First principles study of point defects in diamond

Thesis Booklet

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Introduction

Research and development of quantum technology is a hot topic in the EU and the entire world, which would introduce new sensors for computation or communication and ultrasensitive detectors in the future. One possible realization of quantum bits is the paramagnetic and optically active point defects embedded in solids. Point defects in diamond acting as solid state quantum bits were already successfully created, the nitrogen-vacancy (NV) centre in diamond is one of such examples [Doherty et al., 2013].

A controllable initialization schema for quantum bits is essential. The NV centre exhibits $S = 1$ electronic spin, where the quantum bit is realized as the substates of this electron spin. The initialization of this quantum bit is carried out by optical excitation: the system will be at the $S_z = 0$ spin state upon illumination with green light. This is an optical spin-polarization process, where the system decays from the optically excited electronic state by means of non-radiative transitions into the $S_z = 0$ state with greater probability than into the $S_z = \pm 1$ projection. Nevertheless, the exact physical background of this process is not fully understood [Doherty et al., 2013]. The clarification of the spin-polarization process is essential to understand the physics of NV quantum bits.

In the recent years, beside NV centre, various other point defects have been also proposed for quantum technology. For example, the electronic spin can be coherently manipulated in silicon [Sukachev et al., 2017] and germanium [Bhaskar et al., 2017] related point defects of diamond. Thus it is worthwhile to study other point defects in diamond beside the NV centre for quantum technology applications. Potential quantum bits might emerge in diamonds grown by chemical vapour deposition process (CVD), where the hydrogen, oxygen, silicon are typical contaminants: the CVD diamond growth can be accelerated by additional oxygen to the hydrogen precursor gases, and the silicon is often used as a substrate for heteroepitaxial diamond growth. However, there were only few oxygen centres identified in diamond [Hartland, 2014], and there is little known about the properties of silicon related point defects. It is known from *electron paramagnetic resonance* (EPR) studies, that silicon-vacancy (SiV), silicon-divacancy (SiV) and even its hydrogenated counterparts (SiV:H, SiV_2:H) occur in diamond. However, not all silicon related defects are identified in diamond. One of such examples is the silicon related absorption centre at 1.018 eV, of which origin is yet to be identified [D'Haenens-Johansson, 2011].

It is well known, that the CVD diamond growth is stable under the conditions of 50-50% stoichiometry ratio of O and C atoms in the precursor gases [Bachmann et al., 1991]. Diamond growth without oxygen only goes with at least 99% hydrogen content. As a consequence, the appearance of oxygen and hydrogen related point defects is expected in diamond. Direct identification of oxygen defects is a difficult task because, the abundant ^{16}O isotope does not dot interact with the magnetic field. However, ^{17}O isotope exhibits

an unique hyperfine splitting in the EPR spectra because it has an $I = 5/2$ nuclear spin ^{17}O that can interact with the electron spin. Due to the high cost of ^{17}O isotopes, ^{17}O is usually introduced in diamond by ion implantation. The only unambiguously identified oxygen defect is the KUL12 EPR centre with $S = 1/2$ spin, which was created upon oxygen by ^{17}O ion implantation [Iakoubovskii and Stesmans, 2002]. The exact geometric structure, charge state of this defect has been not known so far. On the other hand, the WAR5 EPR centre was detected in CVD diamond with ^{16}O contamination. The properties of WAR5 is very similar to that of NV: both EPR centres exhibit nearly same hyperfine splitting from ^{13}C neighbours, and exhibit nearly identical zero field splitting, thus the neutral oxygen-vacancy (OV) structure was assigned to WAR5 [Cann, 2009]. Furthermore, the signal of WAR5 was accompanied by an optical transition around 2 eV similar to the NV centre. There were attempts to measure the spin-polarisation in OV, however in spite of many similarities between the WAR5 and NV center, the WAR5 EPR centre did not exhibit any optical spin-polarization [Hartland, 2014]. The physical background of this phenomenon is not known. Numerous EPR centres were tentatively assigned to oxygen in HPHT (*high temperature high temperature*) diamonds, however the presence of oxygen in these defects was not demonstrated [Komarovskikh et al., 2014].

Objectives

During my PhD years, I searched for alternatives beside the NV and SiV centres in diamond for quantum technology applications. My first goal was to study the properties of silicon point defects and silicon-hydrogen complexes embedded in diamond. I calculated their ionization energies and magneto-optical properties and the binding energies of complexes.

The next goal of my research was to study of oxygen and oxygen-hydrogen centres. I was particularly interested in the neutral oxygen-vacancy (OV) centre, which possesses an *isovalent* electronic structure to that of the NV centre, but does not show optical spin-polarization in contrast to NV centre. I calculated the ionization energies of oxygen and oxygen-hydrogen complexes. For the paramagnetic defects I calculated the hyperfine tensors that are fingerprints of defects in the EPR spectrum. I studied the quantum tunneling in various point defects, that significantly affects the EPR spectrum oxygen point defects.

