Abstract of the habilitation thesis

2.1 First name and surname: Pavlo Aleshkevych

2.2 Diplomas and scientific degrees

Master of Science

Donetsk National University (Ukraine), Physics Faculty, 1997. The Master thesis entitled: „*The defect structure and optical properties of ZnS-CdS compounds*" with obtaining specialization: solid state physics

Doctor of Physics

Institute of Physics, Polish Academy of Sciences in Warsaw, 2003. PhD thesis entitled „*Spin waves in manganites films with an excess of manganese*", performed under supervision of Prof. dr hab. Ritta Szymczak.

2.3 Information of employment in scientific institutions

May 2003 – April 2012: assistant professor. Institute of Physics, Polish Academy of Sciences.
May 2012 – Present time: chief specialist. Institute of Physics, Polish Academy of Sciences.

2.4 Indication of the achievement of habilitation procedure

The academic achievement resulting from Article 16 Paragraph 2 of the of Act 14th March, 2003 about the academic degrees and academic title submitted for habilitation procedure is one-subjected series of publications consisting of 9 papers. The theme of this series is ***„Studies of inhomogeneity and defects in single crystals by means of microwave spectroscopy methods".***

The common denominator of chosen works is the use of various microwave spectroscopy techniques (EPR, FMR, non-resonance microwaves absorption) for studying materials having either inhomogeneous magnetic structure or defects. The followed changes were made in comparison to the previous version of the abstract of the habilitation thesis from 2015:

- two publications that were too closely related to my PhD thesis were removed (Acta Physica Polonica A 110 (2006) 57 oraz Physica Status Solidi (a) 203 (2006) 1586);

- two new publications discussing about the experimental limitations of actually used now the ferromagnetic resonance technique were added (IEEE Transactions on Microwave Theory and Techniques 66 (2018) 803 oraz Measurement Science and Technology 29 (2018) 025501).

2.4A List of works that constitute a basis for habilitation procedure

H1. J. Krupka, **P. Aleshkevych**, B. Salski, P. Kopyt, „*Magnetodynamic Study of Spin Resonances in Cylindrical and Spherical YIG Samples*", IEEE Transactions on Microwave Theory and Techniques **66** (2018) 803.

H2. J. Krupka, **P. Aleshkevych**, B. Salski, P. Kopyt, „*Ferromagnetic Linewidth Measurements Employing Electrodynamic Model of the Magnetic Plasmon Resonance*", Measurement Science and Technology **29** (2018) 025501.

H3. A. Wittlin, **P. Aleshkevych**, H. Przybylińska, D. J. Gawryluk, P. Dłużewski, M. Berkowski, R. Puźniak, M. U. Gutowska and A. Wisniewski, „*Microstructural magnetic phases in superconducting $FeTe_{0.65}Se_{0.35}$*", Supercond. Sci. Technol. **25** (2012) 065019.

H4. **P Aleshkevych**, M Baran, S N Barilo, J Fink-Finowicki, H Szymczak, „*Resonance and non-resonance microwave absorption in cobaltites*", J. Phys.: Cond. Matter **16** (2004) L179.

H5. **P. Aleshkevych**, "*On the estimation of the magnetocaloric effect by means of microwave technique*", AIP Advances **2** (2012) 042120.

H6. **P Aleshkevych**, J Fink-Finowicki, M Gutowski, H Szymczak, "*EPR of Mn^{2+} in the Kagomé staircase compound $Mg_{2.97}Mn_{0.03}V_2O_8$*", J. Magn. Res. **205** (2010) 69.

H7. R. Bikas, **P Aleshkevych**, H. Hosseini-Monfared, J. Sanchiz, R Szymczak and T. Lis, „*Synthesis, structure, magnetic properties and EPR spectroscopy of a copper(II) coordination polymer with a ditopic hydrazone ligand and acetate bridges*", Dalton Trans. **44** (2015) 1782.

H8. R. Bikas, H. Hosseini-Monfared, **P. Aleshkevych**, R. Szymczak, M. Siczek, T. Lis, „*Single crystal EPR spectroscopy, magnetic studies and catalytic activity of a self-assembled [2x2] $Cu(II)_4$ cluster obtained from a carbohydrazone based ligand*", Polyhedron **88** (2015) 48.

H9. **P Aleshkevych**, J Fink-Finowicki, T Zayarnyuk, I Radelytskyi, M Berkowski, C Rudowicz, P Gnutek, „*EMR studies of the internal motion of Mn4+ ions in the Sr overdoped (La1-xSrx)(Ga1-yMny)O3 (x/y up to 8) supplemented by magnetic and optical spectroscopy measurements*", J. Magn. Res. **255** (2015) 77.

