Présentée par

Alban LAFUENTE-SAMPIETRO

Thèse dirigée par **L. BESOMBES** et **S. KURODA**
co-encadrée par **H. BOUKARI**

préparée au sein de **l'Institut Néel** et de **l'Université de Tsukuba**

dans **l'École Doctorale de Physique de Grenoble et the School of Pure and Applied Science de l'Université de Tsukuba**

Contrôle optique du spin d'un atome magnétique dans un semiconducteur : spin hybride trou-Manganèse et Chrome

Thèse soutenue publiquement le **26 janvier 2018**,
devant le jury composé de :

Mme. Maria CHAMARRO
Professeur, INSP, Rapporteur
M. Aristide LEMAÎTRE
Directeur de Recherche CNRS, C2N, Rapporteur
M. Bernhard URBASZEK
Directeur de Recherche CNRS, LPCNO, Examinateur
M. Etienne GHEERAERT
Professeur, Université Grenoble-Alpes, Président

M. Yasuhiro TOKURA
Professeur, Faculty of Physics, Université de Tsukuba, Invité
M. Takashi SUEMASU
Professeur, Faculty of Applied Physics, Université de Tsukuba, Invité
M. Kazuaki SAKODA
Managing Researcher, NIMS, Invité

Acknowledgement

I couldn't have finished this PhD if it was not for the help of a lot of person. I cannot have done it alone, and I would like to begin this manuscript taking a step backward to thank everyone that has been there for me, though those times that have not always been easy.

Let's begin with the most obvious one. I want to express my more sincere gratitude to all my thesis supervisors. First, Lucien Besombes, who have been the first one to believe in me, and never let me get content with me. He always asked me to get the best of myself, and even pushed me to do more. Although not always easy to hear, his advices was always precious and helped me to get better, be it while doing experiment or writing my thesis. I also want to thank Pr. Shinji Kuroda, who offered me the possibility to do this double degree PhD, and did a lot so my stay in the University of Tsukuba would be as simple as possible. He helped me pass through the different demands of the university, and really supported me along my research in his laboratory. And finally, I should not forget Hervé Boukari, who helped me a lot on the growth side, and, along with Pr. Shinji Kuroda, supported me on all the link between the two universities. The double degree would have been a lot more difficult without him, if not impossible. And he always had some reassuring words, nice to hear after discussion with Lucien.

The PhD would not have been completed without the juries to judge it. I want to deeply thank the member of my juries, both on the French side and on the Japanese side. The discussion we had during the questions on my defence was really interesting and challenging. A big thank you to Pr. Maria Chamarro and Aristide Brian for having read this thesis and given their honest opinion on it. I also want to thank Pr. Etienne Gheeraert, who has always been there to support me for the link between Grenoble and Tsukuba, and kindly accepted to preside the jury. And finally, for the French side, I want to than Bernhard Urbaszek to have accepted to be part of the jury. On the Japanese side, I want to thank Pr. Yasuhiro Tokura, Pr. Takashi Suemasu and Kazuaki Sakoda to have agreed to be part of my jury.

But the supervisors and the jury are only a part of the people surrounding you during a thesis. Some many more persons make the working environment, and the

thesis would be quite different without them. I would like to thank the person of the NPSC team. I think I was not the most well integrated PhD student, due in part to my long absences caused by my double degree with a Japanese university, but also to my office being a bit far from the usual offices of the team, and my usual difficulties to socialize. Nonetheless, it was always interesting to meet people of the team and discuss with them, be it about physics or other subjects. Among them, I want to extend a special thank to some PhD student Valentin Delmonte, Mathieu Jeannin, Alberto Artioli and Kimon Moratis, with whom I had quite a lot of discussion on a lot of subjects, and who where always interesting. In the permanent of the team, I especially want to thank Joel Cibert, always smiling and helpful, and Henri Mariette, always willing to discuss around a nice table in Japan.

