Summary of the habilitation thesis

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1. Curriculum vitae

1.1. Personal data

First name and surname: Nevill Gonzalez Szwacki
Date and place of birth: 9 September 1973, Merida (Venezuela)
Married, one child

1.2. Academic degrees earned

June 2003

Ph.D. in physics, Institute of Physics, Polish Academy of Sciences in Warsaw. Doctoral thesis entitled: "*Structural, electronic, and optical properties of $GaAs_{1-x}N_x$ and $Ga_{1-x}B_xAs$ alloys: fist principles calculations*", Dissertation advisor: prof. dr hab. Piotr Bogusławski

November 1998

Master's degree in physics, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw. Master's thesis entitled: *"Three-dimensional model of interaction between magnetic layers in the EuTe/PbTe superlattices"*, Thesis advisor: prof. dr hab. Jan Blinowski

1.3. Employment in scientific entities

- *2010- presently* - **Scientific Assistant Professor**, Institute of Theoretical Physics, Faculty of Physics, University of Warsaw
- *2004-2009* - **Robert A. Welch Postdoctoral Fellow**
  - Dept. of Physics, Texas Southern University, Houston, Texas (2008-2009)
  - Dept. of Physics, Texas Tech University, Lubbock, Texas (2006-2008)
  - Dept. of Mechanical Engineering & Material Science, Rice University, Houston, Texas (2004-2006)
- *2003-2006* - **Assistant Professor**, Institute of Physics, Polish Academy of Sciences in Warsaw

N. González Sz.

2. Scientific achievement

- As a scientific achievement, in accordance with Article 16 (2) of the Act of 14 March 2003[I], I indicate a cycle of 8 thematically related publications with a common title:
  Investigation of the influence of transition metal impurities on the properties of classical semiconductors by using first principles calculations

- The cycle of thematically related publications consists of (publications [1–8][II]):

H1. **N. Gonzalez Szwacki** and S. K. Estreicher, "*First-principles investigations of Fe-H interactions in silicon*", Physica B 401-402, 171 (2007).
IF: 0.751, MNiSW score: 20 points

H2. **N. Gonzalez Szwacki**, M. Sanati, and S. K. Estreicher, "*Two FeH pairs in n-type Si and their implications: A theoretical study*", Phys. Rev. B 78, 113202 (2008).
IF: 3.322, MNiSW score: 35 points

H3. **N. Gonzalez Szwacki**, J. A. Majewski, and T. Dietl, "*Aggregation and magnetism of Cr, Mn, and Fe cations in GaN*", Phys. Rev. B 83, 184417 (2011).
IF: 3.691, MNiSW score: 35 points

H4. A. Navarro-Quezada, **N. Gonzalez Szwacki**, W. Stefanowicz, T. Li, A. Grois, T. Devillers, M. Rovezzi, R. Jakieła, B. Faina, J. A. Majewski, M. Sawicki, T. Dietl, and A. Bonanni, "*Fe-Mg interplay and the effect of deposition mode in (Ga,Fe)N doped with Mg*", Phys. Rev. B 84, 155321 (2011).
IF: 3.691, MNiSW score: 35 points

H5. T. Devillers, M. Rovezzi, **N. Gonzalez Szwacki**, S. Dobkowska, W. Stefanowicz, D. Sztenkiel, A. Grois, J. Suffczyński, A. Navarro-Quezada, B. Faina, T. Li, P. Glatzel, F. d'Acapito, R. Jakieła, M. Sawicki, J. A. Majewski, T. Dietl, and A. Bonanni, "*Manipulating Mn-Mg_k cation complexes to control the charge- and spin-state of Mn in GaN*", Sci. Rep. 2, 722 (2012).
IF: 2.927, MNiSW score: 40 points

H6. **N. Gonzalez Szwacki**, J. A. Majewski, and T. Dietl, "*(Ga,Mn)As under pressure: A first-principles investigation*", Phys. Rev. B 91, 184409 (2015).
IF: 3.718, MNiSW score: 35 points

H7. M. Rovezzi, W. Schlögelhofer, T. Devillers, **N. Gonzalez Szwacki**, T. Li, R. Adhikari, P. Glatzel, and A. Bonanni, "*Incorporation of Mn in $Al_xGa_{1-x}N$ probed by x-ray absorption and emission spectroscopy, high-resolution microscopy, x-ray diffraction, and first-principles calculations*", Phys. Rev. B 92, 115308 (2015).
IF: 3.718, MNiSW score: 35 points

H8. **N. Gonzalez Szwacki**, "*Formation of Mn-Si_n complexes in GaN: A first principles investigation*", Solid State Commun. 259, 16 (2017).
IF: 1.549, MNiSW score: 30 points

[I] Law on Academic Degrees and Title and Degrees and Title in the Arts [Dz. U. (Official Journal of Laws) item 882 from 2016 with changes in Dz. U. item 1311 from 2016.].

[II] In Section 6 of the habilitation thesis.

2.1. Introduction

The research on magnetic semiconductors began in the early 1960s with the europium chalcogenides. The EuO, EuS, and EuSe semiconductors exhibit ferromagnetism and EuTe exhibits antiferromagnetism at low temperatures and their magnetic properties have been found to be strongly correlated with their electrical and optical properties[III]. At the end of the 1970s it was discovered that manganese doping could enhance the magnetic properties of CdTe. Magnetic semiconductors, in which magnetic ions replace part of the ions of the nonmagnetic host material, are called diluted magnetic semiconductors (DMSs). Despite the relatively low concentration of magnetic ions, many of the features exhibited by DMSs are similar to those of semiconductors with a high concentration of magnetic ions (for instance the mentioned above europium chalcogenes) due to the *sp-d* exchange interaction between spins of itinerant carriers and spins localized on magnetic ions. Most of the research on magnetic semiconductors is currently conducted on II-VI, III-V, IV-VI, and group IV DMSs, among others.

The advantage of II-VI DMSs (like CdMnTe) is that they can be obtained by the same growth techniques as those used to obtain the host semiconductor as long as the concentration of Mn ions (or other magnetic ions) does not exceed the solubility threshold[IV]. Ferromagnetism in DMSs was described for the first time in IV-VI DMSs for GeTe doped with manganese ions. A high transition temperature of 167 K was reported for $Ge_{1-x}Mn_xTe$ for manganese concentration of $x = 0.50$[V]. The observed ferromagnetism has been explained by an indirect exchange interaction of the Ruderman-Kittel-Kasuya-Yosid (RKKY) type between localized magnetic moments coupled by the interaction with conduction band electrons[VI]. Before the spread of the molecular beam epitaxy (MBE) technique to obtain III-V DMSs, it was already known that transition metal ions introduce acceptor states to III-V compounds. In many cases these are deep acceptor states, except for example Mn, which introduces an acceptor level of ~0.1 eV to the energy gap of GaAs[VII]. Subsequent incorporation of high concentrations of Mn ions in GaAs by the MBE method resulted in obtaining ferromagnetic (Ga,Mn)As with Curie temperature, T_C, of 190 K[VIII]. The ferromagnetic coupling between magnetic moments localized on Mn ions and also a number of experimental results obtained for (Ga,Mn)As were explained within the theoretical *p-d* Zener model in which the indirect exchange interaction between localized spins of Mn *d*-electrons are mediated by valence band holes[IX]. There is lack of consensus in the literature about the nature of the holes, whether they are in the valence band or in the impurity band[X].

In order to observe ferromagnetic or antiferromagnetic ordering in DMSs, a significant amount of magnetic ions should be introduced to the host semiconductor, which usually exceeds its solubility limit, therefore growth techniques capable to produce materials under conditions distant from thermodynamic equilibrium shall be used for the synthesis of III-V magnetic semiconductors. Molecular beam epitaxy is the most commonly used method of preparing such metastable materials. Under normal MBE growth conditions, heavy doping of III-V compounds with transition metal ions results in the segregation of magnetic ions on the growth front and then the formation of unwanted compounds with a crystal structure different from that of the host semiconductor. This makes it impossible to obtain

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[III] F. Matsukura and H. Ohno, in *Handb. Cryst. Growth* (North-Holland, Boston, 2015), pp. 649–682.

[IV] J. K. Furdyna and J. Kossut, *Diluted Magnetic Semiconductors* (Acad. Press, 1988).

[V] R. W. Cochrane, M. Plischke, and J. O. Ström-Olsen, Phys. Rev. B **9**, 3013 (1974).

[VI] W. Dobrowolski, J. Kossut, and T. Story, in *Handb. Magn. Mater.* (Elsevier, 2003), pp. 289-377.

[VII] R. A. Chapman and W. G. Hutchinson, Phys. Rev. Lett. **18**, 443 (1967).

[VIII] T. Dietl and H. Ohno, Rev. Mod. Phys. **86**, 187 (2014).

[IX] T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000).

[X] S. Ohya, K. Takata, and M. Tanaka, Nat. Phys. **7**, 342 (2011).

magnetic semiconductor alloys[XI]. A general strategy to prevent this surface segregation is to reduce the growth temperature. This temperature should be high enough to maintain the epitaxial growth of a single phase and single crystal (Ga,Mn)As, but low enough to inhibit the segregation of Mn ions and the formation of secondary phases, such as MnAs with a NiAs structure, which is a thermodynamically stable phase. When appropriate growth conditions are applied, the Mn ions are mostly incorporated into substitutional positions in the cationic sublattice[XII]. The improvement in growth technology of (Ga,Mn)As resulted in the fact that the reported T_C has been increasing year by year, but it is still below room temperature. For practical applications, a DMS with T_C higher than room temperature is required. In order to increase T_C in (Ga,Mn)As, one needs to increase the effective number of manganese ions involved in the ferromagnetic order. To this end, the problem of self-compensation should be minimized, in which double-donor defects are involved: arsenic antisites, As_{Ga}, and manganese interstitials, Mn_i. In order to reduce the degree of self-compensation, among other things, a number of studies on the effect of annealing on the T_C of (Ga,Mn)As were carried out, which showed that the increase in T_C results from a decrease in the concentration of Mn_i, and thus an increase in the concentration of holes[XIII, XIV]. More recently it has been shown that T_C can be also increased by applying hydrostatic pressure to (Ga,Mn)As[XV].

The observation of relatively high T_C for ferromagnetic (Ga,Mn)As and its compatibility with GaAs-based heterostructures has initiated a large-scale research on DMSs with a wide range of combinations of host semiconductors and magnetic elements as their dopants, in particular DMSs with wide band gap semiconductors such as GaN and ZnO. Extensive research on GaN-based DMSs was also motivated by theoretical work that predicted ferromagnetism at room temperature for heavily doped p-type (Ga,Mn)N[IX]. At the same time, many experimental studies reported ferromagnetism with T_C above room temperature, and many others reported ferromagnetism with T_C below 20 K for GaN doped with transition metal ions. This unclear situation has led to considerable experimental and theoretical efforts to explain the observed magnetism[XVI]. One of the causes of high T_C ferromagnetism in GaN-based magnetic semiconductors may be the experimentally observed aggregation of magnetic ions in GaN, i.e. the coexistence of areas with high and low concentrations of magnetic cation ions[XVII]. Some studies also point to the presence of secondary phases, derived from the low solubility of magnetic ions in GaN, as a source of ferromagnetism. It has also been shown that the aggregation of magnetic ions can be controlled by codoping with shallow donors or acceptors (e.g. Mg or Si). Especially important in this context are the results obtained for (Ga,Fe)N and (Ga,Mn)N, for which a correlation between doping, magnetic properties, and the distribution of magnetic ions was found.