2.4B Presentation of the scientific works and achieved results

The main purpose of the series of works, the habilitation procedure based for, was to investigate the nature of inhomogeneity and defects in magnetic single crystals by means of microwave spectroscopy techniques and determining how they affect the magnetic properties of these materials. The studies focus on the effects resulting from the magnetic inhomogeneity or the defect structure by using the microwave spectroscopy technique in the advanced or nonstandard way. The studies were supplemented with additional, non-microwave, techniques, when it was possible to obtain synergies or additional results which could not have been obtained applying these techniques separately.

The microwave spectroscopy techniques, including the electron paramagnetic resonance (EPR), ferromagnetic resonance (FMR), spin wave resonance (SWR) or non-resonance microwave absorption is well known because of the high sensitivity and efficiency in the characterization of magnetic materials. The relative speediness of the measurement procedure is big advantage also. The development of new materials with desirable magnetic properties increases demands concerning characterization techniques. Rapid technological progress leads not only to discover of new singular materials but in fact to discovery of the whole families of new magnetic materials. It turns out very often, that the realization of the desired electronic, chemical, optical, and other properties leads to the formation of inhomogeneous magnetic structure. The nature of magnetic inhomogeneity can be very different: a) chemical, if there are deviations from the chemical stoichiometry when defect structure emergence is required for charge compensation; b) the coexistence of different crystalline phases with different magnetic properties; c) electronic phase separation in the structurally homogeneous material, being the result of competition between the magnetic and Coulomb interactions. Also, the magnetic inhomogeneity is an inherent peculiarity for geometrically frustrated magnetic materials.

The studied materials

There were different single crystals used in the presented series of works representing various types of magnetic inhomogeneities:

- poly- and single crystals of $Y_3Fe_5O_{12}$ (YIG) [H1,H2] - ferrimagnet with antiparallel ordering of iron atoms, occupying different crystallographic positions.
- Superconducting single crystals $FeTe_{1-x}Se_x$ [H3], characterized by the coexistence of different magnetic phases at the microscopic level due to chemical disorder.
- Cobaltite's $La_{1-x}A_xCoO_3$ (x=0.1-0.2) forming different magnetic phases as a result of doping by divalent A^{2+} atoms; weak ferromagnet $TbBaCo_2O_{5.5}$ [H4].
- Exhibiting colossal magnetocaloric effect $Gd_5Si_2Ge_2$ and $La_{0.7}Ca_{0.3}MnO_3$ [H5],where the structural transition is connected to the magnetic transition.
- The Kagomé pseudo two-dimensional crystal structure $(Mg_{1-x}Mn_x)_3V_2O_8$ (x = 0.01) [H6]-geometrically frustrated magnet.
- New copper-based coordination polymers [H7, H8] - artificially fabricated 2D molecular grid containing multi-atom clusters of exchange coupled copper atoms with different topologies.
- Solid solutions of $(La_{1-x}Sr_x)(Ga_{1-y}Mn_y)O_3$ [H9], where divalent Sr^{2+} ions doping leads to the formation of electronic defects determining the magnetic properties and conductivity.

Experimental equipment

The main of presented here experimental results were obtained using the electron spin resonance spectrometers. The majority of the experimental results were obtained using a Bruker EMX spectrometer located at the Institute of Physics, Polish Academy of Sciences in Warsaw. This is the X-band spectrometer (operating at constant frequency of around 9.3 GHz) with reflection-type TE_{102} resonant cavity, allowing to measure the microwave absorption within temperature range 3.8 - 300 K, and magnetic field sweep scope up to 1.8 T. Measurements of the resonance frequency, Q-factor and transmission coefficient |S21| in [H1, H2] have been performed employing Agilent Technologies PNA-X VNA (vector network analyzer). The magnetic surface anisotropy studies in the thin manganites films were performed using the spectrometer located at the Free University in Berlin. Part of the EPR experiments made on Kagomé structures were performed using Bruker ELEXSYS E-500 Q-band (34 GHz) located at the Institute of Nuclear Chemistry and Technology (Warsaw). Interpretation of experimental results, requiring the numerical computation were carried out based on my own computer programs.

The presented description of a series of work is separated into three main parts: the results derived by the FMR [H1-H3], the results based on the non-resonance absorption [H4, H5] and the results derived by means of EPR technique [H6-H9].

In spite of theories of the ferromagnetic resonance, spin waves, and modes of operation of insulating ferromagnetic resonators have been under development for the last 70 years, there are still experimental limitations restricting the applicability of FMR when new magnetic materials or nonstandard microwave setups are involved. One of the most known theories proposed by Walker in 1958 allows finding the relationship between the resonance frequency and the static internal magnetic field bias of an isolated magnetic spheroid. The solution introduced by Walker are called as quasi-magnetostatic modes (QMS) because was derived under the assumption that the microwave field in the spheroid satisfies magnetostatic conditions. One of the major drawbacks of

the QMS theory, however, is the lack of possibility to account for propagation effects essential especially at higher frequencies, where the influence of metal enclosure and the size of the magnetic sample on resonance frequencies cannot be neglected.