In my third objective, I examined the physical background of the spin-polarization process of NV centre. The optical spin-polarization occurs via non-radiative processes. I studied the electron-phonon and spin-orbit effects simultaneously from first principles, in order to achieve a semi-quantitative description.

Methods

In my research, I studied the point defects in a diamond supercell that consists of 512 carbon atoms. Simulation of a system of half thousand atoms directly from the Schrödinger equation is impossible. In order to limit the computation time to foreseeable time one must apply a series of approximations. During my research I relied mainly on methods based on density functional theory (DFT), in particular I calculated the electronic structure by HSE06 functional within DFT, which predicts the electronic excitation energy of the negatively charged NV(−) and SiV(−) with the precision of 0.1 eV [Gali et al., 2009, Gali and Maze, 2013]. I separated the motion of the nuclei from the electronic structure with the Born-Oppenheimer approximation, but during my research I went beyond this approximation with the characterization of the Jahn-Teller effect on the point defects, where vibration states are entangled with the electronic orbitals. I used computer clusters with massively parallelized codes to carry out the calculations.

New scientific results

1. **Silicon and silicon-hydrogen complexes in diamond lattice**

I have studied the silicon and silicon-hydrogen complexes in diamond by means of density functional theory simulations. I have determined the electronic structure of SiV_2, SiVH, SiV_2H complexes in a 512 carbon atom supercell, and I have relaxed their geometry structures in appropriate charge states. Based on my calculations I have made the following statement:

(a) I have determined the dynamic matrix of the vibrations of the above-mentioned silicon-hydrogen complexes. Next, I have determined the vibration modes localized to the defect centres and their vibration frequency. I have stated that the 1.018(1)eV absorption centre found in bulk CVD diamond samples is related to the $SiV_2H(-)$ open shell singlet $S = 0$ centre, and its side peaks are coupled with the $340\,\mathrm{cm}^{-1}$ localized vibration mode of the Si atom. [T1]

2. **Oxygen and oxygen-hydrogen complexes in diamond lattice**

I have studied the oxygen and oxygen-hydrogen complexes in diamond by means of density functional theory simulations. I have determined the electronic structure of the oxygen interstitial (O_i), substitutional (O_s), vacancy (OV), (O_SH_n), (OVH_n complexes in a 512 carbon atom supercell, and I have relaxed their geometry structures in appropriate charge states. Based on my calculations I have made the following statements:

(a) After the determination of formation energies from first principles, I have proven that, beside the O_SH_n and OVH_n complexes, defect centres with more than one hydrogen atom are also stable. I have proven that the ground state of the neutral $O_s(0)$ point defect is an $S = 0$ singlet, which can be excited optically by approximately 1.38 eV. [T2]

(b) I have calculated the hyperfine structure of the oxygen-hydrogen complexes. Based on the results, I have identified the KUL12 S=1/2 EPR centre with C_{3v} symmetry in CVD thin films as the $O_S(+)$ oxygen substitutional point defect. The symmetry and orientation of main the axes of the theoretical hyperfine tensor, and its principal values ($A_{\parallel} = -223\,\mathrm{MHz}$, $A_{\perp} = -189\,\mathrm{MHz}$) are in agreement with the data of the KUL12 centre observed in experiments ($A_{\parallel} = \pm 238\,\mathrm{MHz}$, $A_{\perp} = \pm 207\,\mathrm{MHz}$). [T2]

(c) I have determined the possible orientations of OVH(0) and $O_S(+)$ point defects in diamond from *ab-initio* calculations, then I have calculated the barrier energies connecting the different orientations on the potential energy surface. Next, I have determined the tunneling rate of hydrogen atoms between the three equivalent carbon dangling bonds of OVH defect centre, then I have determined the tunneling rate for the $O_S(+)$ centre. According to my calculations the tunneling rate in the OVH(0) centre (26 THz) is orders of magnitude faster than the alternation of the electromagnetic field, but for $O_S(+)$ the tunneling frequency (0.3 GHz) is negligible to the frequency of the applied electromagnetic field (X-band ∼10 GHz). Thus I have pointed to that, the EPR signal of the OVH complex with static Jahn-Teller distortion of C_s symmetry is averaged out to C_{3v} symmetry in experiments due to the tunneling of the H atom. On the other hand, the EPR signal of $O_S(+)$ centre does not average from C_{3v} to T_d symmetry, in excellent agreement with the experimental data. [T2]