Group IV magnetic semiconductors are investigated since they are compatible with the existing silicon technology. For example, the growth of polycrystalline manganese doped Si with a concentration of Mn ions exceeding 10% was performed on a Si(001) substrate using MBE[XVIII]. However, it was later

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[XI] D. DeSimone, C. E. C. Wood, and C. A. Evans, J. Appl. Phys. **53**, 4938 (1982).

[XII] R. Shioda, K. Ando, T. Hayashi, and M. Tanaka, Phys. Rev. B **58**, 1100 (1998).

[XIII] T. Wojtowicz, J. K. Furdyna, X. Liu, K. M. Yu, and W. Walukiewicz, Phys. E **25**, 171 (2004).

[XIV] K. W. Edmonds, P. Bogusławski, K. Y. Wang, R. P. Campion, S. N. Novikov, N. R. S. Farley, B. L. Gallagher, C. T. Foxon, M. Sawicki, T. Dietl, M. Buongiorno Nardelli, and J. Bernholc, Phys. Rev. Lett. **92**, 37201 (2004).

[XV] M. Gryglas-Borysiewicz, A. Kwiatkowski, M. Baj, D. Wasik, J. Przybytek, and J. Sadowski, Phys. Rev. B **82**, 153204 (2010).

[XVI] K. Sato, L. Bergqvist, J. Kudrnovský, P. H. Dederichs, O. Eriksson, I. Turek, B. Sanyal, G. Bouzerar, H. Katayama-Yoshida, V. A. Dinh, T. Fukushima, H. Kizaki, and R. Zeller, Rev. Mod. Phys. **82**, 1633 (2010).

[XVII] T. Dietl, Nat. Mater. **9**, 965 (2010).

[XVIII] H. Nakayama, H. Ohta, and E. Kulatov, Thin Solid Films **395**, 230 (2001).

shown that Mn-rich precipitates are formed during the MBE growth[XIX]. This may be due to the tendency of metallic dopants to occupy interstitial positions in silicon, what favors the formation of metallic precipitates. Moreover, the presence of metallic impurities in silicon is not always desirable since they often introduce electrically active centers that act as traps for carriers.

2.2. Aim of the work

My research on the influence of impurities on the properties of classical semiconductors begins with the technologically important issue of passivation of deep impurities in silicon. Deep trap states for charge carriers are formed in silicon in the process of growth of bulk silicon. One of the most common "unwanted" impurities is iron and the method for "getting rid of" the deep states introduced by iron is to passivate these states with hydrogen. In the cycle of 5 publications (articles **H1** and **H2** and [9–11]), I researched the possibility of forming iron clusters and complexes $\{Fe,H_n\}$ in silicon. As next, the position of the impurity states introduced by $\{Fe,H_n\}$ complexes in the energy gap of silicon and the influence of hydrogen on these states were studied. The last stage was to compare the phonon spectra of the resulting complexes with experimental data.

In the following years, I studied the intentional incorporation of magnetic impurities into semiconductors such as GaAs (article **H6**), GaN (articles **H3**, **H4**, **H5**, and **H8**), and the ternary compound $Al_xGa_{1-x}N$ (article **H7**). The magnetic impurities that have been studied are iron, chromium, and manganese for GaN and manganese for GaAs. In particular, I dealt with the phenomenon of chemical phase separation occurring in GaN:TM and GaAs:TM, where TM (transition metal) is one of the transition metals. This was done by means of computer modeling. Chemical phase separation consists in the aggregation of transition metals inside the host material while maintaining the crystal structure of the material. Thanks to first principles calculations, it was possible to establish that the aggregation of impurities takes place already in the phase of sample formation, i.e. on the growth surface. This trend is stronger for the Fe ion than for the Mn and Cr ions, which explains the experimental observation of formation of clusters and iron precipitates already for small iron concentrations in GaN (articles **H3** and **H4**). The effect of magnesium (article **H5**) and silicon (article **H8**) on the aggregation of Mn ions in GaN was also studied. The role of codoping has proved to be very important, because not only potentially increases the number of carriers in the crystal, but, as confirmed by computer modeling, magnesium and silicon form $\{Mn,Mg_n\}$ and $\{Mn,Si_n\}$ complexes with Mn, respectively, what prevents the clustering of manganese in GaN, and thus fosters their more homogeneous distribution in this crystal.

Important conclusions from the habilitation publication cycle:

- Works **H1** and **H2**: There is no systematic way to get rid of iron-related trap states in silicon through the intentional introduction of hydrogen (hydrogen passivation process). Instead of improving the situation, new, deep impurities states are created in the energy gap of silicon associated with the formation of $\{Fe,H_n\}$ complexes. However, hydrogen atoms may indirectly improve the quality of e.g. photovoltaic cells, as their presence increases the probability of formation of mobile at room temperature ions of interstitial iron, and thus increases the possibility of iron precipitation.
- Work **H6**: The influence of hydrostatic pressure on the magnetic interaction of Mn ions in GaAs was an important part of my computer simulations. We obtained that for the Mn concentration of 12.5% and zero pressure T_C is equal to 181 K as established by Monte Carlo simulations, while it

[XIX] Y. Zhang, Q. Jiang, D. J. Smith, and J. Drucker, J. Appl. Phys. **98**, 33512 (2005).

increases linearly with pressure to about 6 GPa. Farther increase in pressure increases also T_C and (Ga,Mn)As becomes ferromagnetic at room temperature at a pressure of the order of 14 GPa.

- Works **H3** and **H4**: Numerical calculations confirm experimental observations indicating the aggregation of magnetic ions (chemical phase separation) of Fe_{Ga}, Mn_{Ga} or Cr_{Ga} in GaN. The tendency to aggregate is theoretically predicted also for Fe_{Ga} ions on the growth surface of wz-GaN. Such a picture is confirmed by experimental observations, according to which 1% of Fe ions in GaN is sufficient to produce precipitates (crystallographic phase separation). Calculations for bulk (Ga,Fe)N suggest that codoping with Mg hinders, while Si promotes the incorporation of Fe ions into zb-GaN, which is consistent with experimental results. Assuming homogeneous distribution of Si or Mg impurities (homogeneous doping), we obtain that the presence of Si impurities prevents aggregation of Fe ions in bulk. This is in contrast to the presence of Mg impurities, which, according to calculations, reinforces the tendency to aggregation of Fe ions, which is the result expected in the case of selective magnesium doping (δMg).
- Works **H5** and **H8**: The codoping of (Ga,Mn)N with magnesium or silicon does not affect the number of free carriers in the semiconductor because these carriers are captured by Mn ions, changing their charge and spin states. The incorporation of these impurities additionally causes that $\{\text{Mn,Mg}_n\}$ or $\{\text{Mn,Si}_n\}$ complexes are created in the GaN cationic sublattice. As a result, a more homogeneous distribution of paramagnetic centers is observed experimentally, showing a variety of possible charge and spin states, the values of which can be controlled by the relative concentration of Mg or Si impurities to the concentration of Mn ions.
- Work **H7**: The distribution of Al and Ga ions in the cationic sublattice in the ternary $Al_xGa_{1-x}N$ compound is random and independent on the concentration, x, of Al ions. In case of doping of the $Al_xGa_{1-x}N$ compound with manganese, the Mn ions preferentially substitute Ga ions. The presence of Mn ions in interstitial positions is in terms of energy less favorable than that of Mn_{Ga} ions. The obtained theoretical results confirm experimental observations concerning the distribution of Mn impurities in $Al_xGa_{1-x}N$. Additionally, the experiment shows that the distribution of these impurities is homogeneous in a wide range of aluminum concentrations reaching up to 82%.

2.3. Calculation methodology

Modeling from first principles the incorporation of transition metal impurities in materials such as Si, GaAs, or GaN is more difficult than in the case of lighter impurities, such as those considered by me H and B in Si (works **H1** and **H2**) or Mg and Si in GaN (works **H4**, **H5**, and **H8**). This is closely related to the partial filling of the 3*d* orbitals, which gives a whole range of possible values of total spin, *S*, and thus localized magnetic moments. The 3*d*-orbital related wave functions are strongly localized and therefore give deep energy levels in the band structure picture. Calculation methods that are based on a plane-wave basis set require a large number of plane-waves to describe these wave functions. In addition, TM ions are known for their complex chemical behavior, giving them the freedom to build themselves into the host crystal at locations with different coordination numbers. This is due to the fact that *s*, *p*, and *d* orbitals are involved in the bonds, which enables a wide variety of possible hybridizations. Depending on the location of the TM ion in the semiconductor, the nature of its bonds with the host crystal atoms may change from strongly ionic, with a small overlap of wave functions and with a large transfer of valence electrons from or to the host material atoms, to strongly covalent ones, with a large overlap of wave functions. The variety of bonds that TM ions form in semiconductors can also lead to significant lattice relaxations or strong interactions of TM ions with defects or atoms of other impurities (H, Mg, ...). Such issues can be best addressed by those first principles methods that allow to minimize the total energy of the system with respect to the coordinates of atoms in the

supercell under consideration. One such method is density functional theory (DFT), which is the basic tool, used by myself in most of the numerical calculations presented in this summary. To sum up, theoretical studies of TM ions in semiconductors must take into account a correct description of a number of possible bonds that these ions form in the semiconductor, which also requires systematic optimization of the geometry of the considered system.

The following subsections provide a brief overview of calculation methods – using various exchange and correlation functionals – that, among others, work well in computational modeling of systems containing TM ions with partially filled 3*d* orbitals (as well as 4*d* and 5*d* orbitals). In addition, it will be shown how to deal with the basic problem of numerical simulations using the DFT method, which to a greater or lesser extent are burdened with an error known in literature[xx] under the name of "self-interaction error".