Rigorous magnetodynamic (MD) study presented in [H1] allows full-wave electromagnetic (EM) study of the MPR mode at any spectral range without any limitations.

Another challenge is related to the calculation of the Q-factors of the modes found with the QMS theory. So far, the Q-factors of resonance cavities containing small magnetic samples have been evaluated employing perturbation theory (PT). However, PT allows to correctly determining the Q-factor of the mode of uniform precession only for small magnetic samples with the ferromagnetic linewidth $\Delta H > 10$ Oe, for which the condition of small perturbation holds. These limitations become apparent when, for example, we deal with the yttrium-iron garnet (YIG) widely used in microwave technology. It is a ferrimagnetic with antiparallel aligning of Fe^{3+} iron ions sublattices. YIG is the material with the lowest magnetic losses producing very narrow resonance lines.

The particular goal of [H1] was to extend the MD study of spin resonances to magnetic samples of cylindrical shape inserted into larger resonant cavities and compare the obtained results with the QMS theory and experimental results. It will help in better understanding of the physical nature of spin resonances that are in fact EM resonances, and establish limits of the QMS theory.

It was shown in [H1] that PT correctly predicts the existence of very large resonance frequency shifts for the effective permeability values μ_r corresponding to the MPR. However, it does not predict existence of two separate resonances (mode splitting) for a fixed value of the static magnetic field corresponding to the MPR resonances. The PT also fails in Q-factor determination of magnetic samples exhibiting very narrow-linewidth ΔH.

In [H2] it was shown how to apply the electrodynamics model of the magnetic plasmon resonance for accurate measurements of the ferromagnetic resonance linewidth ΔH. Two measurement methods are presented. The first one employs Q-factor measurements of the magnetic plasmon resonance coupled to the resonance of an empty metallic cavity. Such coupled modes are known as magnon-polariton modes, i.e. hybridized modes between the collective spin excitation and the cavity excitation. The second one employs direct Q-factor measurements of the magnetic plasmon resonance in a filter setup with two orthogonal semi-loops used for coupling. Q-factor measurements are performed employing a vector network analyzer. In that method, the static magnetic field bias is tuned in a way to get identical Q-factors for the two observed modes. Subsequently, measured data is compared with a look-up table ($1/Q_{min}$ versus ΔH) computed with the electrodynamics model for known diameter and saturation magnetization of the sample.

Rigorous electromagnetic studies shown in [H2] that a narrow-linewidth ferrimagnetic sphere exhibits a high Q-factor at MPR, which decreases with the ferromagnetic linewidth ΔH. This finding is in agreement with experiments; but not with the cavity perturbation theory, which leads to the opposite conclusion that the unloaded Q-factor is proportional to the ferromagnetic linewidth ΔH. This is one of the reasons why the standard methods of the linewidth measurements, based on the use of rectangular metallic resonance cavities operating in TE_{102} mode (i.e., most commercial

spectrometers made by Bruker, Varian), are recommended only for samples with $\Delta H > 10$ Oe.[1]. In [H2] experiments have been performed employing two kinds of resonators: 1) the first one was a rectangular cavity operating at a TE_{102} mode, equipped with an adjustable coupling mechanisms. 2) The second type of resonator was a spherical MPR resonator consisting of the YIG sample under test surrounded with two orthogonal coupling semi-loops.

The methods presented in [H2] allow one to extend the measurement range of the ferromagnetic resonance linewidth ΔH well beyond the limits of the commonly used measurement standards in terms of the size of the samples and the lowest measurable linewidth.

The paper [H3] is an example of effective application of the microwave spectroscopy method to study the magnetic inhomogeneity in volume nonhomogeneous single crystals. The subject of studies was different crystals of $FeTe_{1-x}Se_x$ that, despite similar conditions of growth, showed a big difference in the superconducting properties. Although $FeTe_{1-x}Se_x$ compounds appear to be an almost ideal model system for the study of the phenomenon of superconductivity in iron based compounds, the detailed analysis of data is significantly hindered by crystal disorder which results from a complex structural chemistry and an apparent inherent non-stochiometry. Multi-scale lattice disorder begins at short range atomic level because the Te and Se ions are in slightly different positions in the unit cell. On larger distance scales, crystals of $FeTe_{1-x}Se_x$ tend to have inhomogeneities like clustering, and microstructural foreign phases of Fe chalcogenides. Since some of these phases have distinct magnetic properties they also mask and distort the intrinsic response of the parent compound. Understanding of these phenomena appears to be essential for the elucidation of the underlying mechanism of superconductivity in this system.

