Załącznik nr 3
Appendix No. 3

SUMMARY OF PROFESSIONAL ACCOMPLISHMENTS

Application of microwave spectroscopy to studies of effective mass carriers in selected two-dimensional and three–dimensional crystalline structures.

Agnieszka Wołoś, Ph.D.
University of Warsaw, Faculty of Physics

1. Personal data.

Agnieszka Wołoś

2. Education and scientific degrees.

2005: **Ph.D. degree (with distinction)** obtained at the Faculty of Physics, University of Warsaw.

1999–2004: Ph.D. studies at the Faculty of Physics, University of Warsaw, field: Solid State Physics, title of the Ph.D. Thesis: *Properties of Mn impurity in the selected group III-V semiconductors*, supervisor: Prof. Maria Kamińska.

1999: **M.Sc. degree** obtained at the Faculty of Physics, University of Warsaw.

1994–1999: M.Sc. studies at the Faculty of Physics, University of Warsaw, field: Solid State Physics, title of master's thesis: *Plasmon-phonon coupling in Raman scattering in gallium nitride*, supervisor: Prof. Maria Kamińska.

3. Professional positions.

2011–30.09.2016: adjunct (research, part-time) at the Faculty of Physics, University of Warsaw. From 01.10.2016 adjunct – research and teaching, full-time position.

2007–30.09.2016: adjunct in the Institute of Physics Polish Academy of Sciences.

2005–2006: post–doctoral position at the Johannes Kepler Universität Linz, Institut für Halbleiter- und Festkörperphysik, Linz, Austria.

2004–2005: engineer–technical position at the Faculty of Physics, University of Warsaw.

4. The scientific achievement, in accordance with Article 16, Paragraph 2 of the Act of 14 March 2003 concerning the scientific degrees and titles (Journal of Laws No. 65, item 595, as amended).

4.1. Title of the scientific achievement.

Application of microwave spectroscopy to studies of effective mass carriers in selected two–dimensional and three-dimensional crystalline structures.

4.2. List of publications constituting the scientific achievement.

A1. A. Wolos, A. Drabinska, *Application of microwave spectroscopy to studies of electron transport properties*, J. Cryst. Growth **401**, 314 (2014).

A2. A. Wołoś, W. Jantsch, K. Dybko, Z. Wilamowski, C. Skierbiszewski, *Plasmon-cyclotron resonance in two-dimensional electron gas confined at the GaN/Al$_x$Ga$_{1-x}$N interface*, Phys. Rev. B **76**, 045301 (2007).

A3. A. Wołoś, Z. Wilamowski, C. Skierbiszewski, A. Drabinska, B. Łucznik, I. Grzegory, and S. Porowski, *Electron spin resonance and Rashba field in GaN-based materials*, Physica B **406**, 2548 (2011).

A4. A. Wołoś, Z. Wilamowski, M. Piersa, W. Strupiński, B. Łucznik, I. Grzegory, and S. Porowski, *Properties of metal-insulator transition and electron spin relaxation in GaN:Si*, Phys. Rev. B **83**, 165206 (2011).

A5. A. Wolos, S. Szyszko, A. Drabinska, M. Kaminska, S. G. Strzelecka, A. Hruban, A. Materna, M. Piersa, *Landau-Level Spectroscopy of Relativistic Fermions with Low Fermi Velocity in the* Bi_2Te_3 *Three-Dimensional Topological Insulator,* Phys. Rev, Lett. **109**, 247604 (2012).

A6. A. Wolos, S. Szyszko, A. Drabinska, M. Kaminska, S. G. Strzelecka, A. Hruban, A. Materna, M. Piersa, J. Borysiuk, K. Sobczak, M. Konczykowski, *g-factors of conduction electrons and holes in* Bi_2Se_3 *three-dimensional topological insulator,* Phys. Rev B **93**, 155114 (2016).

4.3. Description of the scientific goal of the selected series of publications and achieved results with description of their possible use.

4.3.1. Introduction.

The scientific goal of the series of publications is to discuss application of microwave spectroscopy technique to studies of effective mass carriers in selected two- and three-dimensional crystalline materials.