2.3.1. Exchange and correlation functionals

The main drawback of the DFT method is the lack of an exact form of the exchange and correlation functional. Therefore, in the literature[xx] there is a whole range of approximate functionals that perform better or worse, depending on the system that is being considered (its chemical composition, dimensionality) and/or the physical quantity that we want to calculate. The main disadvantage of the DFT method is the lack of universal approximation to the exchange and correlation functional. The advantage, however, is the speed of calculation and its accuracy, sometimes comparable to that of the Möller-Plesset method (MP2). The exchange and correlation functionals used by myself can be divided into three main classes. The first class of functionals are those based on the homogeneous electron gas model, i.e. the method of local density approximation (LDA) or local spin density approximation (LSDA). The use of LDA (or LSDA) functional is often the starting point for calculations of structural and electronic properties of solids. The most popular local functional is the so-called SVWN functional (exchange of Slater and correlation of Vosko, Wilks, and Nusair). Another group of functionals are those taking into account the dependence of energy on electron density and its gradient, the so-called generalized gradient aproximation (GGA). In this class of functionals the most frequently used is the PBE (Perdew, Burkeg, and Ernzerhof) functional. The third class are hybrid HF/DFT functionals, in which the expression for the exchange energy contains a share of exchange energy from the Hartree-Fock method (HF). This class includes, among others, PBE0, HSE, and B3LYP. The PBE0 functional is a one-parameter mixture of PBE and 25% of HF. The HSE (Heyd, Scuseria, and Ernzerhof) functional was developed on the basis of PBE0, in which an additional adjustable parameter controlling the short-rangeness of the interaction, thanks to which the exchange interaction is calculated only at a certain distance from a given atom. The three-parameter hybrid B3LYP (Becke, Lee-Yang-Parr) functional, like the previous two, contains some addition (20%) of the exact exchange energy taken from the HF method. It is added to the exchange and correlation energy coming from the mixture of DFT functionals. The parameters describing the contribution of individual terms in such a functional are adjusted so as to reproduce the experiment or thermochemical data. The last group of functionals in some cases allows obtaining more accurate results, among other things, as a result of reducing the so-called self-interaction error, which is one of the drawbacks of DFT methods.

[xx] D. Sholl and J. A. Steckel, *Density Functional Theory: A Practical Introduction* (Wiley, 2011).

2.3.2. Self-interaction error in DFT calculations

The electron-electron interaction in the density functional theory consists of the Coulomb repulsion term (Hartree term), E_H, and the exchange-correlation term (of unknown form), E_{xc}. While the E_H term correctly describes the Coulomb repulsion of electrons using the total electron density, it also includes the Coulomb repulsion between the electron and its own charge density. This false self-interaction is exactly cancelled by the exchange term in some methods, such as the above mentioned Hartree-Fock theory, but is only partially cancelled by the exchange term in LDA (or GGA), which is known in the DFT methodology as the self-interaction error. This error is one of the most important reasons for underestimating the energy gap, E_g, in DFT calculations based on LDA (or GGA). In many cases, the self-interaction error has little effect on properties other than E_g, but it can be an important problem when simulating systems with localized electrons, e.g. on impurities. Since the self-interaction energy is always positive, it increases the energy of localized states and the consequence is the spatial delocalisation of electrons. This error is common in computer simulations taking into account the elements of *d*- and *f*-blocks and may cause e.g. unwanted metallisation of the system or incorrect values of the magnetic moments localized on these atoms.

A number of methods have been proposed to alleviate the problem of self-interaction. One of the methods used by myself is the LDA+*U* or DFT+*U* method, in which a repulsion between electrons (usually from *d* or *f* orbitals) localized on a given atom is introduced. This repulsion can lead to breaking of symmetry causing the opening of the energy gap. The repulsive term is similar to that of the Hubbard model and is usually referred to as the Hubbard-*U* term. The calculation cost of such a method is low and it can also be used during structural relaxation of the system under study. Application of the DFT+*U* method does not eliminate the problem of self-interaction itself, but it can improve e.g. the resulting delocalisation of deep impurity states or eliminate errors in the predicted magnetic structure.

The last approach used by myself is the use of the aforementioned hybrid HF/DFT functionals related to the Hartree-Fock theory. In the HF method, the non-local exchange energy (Fock term) is not a functional of electron density, but depends on one-particle states. This exchange term accurately cancels the false self-interaction occurring in the Hartree part, but does not take into account the electron correlation. The exchange itself has a long-range nature (decreases as $1/r$) and is unscreened, which leads to unrealistically high excitation energies and a large overestimation of E_g. The combination of HF and LDA (or GGA) is motivated by the observation that HF calculations overestimate E_g, while DFT calculations underestimate E_g. The combination of the two methods, HF and DFT, gives more realistic values of energy gaps, which is the main advantage of using hybrid functionals. The method itself (expensive in terms of calculation time) alleviates, but does not fully eliminate the consequences of the self-interaction error.

2.4. Description of the habilitation thesis

2.4.1. Interaction of Fe with hydrogen in Si (articles **H1** and **H2**)

One of the early motivations for the study of hydrogen in semiconductors was its ability to "get rid of" deep impurity states. The term 'hydrogen passivation' is often used when the energy level associated with a dopant or defect disappears from the energy gap after hydrogenation of the sample. In the case of silicon, it has been demonstrated that exposure of the sample to hydrogen plasma can eliminate impurity levels associated with some TM[XXI] impurities. However, in early studies little was known about

[XXI] G. Kissinger and S. Pizzini, *Silicon, Germanium, and Their Alloys: Growth, Defects, Impurities, and Nanocrystals* (Taylor & Francis, 2014).

the microscopic properties of hydrogenated defects and how hydrogen affects electron states. A $\{X,H\}$ complex, where X stands for dopant or defect, does not have to be electrically inactive. In fact, in many cases hydrogen only partially passivates deep impurity states or those caused by defects, especially those related to unsaturated bonds often found on surfaces, interfaces, metallic contacts or grain boundaries. An important example of full passivation is the case of interaction between silicon and native oxide, which is usually formed on its surface. Hydrogen effectively passivates unsaturated bonds of Si at the Si/SiO$_x$ boundary[XXI]. The main reason for the not always effective passivation of TM ion dopants with hydrogen is due to the fact that H-atoms bind directly to the dopant. For example, the substitutional TM is already four times coordinated (four TM—Si bonds). After hydrogenation, the TM becomes 5-, 6-, and even 7-times coordinated. Large coordination numbers for TM ions are not uncommon in chemical compounds[XXI]. Such configurations include many *s-p-d* hybrid orbitals and only a few of them are passivated by hydrogen. As a result, many $\{TM,H_n\}$ complexes are electrically active.

On the experimental side, wet chemical etching is the most commonly used technique to introduce hydrogen into thin silicon layers, which also contain TM ion contamination[XXI]. The formation of $\{TM,H_n\}$ complexes themselves is confirmed experimentally by deep level transient spectroscopy (DLTS)[XXI] and theoretically **[H1] [H2]** [10,11][XXI]. In these studies it was found, for example, that there are families of complexes that contain different numbers of H-atoms, such as $\{Fe_s,H_n\}$ (n = 1 to 4) or $\{Fe_i,H\}$ **[H1]** **[H2]** [10,11], where Fe_s and Fe_i denote iron ions in the substitutional and interstitial positions in silicon, respectively. The Fe—H bond energies for Fe_s are in the order of 1.4-1.8 eV **[H1]** **[H2]**, while for Fe_i it is in the order of 0.8 eV **[H1]** [11]. It is well known that the introduction of hydrogen in silicon photovoltaic cells improves the lifetime of minority carriers. The general explanation for this fact is that some defects are passivated by hydrogen atoms. One example is the highly harmful contamination of photovoltaic cells by iron atoms, for which the mechanism of 'neutralisation' by the introduction of hydrogen is not exactly known.

Unlike the isolated Fe atom, which has a magnetic moment of $4\mu_B$, iron on a substitutional position in intrinsic silicon has a zero magnetic moment, because the unpaired electrons from the *d* orbitals strongly interact with the four adjacent silicon atoms. The Fe_s dopant does not introduce into the energy gap any impurity states **[H1]**. The most common position of iron in silicon, however, is the interstitial position and in this position in intrinsic silicon it has a magnetic moment of $2\mu_B$. The same magnetic moment is also found in n-type silicon, while in p-type silicon the moment increases to $3\mu_B$. The Fe_i ion introduces a deep donor level **[H1]** to the silicon energy gap.

The calculations of the interaction between hydrogen and iron in the interstitial position in silicon show that in the case of p-type silicon it is unlikely that positively charged interstitial hydrogen and Fe_i^+ will form a bond **[H1] [H2]** [11]. However, in the case of intrinsic or n-type silicon, interaction between neutral Fe_i^0 and hydrogen becomes possible. In this case hydrogen can diffuse as H_{BC}^0 (hydrogen atom in the center of the Si—Si bond; BC, bond centered) or less probably as H_T^- (hydrogen ion in the interstitial tetrahedral position, T) **[H2]**. The resulting pair is $\{Fe_i,H\}$ characterized by the fact that Fe_i moves to the hexagonal interstitial position with the attached H pointing in the direction of the T position along the trigonal axis with the Fe—H bond length equal to 1.51 Å. The calculated binding energy for the process ${}^{1}Fe_i^0 + {}^{1/2}H_{BC}^0 \rightarrow {}^{1/2}\{Fe_i,H\}^0$ is 0.82 eV. The ${}^{S}X^{q}$ or ${}^{S}\{\ \}^{q}$ notation used here denotes the dopant or complex, respectively, with a total spine S and in a charge state q. This pair has both the donor level, with energy E_v + 0.36 eV, and the acceptor level, with energy E_c – 0.26 eV, where E_v and E_c denote the energies of the valence band maximum and the bottom of the conduction band **[H2]**, respectively. In plus and minus charge states, the $\{Fe_i,H\}$ complex has S = 1, and the binding energy of the iron ion and hydrogen pair is 0.4 eV smaller than in the case of ${}^{1/2}\{Fe_i,H\}^0$.

The possibility of formation of pairs consisting of hydrogen and substitutional iron [**H1**] [**H2**] [11] was also studied and it was shown that hydrogen binds directly to Fe_s without interfering in any of the four Fe_s—Si bonds. The calculated binding energy is 1.39 eV for the ${}^{1/2}\{Fe_s,H\}^0$ pair [**H2**], which turned out to be more stable than the previously analyzed $\{Fe_i,H\}$ pair. This corresponds to a annealing temperature of 225°C [**H2**]. The $\{Fe_s,H\}$ complex does not introduce a donor level to the energy gap, but has an acceptor level, with energy $E_c - 0.62$ eV. The states with the lowest energy are ${}^{1/2}\{Fe_s,H\}^0$ (Fe_s—H along the <100> direction) and ${}^{0}\{Fe_s,H\}^-$ (Fe_s—H along the <111> direction). The first one is sensitive to the electron paramagnetic resonance (EPR) spectroscopy [**H2**]. The EPR studies and calculations show that $\{Fe_s,H\}$ has on average a tetrahedral symmetry with rotating (or tunnelling) H around Fe_s. The second H can also be bound to Fe_s according to the process: ${}^{1/2}\{Fe_s,H\}^0 + {}^{1/2}H^0_{BC} \rightarrow {}^{0}\{Fe_s,H_2\}^0 + 1.75\ \text{eV}$. In this case both hydrogen atoms rotate around Fe_s with activation energy of 0.22 eV. Such a system introduces an acceptor level at $E_c - 0.71$ eV to the energy gap [**H2**]. An analogous description also applies to the case of $\{Fe_s,H_n\}$ complexes with higher than 2 hydrogen atoms [**H1**].