The magnetic resonance spectra were collected on the plate-shaped crystalline samples selected from cleaved pieces from the bulk material. Many such samples have been investigated and the two representative group of crystals A and B were chosen. The spectra were recorded at room temperature with magnetic field oriented perpendicularly to the crystallographic *c*-axis. In both groups of crystals, two broad, poorly resolved, asymmetric resonances are observed, with the resonance fields varying slightly with a crystal orientation with respect to the external magnetic field applied.

The microwave absorption spectra were attributed to the collective magnetic excitation, ferromagnetic resonance (FMR) and were analyzed with the use of the procedure suitable for broad resonance lines, which takes into account that linearly polarized microwave field in the resonant cavity like TE_{102} contains both clockwise and counterclockwise polarization directions, affecting the measured line shape. The single resonance line shape is described by:

$$\frac{dP}{dH} = \frac{1}{2}\frac{d}{dH}\left(\chi''_+ + \chi''_-\right), \tag{1}$$

[1] ASTM A883/A883M-01 "Standard test method for ferrimagnetic resonance linewidth and gyromagnetic ratio of nonmetallic magnetic materials"; U.S. National Bureau of Standards, Technical Note 173 "Tables to facilitate the determination of the ferrimagnetic resonance linewidth of nonmetallic magnetic materials"; IEC 556 1982; IS 8426:2001

where P is the absorbed microwave power and $\chi''_{\pm}$ are Lorentzian line profiles for +/- polarization of the microwave field. Each of experimental spectrum was fitted with the sum of two different Lorentzians. It was found that angular variation of one of the resonance line position shows the 6-fold symmetry in plane perpendicular to the c-axis.

Such a variation of the resonance fields with angle is not expected for a tetragonal symmetry lattice. In contrast, it is characteristic of magnetocrystalline anisotropy with hexagonal symmetry. Thus, the observed resonances dominating typically in the FMR spectra of both crystals A and B must stem from inclusions of a different crystallographic phase than the host lattice. Moreover, such distinct magnetocrystalline anisotropy can be only observed if all the inclusions are identically oriented crystallographically. The broadness of the resonance lines, however, points out to a considerable shape distribution of the particles. A distribution of resonance linewidth in different crystals allowed for fast estimation of structural inhomogeneity. Structural studies carried out later by other techniques (including TEM, magnetic studies), confirmed the FMR results. In particular, it was found, that all crystals contain inclusions of Fe_3O_4 impurity phases, as well hexagonal symmetry nanometer scale grains, identified as $Fe_7(Te,Se)_8$ incorporated in the tetragonal host lattice as a result of an extensive defect process held upon the crystal growth. The observed structural differences among the studied crystals were partially attributed to the different growth rate. The results in paper [H3] suggest that inhomogeneous distribution of host atoms is an intrinsic feature of superconducting FeTeSe chalcogenides. In particular, the obtained data support an observation, that inhomogeneous spatial distribution of ions and small inclusions of hexagonal phase with nanoscale phase separation seems to enhance the superconductivity.

The magnetic inhomogeneities in single crystals of cobaltites $La_{1-x}A_xCoO_3$ (x=0.1-0.2, A = Sr, Ca,…) and $TbBaCo_2O_{5.5}$ were studied in paper [H4].

$La_{1-x}A_xCoO_3$ crystals have Co ions in mixed valence: 3+ and 4+. Depending on the spin state of considered ions, the Co^{3+}- Co^{4+} pairs can interact ferromagnetically due to the double-exchange interaction, while the Co^{3+}- Co^{3+} and Co^{4+}- Co^{4+} pairs can be coupled antiferromagnetically due to the superexchange interaction. The coexistence and competition of antiferromagnetic and ferromagnetic interactions lead to the frustration, which is responsible for spin-glass ordering observed in cobaltites. In the case of low doping it is assumed that the system is separated into hole-rich metallic ferromagnetic clusters with Co^{3+}- Co^{4+} coupling and the hole-poor matrix (phase separation). With the increase of doping, the interaction between the hole-rich regions begins and the cluster glass can appear.

Note, that at the time the paper [H4] was published, no EPR studies were found in single crystalline cobaltites, in spite of the fact that microwave resonance techniques could provide direct identification of the spin state of Co ions.

The presented EPR data in $La_{0.9}Ca_{0.1}CoO_3$ confirmed the presence of cobalt ions in different spin states. The single EPR line observed in the crystal indicates that effective spin of the paramagnetic center S_{eff}= 1/2. This suggests that the resonance would be related to Co^{4+} ions in the low spin state (t_{2g}^5, S=1/2). The Co^{3+} ions could be in the low spin state (t_{2g}^6, S=0) or in the intermediate spin ($t_{2g}^5e_g^1$, S=1) state. In the first case (non magnetic state of Co^{3+} ions), both the integral intensity of

EPR line I(T) as well as the magnetic susceptibility $\chi(T)$ of the sample should be described by the same temperature dependence. However, as it was shown in paper [H4], these dependences exhibits different behavior. It means that a part (or even all) of Co^{3+} ions are not in the low spin state (S > 0), however, because of strong coupling to the lattice, they are being practically invisible in standard X-band EPR experiment.