Many research laboratories in the world are equipped with electron paramagnetic resonance (EPR) spectrometers dedicated to investigations of paramagnetic defects in crystalline materials. This is the most common application of these spectrometers, but not the only one. It turns out that conducting samples placed in a microwave cavity of the spectrometer can show also features related to their magnetoconductivity. Presence of electric component of microwave field in the spot where the investigated sample is placed is a condition necessary to observe these types of signals. This may require the use of specially designed resonators. It turns out, however, that in a popular TE_{102} rectangular cavity dedicated to investigations of magnetic dipole transitions, and thus such requiring absorption of a quantum of magnetic part of microwave electromagnetic field, the electric field component of microwaves occurs spontaneously in the center of the cavity due to disruption of the perfect distribution of microwave field by the presence of the sample and quartz elements of the cryostat. In such resonators, signals related to magnetoconductivity are observed, which may constitute an undesired background or, in opposite, interesting objects for studies. In the selected series of publications, signals of that type are discussed, that were detected using EPR spectrometers in materials: $GaN/Al_xGa_{1-x}N$ heterostructures, graphene and topological insulators. The effects that can be investigated by this method are cyclotron resonance, Shubnikov–de Haas oscillations (SdH), quantum effects of weak localization and antilocalization, where the two last are non–resonant signals. These effects are related to electric transport and so with delocalized electron or hole states in a crystal– the effective mass carriers. The overview of these results has been published in the work **A1**. The works **A2** and **A3** contain detailed discussion of the plasmon–cyclotron resonance and Shubnikov–de Haas oscillations detected in $GaN/Al_xGa_{1-x}N$ heterostructures. The work **A5** contains discussion of the cyclotron resonance and Shubnikov–de Haas oscillations detected in topological insulator Bi_2Te_3. The work **A1** contains additionally the analysis of the weak localization and antilocalization effect in $GaN/Al_xGa_{1-x}N$.

More classical examples of application of microwave spectroscopy, to studies of spin resonances of effective mass carriers, are discussed in works **A4** and **A6**. Spin resonance of electrons localized on silicon donors in GaN is discussed in the work **A4**, whereas the work

A6 discusses spin resonance of conducting electrons and holes in Bi_2Se_3 topological insulator.

The presented results were obtained using commercial EPR spectrometers housed in different scientific institutions (Johannes Kepler Universität, JKU, Linz, Austria; Institute of Physics Polish Academy of Sciences, IF PAS; University of Warsaw, UW). All the spectrometers worked in the X–band (f = 9.5 GHz), with TE_{102} resonance cavity and were equipped with the continuous–flow Oxford cryostat allowing work in temperatures between 5 and 300 K. Magnetic field was swept up to 1.7 T (spectrometers at UW and JKU), additionally spectrometer at UW allowed changing the direction of the magnetic field. Due to the use of the lock–in technique and magnetic field modulation, the registered signals are proportional to the first derivative of the power lost in the microwave cavity.

4.3.2. Plasmon–cyclotron resonance and Shubnikov–de Haas oscillations in GaN/$Al_xGa_{1-x}N$ heterostructures.

In the work **A1**, I discussed observation of effects related to electric transport using EPR spectrometer. Previous literature reports from the 90s and later concerning observation of cyclotron resonances (or plasmon–cyclotron resonances) and Shubnikov–de Haas oscillations include research on: $Al_xGa_{1-x}As/GaAs$ heterostructures [1], $Ga_{1-x}Al_xSb/InAs$ [2], $In_xGa_{1-x}As/InP$ [3,4], $GaAs/In_xGa_{1-x}As/Al_yGa_{1-y}As$ quantum wells [5], $GaN/Al_xGa_{1-x}N$ heterostructures [**A1,A2,A3**], Si/SiGe quantum wells [6,7] and bulk silicon [8,9], $Mg_xZn_{1-x}O/ZnO$ heterostructures [10], graphene [11,12,13,14], topological insulator Bi_2Te_3 [**A5**]. This is fairly substantial list of materials whose common feature is high structural quality and related to high mobility of the electron (or hole) gas, but publications concerning particular material are single, which indicates still low prevalence and use of this convenient and non–contact measurement method.

Cyclotron resonance and Shubnikov–de Haas oscillations occur very often on the same spectrum; wherein the Shubnikov–de Haas signal appears for magnetic fields above the cyclotron resonance. While the cyclotron resonance is a strong electric–dipole resonant transition, exceeding fairly in amplitude typical spin (magnetic–dipole) resonances in semiconductors, the Shubnikov–de Haas oscillations are much weaker non–resonant signals (independent on microwave frequency), requiring setting larger modulation amplitude and microwave power. Care, however, should be taken in order to avoid excessive heating.

It is not entirely clear, weather magnetooscillations observed using EPR spectrometers, in particular these equipped with the TE_{102} cavity, are indeed Shubnikov–de Haas effect due to magnetoconductivity, or de Haas–van Alphen effect due to changes in magnetic susceptibility. In TE_{102} cavity, the sample is placed at the maximum of the microwave magnetic field, which is simultaneously the node of the electric field, which would rather point at de Haas–van Alphen effect. This ideal microwave field distribution can be, however, strongly disturbed, in particular for highly conducting samples. Simultaneous observation of cyclotron or magnetoplasma resonance signals proves that there exists non–zero microwave electric field at the place where the sample is set. Moreover, the microwave electric field must have a component in sample plane (in the the two–dimensional case), in order to accelerate electrons in their cyclotron motion. The detection technique has been discussed in Ref. [3]; the main conclusion from this work can be summarized as follows: if only the impedance of the waveguide properly matches the impedance of the cavity, microwave power reflected from the cavity (the quantity directly measured by electronic unit of the spectrometer) is proportional to the longitudinal conductivity of the sample. It is thus commonly accepted to call the magnetooscillations Shubnikov–de Haas effect.