According to calculations, $\{Fe,H_n\}$ type complexes are electrically active, i.e. the formation of such complexes does not contribute to the improvement of the situation of e.g. photovoltaic cells. The experimentally observed improvement in the lifetime of minority carriers in silicon after the introduction of hydrogen must have a more complex explanation. Since most currently produced silicon photovoltaic cells of p-type contain born impurities, still not fully understood process can take place here, in which an indication can be the suggested by theory [**H1**] [11] dissociation of $\{Fe_i,B_s\}$ pairs and formation of $\{B,H\}$ pairs and isolated Fe_i ions while injecting hydrogen at lower temperatures[XXI]. At higher temperatures, used to passivate photovoltaic cells, the presence of H^+ can stabilize higher concentrations of interstitial Fe, which during cooling can increase Fe_i precipitation[XXI]. Considering that the activation energy for Fe_i diffusion is in the range of 0.69-0.84 eV[XXII], i.e. these ions are mobile at room temperature, hydrogen would indirectly contribute to the improvement of photovoltaic cells through the precipitation process of these ions.

2.4.2. Pressure effects on magnetic properties of Mn doped GaAs (article **H6**)

The most intensively tested diluted magnetic semiconductor is manganese-doped GaAs. Gallium arsenide itself is a widely used material for the manufacture of optoelectronic instruments such as infrared radiation sources and detectors[XXIII]. Attempts to obtain a semiconductor with ferromagnetic properties at room temperature from manganese-doped GaAs have been an additional source of interest in this material for many years. Such a possibility was suggested by the predictions within the theoretical *p-d* Zener model[IX]. However, the highest Curie temperature, T_C, for the transition from ferromagnetic to paramagnetic state, which so far has been achieved for (Ga,Mn)As experimentally is about 190 K[VIII]. However, the possibility of influencing the magnetic state of (Ga,Mn)As has been experimentally demonstrated through the application of electric voltage[XXIV], the possibility of shifting the domain wall under the influence of electric current[XXV], and the change of magnetic anisotropy under the influence of electric field[XXVI]. The effect of hydrostatic pressure on magnetic properties of (Ga,Mn)As was also studied experimentally[XV].

[XXII] A. A. Istratov, H. Hieslmair, and E. R. Weber, Appl. Phys. A **69**, 13 (1999).

[XXIII] S. Adachi, *GaAs and Related Materials: Bulk Semiconducting and Superlattice Properties* (World Scientific, 1994).

[XXIV] H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl, Y. Ohno, and K. Ohtani, Nature **408**, 944 (2000).

[XXV] M. Yamanouchi, D. Chiba, F. Matsukura, and H. Ohno, Nature **428**, 539 (2004).

[XXVI] D. Chiba, M. Sawicki, Y. Nishitani, Y. Nakatani, F. Matsukura, and H. Ohno, Nature **455**, 515 (2008).

Until the publication of the article **H6** there was no significant theoretical contribution to the study of the influence of pressure on the electronic structure of (Ga,Mn)As and its magnetic properties. The paper **H6** presents, among others, the dependence of T_C on pressure for $Ga_{1-x}Mn_xAs$ with experimentally realistic concentrations of Mn ions 6.25% and 12.5%.

Atoms of gallium, manganese and arsenic have electron configurations of $[Ar]3d^{10}4s^24p^1$, $[Ar]3d^54s^2$, and $[Ar]3d^{10}4s^24p^3$ respectively. If Mn replaces Ga in the GaAs cationic sublattice then two 4*s* manganese electrons can replace two 4*s* gallium electrons in the bond formation. Thus, the manganese ion in the substitutional position is in the charge state 2+. Due to the lack of electron on the 4*p* orbital (compared to the As ion), manganese at the limit of weak doping acts as a shallow acceptor with energy ~0.1 eV above the top of the valence band[VIII]. As the concentration of Mn ions increases, the width of the impurity band increases to finally merge with the valence band. In addition to the hole band, Mn_{Ga} ions are also a source of localized magnetic moments (of $5\mu_B$ each).

For zero pressure and Mn ion concentration of 6.25%, the deep Mn 3*d* band states and higher in energy states induced by Mn are located 5 and 0.4 eV, respectively, below the Fermi energy, which is consistent with photo-emission experiments[VIII]. For higher pressures, both levels associated with Mn (deep and induced) and the Fermi level move in the direction of higher energies, however, the position of the induced level in relation to Fermi energy remains constant due to the interaction of Mn 3*d* levels with the levels of the valence band, which is mainly built of As 4*p* orbitals. The calculations also show that the part of the impurity band, which in the spin-polarized band structure description occurs up to ~0.3 eV above Fermi level in the "up" spin band, is not "detached" from the valence band and, what is more, it behaves with pressure similarly to the top of the valence band of GaAs. These calculations confirm, therefore, that the electronic states related to the Mn ion with energies above the Fermi level are band-like rather than localized states, which is an important result from the point of view of the discussion in the literature on the nature of these states[VIII].

By analyzing the behavior of T_C with the increase in hydrostatic pressure, we obtained that for the Mn concentration of 12.5% and zero pressure T_C is equal to 181 and 258 K for calculations performed with Monte Carlo (MC) and mean field approximation (MFA) methods, respectively, while it increases linearly with pressure to about 6 GPa. Farther increase in pressure increases also T_C and (Ga,Mn)As becomes ferromagnetic at room temperature at a pressure of the order of 14 GPa as established by MC simulations.

The theoretically determined values for the pressure derivative of the critical temperature, dT_C/dp, agree well with those found experimentally for $Ga_{0.93}Mn_{0.07}As$ in a regime in which the effects associated with hole localization are of less importance. Namely, our results show that the pressure induced T_C changes estimated for the Mn concentration of 6.25% are +2.2 and +3.5 K/GPa for MC and MFA calculations, respectively, and the experimental value for dT_C/dp, estimated using the Zener's *p-d* model, is of the order of 2-3 K/GPa[XV].

2.4.3. Chemical phase separation in Fe, Mn, or Cr doped GaN (articles **H3** and **H4**)

The application of modern nano-characterization methods (including synchrotron ones) made it possible to visualize in the nanoscale the aggregation of transition metal cations in various semiconductors (e.g. those investigated by us GaN and GaAs[XXVII]). This opens up new opportunities for nanomagnetism and nanospintronics provided that the formation of ferro and/or antiferromagnetic nanocrystals in the bulk of the host semiconductor can be controlled on a nanometre scale, e.g. by means of n- and/or p-type doping with shallow impurities (e.g. Mg or Si).

[XXVII] T. Dietl, K. Sato, T. Fukushima, A. Bonanni, M. Jamet, A. Barski, S. Kuroda, M. Tanaka, P. N. Hai, and H. Katayama-Yoshida, Rev. Mod. Phys. **87**, 1311 (2015).

Aggregation of magnetic ions at the nanoscale can lead to chemical phase separation, in which ion dopants usually occupy substitutional positions in the cationic sublattice, one adjacent to the other, forming ion aggregates[XXVII]. The consequence of this aggregation of magnetic ions is the presence of strong exchange interactions between magnetic ions. Another effect of the accumulation of magnetic ions can be a crystallographic phase separation, which consists in precipitation of a crystal with a different crystal structure than that of the host material.

In the paper **H3** the tendency to form clusters (aggregation of magnetic ions) of Fe_n, Mn_n, or Cr_n (for $n \leq 4$) in GaN was studied, both on the surface and inside of the material, in the case when these ions substitute Ga ions. In the work **H3**, we show that regardless of the type of magnetic dopant (Fe, Mn, or Cr) in GaN there is a strong tendency to accumulate ions in the bulk of the material, because the pairing energy for a pair of Fe, Mn, or Cr ions in GaN with a wurtzite (wz) or zinc blend (zb) structure is always negative. For example, the pairing energies for Mn and Fe in wz-GaN are -672 and -161 meV, respectively (similar values were also obtained for zb-GaN). These results indicate that transition metal ions want to be at a distance of nearest neighbors (NNs). An obstacle for such pairing of ions may be kinetic barriers for ion diffusion in bulk gallium nitride. Assuming that these barriers are much smaller on the surface of crystal growth, the pairing energy was calculated for the same magnetic ions on the gallium terminated (0001) surface of wz-GaN and it turned out that it is negative only for iron ions, i.e. on the surface only Fe ions tend to aggregate, while Mn or Cr ions repel each other. Such an image is consistent with experimental observations[XXVII], according to which 1% of Fe ions in GaN is sufficient for crystallographic phase separation to take place. In the case of Mn and Cr ions, the pairing energy on the surface is positive, which suggests that these ions should be more evenly distributed in the bulk of the crystal. Such an image is consistent with the experiment[XXVII], because much larger amounts (up to about 12%) of these ions can be introduced into the GaN without the presence of crystallographic phase separation.

As far as the magnetic properties of transition metal aggregates are concerned, regardless of the number of Fe ions in the Fe_n cluster, they are interfacing antiferromagnetically. The ions in the Mn_n and Cr_n clusters, on the other hand, are coupled ferromagnetically. An interesting fact is that on the gallium surface, the Mn pair is coupled antiferromagneticly.

In the experimental-theoretical work **H4,** we examined the effect of magnesium (or silicon) doping on the distribution of Fe ions in GaN and the resulting magnetic properties of (Ga,Fe)N:Mg, with particular emphasis on the role of doping – homogeneous or selective in a very limited area, δMg (so called delta doping or planar doping). In the case of homogeneous codoping of (Ga,Fe)N with Mg, the competition between Mg and Fe for substitutional positions in the host crystal makes that the presence of Mg impurities reduces the amount of Fe ions compared to the situation in the reference (Ga,Fe)N sample. In contrast, selective magnesium doping (δMg) favors the incorporation of Fe ions and induces their aggregation. As a consequence of reduced efficiency of Fe ion incorporation in homogeneously doped magnesium layers, the system becomes diluted (with homogeneous distribution of Fe ions), and its magnetic response is purely paramagnetic. However, with δMg doping, the tendency of Fe ions to aggregation is enhanced and the system becomes ferromagnetic due to the presence of ferromagnetic nanocrystals: ε-Fe3N and $Fe_{1-x}Ga_x$ (galfenol, i.e. iron and gallium alloy).

The numerical calculations carried out by me in the work **H4** can be summarized as follows:

(i) They confirm the tendency to aggregation of Fe ions on the growth surface of wz-GaN in the presence of Mg impurities.

(ii) Calculations for bulk (Ga,Fe)N suggest that the co-presence of Mg impurities makes it difficult, while Si promotes the incorporation of Fe ions into zb-GaN, which is consistent with experimental observations.