As I said, my office was a bit far from the main offices of the team NPSC. It made the contact with my team a bit more difficult, but it also gave me the possibility to meet a lot of PhD student from other team. Among them, I especially want to thank Yann Périn, André Dias and Dayane De-Chouza-Chaves, with whom I shared an office for two or three years. It was a really lively, and always fun to be here. We had some great discussion, and often some great laugh. I will with no doubt miss the atmosphere of this open space. The arriving of Hawa Abdul-Latiff in the office was quite a good surprise too, and I want to thank her particularly. We bonded quite quickly, in part thank to our shared experience being double degree student between the university of Grenoble and the university of Tsukuba. This year and a half we shared seems way to short and it would be pleasure to meet again to continue our discussion. Speaking of encounter started in Grenoble thanks to my Japanese experience, I do not want to forget Ryogen Fujiwara. It was really nice to be able to discuss our two countries and to exchange about our experience.

The Tsukuba side is not to be neglected. I meet several great persons during my time there. First, I want to thank the whole Kuroda team. I had some really great moment with them, and the whole have always been helpful every time I had a problem. They also was really accepting about the small error I did in Japanese etiquette, and I was able to learn a lot thank to them. I especially want to thank the whole dot team in the Kuroda lab: Hayato Utsumi, Masahiro Sunaga and Kenji Makita. It was a pleasure to work with them, and also to meet them outside of work. Even though the language was sometimes a problem, we found ways to have nice discussions. I also want to deeply thank Ryo Ishikawa and Takuma Nakamura. They did a lot to help me while I was there, and to go through the Japanese administrative side. I could not have done anything without them.

The completion of this PhD and all these travels would not have been possible without the help of the administrative. I would like to thank especially Aurélie Laurent on Grenoble side, which always was of great help to prepare my travel,

Introduction

Building a quantum computer is one of the challenges of this century. The core component of such a computer is the *qubit*, the quantum bit. Instead of regular bits, which can take the states (values) $|0\rangle$ and $|1\rangle$, the *qubits*, being quantum devices, can also be in a superposition of states, $\alpha|0\rangle + \beta|1\rangle$. An important step in the realization of the computer is to find a system to store and control these quantum states, which do not exist yet. The two main criteria for this system are its characteristic time, that must be long enough to do the operation and store the result, and the speed of preparation in a given state, determining the speed of each operation. Moreover, it has to be possible to build gate of one or two *qubits*. The system has also to be scalable, in order to be able to build quantum component with a large number of *qubits*.

Several approaches exist for the fabrication of a *qubit*, such as cold atoms, superconductors... A promising system for their realization is a single quantum dot (QD), nanometer-sized objects designed to confine carriers in all three dimensions. This confinement leads to a quantization of the carrier energy, akin to the energy level of the electron in an isolated atom.

Multiple methods exist to form such devices: gate trapping of single electron between electrodes, nanometer-sized grains formed by the precipitation of semiconductors in a solution (colloidal dots), thickness variation of a quantum well, strain relaxation of a semiconductor layer... I will focus in this thesis on the later type of QDs, usually grown by Molecular Beam Epitaxy (MBE). They are formed by small island, with a characteristic size of a few nanometers, of a small gap semiconductor inserted in a wide gap semiconductor. Well-known examples are InAs/GaAs (for III-V semiconductors), CdSe/ZnSe or CdTe/ZnTe (for II-VI semiconductors). More specifically, in this thesis, I studied optically active QDs: carriers can be injected in the QD by a laser excitation, and their relaxation occurs with the emission of a photon.

The spin of the carriers injected in a QD is a good candidate for the realization of a two level quantum system. For a single gate *qubit*, coherence time of the electrons as long as 1 μs was found [1]. Moreover, it has been demonstrated that QDs can be used to control electrically (for the gate *qubit*) or optically (for the

optically active dots) the spin of the injected carriers [2, 3]. Finally, the optical preparation of the carrier spin state takes only a few nanoseconds. All of this makes the spin of carriers trapped in a QD a promising system for the fabrication of *qubits* [4–7]. However, the dephasing time of an ensemble of QDs is a lot shorter than the coherence time of single QD, falling to about 10 ns [8–10]. This is too short to do any significant data storage or processing.

Exiting the world of QDs, several systems were proposed to get longer spin coherence time, such as Nitrogen-Vacancy (NV) centers in diamond [11] or atomic spins directly inserted in the semiconductors [12]. In NV centers, electronic spin coherence time in the milliseconds range was found in ultrapure isotopically purified diamonds [13]. However, the preparation of the electronic spin of the NV center takes hundreds of nanoseconds, which would slow the calculations down [11]. The same kind of coherence and manipulation time can be expected for the atomic spins.