In the work **A2,** I discussed plasmon–cyclotron resonance in GaN/$Al_xGa_{1-x}N$ heterostructures, which has been observed and described here for the first time. Two–dimensional electron gas in GaN/$Al_xGa_{1-x}N$ heterostructures occurs spontaneously at the interface due to difference in polarization of GaN and $Al_xGa_{1-x}N$. Typical electron concentrations are of the order of 10^{12}–10^{13} cm^{-2}, which causes that the plasma frequency in mm-sized samples is close to (slightly higher) than the frequency of the popular X-band (9.5 GHz). It allows to observe edge magnetoplasma resonance (related to the lower branch of the coupled plasmon–cyclotron resonance). In the work **A2**, I described the resonance position and the shape of the signal basing on the theory of size–dependent plasmon–cyclotron coupling [15] and the Drude model of momentum relaxation [16]. This model was tested as a function of sample size (plasma frequency of the two–dimensional electron gas depends on the lateral size of a sample) and concentration and mobility of the carriers. The measurement of plasmon–cyclotron coupling is a contactless method for determination of electric parameters of the two-dimensional gas, concentration and mobility. This method is particularly useful when we deal with samples having conducting substrate or conducting buffer layers, that make it impossible to determine electric parameters of the two–dimensional electron gas using classical methods of electric transport. The discussed method was applied to determine electric parameters of first GaN/$Al_xGa_{1-x}N$ samples obtained in the laboratories of the Institute of Physics PAS. It turned out later, that similar conditions for observation of the plasmon–cyclotron resonance can be fulfilled in $Mg_xZn_{1-x}O$/ZnO [10] and Si-based materials [9].

4.3.3. Rashba field in GaN–based materials.

The work **A3** contains further examples of plasmon–cyclotron resonances in GaN/$Al_xGa_{1-x}N$ heterostructures, but its main purpose is to discuss problem of Rashba field in materials based on gallium nitride. I performed systematic studies of both heterostructures and bulk samples using EPR technique, and basing on that I discussed conclusions on the Rashba field in these materials.

Spin splitting of conduction band in bulk GaN and in GaN–based heterostructures has recently attracted considerable interest due to expected long electron spin coherence times in these materials [17,18]. Long spin relaxation times are highly desired for spintronic applications to maintain information about spin while spin current travels through a semiconductor. Spin relaxation times depend crucially on the magnitude of spin–orbit interactions, being the longer the weaker is the coupling [19]. Gallium nitride is expected to show weak spin–orbit coupling as both Ga and particularly N are rather light elements. Low–temperature spin lifetimes in bulk GaN have been demonstrated to range up to about 20 ns, despite high dislocation density [17]. On the other hand GaN is a polar semiconductor showing effects of spontaneous and piezoelectric polarization resulting in strong electric fields. Any electric field acts on the spin of a moving electron due to spin–orbit coupling mechanism. Thus it cannot be excluded that the polarization–induced electric fields can enhance the magnitude of conduction band spin splitting. In GaN/$Al_xGa_{1-x}N$ heterostructures grown along GaN **c**–axis, with polarization–induced two–dimensional electron gas at the interface, the spin–orbit Rashba effect has been demonstrated to be surprisingly large [20]. The Rashba spin–orbit coupling parameter α has been shown to be equal between 5.5–10 ×

10^{-11} eVcm with the resulting low–temperature spin scattering times being at the order of a ps [21,22,23,24]. For comparison, in modulation doped Si/SiGe quantum wells it is two orders of magnitude weaker, α equals to 5×10^{-13} eVcm, with spin scattering times ranging up to a microsecond [7].

The dependence of the Rashba parameter on the electric field in a heterostructure is controversial and widely discussed for many years. In general there are two contributions to the value of parameter α, $\alpha = \alpha_{BIA} + \alpha_{SIA}$: bulk inversion asymmetry contribution, BIA, and structure induced asymmetry, SIA. De Andrada e Silva et al. have shown that Rashba parameter can be derived from **k·p** model [25]; in a uniform electric field, E, and neglecting interface effects, the structure–related α_{SIA} parameter equals to $\alpha_{SIA} = \alpha_0 E$. The proportionality parameter, α_0, is a constant characteristic for the particular semiconductor, dependent on its energy gap and spin–orbit splitting of the valence band. Pikus and Pikus [26] have noticed that the electric field, E, should be replaced by its average value for more general cases. This, however, gives $\alpha_{SIA} = 0$ if the effective mass approximation would have been valid throughout the entire well, including the barriers. Following the problem, Pfeffer and Zawadzki [27] have calculated spin splitting for $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ heterostructure, including in their **k·p** Hamiltonian effects of potential discontinuity at the interface. They have concluded that the average electric field in the heterostructure contributes only to 3% of the total SIA spin splitting, while the dominant contribution comes from the interface. The latter depends only on valence bands offsets and on the envelope function at the interface. It is now agreed that effects of interface play an important role in spin–orbit splitting of the Rashba type in asymmetric heterostructures.