(iii) Assuming homogeneous distribution of Si or Mg impurities (homogeneous doping), the presence of Si impurities prevents the aggregation of Fe ions in the bulk of zb-GaN. This is the opposite to the presence of Mg, which according to calculations strengthens the tendency to aggregation of Fe ions, which is the result expected in the case of selective doping with Mg, for which the process of interdiffusion of atoms is important.

To sum up, a combination of experimental and theoretical results allows us to predict how the different ways of codoping can be used to control the formation of magnetic nanostructures in the host semiconductor.

2.4.4. Formation of $\{Mn,Mg_n\}$ and $\{Mn,Si_n\}$ complexes in GaN (articles **H5** and **H8**)

Magnesium in GaN is a shallow acceptor hoping to achieve a sufficiently high concentration of holes in (Ga,Mn)N to activate the mechanism of long range coupling of magnetic ions, which, according to the theoretical *p-d* Zener model, takes place through free holes and consequently allows to obtain ferromagnetic order of these ions[XVII]. However, experiment shows that codoping of (Ga,Mn)N with magnesium does not lead to the ferromagnetism of this compound[XXVIII]. Investigations of magnetic and optical properties and also synchrotron radiation studies showed, however, that the concentration of Mg impurities affects the charge state of manganese, Mn^{k+} ($3 \le k \le 5$), and its spin, S ($2 \ge S \ge 1$) **[H5]**. The holes introduced by Mg are captured by Mn^{3+} ions, changing their charge state to Mn^{4+} and even Mn^{5+}, and in addition, $\{Mn,Mg_n\}$ complexes are formed in the cationic sublattice. Therefore, due to the variety of possible charge states and spins and the different ways of coupling with the environment, the paramagnetic centers in GaN can show a rich spectrum of properties and functionality and can be used in commercial light emitters and even be used in quantum information technology. Moreover, the properties of $\{Mn,Mg_n\}$ complexes allow extending to infrared the already significant optical capabilities of nitrides, opening the way to their wider application, among others, in solotronics. The experimental results have been confirmed and explained by numerical calculations [**H5**], in which I showed that codoping of (Ga,Mn)N with Mg allows to control the charge and spin states of Mn^{k+} ion in ranges similar to the experimental ones. According to theoretical results, this exceptional degree of tunability results from the formation of $\{Mn,Mg_n\}$ cationic complexes, in which the number of ligands, n, is in the experiment pre-determined by the growth conditions. One of the growth parameters is of course the ratio of Mg to Mn concentration, $y = x_{Mg}/x_{Mn}$. Each of the Mg ions is connected to the Mn ion in the cluster through a nitrogen ion. From numerical calculations it was estimated that pairing energy values are negative for up to four Mg ions, which are NNs of the Mn ion in the cationic sublattice, which indicates the tendency of magnesium to form $\{Mn,Mg_n\}$ complexes with manganese. Taking into account the statistical distribution of n, which means that for a given y different complexes can coexist, we have obtained, without introducing any adjustable parameter, the correspondence between experimental results and theoretical predictions both on the number of bonded Mg ions and on the length of the Mn—N bond (for nitrogen simultaneously bonded with magnesium) as a function of the y parameter. Shortening of the Mn—N bond is the largest for the (Mn,N) pair closest to the Mg dopant. This is mostly due to the large charge transfer in the $\{Mn,Mg_n\}$ complexes, which leads to the occurrence of Coulombic attraction between ionized Mg acceptors and the Mn donor.

The procedure of theoretical calculations was as follows. In the first step, the possibility of formation of $\{Mn,Mg\}$ pairs at the gallium (0001) surface of wz-GaN was examined. The pairing energy obtained in this case is positive (233 meV), which suggests that no such pairs are formed on

[XXVIII] V. Dierolf, I. Ferguson, and J. M. Zavada, *Rare Earth and Transition Metal Doping of Semiconductor Materials: Synthesis, Magnetic Properties and Room Temperature Spintronics* (Elsevier Science, 2016).

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the surface. A similar result was obtained earlier for the $\{Fe,Mg\}$ pair in the work **H4**. In the next step, the possibility of formation of $\{Mn,Mg_n\}$ (n = 1-5) complexes in bulk wz-GaN was studied. In order to do this, it was necessary to determine the preferred places where Mn and/or Mg ions build up in wz-GaN. It has been assumed that the possible positions are: substitutional for Ga, X_{Ga}, interstitial with tetrahedral environment, $X_{i\text{-}T}$, and interstitial with octahedral environment, $X_{i\text{-}O}$. The smallest formation energies were obtained for the cases of Mn_{Ga}, Mg_{Ga}, and the $\{Mn_{Ga},Mg_{Ga}\}$ pair. Therefore, in the further part of the study it was assumed that both Mn and Mg take substitutional positions in the Ga sublattice.

In the wurtzite and zinc blende structures of GaN, manganese in the substitutional position (Mn_{Ga}) has 12 gallium NNs divided into two groups, 6 in the plane and 6 out of the plane [we refer here to the {111} and (0001) planes in the zb and wz structures, respectively]. In wz-GaN the experimental value for the lattice constants ratio $c/a = 1.627$ [XXIX] is very close to the ideal value of $c/a = 1.633$, which means that the NNs that are out of the plane are less than 0.3% closer to a given Ga ion than the NNs that are lying in the plane. Thus, the two above mentioned groups of NN ions are almost equivalent in distance to Mn_{Ga}, i.e. the structural anisotropy is very small. According to our results for the simplest case of one Mg ion being NN of Mn, there are three structurally inequivalent $\{Mn,Mg\}$ configurations, which are, however, close to each other in energy.

For larger $\{Mn,Mg_n\}$ (n = 2-5) complexes, several configurations have to be considered. However, there are two limitations that help to identify low-energy structures. First, two Mg ions "repel" each other if they are placed as NNs because they have a positive pairing energy in GaN **[H4]**. Secondly, larger $\{Mn,Mg_n\}$ complexes form from smaller $\{Mn,Mg_{n-1}\}$ one by adding one Mg ion at a time. These two limitations reduce the number of different configurations to consider in order to obtain the most stable cases. According to my calculations, the largest $\{Mn,Mg_n\}$ complex that can be formed is that containing up to about four Mg ions. For n = 5 the pairing energy is negative but small in absolute value (~95 meV), which means that the fifth Mg ion will be "loosely bound" to the $\{Mn,Mg_4\}$ complex.

In terms of magnetic properties, the magnetic moment (calculated per unit cell) is, in each case, almost entirely localized on the Mn ion (with a small contribution of the 4 nitrogen ions, which are NNs of the Mn ion). Without magnesium doping, the charge state of the Mn ion is 3+ and changes to 4+ and 5+ in the presence of one and two Mg ions, respectively. A further increase in the number of Mg ions in the complex does not have such a clear impact on the charge status of the Mn ion. Finally, it should be mentioned that the Mn ion has the same charge state when Mg_{Ga} is NN of Mn_{Ga} as when Mg_{Ga} is at some distance from Mn_{Ga}. However, this is not the case of (Ga,Mn)N:2Mg, for which two ions of Mg as NNs of Mn induce a charge state of 5+, but if they are at a certain distance from Mn, they induce a charge state of 4+. This result is an additional confirmation of the existence of $\{Mn,Mg_2\}$ complexes in the experiment, for which Mn ions with a charge state of 5+ are observed.

In the paper **H8,** I extended the previously presented results for (Ga,Mn)N:Mg **[H5]** by the important issue of (Ga,Mn)N doping with silicon, that is with a donor impurity. The question arose whether also in this case we are dealing with the formation of clusters of the $\{Mn,Si_n\}$ type, and if so, where the formation of these clusters takes place: on the surface or in bulk. As for the position of Mn ions in GaN, there seems to be a consensus, in both experiment[XXVII] and theory **[H5]**, that these ions mostly occupy substitutional positions replacing Ga ions. However, there is a discrepancy in the presented values of the charge state of the Mn^{k+} ion, which, according to the experimental literature[XXVII], may be: 3+, 2+, and even 0. The numerical calculations show that manganese replacing

[XXIX] H. Morkoç, *Handbook of Nitride Semiconductors and Devices: Materials Properties, Physics and Growth* (Wiley, 2009).

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in GaN a trivalent atom supplies an ion with spin $S = 2$ and a charge state of 3+. However, both the experiment[XXX] and the theory show that the incorporation of Si_{Ga} ions (donors) causes some of the Mn ions to have a high spin $S = 5/2$ and a charge state of 2+.

An important contribution of my calculations was to determine the mutual location of Mn_{Ga} and Si_{Ga} ions both on the surface and in the bulk of wz-GaN. In the first step of the calculations, the possibility of formation of $\{Mn,Si\}$ pairs in which Mn and Si ions are at neighboring substitutional positions on the gallium (0001) surface of wz-GaN was examined. The obtained pairing energy is negative (-77 meV), thus suggesting the probability of formation of such pairs on the growth surface. A similar trend was obtained earlier for the $\{Fe,Si\}$ pair **[H4]**. On the other hand, the $\{Si,Si\}$ pairs do not want to form on the surface, because for them the pairing energy is positive (399 meV). The same is also true for the $\{Mn,Mn\}$ pairs that, according to our earlier results **[H3]**, are unlikely to form on the gallium surface of wz-GaN during crystal growth. In addition, the obtained results may also suggest that codoping with silicon may contribute to a more homogeneous distribution of Mn ions in the gallium sublattice, i.e. it may prevent the formation of atomic aggregates.

In the next step, the formation energies for different Si ion positions in bulk wz-GaN were compared. These energies for $Si_{i\text{-}T}$, $Si_{i\text{-}O}$, and Si_{Ga} are 11.21 eV, 10.27 eV, and 0.9 eV, respectively (the last value was taken from the work published by Bogusławski and Bernholc[XXXI]). For comparison, the energies for the same positions of the Mn ion, i.e. $Mn_{i\text{-}T}$, $Mn_{i\text{-}O}$, and Mn_{Ga}, are 6.73 eV, 6.59 eV, and 1.87 eV, respectively **[H5]**. These results suggest that both ions will prefer substitutional positions in the cationic sublattice, which is also consistent with experimental observations[XXX]. The calculations also show that the codoping of (Ga,Mn)N with silicon leads to the formation of $\{Mn,Si\}$ pairs, not only on the Ga surface, but also in bulk. This is suggested by a negative pairing energy of -2.27 eV. The $\{Mn,Si_n\}$ complexes with two Si ions are also possible, but less likely. As a result of codoping of (Ga,Mn)N with silicon, the Mn ion can occur in two different charge states, 2+ and 3+, if the Si to Mn concentration ratio is less than one. However, it should be noted that the charge state of Mn does not depend on the mutual position of the Mn_{Ga} and Si_{Ga} ions in the cationic sublattice. The magnetic moment of the Mn ion, which at the absence of Si is $4\mu_B$, increases to $5\mu_B$ in the presence of Si.

