic is the shift of the NV optical spectrum ($\sim 100 \text{ nm}$ at 90 GPa), both in emission and absorption, that requires used optical elements to function on an extensive range of wavelengths, changing as the experiment proceeds. We are currently improving our optical setup so it can be as efficient and practical to use above the megabar as it is at few-gigapascal pressures. The main results of our investigation of NV ESR into the megabar regime will be published in an article currently in preparation.

These results open the way to NV measurement of magnetic phenomena in the megabar range, confirming that they provide a realistic method to potentially settle the debate of hydride superconductivity in the near future. The first test performed here on a single geometry for the anvil micro-structure will, of course, also need to be completed by further exploration of this method to engineer the stress distribution in the anvil culet. We, for instance, plan to explore micro-machining geometries with wider extension to retain hydrostaticity within the anvil while keeping widefield magnetic cartography capabilities. NV centers could be used in much more detailed magnetic field configurations to retrieve spatially resolved maps of the total stress tensor inside the diamond anvil, providing rare direct measurements to inform future improvements to the design of the anvils themselves to expand the pressure limits of the DAC in the multi-megabar regime.

Our extremely fruitful collaboration with the high-pressure group at CEA also leads us to more exploratory research lines, both on the quantum optics and the NV-magnetometry side. We recently started exploring the behavior of other promising luminescent point defects of diamond under pressure, Silicon-Vacancy (SiV) and Germanium-Vacancy (GeV) centers, that exhibit properties different from the NV center, which could be helpful in the high-magnetic field or multi-megabar regimes [Vindolet et al., 2022]. On the magnetometry side, high-pressure NV magnetic sensing can be applied to probe almost any magnetic behavior susceptible to change under pressure. Results have, for instance, shown that the currently very active field of 2D materials, and more precisely 2D magnets like CrI₃, can be strongly affected by the application of even moderate pressures of a few gigapascals [Song et al., 2019]. The community studying 2D materials under pressure is growing rapidly and could benefit from the magnetic diagnosis NV centers can provide to complete transport and optical measurements currently being performed at high pressure [Pei et al., 2022].

On the fundamental aspect of NV centers, we believe that studying them under these very high-stress conditions can provide exciting insights into the mechanisms giving them their unique properties. The appearance of positive contrast ESR lines in strong anisotropic stress and off-axis magnetic field is a clear indicator that stress allows us to explore distortion regimes unreachable through other perturbations, possibly shedding some light on the complex room temperature excited state behavior, for instance. Further investigation of all the NV mechanisms that have been explored at ambient pressure by the vast NV center community (low temperature, high magnetic field, pulsed protocols, coherence assessment, polarization resolved studies ...) should be now extended to add stress(es) as a new parameter to further our understanding of these truly extraordinary quantum sensors.

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