The temperature dependence of the resonance linewidth in $La_{0.9}Ca_{0.1}CoO_3$ was investigated in the paper [H4]. Two models were proposed to describe experimental data. The first, assuming that the change in linewidth is attributed to the spin-glass to paramagnet transition at finite phase transition temperature. The second approach based on assumption that the broadening of resonance line is due to the spatial inhomogeneity which must be present when there are random distribution of Ca ions, and which results in an effective clustering of Co atoms. Comparing the fitting results, it was concluded that the second model better describes the linewidth variation on temperature (using the simpler expression with 3 parameters, whereas the first model needs 4 parameters).

The thermal variations of the EPR linewidth in $La_{1-x}Ca_xCoO_3$ single crystals (x = 0.1), as well as an asymmetrical profile of the resonance line are typical of the spin-glass-like systems. The observed resonance line is an envelope of all individual lines contributed by separated magnetic complexes/clusters containing Co^{4+} ions. The sharp increase of the linewidth is due to a growth of local magnetic inhomogeneities, attributed to the competition between long-range dipolar interactions and short-range exchange interactions. With lowering of temperature the number of clusters grows intensifying the resonance absorption.

A non-resonance absorption was observed in the crystal with a bigger level of Ca-doping $La_{0.8}Ca_{0.2}CoO_3$, which has been associated with microwave losses on metallic clusters. These losses are strictly related to the conductivity. With the decreasing of temperature the volume and number of spin clusters are increasing thus the total absorption surface is increasing where microwave power can be dissipated/absorbed. It gives growth in absorption when temperature decreases from 100K down to ~55K. At the further decreasing of temperature, interaction between clusters begins and then a percolation threshold could be reached. In that case, a microwave field cannot penetrate all crystal because of its shielding by spreading/growing metallic surface.

The dependence of the absorption amplitude on the magnetic field strength was analyzed in the paper [H4], which was associated with magnetoimpedance (MI) effect. This effect was already studied extensively in Co-based amorphous alloys. In terms of MI effect description, an application of magnetic field leads to the growth of initial complex surface impedance that, in turn, suppresses microwave absorption.

The properties of other $TbBaCo_2O_{5.5}$ cobaltite were studied in the second part of paper [H4] where also a non-resonance microwave absorption was observed. However, in case of this single crystal, a different, not involving MI effect, mechanism explaining the non-resonance absorption was proposed. Firstly, the experimental data have shown that the absorption is very anisotropic and appears only for a specific crystal orientation with respect to both: static and microwave magnetic fields. Secondly, large enough static magnetic field completely destroys the absorption of microwaves. In view of these facts, the experimental microwave absorption in $TbBaCo_2O_{5.5}$ was connected with the presence of magnetic domain structure. There was no theoretical approach, up to

the moment of publishing the paper [H4], describing the dynamics of a magnetic domain in a microwave magnetic field for weak ferromagnets, therefore the theory developed for ferromagnets was adapted, [2] where, in addition to a well known low-frequency branch of domain wall translations, it predicts the existence of high-frequency branches in the spectrum of the wall excitations. By measuring the absorption as a function of frequency, it would be possible to find the value of the high-frequency branch resonance frequency directly. In [H4] the spectrometer with fixed microwave frequency was used, that is why the data, reported in this paper, were related to the non-resonance absorption.

A new experimental method for studying the magnetocaloric effect, based on measurements of microwave absorption was proposed in [H5]. The method has been tested on two examples: a) polycrystalline $Gd_5Si_2Ge_2$ compound and b) single crystal of $La_{0.7}Ca_{0.3}MnO_3$ manganite. Both of these compounds, while being ferromagnetic, are characterized by a strong magnetic inhomogeneity associated with the presence of phase separation, whether it is an electronic phase separation like in the $La_{0.7}Ca_{0.3}MnO_3$ or structural phase separation as in $Gd_5Si_2Ge_2$. Strong competition between phases is a source of various magnetic effects and, particularly, the colossal magnetocaloric effect.

It was shown in paper [H5] that, in the vicinity of the magnetic phase transition, there is a simple, functional relationship between the magnetization and non-resonance microwave absorption. The underplaying reason for this relationship in both materials is found to be the colossal magnetoresistance effect. The study shows how by replacing the magnetization measurements with microwave absorption measurements, one can still use the standard differential thermodynamic equation of Maxwell, binding the entropy variation with the variation of the magnetization, in order to estimate the entropy change under the influence of an applied magnetic field.