Results presented in the work **A3** concern bulk GaN and $GaN/Al_xGa_{1-x}N$ heterostructures. In $GaN/Al_xGa_{1-x}N$ heterostructures, a strong plasmon–cyclotron resonance is observed that has been earlier described in the work **A2**. The resonance confirms presence of high–mobility two–dimensional electron gas in investigated samples. In samples having lower mobility, a zero-field signal is observed that originates from weak antilocalization (**A1**). This effect was systematically investigated using classical methods of electric transport [21,22,23,24]. Thanks to the observation of the so called antilocalization minimum, it is possible to determine value of the Rashba parameter, therefore evaluate the magnitude of the Rashba splitting. As I have already mentioned, α determined in these experiments equals between $5.5 - 10 \times 10^{-11}$ eVcm, which for typical concentrations of the two-dimensional electron gas of the order of 2×10^{-12} cm^{-3} corresponds to the Rashba field of the order of B_R = 40 000 G and spin splitting at zero magnetic field (the Rashba splitting) about 0.4 meV. The energy of the zero–field spin splitting falls far beyond the resonance condition for the X–band. This explains the fact that the spin resonance signals has never been observed in microwave experiments.

It is worth to mention, that effects of weak localization and antilocalization that has been typically investigated using electric transport method, may be also observed using microwave spectroscopy technique. In the work **A1,** I showed an example of such a signal detected for a $GaN/Al_xGa_{1-x}N$ heterostructure. The signal is visible for low-mobility samples, for which plasmon–cyclotron resonance is not observed due to too high width of the resonance line. The mobility of the electron gas in sample discussed in the work **A1** is 3 000 $cm^2/(Vs)$, that corresponds to elastic scattering rate $1/\tau = 3 \times 10^{12}$ s^{-1}. Comparing it to the experimentally set X-band microwave frequency, $f = 9.5 \times 10^9$ s^{-1}, assures us that the experiment fulfills criteria for a DC measurement. Low electron mobility places simultaneously the sample in a diffusive transport limit (for the magnetic field range that is interesting for us) which is most suitable for studies of quantum interference phenomena. The signal discussed in the work **A1** originates from two contributions, spin relaxation due to spin–orbit coupling and dephasing. The interplay of the two contributions results in negative magnetoconductivity at lower magnetic field (weak antilocalization) which turns to positive magnetoconductivity (weak localization) at higher magnetic field; characteristic weak antilocalization minimum appears. What is interesting, the antilocalization minimum occurs at about 2 mT almost independent of Al composition, conductivity, or electrostatic gating, indicating that spin–orbit coupling very weakly depends on these parameters as well [21,22,23,24]. The analysis of the signal registered using EPR spectrometer, based on models proposed in Ref. [21,28], allowed (the work **A1**) to determine parameters describing spin–orbit interaction, among others the Rashba parameter $\alpha = 6.8 \times 10^{-11}$ eVcm, in good agreement with literature data. The application of microwave spectroscopy to studies of quantum interference phenomena may constitute a contactless option for the classical electric transport measurements. This method has been for the first time described in the work **A1** and Ref. 11, then applied wider to studies of graphene [12,13,14].

Electron spin resonance is a natural way to study spin–orbit interactions. Rashba type of spin splitting has been systematically studied by EPR in Si/SiGe quantum wells [7,29,30]. It turned out that the Rashba field, which is of the order of a few hundred Gauss in these materials, influences both the g-factor and the linewidth of the resonance signal. In the work **A3,** I employed the formalism applied earlier successfully to Si/SiGe quantum wells to analysis of spin resonance of electrons localized on Si donors in GaN, and to new resonance signal which was attributed to electrons localized in accumulation layer on the GaN surface. I obtained in that way evaluation of the upper limit for the Rashba field, which cannot exceed 400 G. The upper limit for the α_{BIA} is thus of the order of 4×10^{-13} eVcm, which is in contrast to GaN/$Al_xGa_{1-x}N$ heterostructures, for which the Rashba field is of the order of 40 000 G. It reminds the situation discussed in Ref. [27] for the case of $In_{0.53}Ga_{0.47}As/In_{0.52}Al_{0.48}As$ where α_{SIA} strongly dominated over α_{BIA} and the main contribution originated from the properties of the interface. On the other hand, Stefanowicz *et al.* [3131] described recently the effect of weak antilocalization, with clearly visible characteristic minimum at 2 mT, detected for thin GaN:Si layer above the critical concentration for metal-insulator transition. The analysis of this signal allowed to determine the Rashba parameter $\alpha_{BIA} = 4.5 \times 10^{-13}$ eVcm, comparable to the values determined earlier for GaN/$Al_xGa_{1-x}N$ heterostructures, which would mean that the α_{BIA} dominates over α_{SIA} in that case, and the Rashba field is significantly different for electrons localized on donors and for these above metal–insulator transition.