Another approach comes from the Diluted Magnetic Semiconductors (DMS). In these materials, a low density of magnetic atoms is inserted in the semiconductor lattice. The semiconductor keeps its conventional optical and electrical properties and new ones arise from the presence of the magnetic atoms. It was shown that there is a strong exchange interaction between the carriers and the magnetic atom spins. When inserting magnetic atoms in a quantum dot, the carriers are confined with them. Their interaction is enhanced, enabling the control of the magnetic atoms spins via the injected carriers. In this thesis, this reasoning is pushed to its limit, inserting a single magnetic atom in a QD, and controlling its spin optically. Such individual spins are promising for the implementation of emerging quantum information technologies in the solid state [14–16]. They were to present many desirable features for the realization of spin *qubits*, such as reproducible quantum properties, stability, and potential scalability by coupling dots [17]. Thanks to their point-like character, a longer spin coherence time (compared to carriers' spins) can also be expected at low temperature. All of this makes single magnetic dopants in QDs a good candidate to store quantum information.

The control of the spin state of individual [18–23] or pairs [24, 25] of magnetic atoms has been demonstrated. The spin of a magnetic atom in a QD can be prepared by the injection of spin polarized carriers and its state can be read through the energy and polarization of the photons emitted by the QD [26–28]. The insertion of a magnetic atom in a QD where the strain or the charge states can be controlled also offers degrees of freedom to tune the properties of the localized spin such as its magnetic anisotropy [29].

Tab. 1 lists some magnetic atoms that can be inserted in a semiconductor lattice. Each of those atoms has a unique set of electronic spin, nuclear spin and orbital momentum. For a given semiconductor structure, those properties

Table 1: List of different possible transition metals and their key properties in the context of our study.

Inserted atom	V^{2+}	Cr^{2+}	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
d-shell	d^3	d^4	d^5	d^6	d^7	d^8	d^9
Electronic spin	3/2	2	5/2	2	3/2	1	1/2
Nuclear spin	7/2	0	5/2	0	7/2	0	3/2

change the magnetic atom behaviour. Each can be used for different applications, such as the realization of a spin mechanical *qubit* for the elements with an orbital momentum. The first atom to have been inserted in a quantum dot is the Mn, first in II-VI (2004) [18], and then in III-V (2007) [20]. Since then, other magnetic atoms have been embedded in II-VI QDs and studied: Co (2014) [30] and Fe (2016) [31]. They have not been inserted successfully in III-V semiconductors yet.

Mn in II-VI semiconductors has been widely studied in the last decades. In bulk semiconductors, its relaxation time was found to reach the milliseconds range, for vanishing Mn concentration [32, 33]. Inserted in II-VI QDs, it was demonstrated that a single Mn spin could be optically prepared in a few tens of nanoseconds, depending on the laser power [34]. At the same time, a relaxation time of the Mn spin of a few microseconds was found [26]. The dynamic of a Mn spin was also probed in a positively charged QD, forming a hybrid spin by coupling with the resident hole [35], and in a strain-free environment [36].

Single Cr atom in a QD is also of particular interest: thanks to its orbital momentum, it should be very sensitive to strains. This opens new ways to manipulate the spin state of this magnetic atom without having to use optical excitation. It also opens the possibility to realize spin mechanical system where the Cr is used as a *qubit* coupled to an oscillator. Cr could be used to probe the movement of the oscillator, cool the oscillator down or create non-classical states of the oscillator. Moreover, the Cr atom in a II-VI matrix presents no nuclear spin. There is therefore no hyperfine interaction for Cr atom in a CdTe/ZnTe QD. This simplifies the Cr spin structure and leads to an expected longer coherence time.