There are, mostly, two reasons of existence the meaningful non-resonant absorption, depending on the magnetic field: conductivity and initial magnetization processes. The observed, in paper [5], non-resonance microwave absorption was attributed to conductivity. The conducting character of both tested crystals is reflected in the asymmetry of the resonance absorption derivative. This is well-known in the literature the Dysonian lineshape that is essentially a combination of the absorption and the dispersion components of a symmetric Lorentzian line.

This asymmetry is due to the inhomogeneity of the microwave field, whose intensity decreases exponentially within the conductor. The study shows that, in case of few physical conditions fulfillment, there is a simple relation between the imaginary part of the AC susceptibility and the conductivity. In the narrow temperature range where the slope of magnetization is maximal, it was established a functional relationship between the microwave absorption and the entropy change. This method allows the study of inhomogeneity based on the shape of the microwave absorption and based on the temperature changes of measured magnetocaloric effect.

Magnetic materials with geometrical frustration have recently attracted much attention in the last years. The magnetic inhomogeneity in such materials due to specific geometry leading to high order of degeneracy and complexity of magnetic ground states. The $(Mg_{1-x}Mn_x)_3V_2O_8$ (x=0.01) single crystals were studied in the paper [H6] by means of EPR technique. The single crystal has buckled

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[2] Gilinskii A *Sov. Phys. JETP* 41 (1975) 511

two-dimensional (2D) Kagomé lattice. Magnetically concentrated materials with Kagomé structure show rich magnetic field-temperature (H-T) magnetic phase diagrams because of buckled Kagomé lattice breaks ideal triangle symmetry pushing the competitive magnetic ordered states closer together. Also in all mentioned systems (H-T) diagrams show strong anisotropic behavior depending of magnetic field direction with respect to the crystallographic axes. The strong anisotropy observed even in the MnV_2O_8 where Mn^{2+} has orbital singlet ground state. Therefore, the main purpose of this paper was to study the single-ion anisotropy contribution to the overall anisotropy. Work had model character, because the nonmagnetic matrix of the Kagomé structure was intentionally doped with a small amount of manganese ions to reduce the exchange interactions.

The experimentally observed resonance absorption was attributed to the Mn^{2+} ion occupying two crystallographically non-equivalent positions "spine" and "cross-tie". Well-resolved signals from different positions allowed to determine the crystal field parameters for each position. From the analysis of the microwave absorption intensity of different crystallographic position it was concluded that dopant Mn^{2+} ions are randomly distributed in the crystal, occupying stoichiometric position of Mg ions. The resonance lines are very anisotropic, therefore, the angular variation of the resonance spectrum in three mutually perpendicular planes was studied. The analysis of experimental data of single Mn^{2+} ion has been described by a theoretical spin-Hamiltonian composed of Zeeman, hyperfine and terms, describing the initial splitting of spin levels without magnetic field (ZFS). The main values of the g-factors and hyperfine structure as well as microscopic parameters of the crystal filed are determined for both Mn^{2+} positions. It was found that the local symmetry of oxygen octahedron surrounding Mn ions in "cross-tie" and "spine" positions are different: axial, for "cross-tie" and rhombic, for "spine". Besides main resonance lines, the weak resonance lines attributed to Mn^{2+} pairs were observed. The isotropic exchange constant J = 41 K was found by analyzing the temperature dependence of the resonance lines integral intensity. Additionally, the anisotropic and biquadratic exchange interactions are also estimated.

The electron paramagnetic resonance method was used in [H7, H8] to study magnetic structure in the newly discovered coordination polymers containing organic complexes with transition group elements. The great interest to these compounds in the recent years is associated with the ability to produce the coordination polymers at a predetermined crystal structure, physical and magnetic properties in a controlled way. Often, the magnetic structure of these compounds has been inhomogeneous because of the diversity of exchange interactions between magnetic ions, when the exchange interactions take place through a various ligand bridges. It should be noted that, usually, in the field of inorganic chemistry the predominant way of magnetic properties studies is magnetic measurements and, in particular, measurements of magnetic susceptibility on, mostly, powdered materials.

The papers [H7, H8] presents the results of measurements in polymer crystals. Additionally, the powdered sample in [H7] was also studied by means of EPR technique.

The one dimensional coordination polymer [Cu4(L)2(µ1,1-OAc)2(µ1,3-OAc)4]n was studied in paper [H7]. The temperature dependence of resonance line was measured in the powdered sample and the angular dependence of resonance line in the single crystal. To describe the experimental

data, there was proposed a model where non-uniform magnetic structure of the polymer comprises two different types of Cu-Cu pairs, combined with exchange interactions (dimers). One of the Cu-Cu pair is characterized by a ferromagnetic interaction while the second type of exchange pairs is antiferromagnetically coupled. The principal values of g-tensor and parameters of zero field splitting were determined for the antiferromagnetic coupled dimers. These results together with magnetic susceptibility data were used next to evaluate the exchange integrals for both types of exchange pairs.