4.3.4. Metal–insulator transition and electron spin relaxation in GaN:Si

In the work **A4** I applied the technique of microwave spectroscopy, supplemented with Hall effect measurements, to studies of the properties of gallium nitride doped with Si at the metal–insulator transition. Gallium nitride is a wide–bandgap semiconductor finding application in blue and UV optoelectronics [32] and high power electronics [33]. It is also being investigated for use in spintronics due to its weak spin–orbit interaction and expected long electron spin coherence [17]. There is also considerable interest in doping GaN with transition metals in order to combine magnetic and semiconducting properties, likewise for use in spintronic devices [34]. Silicon as a popular shallow donor in GaN serves as a source of effective–mass electrons, allowing us to obtain *n*–type material. As both electron transport and spin coherence in *n*–type semiconductors are practically determined by the properties of donor bands, in the work **A4** I present systematic studies of the Si doping–induced bands in GaN.

The critical Si concentration for the metal–insulator transition in GaN has already been theoretically estimated, however the exact nature of the transition has not been investigated experimentally. In the work **A4**, I present a classical analysis of electron transport close to the metal–insulator transition, evaluating activation energies of the resistivity and the Hall concentration. Their dependence on the doping allowed to determine the critical concentration for the metal–insulator transition. The electron transport data were analyzed within Shklovskii's formalizm, which distinguishes the following three activation energies: E_1, to the GaN conduction band; E_2, the activation energy to double-occupied donor states; and E_3, the hopping activation energy. I showed that while increasing the doping concentration, Si–related bands are formed below the bottom of the GaN conduction band. The D_0 band of single–occupied Si donor sites is centered 27 meV below the bottom of the GaN conduction band, and the D_- band of double–occupied Si states is centered at 2.7 meV below the bottom of the GaN conduction band. The metal–insulator transition occurs at the critical concentration of uncompensated donors equal to about 1.6×10^{18} cm^{-3}.

Electron spin resonance provides a deeper understanding of the nature of the metal–insulator transition in GaN:Si. The measurements show that the electronic magnetic moment is damped when approaching the critical concentration for the metal–insulator transition, which is consistent with filling nonmagnetic double–occupied donor states (D_-). Simultaneously, the electron lifetime in the single–occupied donor band (D_0) becomes shortened due to excitations to the D_- band. In metallic samples being well beyond the metal–insulator transition, all the conducting electrons occupy nonmagnetic electronic states.

A number of theoretical approaches have been developed for the metal–insulator transition [35]. In the work **A4**, I showed that the real metal–insulator transition in GaN:Si shows many features characteristic of the Mott–Hubbard type of the metal–insulator transition: the existence of a paramagnetic D_0 band of single–occupied donor sites and a nonmagnetic D_- band of double–occupied electronic states. The metal–insulator transition corresponds to simultaneously closing the gap between the two subbands and a vanishing of the activation energy for electron transport in the GaN conduction band. This occurs at the critical concentration of uncompensated Si donors equal to about 1.6×10^{18} cm^{-3}.

The studies described in the work **A4,** and the two previous works **A3** and **A2**, were supported by the MNiSW grant *Two-dimensional electron gas in GaN/AlGaN heterostructures for spintronic applications,* POL-POSTDOC III, PBZ/MNiSW/07/2006/39, 25.06.2007-24.12.2010, where I was a principal investigator.

4.3.5. Landau level spectroscopy in three-dimensional topological insulator Bi_2Te_3.

In the year 2012, I started works on topological insulators, to which the next work, **A5**, is related. Topological insulators are recently discovered new kind of condensed matter phase, which is fascinating for fundamental physics research, and carrying possibility for application in spintronics and quantum information processing. Quantum memory and quantum computation in media of topologically ordered states may potentially be fault tolerant. This is why topological insulators are really in core of worldwide research nowadays, and similarly to graphene they are on covers' and are subject of many articles in leading scientific journals. These materials are quite different from ordered classical phases which we have gotten used to for many years, and which were related, according to Landau's description, to spontaneous breaking of symmetry (e.g. crystals break continues translational and rotational symmetries of vacuum, magnets break time-reversal and rotational symmetries in spin space). A class of topological insulators is an example of ordered phase beyond symmetry breaking, possessing a new kind of organization on quantum level, which leads typically to system response in units of fundamental constants. In some configurations topological insulators carry also hope for observations of new fascinating phenomena, like exotic elementary particles - expected presence of Majorana Fermions [36,37].