(d) I have determined the geometry and electronic structure of the optical excited state of the OV(0) point defect. I have determined the zero field splitting ($D = 2989\,\mathrm{MHz}$) of the OV(0) centre with $S = 1$ spin and the hyperfine tensor of the ^{17}O nucleus ($A_{\parallel} = \pm 188\,\mathrm{MHz}$, $A_{\perp} = \pm 102\,\mathrm{MHz}$), which data are in good agreement with the data of the WAR5 centre ($D = 2888\,\mathrm{MHz}$, $A_{\parallel} = \pm 197\,\mathrm{MHz}$, $A_{\perp} = \pm 118\,\mathrm{MHz}$) as expected. Thus, I have proven the former presumption that the microscopic structure of the WAR5 centre is the OV(0) system. Consequently, the ground states of OV(0) and NV(−) are *isoelectronic*, they possess nearly the same hyperfine parameters and zero field splitting. On the other hand, this can not be stated about their optically excited state: the electronic structure of OV(0) and NV(−) centres are significantly different. According to my calculations, the geometry of the excited state of OV(0) is not stable, there is a direct relaxation path on the potential energy surface from the excited state down to the ground state. As contrary to the initial presumptions, my calculations indicates that the WAR5 EPR centre is not linked with the 2.282 eV photoluminescence centre. The de-excitation of OV(0) occurs via non-radiative relaxation path, which is faster than the optical emission, in constrast to the NV(−) centre, where this type of instability does not occur. [T2]

3. **Spin-orbit interaction in the NV(-) center.**

(a) I have proven that the *intrinsic* value of spin-orbit interaction in NV(−) defect converges with an exponential decay ($\lambda_z^{\star}(L) = Ae^{-aL} + \lambda_z$) as a function of the L super-lattice constant to the infinite bulk limit of spin-orbit splitting. [T3]

(b) I have determined that for optically excited state of NV($-$), its *intrinsic* ($\lambda_z = 15{,}8$ GHz) spin-orbit interaction is damped by the dynamic Jahn-Teller effect through the $p = 0{,}304$ Ham reduction factor. The reduced spin-orbit interaction ($p \times \lambda_z = 4{,}8$ GHz) calculated from first principles agrees well with the $\lambda_z^{\text{exp.}} = 5.3$ GHz experimental data. [T3]

(c) The combined effect of spin-orbit and electron-phonon interactions lead to the non-radiative $\Gamma_{E_{1,2}}$ and Γ_{A_1} transitions of NV($-$) centre, by which I have proven that, they are governed by the Jahn-Teller effect. My quantitative results are consistent with the experiments, where I have explained the $\Gamma_{E_{1,2}}/\Gamma_{A_1} \approx 0,5$ ratio of the two scattering rates from fully *ab initio* calculations. [T3]

Impact of results

My results would greatly contribute to the realization of an optimal solid state quantum bit, which can be useful in the area of transmission of quantum information or creation quantum memory. Additionally the point defects that I have studied can be applied in the field of ultrasensitive sensors, or as biological contrast agents in medical sciences.

Publications related to thesis points:

- [T1] Gergő Thiering and Adam Gali. Complexes of silicon, vacancy, and hydrogen in diamond: A density functional study. *Physical Review B*, 92(16), oct 2015.

- [T2] Gergő Thiering and Adam Gali. Characterization of oxygen defects in diamond by means of density functional theory calculations. *Physical Review B*, 94(12), sep 2016.

- [T3] Gergő Thiering and Adam Gali. Ab initio calculation of spin-orbit coupling for an NV center in diamond exhibiting dynamic Jahn-Teller effect. *Physical Review B*, 96(8), aug 2017.

Further publications:

- [4] Gergő Thiering, Elisa Londero, and Adam Gali. Single nickel-related defects in molecular-sized nanodiamonds for multicolor bioimaging: an ab initio study. *Nanoscale*, 6(20): 12018-12025, 2014.

- [5] Adam Gali, Tamás Demján, Márton Vörös, Gergő Thiering, Elena Cannuccia, and Andrea Marini. Electron-vibration coupling induced renormalization in the photoemission spectrum of diamondoids. *Nature Communications*, 7:11327, apr 2016.

- [6] Matthias Pfender, Nabeel Aslam, Patrick Simon, Denis Antonov, Gergő Thiering, Sina Burk, Felipe Fávaro de Oliveira, Andrej Denisenko, Helmut Fedder, Jan Meijer, Jose A. Garrido, Adam Gali, Tokuyuki Teraji, Junichi Isoya, Marcus William Doherty, Audrius Alkauskas, Alejandro Gallo, Andreas Grüneis, Philipp Neumann, and Jörg Wrachtrup. Protecting a diamond quantum memory by charge state control. *Nano Letters*, 17(10): 5931-5937, sep 2017.

- [7] Stefan Häußler, Gergő Thiering, Andreas Dietrich, Niklas Waasem, Tokuyuki Teraji, Junichi Isoya, Takayuki Iwasaki, Mutsuko Hatano, Fedor Jelezko, Adam Gali, and Alexander Kubanek. Photoluminescence excitation spectroscopy of SiV- and GeV- color center in diamond. *New Journal of Physics*, 19(6):063036, jun 2017.

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