Comparing cases of (Ga,Mn)N codoped with Mg or Si, we can say that in both cases there is a clear tendency for the formation of Mg or Si complexes with Mn ions, with the difference that $\{Mn,Mg_n\}$ complexes may contain up to four Mg ions, while $\{Mn,Si_n\}$ complexes up to two Si ions only. The $\{Mn,Si\}$ and $\{Mn,Mg_2\}$ complexes have the largest absolute pairing energy. On the other hand, the pairing energy for $\{Mn,Si_2\}$ is in absolute value about twice smaller than the pairing energy for $\{Mn,Mg_2\}$, i.e. -0.31 eV and -0.58 eV, respectively.

2.4.5. Mn doping of the $Al_xGa_{1-x}N$ ternary compound (article **H7**)

Apart from the studies on transition metal doping of binary semiconductors (articles **H3**, **H4**, **H5**, **H6**, and **H8**), the case of manganese doping of the ternary aluminum gallium nitride compound ($Al_xGa_{1-x}N$) was also analyzed. This compound is an important semiconductor from the optoelectronics point of view, because it is used to produce diodes working in the range from blue light to ultraviolet. It is also used for the production of e.g. blue semiconductor lasers and high electron mobility transistors

[XXX] A. Bonanni, M. Sawicki, T. Devillers, W. Stefanowicz, B. Faina, T. Li, T. E. Winkler, D. Sztenkiel, A. Navarro-Quezada, M. Rovezzi, R. Jakieła, A. Grois, M. Wegscheider, W. Jantsch, J. Suffczyński, F. D'Acapito, A. Meingast, G. Kothleitner, and T. Dietl, Phys. Rev. B **84**, 35206 (2011).

[XXXI] P. Bogusławski and J. Bernholc, Phys. Rev. B **56**, 9496 (1997).

(HEMTs)[XXXII]. Incorporation of manganese is extending the rich list of applications of $Al_xGa_{1-x}N$ compound with magnetic properties.

As first, the distribution of Al and Ga ions in the $Al_xGa_{1-x}N$ compound was examined for few Al concentrations, i.e. for different x-values. This makes it possible to determine whether the compound is separated locally into sub-areas where GaN or AlN dominates, or whether the distribution of Al and Ga ions is random in the cationic sublattice. For this purpose, for intermediate concentrations of Al ions, $x = 0.25$, 0.5, and 0.75, we compare the total energies for several structures with a random distribution of Al and Ga ions in the cationic sublattice. This means that for a given concentration of Al ions – i.e. for a given number of Al ions in the supercell – we randomly change the position of Al and Ga ions and for such configurations we compare their total energies. Calculations have shown that regardless of the concentration of Al ions, the total energies of these configurations do not differ by more than 50 meV. Based on this result, we conclude that regardless of the aluminum concentration in the $Al_xGa_{1-x}N$ compound, the Al and Ga ions have random positions in the cationic sublattice.

The second step was to examine the formation energies of the Mn dopant at substitutional or interstitial positions in $Al_xGa_{1-x}N$. In the substitutional case, it is assumed that for $x \leq 0.5$ Mn ions replace mainly Ga ion sites, while for $x > 0.5$ Mn ions replace Al ion positions. We obtained that Mn_{Ga} ($x \leq 0.5$) has a constant formation energy of 3.5 eV, while for Mn_{Al} ($x > 0.5$) we obtained a sudden increase in formation energy to 5.5 eV. This result indicates that, according to the values of formation energies, Mn tends to replace Ga rather than Al ions in $Al_xGa_{1-x}N$. This result could also suggest that high quality AlN:Mn epitaxy is difficult. On the other hand, the energetics on the growth surface is not taken into account, which plays a key role during epitaxial growth **[H3]** **[H4]**. In the case of tetrahedral, $Mn_{i\text{-}T}$, and octahedral, $Mn_{i\text{-}O}$, interstitial positions, we always find formation energies higher than those for Mn_s ions. After structural relaxation, $Mn_{i\text{-}O}$ remains at the point of insertion in the center between the NNs that form the octahedron, with a linearly increasing, from 6.5 eV ($x = 0$) to 9.25 eV ($x = 1$), formation energy with concentration x. On the other hand, the $Mn_{i\text{-}T}$ ion is unstable in the tetrahedral position and tends to move towards the octahedral interstitial position; its formation energy is 8.25 eV, regardless of x. The results of the numerical calculations show that it is preferable the incorporation of the Mn dopant into $Al_xGa_{1-x}N$ on a substitutional position, what is consistent with experimental results. In addition, an important experimental result is the fact that Mn ions are evenly distributed in $Al_xGa_{1-x}N$, without aggregation of Mn ions or formation of precipitates, for aluminum concentrations up to 82% **[H7]**.

[XXXII] R. Quay, *Gallium Nitride Electronics* (Springer Berlin Heidelberg, 2010).

3. Other scientific and research achievements

3.1. Bulk structures

During my PhD studies at the Institute of Physics of the Polish Academy of Sciences, under the supervision of Prof. Piotr Bogusławski, I dealt with computer modeling of physical phenomena based on DFT. The PhD thesis was entitled "Structural, electronic, and optical properties of $GaAs_{1-x}N_x$ and $Ga_{1-x}B_xAs$ alloys: first principles calculations" (defended in 2003) and concerned the alloys GaAsN and GaBAs, i.e. materials with new and interesting physical properties, which, on the other hand, are important materials in applications in optoelectronics. In my doctoral thesis, I conducted an analysis of the crystal and electronic structure of these alloys on the basis of first principles calculations. It has been shown that the difference between the values of the energy gaps of the GaAsN and GaBAs alloys results mainly from the difference in the influence of atomic relaxation on the wave function from the bottom of the conduction band and from differences in the atomic structure of nitrogen and boron. It was also shown that both, the size of the so-called bowing, i.e. the non-linear dependence of the energy gap as a function of composition x and the fact that the bowing is stronger for GaAsN than for GaBAs, are in good accordance with experimental data. The analysis of the electronic structure in the reciprocal space showed that both, bowing and non-linear dependence of the GaAsN and GaBAs energy gaps on pressure, result from the interaction of the bottom of the conduction band with side minima in the Brillouin zone. The work also explained the nature of the experimentally observed additional optical transition E_+, which occurs in addition to the basic transition E_0 from the top of the valence band to the bottom of the conduction band. The results of research on these alloys have been published in several articles [12–14].

After obtaining my PhD degree in 2003, I was employed at the Institute of Physics of the Polish Academy of Sciences as an assistant professor. In cooperation with Prof. P. Bogusławski, I continued my research on bulk materials and the results were presented in three articles [15–17] published in the years 2003-2006. In particular, these were calculations from first principles concerning structural and elastic properties of ZnTe, MnTe, and ZnMnTe semiconductors in the structures of zinc blende, NiAs, and wurtzite, where we studied the relative stability of phases for the full range of concentrations x in $Mn_{1-x}Zn_xTe$ [15,16].

3.2. Zero-, one-, and two-dimensional structures

At the beginning of 2004, I went for a postdoctoral internship to Prof. B. Yakobson's group from Rice University in Houston. During this internship, I initially studied the structure and electronic properties of nanowires of transition metal disilicides using first principles calculations. The results of these calculations have confirmed experimental observations, which show that nanowires, e.g. of YSi_2, are structurally stable and conductive (articles [18,19]). The next topic that I dealt with at Rice University was the identification and investigation of the properties of all-boron molecular allotropes. The boron atom has a very similar electronic structure (atomic orbitals) to that of carbon, so one could expect that, like carbon, boron can form atomic clusters like fullerenes or to occur in the form of nanotubes. One of my greatest achievements was to identify and describe the whole family of such structures (articles [20–22]). One of the described clusters, B_{80}, is currently known in scientific literature as the "boron buckyball" because of the structural (e.g. the same symmetry) and electronic similarities (e.g. the same number of electrons and a similar size of HOMO-LUMO gap) to its carbon counterpart C_{60}.

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The existence of boron fullerenes and 2D crystals with a structure similar to that suggested by computer simulations carried out by me has been experimentally[XXXIII] confirmed quite recently.

In 2008, I started cooperation with Prof. C. J. Tymczak from Texas Southern University in Houston, which lasted for three consecutive years. Professor Tymczak specializes in quantum chemistry and in his group I continued work on low-dimensional all-boron systems and also structures based on boron, such as small flat atomic clusters of $B_{12}H_6$ type (borozene – benzene equivalent, article [23]). Flat (or quasi-flat) atomic clusters are quite rare in nature and their structure is often associated with electron delocalization, a phenomenon that in chemistry is referred to as aromaticity. The degree of cluster or molecule aromaticity is often an indicator of the stability of the structure, and thus the possibility of its synthesis. The study of such small clusters is also important from the point of view of the type of bonds that boron creates in clusters, which in turn allows for the identification of stable "building blocks" of larger clusters and even bulk structures. After returning from the postdoctoral internship, I continued a cooperation with Professor Tymczak, which resulted in two further publications (articles [24,25]). In the article [24], we examined the stability of flat clusters $B_{12}H_n$ and $B_{12}F_n$ in comparison with their three-dimensional equivalents (of a shape similar to a regular icosahedron). In this study, we obtained that neutral $B_{12}H_n$ and $B_{12}F_n$ clusters will be energetically more stable as flat structures only for $n \leq 4$. Special cases are the $B_{12}H_6$ and $B_{12}F_6$ structures, which as positive double ionized clusters have a "chance" to take a flat form.

In the article [25] symmetry of previously obtained theoretically B_{80} fullerene, which for some time was the subject of controversy[XXXIV], was examined in detail. It was not entirely clear whether the symmetry of this cluster is I_h or T_h, because the differences in the positions of atoms, in the case of one or the other symmetry, were very small. In addition, differences in total energies for both configurations were minimal and indicated a slight preference for the T_h symmetry. The question arose whether the cluster is really distorted to a smaller symmetry, or whether it is an artifact of the applied calculation methods. In particular, in an earlier article [20], we used two exchange and correlation functionals: PBE and hybrid PBE0. The conducted research shows that the symmetry of the studied atomic cluster depends to a large extent on the level of accuracy, at which the electron correlation in this system is described. In the article [25], the hybrid B3LYP functional was compared with the computationally expensive MP2 method. The B3LYP functional is often used to perform quantum-mechanical calculations for atomic clusters (especially those composed of light atoms). In the paper [25], we showed that the use of the popular B3LYP functional did not bring any new quality over what was obtained in the article [20] with the use of other functionals (e.g. PBE and PBE0). Only taking into account the correlation at the level of MP2 method gave as a result a homogeneous charge distribution around the entire cluster, and thus, showed that the cluster assumes the highest possible symmetry. This result was also of great importance in predicting the structure and electronic properties of boron nanotubes, which are structures related to fullerenes. Experimental data do not give a clear answer on the structure of boron nanotubes, but they suggest that they are metallic[XXXV], which is not clear from the theoretical point of view. Numerical calculations based on PBE predict that, depending on the diameter, boron nanotubes are either semiconductor or metallic. The greater the distortion (buckling) of the nanotubes, the greater the value of the energy gap is. In the paper [25], we showed, on the example of finite length nanotubes, that the distortions of atoms in nanotubes are also the result of insufficient description of correlation effects, i.e. they are a computational artifact. Thus, we have

[XXXIII] T. Kondo, Sci. Technol. Adv. Mater. **18**, 780 (2017).