In this thesis, I will present a detailed study of the hole-Mn hybrid spin, and to start the study of a single Cr atom in a QD. Those two systems are promising for the realization of spin *qubit* coupled to strains. Growth of the Mn-doped QDs was done in Grenoble, in the INAC-CNRS joined team NPSC, by Hervé Boukari. The Cr-doped QDs were grown in Tsukuba, in the team of Pr. Shinji Kuroda, by Hayato Ustumi, Masahiro Sunaga and myself. The optical study of the magnetic QDs was performed at the Néel Institut in Grenoble, where an optical setup for the study of single quantum dots doped with a single magnetic atom had been developed.

This thesis is organized as follows:

Chapter I This chapter focuses on the theoretical background of this thesis. I begin to discuss the properties of a semiconductor crystal. This discussion is then used as a basis to present the physics of the QDs and their properties. Then the interaction between carriers and magnetic atom in a diluted magnetic semiconductor is presented. Particular attention is given to the interaction between the carriers and the two atoms studied in this thesis: the Mn and the Cr. I also show how the inclusion of these magnetic atoms in a crystal affects their spin energy structure. Finally, I present a short example of application of these theories on CdTe/ZnTe QDs doped with single Mn.

Chapter II The growth of Cr doped QDs was an important part of this thesis. I present here the techniques used to grow the samples studied optically. I begin with a general explanation of the MBE process. I then explain how the Cr-doped QDs were grown and how they are formed using Stranski-Krastanov (SK) relaxation. I also present some tests that were done for the growth of two other kinds of Cr-doped samples: charge tunable sample, and strain-free dots formed by the thickness variation of a quantum well. For each kind of sample, I present basic optical characterization.

Chapter III I discuss in this chapter the dynamic of the hole-Mn hybrid spin. I show that spin states form optical Λ-level systems. Two hole-Mn ground states are connected to one X^+-Mn excited state via two transitions of opposite polarizations. They were used to study the dynamics of the hole-Mn hybrid spin. A fast hole-Mn spin relaxation, in the nanoseconds range, caused by the interplay between acoustic phonons and the hole-Mn exchange interaction is evidenced. I also show that two X^+-Mn level can be coupled by the in-plane strain anisotropy and study this strain induced coherent dynamics.

Chapter IV In this chapter, I show that it is possible to include single Cr spin in CdTe/ZnTe QDs and probe its spin optically. The Cr spin structure is deduced from magneto-optical experiments. It is confirmed that the Cr spin is strongly coupled to strains. A value of the magnetic anisotropy D_0 between 2 and 3 meV is extracted. This is two orders of magnitude higher than what is found in Mn-doped QD or in NV centers in diamond. The sign of the hole-Cr exchange interaction is also extracted from these experiments and found to be anti-ferromagnetic.

Chapter V This chapter explore the dynamics of the Cr spin in a QD. The study begins with photon correlation experiments. In order to get more precise results, resonant optical pumping experiments were performed. The optical

setup is first presented, before discussing the results. The success of this experiment shows the possibility to prepare the Cr spin by spin pumping. A strong influence of phonons on the Cr spin dynamics is evidenced. A Cr spin relaxation time under excitation in the 10 nanoseconds range is extracted from the experiments. In the dark, the relaxation time of the Cr is found to be in the microsecond range. Finally, I also demonstrate the possibility to tune the energy of the Cr spin by optical Stark effect.

Contents

xi

Bibliography

[1] J. R. Petta, A. C. Johnson, J. M. Taylor, E. A. Laird, A. Yacoby, M. D. Lukin, C. M. Marcus, M. P. Hanson, and A. C. Gossard, "Coherent manipulation of coupled electron spins in semiconductor quantum dots", Science **309**, 2180–2184 (2005).

[2] A. Greilich, D. R. Yakovlev, A. Shabaev, A. L. Efros, I. A. Yugova, R. Oulton, V. Stavarache, D. Reuter, A. Wieck, and M. Bayer, "Mode locking of electron spin coherences in singly charged quantum dots", Science **313**, 341–345 (2006).

[3] D. Press, T. D. Ladd, B. Zhang, and Y. Yamamoto, "Complete quantum control of a single quantum dot spin using ultrafast optical pulses", Nature **456** (2008).

[4] D. Loss and D. P. DiVincenzo, "Quantum computation with quantum dots", Phys. Rev. A **57**, 120–126 (1998).