The single crystal of $C_{60}H_{60}Cu_4N_{24}O_4(NO_3)_4$ where, according to the crystallographic data, the copper atoms are self-organizing in a clusters making a 2x2 grid with symmetrically arranged ligands was studied in paper [H8]. Inside such 2x2 ring (tetramer) the copper atoms are strongly exchange coupled, while between tetramers, due to the large distance, the long-ranged dipole interaction remains the only meaningful magnetic interaction. The recent great attention to compounds with strongly exchange coupled clusters stems from the fact that they may show behavior typical for single molecule magnet. Also, it is important to understand the nature of magnetism in such self-organizing magnetic structures. The exchange clusters of magnetic ions are the simplest ferromagnet or antiferromagnet where the exchange interaction between a small number of magnetic ions has to be taken into account. On the other hand, their magnetic properties depend strongly on the symmetry, electronic nature of the magnetic ions and the structure of the nearest neighboring ligands. These factors strongly affect the EPR spectrum, therefore the microwave spectroscopy technique should play important role in studies of such materials.

The temperature evolution of EPR spectrum was studied in these materials in paper [H8]. It turned out the EPR spectrum comprises several resonant lines which behave differently with temperature. Analysis of experimental data allowed to identify two different sources of microwave absorption. One of them associated with single Cu^{2+} ions, exposing typical for paramagnet behavior. This small fraction of isolated Cu^{2+} is attributed to an uncontrolled impurities associated with an microcrystallites of copper nitrates precipitated on the crystal faces. The other major source of microwave absorption is antiferromagnetically coupled Cu_4 tetramers. The resonance signal of tetramers shows anisotropic fine structure composed of several resonance lines with non-linear temperature dependence. The tetramer spectrum analysis was carried out by using following spin-Hamiltonian:

$$\hat{\mathcal{H}} = \sum_{i=1}^{4} \mu_B \vec{H}\tilde{g}_i\hat{\vec{S}}_i + \hat{\vec{S}}_1\tilde{J}\hat{\vec{S}}_2 + \hat{\vec{S}}_1\tilde{J}\hat{\vec{S}}_4 + \hat{\vec{S}}_2\tilde{J}\hat{\vec{S}}_3 + \hat{\vec{S}}_3\tilde{J}\hat{\vec{S}}_4 \qquad (2)$$

where $\tilde{J}$ – the second rank dyadic tensor containing all the relevant exchange parameters involves into the bilinear exchange.

The exact numerical diagonalization of the spin-Hamiltonian (2) was used to calculate the resonance line positions by using the self-developed computer program. The calculated positions of eight resonance transitions within the tetramer spectrum reproduce very well the experimental angular dependence. The isotropic part of exchange interaction was found by analyzing the temperature dependence of the integral intensity of resonance transitions within tetramer multiplets. The presence of fine structure indicates that degeneracy of each of the multiplets is lifted because of

zero-field splitting. Neither isotropic exchange nor crystal field acting on Cu^{2+} cannot lift the degeneracy within the multiplets and explain the presence of the fine structure. It was proposed in paper [H8] that main contribution to the zero-field splitting is caused by small off-diagonal elements of tensor $\tilde{J}$ (J_{ij}, with i $\neq$ j) related to anisotropic exchange.[3] Due to high S_4 symmetry of Cu_4 cluster, it is assumed that antisymmetric part of anisotropic exchange related to Dzyaloshinsky-Moria interactions is zero (J_{ij}- J_{ji}=0) and in the first approach every off-diagonal elements of elements of $\tilde{J}$ can be reduced to the single parameter $J_{ij}= J_{ji\ (i<>j)} = D$ accounting the symmetrical part of anisotropic exchange. Using the least-square procedure, the spin-Hamiltonian (2) parameters were determined.

The effect of Sr^{2+} doping on the electronic structure in single crystals of $(La_{1-x}Sr_x)(Ga_{1-y}Mn_y)O_3$ solid solutions (LSGM) was studied in paper [H9]. The ratio x(Sr)/y(Mn) of the Sr concentration (x) and the Mn concentration (y) is a crucial parameter in this study. Two set of samples with two different Mn concentrations were made with expectation to achieve the transport solely by hole delocalization and not by ferromagnetic double-exchange mediation as it is the case, e.g. in $La_{1-x}Sr_xMnO_3$. The legitimacy of such expectations was based on the intriguing fact that the starting undoped (i.e. 'parent') compound for either manganites, characterized by colossal magnetoresistance ($LaMnO_3$), or (La_2CuO_4) are both antiferromagnets and insulators upon doping by divalent ions (e.g., Ca^{2+}, Sr^{2+}) is undergo a simultaneous change of both magnetic ordering as well as conductivity (non-metal to metal transition). By introducing an isolated magnetic ion (Mn) into the non-magnetic matrix of perovskite structure ($LaGaO_3$), it was possible to investigate changes of this electronic structure under a gradually increasing concentration of the Sr^{2+} dopant ions. The microwave studies in paper [H9] was complemented by magnetic susceptibility and optical studies.