[XXXIV] G. Gopakumar, M.T. Nguyen, and A. Ceulemans, Chem. Phys. Lett. **450**, 175 (2008).

[XXXV] V. Bezugly, J. Kunstmann, B. Grundkötter-Stock, T. Frauenheim, T. Niehaus, and G. Cuniberti, ACS Nano **5**, 4997 (2011).

shown that regardless of their diameter, all boron nanotubes are metallic, as opposed to carbon nanotubes, whose electron properties depend on their chirality.

As in the paper [25], in paper [26] the results concerning the predictive power of exemplary exchange and correlation functionals in comparison to the quantum Monte Carlo method in terms of predicting the relative energetic stability of small Si-C atomic clusters are presented. Our research suggests that, unlike periodic systems where DFT methods generally perform well, comparing the energy of small, covalently bonded Si_nC_m atomic clusters calculated using DFT methods does not always give correct results for the relative stability of those clusters. In paper [26], we compared results obtained using local LDA (in this case SVWN), semi-local GGA (in this case PBE), and hybrid HF/DFT (in this case B3LYP) functionals to diffusion Monte Carlo (DMC) simulations. It turns out that only the LDA functional gives similar trends in relative stability of isomers as the DMC approach, and this may suggest that it is qualitatively more accurate in predicting the properties of small Si_nC_m clusters than the GGA functional or a hybrid one. Thus, we have shown that, in principle, the simplest approximation of the exchange and correlation functional, in which both the exchange and correlation are local in character, gives the best result in this particular case, which can only result from the self-cancelation of errors resulting from the approximate form of the exchange and correlation functionals.

Two-dimensional crystals were the subject of a recently completed NCN project (2013/11/B/ST3/04273) led me. The work on these structures began by exploring the possibility of graphene doping with boron. We were interested in determining the limit concentration at which the honeycomb structure would be preserved despite a heavy doping of graphene with boron atoms (article [27]). An interesting fact turned out to be that C-B alloys retain a structure similar to the honeycomb structure even for the half-to-half mixing of carbon and boron. Moreover, it has been established that boron atoms modify the electron properties of graphene and the half-metal system becomes metallic. In the next paper (article [28]), we dealt with the analysis of flat atomic clusters, which can be considered as fragments of 2D crystals composed of boron atoms arranged in a hexagonal lattice (or colloquially referred to as triangular lattice). In these structures, not all the lattice nodes are filled with boron atoms, giving a potentially large margin for maneuver when it comes to the arrangement of atoms. The paper [28] presents the results of investigations of two 2D boron crystals marked as α and β, which differ in surface density. We have shown that fragments of denser α crystal are usually more energetically stable than fragments of the β crystal, but they have a greater tendency to structural distortions and sometimes differ significantly from the initial flat structure. On the other hand, fragments of the β crystal, of lower density, retain their flat character even for a relatively small number of atoms in the cluster (above about 30 boron atoms). Such analysis is important from the point of view of the production of free-standing fragments of these crystals, i.e. those that can be separated from the growth substrate (at present 2D boron crystals are obtained on metallic surfaces[XXXVI]).

Presently I am also working on two-dimensional boron crystals. As in the case of bulk boron, which occurs in many allotropic forms – of which the most known and used are α and β with 12 and 108 atoms in the elementary unit cell, respectively – boron in 2D is also characterized by a large number of allotropic forms. In one of the most recent papers published by myself and collaborators [29], an apparent discrepancy between experimental observations[XXXVI] and theoretical predictions has been explained. The metallic surface on which 2D boron crystals are obtained in the experiment enforces only some forms of these crystals. This is due to the transfer of electric charge from the surface to the crystal as well as the stress caused by the surface itself. Both factors stabilize

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[XXXVI] G. P. Campbell, A. J. Mannix, J. D. Emery, T.-L. Lee, N.P. Guisinger, M.C. Hersam, and M.J. Bedzyk, Nano Lett. **18**, 2816 (2018).

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only certain allotropic forms of 2D crystals. In the paper [29], we also developed a model that allows to predict the most stable 2D boron structures. The model assumes that the total energy (or binding energy) of a given 2D boron structure can be presented as a sum of energy inputs coming from atoms with a given coordination number. These contributions (energies per atom) can be determined from independent first principles calculations for structures, where each boron atom has only a given number of NNs (coordination number). In this way, for any arrangement of boron atoms on a hexagonal lattice, it is possible to find an approximate value of the binding energy, and thus, to separate only those structures that have the highest binding energies. Despite a very simplified character of the proposed model its accuracy in comparison with first principles calculations was about +95 meV/atom, i.e. the underestimation of the binding energy for the tested structures did not exceed 95 meV/atom (which is about 1% of the binding energy value). What is more, the model also proved to be useful for predicting the binding energy for negatively charged 2D structures. This makes it possible to estimate the effect of the metallic surface on the stability of 2D boron crystals.

4. Scientific activities

4.1. Publications after completion of PhD

I am the author or co-author of **28** articles (after obtaining the PhD degree) published in journals on the Philadelphia's list (JCR) with the Impact Factor (IF) in the year of publication of **69.97**. Table 1 presents a comparison of articles written after obtaining the PhD degree together with bibliographical data. The full list of publications can be found in Section 6.

Table 1: Publications after PhD (habilitation thesis publications are indicated in bold).

My position on the list of authors	Journal title	Year of publication	IF in the year of publication	Citations (WoS, 11.01.2019)	MNiSW score (2016)
4	Physical Review B	2018	3.813*	0	35
3	FlatChem	2018	-	0	-
1	Computational Condensed Matter	2017	-	1	-
1	Scientific Reports	2017	4.122	1	40
1	**Solid State Communications**	**2017**	**1.549**	**0**	**30**
1	Journal of Magnetism and Magnetic Materials	2016	2.630	1	30
1	Acta Physica Polonica A	2016	0.469	0	15
4	**Physical Review B**	**2015**	**3.718**	**0**	**35**
1	**Physical Review B**	**2015**	**3.718**	**9**	**35**
1	Acta Physica Polonica A	2014	0.530	1	15
3	**Scientific Reports**	**2012**	**2.927**	**17**	**40**
1	Nanoscale Research Letters	2012	2.524	6	35
1	Acta Physica Polonica A	2011	0.444	1	15
2	**Physical Review B**	**2011**	**3.691**	**14**	**35**
1	**Physical Review B**	**2011**	**3.691**	**26**	**35**
1	Chemical Physics Letters	2010	2.282	31	30
1	Nanoscale Research Letters	2009	2.894	34	35
1	**Physical Review B**	**2008**	**3.322**	**4**	**35**
3	Physical Review B	2008	3.322	45	35
1	Nanoscale Research Letters	2008	1.731	54	35
3	Solid State Phenomena	2008	0.493**	7	10
1	**Physica B**	**2007**	**0.751**	**2**	**20**
2	Physical Review B	2007	3.172	40	35
1	Physical Review Letters	2007	6.944	301	45
1	Physical Review B	2007	3.172	6	35
2	Physical Review Letters	2006	7.072	8	45
1	Acta Physica Polonica A	2004	0.495	24	15
5	Acta Physica Polonica A	2004	0.495	9	15
		Total	69.971	642	785

*last known IF2017 **last known IF2005

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The total number of publications is **30** articles (listed in Section 6), **1** academic textbook (two editions [30,31]), and **2** chapters in scientific books [10,19].

4.2. Hirsch index and total number of citations

My publications according to the Web of Science database have been cited **731 times** (712 without self-citations), and my Hirsch index (iH) is **iH = 12** (as of January 11, 2019).

4.3. Team building and management skills

4.3.1. Supervision and co-supervision of students

- I am a co-supervisor of a PhD student – Tomasz Tarkowski, MA – at the Institute of Theoretical Physics of the Faculty of Physics of the University of Warsaw; the title of doctoral thesis is: "Crystal structure prediction of nanowires using evolutionary computations". Mr. Tarkowski's doctoral dissertation was opened on December 19, 2018. The work concerns a meta-heuristic way of predicting the crystal structure of nanowires using evolutionary algorithms combined with first principles calculations.
- I am a supervisor of a bachelor's student at the Faculty of Physics of the University of Warsaw – Mr. Filip Kowalski; the title of bachelor's thesis is: "Recombination and mutation operators in predicting the crystal structure of nanowires using evolutionary algorithms". Mr. Kowalski's bachelor's thesis was defended on July 27, 2018. The thesis presents mutation and recombination operators potentially useful for prediction of the crystal structure of nanowires using evolutionary algorithms.

4.3.2. Scientific project management

- Currently I am the principal investigator of the project entitled "*Predicting the structure of boron and boron-related nanowires by using first-principles based evolutionary search algorithms*". Duration period: from 27-07-2017 to 26-07-2020, Funding agency: NCN, OPUS, PLN 671 580. The results of the project were presented at 6 conference presentations (including all collaborators involved in the project).
- I was the principal investigator of the project entitled "*The structure and properties of two-dimensional boron and boron-related compounds*". Duration period: from 23-09-2014 to 22-03-2018, Funding agency: NCN, OPUS, PLN 542 880. The results of the project were presented in 7 publications in scientific journals **[H8]** [28,29,32–35] and in 10 conference presentations (including all collaborators involved in the project).

4.4. Participation in research and development projects

The most important post-doctoral projects in which the habilitation student has taken or is currently participating are:

- Predicting the structure of boron and boron-related nanowires by using first-principles based evolutionary search algorithms, 2016/23/B/ST3/03575, duration period: 07.2017-07.2020, funding agency: NCN, OPUS, manager: **dr N. Gonzalez Szwacki**, budget: PLN 671 580, tasks:
  - administration of the project; performing first principles calculations and preparation of the results; promotion of the results and exchange of knowledge.