Topological properties of the family of bismuth compound crystals, i.e., Bi_2Te_3 [38], Bi_2Se_3 [39], and Bi_2Te_2Se [40], have been confirmed in spectacular angle resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy and spectroscopy [41] experiments. Other experiments, including electric transport or optical measurements, are difficult to perform because of high bulk conductance due to native crystal lattice defects. In order to suppress the contribution of the conducting bulk states and expose the surface states in the experiment, technological works are undertaken dedicated to the growth of crystals with lower bulk carrier concentration (using compensating doping, growth in non–stoichiometric conditions, growth of crystals with mixed composition), illumination with electrons creating compensating defects, or formation of very thin structures which is often combined with electrostatic gating. I applied an alternative approach in the work **A5**, where I used the microwave spectroscopy technique to studies of cyclotron resonance of the surface states in Bi_2Te_3 topological insulator. The microwave penetration depth in the applied experimental conditions ranges from 4 to 40 μm. The technique can actually probe independently both bulk and surface properties, being partly insensitive to the detrimental influence of the metallic bulk conductivity. Similar approach has been recently applied to study surface states in Bi_2Se_3 topological insulator, where 2D cyclotron resonance has been revealed thanks to the application of the microwave cavity transmission technique [42].

In the work **A5** I discussed cyclotron resonance of the surface states in topological insulator Bi_2Te_3. I showed that the nature of the states responsible for the resonance is unambiguously topological with linear dispersion, which is in turn connected to the root dependence of the Landau levels energy on the magnetic field (in the case of classic materials this dependence is linear). The most striking result in this work is low value of the Fermi velocity determined from the experiment, which is two orders of magnitude lower than the results obtained from ARPES. The discrepancy may be explained by the fact that the measured samples were exposed to ambient conditions, whereas ARPES experiment is conducted in ultra-high vacuum. Contamination of the surface with atmospheric gases may influence surface states. The problem requires undoubtedly further studies, in particular theoretical. Besides the cyclotron resonance due to surface states I detected signals from the Shubnikov–de Haas oscillations, which allowed to estimate Fermi level position in investigated samples. It turns out that occupation of topological surface states depends not only from the position of the Fermi level in bulk (e. g. from the crystal doping), but also strongly from the band bending at the surface.

4.3.6. g-factors of conduction electrons and holes in topological insulator Bi_2Se_3.

Continuing works on topological insulators in the work **A6**, I discussed spin resonance due to conducting electrons and holes in the bulk of Bi_2Se_3. The investigations showed that electrons in the conduction band and holes in the valence band both have spin 1/2. The effective g-factors for conduction electrons are equal to 27.3 ± 0.15 for magnetic field parallel to the **c** axis and 19.48 ± 0.07 for magnetic field perpendicular to the **c** axis, whereas for conduction holes 29.90 ± 0.09 for magnetic field parallel and 18.96 ± 0.04 for magnetic field perpendicular to the **c** axis, respectively. Nonparabolicity effects were not observed in the investigated low carrier concentration range, below 8×10^{17} cm^{-3}. Large g-factors, higher by an order of magnitude than the free electron value, are due to strong spin-orbit interactions in Bi_2Se_3. The striking similarity of the spin resonances due to conduction electrons and holes confirms the peculiar symmetry between the conduction and valence bands of Bi_2Se_3, both having similar effective masses and spin character.

Bi_2Se_3 band structure was studied in the 1970's, even before the discovery of topological properties of this material, in a series of papers by Köhler based on Shubnikov–de Haas experiments [43,44,45]. It has been shown that the Fermi surface of the Bi_2Se_3 conduction band at low carrier concentration can be assumed to be an ellipsoid of revolution around the trigonal **c** axis, with the center of the Fermi surface at the Γ point. Only a small amount of trigonal warping (for rotation around the **c** axis) has been reported, and nonparabolicity effects become significant only for an electron concentration beyond 10^{19} cm^{-3}. The anisotropic g-factor has been estimated as 32 ± 3 for **B** || **c** and 23 ± 3 for **B** ⊥ **c**. The results of the Shubnikov–de Haas and the spin resonance measurements reported in **A6** are consistent, confirming that in both experiments conduction electrons were present in Bi_2Se_3. A slight discrepancy in the g-factor values can be accounted for a lower precision of the Shubnikov–de Haas method.

More recently, Zhang et al. and Liu et al. [46,47] presented a model Hamiltonian for Bi_2Se_3 and other three–dimensional topological insulators from this family. Starting from the atomic orbitals of Bi and Se, they included the layered quintuple structure of Bi_2Se_3, the effect of the bond creation, the crystal field splitting, and finally the influence of the spin-orbit coupling, eventually leading to the band inversion (around the Γ point) necessary to obtain the topological insulator phase. The conduction band thus has a selenium like character, while the valence band's character is bismuth like. What is important in the context of spin resonance experiment, both the conduction and valence bands are doubly spin degenerate, having spin 1/2, consistent with electron spin resonance data presented in **A6**.