[5] A. Imamoḡlu, D. D. Awschalom, G. Burkard, D. P. DiVincenzo, D. Loss, M. Sherwin, and A. Small, "Quantum information processing using quantum dot spins and cavity qed", Phys. Rev. Lett. **83**, 4204–4207 (1999).

[6] D. D. Awschalom and N. Samarth, "Optical manipulation, transport and storage of spin coherence in semiconductors", in *Semiconductor spintronics and quantum computation*, edited by D. D. Awschalom, D. Loss, and N. Samarth (Springer Berlin Heidelberg, Berlin, Heidelberg, 2002), pp. 147–193.

[7] S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnár, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, "Spintronics: a spin-based electronics vision for the future", Science **294**, 1488–1495 (2001).

[8] M. V. G. Dutt, J. Cheng, B. Li, X. Xu, X. Li, P. R. Berman, D. G. Steel, A. S. Bracker, D. Gammon, S. E. Economou, R.-B. Liu, and L. J. Sham, "Stimulated and spontaneous optical generation of electron spin coherence in charged gaas quantum dots", Phys. Rev. Lett. **94**, 227403 (2005).

[9] A. S. Bracker, E. A. Stinaff, D. Gammon, M. E. Ware, J. G. Tischler, A. Shabaev, A. L. Efros, D. Park, D. Gershoni, V. L. Korenev, and I. A. Merkulov, "Optical pumping of the electronic and nuclear spin of single charge-tunable quantum dots", Phys. Rev. Lett. **94**, 047402 (2005).

[10] P.-F. Braun, X. Marie, L. Lombez, B. Urbaszek, T. Amand, P. Renucci, V. K. Kalevich, K. V. Kavokin, O. Krebs, P. Voisin, and Y. Masumoto, "Direct observation of the electron spin relaxation induced by nuclei in quantum dots", Phys. Rev. Lett. **94**, 116601 (2005).

[11] G. D. Fuchs, G. Burkard, P. V. Klimov, and D. D. Awschalom, "A quantum memory intrinsic to single nitrogen–vacancy centres in diamond", Nature Physics **7** (2011).

[12] M. Pierre, R. Wacquez, X. Jehl, M. Sanquer, M. Vinet, and O. Cueto, "Single-donor ionization energies in a nanoscale CMOS channel", Nature Nanotechnology **5** (2009).

[13] L. Childress, M. V. Gurudev Dutt, J. M. Taylor, A. S. Zibrov, F. Jelezko, J. Wrachtrup, P. R. Hemmer, and M. D. Lukin, "Coherent dynamics of coupled electron and nuclear spin qubits in diamond", Science **314**, 281–285 (2006).

[14] M. Veldhorst, C. H. Yang, J. C. C. Hwang, W. Huang, J. P. Dehollain, J. T. Muhonen, S. Simmons, A. Laucht, F. E. Hudson, K. M. Itoh, A. Morello, and A. S. Dzurak, "A two-qubit logic gate in silicon", Nature **526** (2015).

[15] K. Saeedi, S. Simmons, J. Z. Salvail, P. Dluhy, H. Riemann, N. V. Abrosimov, P. Becker, H.-J. Pohl, J. J. L. Morton, and M. L. W. Thewalt, "Room-temperature quantum bit storage exceeding 39 minutes using ionized donors in silicon-28", Science **342**, 830–833 (2013).

[16] N. Bar-Gill, L. Pham, A. Jarmola, D. Budker, and R. Walsworth, "Solid-state electronic spin coherence time approaching one second", Nature Communications **4** (2013).

[17] P. M. Koenraad and M. E. Flatte, "Single dopants in semiconductors", Nature Materials **10** (2011).

[18] L. Besombes, Y. Léger, L. Maingault, D. Ferrand, H. Mariette, and J. Cibert, "Probing the spin state of a single magnetic ion in an individual quantum dot", Phys. Rev. Lett. **93**, 207403 (2004).

[19] C. Le Gall, A. Brunetti, H. Boukari, and L. Besombes, "Optical stark effect and dressed exciton states in a Mn-doped CdTe quantum dot", Phys. Rev. Lett. **107**, 057401 (2011).