- The structure and properties of two-dimensional boron and boron-related compounds, 2013/11/B/ST3/04273, duration period: 09.2014-03.2018, funding agency: NCN, OPUS, principal investigator: **dr N. Gonzalez Szwacki**, budget: PLN 542 880, tasks:
  - administration of the project; performing first principles calculations and preparation of the results; promotion of the results and exchange of knowledge.
- Theory of graphene derived layer structures coupled to metals and insulators, 2013/10/M/ST3/00793, start date (duration): 05.2014 (36 months), funding agency: NCN, HARMONIA, principal investigator: prof. dr hab. Jacek A. Majewski, budget: PLN 749 876, role in the project: researcher, tasks:
  - performing first principles calculations and preparation of the results.
- Magnetic spectroscopy and spectro-microscopy of the low-dimansional magnetic structures, 2011/03/D/ST3/02654, starting date (duration): 08.2012 (48 months), funding agency: NCN, SONATA, principal investigator: dr Iwona Kowalik, budget: PLN 937 200, role in the project: researcher, tasks:
  - performing first principles calculations and preparation of the results.
- Functionalisation of Diluted Magnetic Semiconductors, FunDMS, duration period: 01.2009-12.2013, funding agency: FP7-IDEAS-ERC, principal investigator: prof. dr hab. Tomasz Dietl, budget: EUR 2 440 000, role in the project: researcher, tasks:
  - performing first principles calculations to study the prosperities of GaN doped with transition metals and preparation of the results.

4.5. Reviews

4.5.1. Reviews of articles for scientific journals

- ACS Nano (IF: 13.709, 2011)
- Acta Physica Polonica A (IF: 0.857, 2008 – two reviews, 2010, 2014, 2016)
- Computer Physics Communications (IF: 3.936, 2010)
- Chemical Society Reviews (IF: 40.182, 2011)
- Computational Materials Science (IF: 2.292, 2017)
- Computer Science, Automation, Measurements in Economy and Environmental Protection (2015)
- Journal of Alloys and Compounds (IF: 3.779, 2017)
- Journal of Applied Physics (IF: 2.176, 2018)
- Journal of Magnetism and Magnetic Materials (IF: 3.046, 2014)
- Journal of Material Chemistry (IF: 6.626, 2011)
- Journal of Superconductivity and Novel Magnetism (IF: 1.142, 2012)
- Nanoscale Research Letters (IF: 3.125, 2010)
- Physica B: Condensed Matter (IF: 1.453, 2013)
- Physical Chemistry Chemical Physics (IF: 3.906, 2011, 2013 – two reviews, 2015)
- Scientific Reports (IF: 4.122, 2014)
- Solid State Communications (IF: 1.549, 2013, 2017, three reviews each year of: 2014, 2015, and 2016)
- The European Physical Journal B (IF: 1.465, 2012 – two reviews)

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4.5.2. Reviews of research projects

- Katholieke Universiteit Leuven, Belgium (research programme: Research Council of K. U. Leuven, 2011)
- National Science Centre (research programme: OPUS, 2012)

4.6. Teaching and popularization activities

Perhaps my most important didactic activity was writing (in cooperation with Prof. T. Szwacka) a textbook on crystallography entitled "*Basic Elements of Crystallography*". The first edition of the textbook was published in 2010, and the second edition in 2016. The textbook is intended for students who study solid state physics, materials engineering, nanotechnology, and related subjects.

In the summer semesters of 2005 and 2006 I gave several lectures in place of Prof. B. Yakobson at Rice University for the course entitled "*Physical Properties of Solids*". In addition, I conducted practical classes for the following courses:

- Quantum mechanics II with elements of theoretical chemistry and molecular spectroscopy (University of Warsaw, summer semester of 2015),
- Modeling of Nanostructures and Materials (University of Warsaw, winter semester of 2014),
- Solid State Physics (Cardinal Stefan Wyszyński University, winter semester of 2001 and summer semester of 2002),
- Electronic Structure of Solids (School of Exact Sciences – Polish Academy of Sciences, summer semester of 2001),
- Numerical Methods (School of Exact Sciences – Polish Academy of Sciences, winter semester of 1999 and summer semester of 2000).

I am also engaged in popularization of physics. I co-organized or helped during hands-on experiments at two editions of the Science Picnic (in 2016 and 2018) and the Science Festival (in 2002 and 2013). For the fourth year in a row, I also prepare school students for the mock exams in physics within the International Baccalaureate Diploma Programme.

5. Participation in conferences (posters, oral presentations, and invited talks)

- N. Gonzalez Szwacki, "*Structure and properties of 2D borocarbonitrides as predicted by first-principles calculations*", Materials Science & Technology 2018, Columbus, USA, October 14–18, 2018. (invited talk)
- T. Woźniak, A. Siklitskaya, M. Birowska, and N. Gonzalez Szwacki, "*Stability and properties of nitrogen-rich carbon nitride 1D nanostructures*", European Materials Research Society Fall Meeting, (E-MRS), Warsaw, Poland, September 17-20, 2018. (poster)
- N. Gonzalez Szwacki, I. A. Kowalik, M. A. Niño, F. J. Luque, and D. Arvanitis, "*Room temperature antiferromagnetism in FeN and Fe_2N nanocrystals on GaN*", European Materials Research Society Fall Meeting, (E-MRS), Warsaw, Poland, September 17-20, 2018. (oral presentation)
- N. Gonzalez Szwacki, "*Boron, the most multi-structure material ever: a first principles study*", The 4th EMN Meeting on Computation and Theory, San Sebastian, Spain, September 3-7, 2018. (invited talk)
- N. Gonzalez Szwacki, "*Theoretical studies using DFT-based methods of one-, two-, and three-dimensional systems*", XII Symposium of the Institute of Theoretical Physics, Faculty of Physics, University of Warsaw, Poland, December 8-9, 2017. (oral presentation)
- N. Gonzalez Szwacki, "*Boron - the most multi-structure material known to date*", 44th Congress of Polish Physicists, Wrocław University of Science and Technology, Wrocław, Poland, 10-15 September 2017. (poster).
- N. Gonzalez Szwacki, "*Borophene in its multiple forms: structure, properties, and possible applications*", Materials Science & Technology 2017, Pitchburg, Pennsylvania, USA, October 8-12, 2017. (invited talk)
- T. Tarkowski, A. Dudek, and N. Gonzalez Szwacki, "*Will borophene outperform graphene?*", 9th International conference on Advanced Nanomaterials, University of Aveiro, Portugal, July 19-21, 2017. (oral presentation)
- T. Tarkowski, J. A. Majewski, and N. Gonzalez Szwacki "*Energy Decomposition Analysis of 2D Boron Crystals from First Principles*", Materials Science & Technology 2016, Salt Lake City, Utah, USA, October 23-27, 2016. (oral presentation)
- N. Gonzalez Szwacki "*Effects of Static Charging on the Stability and Properties of Layered Boron Crystals*", Materials Science & Technology 2015, Columbus, USA, October 4-8, 2015. (oral presentation)
- N. Gonzalez Szwacki, T. Tarkowski, and J. A. Majewski, "*2D Boron Allotropes: Structure, Properties, and Computational Hints Towards an Experimental Realization on a Large Scale*", 44th "Jaszowiec" International School and Conference on the Physics of Semiconductors, Wisła, Poland, June 20th - 25th, 2015. (poster)
- N. Gonzalez Szwacki and J. A. Majewski, "*Structural, Electronic, and Magnetic Properties of the Two-Dimensional Graphene-BN System Studied by First-Principles Simulations*", 44th "Jaszowiec" International School and Conference on the Physics of Semiconductors, Wisła, Poland, June 20th - 25th, 2015. (poster)
- N. Gonzalez Szwacki and J. A. Majewski, "*2D $B_xC_yN_z$ layers as predicted by the cluster-expansion approach*", 43rd "Jaszowiec" International School and Conference on the Physics of Semiconductors, Wisła, Poland, June 7th - 12th, 2014. (poster)
- N. Gonzalez Szwacki and J. A. Majewski, "*2D $B_xC_yN_z$ layers as predicted by the cluster-expansion approach*", (E-MRS), Warsaw, Poland, September 15-18, 2014. (oral presentation)

- N. Gonzalez Szwacki, J. A. Majewski, and T. Dietl, "*Pressure induced room temperature ferromagnetism of (Ga,Mn)As: a first-principle investigation*", 42nd "Jaszowiec" International School and Conference on the Physics of Semiconductors, Wisła, Poland, June 22nd - 27th, 2013. (poster)
- N. Gonzalez Szwacki and J. A. Majewski, "*Structural and electronic properties of the silicon carbide allotropes as predicted by exact exchange calculations*", European Materials Research Society Fall Meeting, (E-MRS), Warsaw, Poland, September 17-21, 2012. (oral presentation)
- N. Gonzalez Szwacki and J. A. Majewski, "*Ab initio sdudies of* $Co_2FeAl_{1-x}Si_x$ *Heusler alloys*", 6th Joint European Magnetic Symposia, (JEMS 2012), Parma, Italy, September 9 -14, 2012. (poster)
- N. Gonzalez Szwacki, J. A. Majewski, and T. Dietl, "*Properties of TM pairs at the surface of GaN and GaN:Si,Mg*", 31st International Conference on the Physics of Semiconductors, (ICPS 2012), Zürich, Switzerland, July 29 – August 3, 2012. (poster)
- N. Gonzalez Szwacki, J. A. Majewski, and T. Dietl, "*The influence of Si and Mg codoping on the magnetism of (Ga,Mn)N and (Ga,Fe)N*", 41st "Jaszowiec" International School and Conference on the Physics of Semiconductors, Krynica, Poland, June 8th - July 15th, 2012. (oral presentation)
- N. Gonzalez Szwacki and J. A. Majewski, "*Structural and electronic properties of the silicon carbide allotropes as predicted by exact exchange calculations*", 41st "Jaszowiec" International School and Conference on the Physics of Semiconductors, Krynica, Poland, June 8th - July 15th, 2012. (poster)
- N. Gonzalez Szwacki, J. A. Majewski, and T. Dietl, "*Properties of transition metal pairs at the surface of GaN and GaN:Si,Mg*", Joint Polish-Japanese Workshop, Spintronics-from New Materials to Applications, Warsaw, Poland, November 15-18, 2011. (oral presentation)
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- N. Gonzalez Szwacki and Boris I. Yakobson, "*Energy Decomposition Analysis of Metal Silicide Nanowires*", Spring Meeting of the Materials Research Society, San Francisco, California, USA, April 17-21, 2006. (poster)
- N. Gonzalez Szwacki, "*Determination of electronic, crystal, and magnetic properties of Ga(As,N) and (Mn,Zn)Te compounds by ab initio calculations*", invited seminar presented at the University of Modena and Reggio Emilia, Modena, Italy, November 21, 2004. (oral presentation)
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- N. Gonzalez Szwacki, E. Przeździecka, E. Dynowska, and P. Bogusławski, "*Elastic properties and structural stability of MnTe, ZnTe, ZnO, and ZnMnTe*", XXXIII International School on the Physics of Semiconducting Compounds "Jaszowiec 2004", Jaszowiec, Poland, May 28 - June 4, 2004. (poster)
- N. Gonzalez Szwacki and P. Bogusławski, "*Segregation of dopants and defects in AlAs/GaAs heterostructures*", XXXII International School on the Physics of Semiconducting Compounds "Jaszowiec 2003", Jaszowiec, Poland, May 30 - June 6, 2003. (poster)
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