Orlita et al. [48] applied the Dirac–type Hamiltonian of Zhang and Liu to explain magneto–optic results (Landau–level spectroscopy) for bulk states in Bi_2Se_3. They showed that the multiparameter Hamiltonian can be simplified to yield a unique property in a magnetic field, namely spin splitting equal to twice the cyclotron energy, consistent with their magneto–optic studies and earlier experimental reports [45,49]. Consequently, the conduction and valence bands of Bi_2Se_3 are both parabolic and characterized by approximately the same effective mass and effective g–factor. The simplified Hamiltonian contains only two parameters: the band–gap energy 2Δ and velocity parameter v_D. The common effective mass for electrons and holes then equals $m_e \approx m_h \approx 2\Delta/v_D$ which is twice the Dirac mass $m_D = \Delta/v_D$. The effective g–factor for electrons and holes can be also expressed in terms of the Dirac mass $g_e \approx g_h \approx 2m_0/m_D$. The Dirac mass, experimentally determined in Ref. **Błąd! Nie zdefiniowano zakładki.** as $m_D = (0.080 \pm 0.005)m_0$ yields an effective g-factor ge ≈ gh ≈ 25. This is in very good agreement with the results of **A6**, where the average g–factor for electrons is 23.4, and 24.4 for holes. The main effect on the g-factor thus comes from the spin–orbit interaction that increases it by an order of magnitude from the free electron value. The resonance signals show some anisotropy, which must be attributed to the influence of remote bands.

The studies of topological insulators were supported by the NCN grant: *3D topological insulators as a new quantum phase of matter – growth and investigations of* Bi_2Te_3*,* Bi_2Se_3 *and* Bi_2Te_2Se – NCN,OPUS2, where I was a principal investigator.

5. Description of other scientific achievements.

5.1. Research before obtaining PhD degree.

I have started my scientific activity during my PhD studies which I did under the supervision of Prof. Maria Kamińska in Solid State Physics Division in the Faculty of Physics of the University of Warsaw in the years 1999–2004. I have initially dealt with investigations of the influence of Be doping on the properties of non-stoichiometric GaAs grown at low temperatures (~ 200 °C). Thanks to the non–equilibrium growth conditions, high concentration of antisite defect are observed in this material, which are interesting physical object and at the same time open possibility for application in electronics. Works that I carried out were part of the European project FP IV DUO (*Devices for ultrafast optoelectronics made from low–temperature grown GaAs and related materials, DUO* EU FP IV, 2000-2002), conducted together with the university centers in Chambery, Stockholm and Vilnius, and the domestic project *Low temperature grown GaAs (LT–GaAs) – material for optoelectronics and spintronics*, KBN, No 7 T08A 04920, 2001/2002, where I was a principal investigator. The aim of these projects was to determine usefulness of GaAs:Be for application in ultrafast optoelectronics. My task was to investigate structural properties of this material using transmission electron microscopy and to study antisite arsenic defects using optical absorption and electron paramagnetic resonance. The results of the studies allowed to model relaxation processes of photo-excited carriers. The works published from these studies are [50,51,52].

In the next part of my PhD studies, I dealt with properties of manganese impurity in semiconductors from III–V group, which became the topic of my PhD thesis. These works were carried out in the frame of the European project FP V FENIKS (*Ferromagnetic semiconductors and novel magnetic semiconductor heterostructures for improved knowledge on spintronics* - FENIKS, FP V, No 115/E-343/SPUB-M/5.PR UE/D, 2001-2005) and the domestic project *Spin electronics – new materials for electronics* PBZ-KBN-044/P03/2001, 16.09.2002-30.06.2005. These projects were conducted with many partners both from Warsaw (Institute of High Pressure Physics Unipress, Institute of Electronic Materials Technology) and abroad and located in a new field of science and electronics–spintronics. Spintronics, in contrast to classic electronics, sets itself a task to utilize both the electron charge and its spin. The requirements has been defined that must be fulfilled in order to realize spintronic ideas. One of the requirements is fabrication of a semiconductor having ferromagnetic properties at room temperature. Current record of Curie temperature belongs to GaAs doped with Mn (~ 180 K). Using analogy of this material to other semiconductors from the III-V family, the idea has raised of high–temperature ferromagnetism in wide band gap semiconductors doped with Mn–this motivated me to undertake the research on this group of materials. GaN:Mn was in a particular center of interest. Samples for these studies were obtained thanks to the cooperation with Institute of High Pressure Physics Unipress, Warsaw. I used many experimental techniques in my works: EPR, optical absorption, electric transport measurements, magnetooptic measurements, transmission electron microscopy. I performed most of the studies in Warsaw, some of the works in foreign centers. I performed magnetooptic measurements and some of the electron paramagnetic resonance measurements in Grenoble High Magnetic Field Laboratory, magnetotransport measurement in in Australian National University. The most important results from the PhD are: (i) determination of the charge and spin states of Mn in GaN, (ii) determination of the location of Mn acceptor level in the GaN band gap, (iii) description of new absorption bands and magnetoabsorption spectra basing on the crystal field model, (iv) quantitative study of hopping over Mn centers and determination of the effective radius of the neutral Mn acceptor in GaAs, GaP, and GaN, (v) determination of the s–d exchange constant in GaN, (vi) quantitative study of the influence of Mn doping on the formation of antisite defect in GaAs. The most important publications from this field are: [53,54,55,56,57,58,59]. My investigations were supported by the PhD project: *Properties of Mn impurity in GaN*, KBN 1P03B00826, 17.03.2004-16.02.2005.