[20] A. Kudelski, A. Lemaître, A. Miard, P. Voisin, T. C. M. Graham, R. J. Warburton, and O. Krebs, "Optically probing the fine structure of a single mn atom in an inas quantum dot", Phys. Rev. Lett. **99**, 247209 (2007).

[21] O. Krebs, E. Benjamin, and A. Lemaître, "Magnetic anisotropy of singly mn-doped InAs/GaAs quantum dots", Phys. Rev. B **80**, 165315 (2009).

[22]E. Baudin, E. Benjamin, A. Lemaître, and O. Krebs, "Optical pumping and a nondestructive readout of a single magnetic impurity spin in an InAs/GaAs quantum dot", Phys. Rev. Lett. **107**, 197402 (2011).

[23]J. Kobak, T. Smolenski, M. Goryca, M. Papaj, K. Gietka, A. Bogucki, M. Koperski, J.-G. Rousset, J. Suffczynski, E. Janik, M. Nawrocki, A. Golnik, P. Kossacki, and W. Pacuski, "Designing quantum dots for solotronics", Nature Communications **5**, 3191 (2014).

[24]L. Besombes, C. L. Cao, S. Jamet, H. Boukari, and J. Fernández-Rossier, "Optical control of the spin state of two Mn atoms in a quantum dot", Phys. Rev. B **86**, 165306 (2012).

[25]O. Krebs and A. Lemaître, "Optically induced coupling of two magnetic dopant spins by a photoexcited hole in a mn-doped InAs/GaAs quantum dot", Phys. Rev. Lett. **111**, 187401 (2013).

[26]L. Besombes, H. Boukari, C. L. Gall, B. Brunetti, C. Cao, S. Jamet, and B. Varghese, "Optical control of the spin of a magnetic atom in a semiconductor quantum dot", Nanophotonics **4**, 75 (2015).

[27]D. E. Reiter, V. M. Axt, and T. Kuhn, "Optical signals of spin switching using the optical stark effect in a mn-doped quantum dot", Phys. Rev. B **87**, 115430 (2013).

[28]M. Goryca, T. Kazimierczuk, M. Nawrocki, A. Golnik, J. A. Gaj, P. Kossacki, P. Wojnar, and G. Karczewski, "Optical manipulation of a single Mn spin in a CdTe-based quantum dot", Phys. Rev. Lett. **103**, 087401 (2009).

[29]J. C. Oberg, M. Reyes Calvo, F. Delgado, M. Moro-Lagares, D. Serrate, D. Jacob, J. Fernandez-Rossier, and C. F. Hirjibehedin, "Control of single-spin magnetic anisotropy by exchange coupling", Nature Nanotechnology **9** (2013).

[30]J. Kobak, T. Smoleński, M. Goryca, M. Papaj, K. Gietka, A. Bogucki, M. Koperski, J.-G. Rousset, J. Suffczyński, E. Janik, M. Nawrocki, A. Golnik, P. Kossacki, and W. Pacuski, "Designing quantum dots for solotronics", Nat. Comm. **5**, 3191 (2014).

[31]T. Smoleński, T. Kazimierczuk, J. Kobak, M. Goryca, A. Golnik, P. Kossacki, and W. Pacuski, "Magnetic ground state of an individual Fe^{2+} ion in strained semiconductor nanostructure", Nat. Comm. **7**, 10484 (2016).

[32]D. Scalbert, J. Cernogora, and C. A. L. Guillaume, "Spin-lattice relaxation in paramagnetic CdMnTe", Solid State Communications **66**, 571–574 (1988).

[33]T. Dietl, P. Peyla, W. Grieshaber, and Y. M. d'Aubigné, "Dynamics of spin organization in diluted magnetic semiconductors", Phys. Rev. Lett. **74**, 474–477 (1995).

[34]C. Le Gall, "Dynamics and Optical contrôl of a single spin in a Quantum Dot", Theses (Université de Grenoble, Nov. 2011).

[35]B. Varghese, H. Boukari, and L. Besombes, "Dynamics of a Mn spin coupled to a single hole confined in a quantum dot", Phys. Rev. B **90**, 115307 (2014).

[36]L. Besombes and H. Boukari, "Resonant optical pumping of a Mn spin in a strain-free quantum dot", Phys. Rev. B **89**, 085315 (2014).