5.2. Research after obtaining PhD degree.

After my doctorate, I obtained two–year post–doctoral position in Institut für Halbleiter- und Festkörperphysik at the Johannes Kepler University, Linz, Austria, years 2005–2006. I worked in group of Prof. Wolfgang Jantsch who specializes in the technique of electron paramagnetic resonance. I took part in studies of Fe impurity in GaN, with close cooperation with the team of crystal growth technologists. This project, similar to studies of Mn in GaN, was motivated by search for high–temperature ferromagnetic semiconductor. My task was to perform electron paramagnetic resonance measurements in order to determine charge state of Fe, concentration of paramagnetic centers, and to monitor formation of precipitates of iron compounds. The investigations allowed to determine solubility limit of Fe in GaN. Ferromagnetic interactions were not observed in samples with homogenously distributed Fe, below solubility limit. Ferromagnetic properties were instead observed in highly doped crystals with clearly non–uniform distribution of dopants. The nature of this ferromagnetism and its theoretical description are still the subject of discussion in the international scientific environment [60, 61].

During my stay in Linz, I became interested in possibility of application of microwave spectroscopy technique to studies of conduction electrons in two–dimensional structures. I investigated plasmon–cyclotron resonances in two–dimensional electron gas occurring spontaneously at the GaN/$Al_xGa_{1-x}N$ interface. This technique, for a certain class of materials, may constitute a contactless option to electric transport measurement, providing information about concentration and mobility of conducting electrons. The details of application of microwave spectroscopy to studies of electric transport properties are described in Chapter 4.

After my return to the country in a year 2007, I started working in the Institute of Physics Polish Academy of Sciences in the Microwave Spectroscopy division guided by deceased now prof. Zbysław Wilamowski. In a year 2011, I established again the cooperation with prof. Maria Kamińska, due to running new electron paramagnetic resonance laboratory at the Faculty of Physics of the University of Warsaw. I participated in setting up, installing and till now I custody of the EPR apparatus and deal with its development. Besides topics described in detail in Chapter 4, I took part in studies of graphene and materials used in organic photovoltaics. The application of microwave spectroscopy technique to studies of graphene allowed to investigate the effect of quantum antilocalization and/or localization, to connect coherence lengths with growth conditions of graphene sheets and their functionalization [11,12,13,14]. The studies were performed in the frame of the projects *Contactless investigations of quantum effects in graphene,* NCN, OPUS4, 25.07.2013-24.07.2015 and *Graphene, generative flow sensors*, NCBiR, GRAF-TECH, 01.12.2012-30.11.2015, in cooperation with the Institute of Electronic Materials Technology, Warsaw.

The studies on organic photovoltaics were carried out in cooperation with Electrotechnical Institute, Division of Electrotechnology and Materials Science, Wrocław. Combining two techniques, microwave spectroscopy and time resolved photoluminescence, we carry out studies of charge transfer processes in active layers of heterojunctions built of a mixture of polymers and fullerenes [62,63]. The works were supported by the grant *New polymer photovoltaic cells: studies of the influence of the polymer structure, cell architecture, and doping on the efficiency of polymer solar cells based on polyazomethine and polytiophene,* NCBiR, 01.12.2012 – 30.11.2015.

Topological insulators are important group of materials that I study recently. They are solid quantum phases with metallic surface states which have Dirac band structure and are immune to disorder. The charged defects of the crystal lattice, however, pull the Fermi level into the bulk bands, making it difficult to measure surface charge transport. In the framework of cooperation with the Institute of Electronic Materials Technology in Warsaw, Ecole Polytechnique, Palaiseau, France and The City College of New York, USA we demonstrated that irradiation with swift (~ 2.5 MeV energy) electron beams allows to compensate these defects, bring the Fermi level back into the bulk gap and reach the charge neutrality point. Controlling the beam fluence, we tuned bulk conductivity from p- to n-type, crossing the Dirac point and back, while preserving the Dirac energy dispersion. The charge neutrality point conductance has a two–dimensional character on the order of ten conductance quanta and reveals, both in Bi_2Te_3 and Bi_2Se_3, the presence of only two quantum channels corresponding to two topological surfaces [64]. Other achievements related to studies of topological insulators were described in works **A5** and **A6**.

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