It was found that even at the lowest level of Mn concentration, there is the evidence of AFM interactions between Mn, as well as, an inhomogeneous distribution of manganese ions and their segregation in exchange-coupled pairs or larger clusters. Upon gradual increase of the Sr doping, but at a fixed Mn concentration, a simultaneous increase in the value of μ_{eff} per Mn atom and a decrease in the intensity of Mn^{4+} resonance, is observed. There were no signs of easily detectable spectra of Mn^{2+} in the Sr overdoped compounds, therefore it was assumed that the Sr doping leads to a dynamic change of the Mn valence state from initial Mn^{4+} up to the Mn^{3+}.

Analysis of the experimental data indicated that, with increasing Sr doping levels the charge compensation mechanism occurs solely due to the increasing number of electronic defects (holes). The results provide strong evidence for hole delocalization for the compositions with the ratio x/y > 1. The analysis of temperature variation of resonance linewidth shows an abrupt change from the nearly temperature independent behavior for the x/y=1 to the thermally activated narrowing for x/y > 1. The narrowing of the line was connected with the internal motion of Mn^{4+} ions, that has been associated with the vibrations within the MnO_6 complex induced by the dynamic valence change $Mn^{4+} <-> Mn^{3+}$. A sharp decrease in the self-trapping hole energy upon the Sr doping was deduced from EMR data. The experimental studies of Mn ions in LSGM solid solution have been complemented by theoretical superposition model analysis of the ZFS parameters for Mn^{4+} ($S = 3/2$)

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[3] I. Dzyaloshinsky, Phys. Chem. Solids 4 (1958) 241-255.

ions. The theoretical predictions based on an orthorhombic symmetry approximation corroborate the experimental findings.

Conclusions

In the presented series of publications, the results of experimental studies of magnetic structure in selected crystals by using the microwave spectroscopy technique were shown. A large part of this research concerns the fundamental phenomena in magnetism and is essential for cognitive process and application.

The most important findings include:

The two methods applicable to the measurement of the ferromagnetic linewidth proposed in this paper allow one to improve accuracy and extend measurement limits of narrow linewidth magnetic materials below the limits of the standard methods. Samples that can be measured with the proposed methods may have larger size (diameter the order of 1– 1.5mm) as compared to the size of the samples that are used in the standard methods that are based on the perturbation theory. The proposed methods would be essential for improvement of technological processes for ferromagnetic materials having very narrow linewidth.

Detection of complex defect structure in the crystal $FeTe_{1-x}Se_x$ associated with inhomogeneous distribution of the Te, Se atoms in the crystal lattice. The presence of two distinct magnetic phases: a hexagonal grains of magnetic phase Fe_7Se_8 embedded in a host matrix and a crystalline precipitate of Fe_3O_4 on the surface of the crystal identified by using the ferromagnetic resonance technique.

Identification of the different cobalt spin states in the cobaltite $La_{1-x}Ca_xCoO_3$ (x = 0.1, 0.2). Showing that the resonance line broadening is due to spatial inhomogeneity, which must be present at the random distribution of calcium ions, contributing in this way to effective clustering of cobalt atoms. Observation of non-resonance absorption in two cobalitites: $La_{0.8}Ca_{0.2}CoO_3$ and $TbBaCo_2O_{5.5}$, The absorption in the case of the first crystal has been associated with the dissipation of microwaves on the surface layer of ferromagnetic metal clusters, while in the case of second one - with the presence of domain structure.

Presentation of a new method for the experimental determination of the magnetocaloric effect value based on measurement of microwave non-resonance absorption. Showing that, in the vicinity of the magnetic phase transition, there is a simple, functional relation between the magnetization and the non-resonance microwave absorption, which allows the use of the standard differential thermodynamic equation of Maxwell, connected the variation of entropy to the variation of magnetization to estimate the entropy change under the influence of applied magnetic field.

The determining the symmetry of the local environment of the Mn^{2+} ion and the spin Hamiltonian parameters for two crystallographic not-equivalent position in the Kagomé crystal $(Mg_{1-x}Mn_x)_3V_2O_8$ (x=0.01) by means of electron paramagnetic resonance. The observation of microwave absorption from exchange coupled Mn^{2+} - Mn^{2+} pairs, and estimating the values of both: isotropic and biquadratic exchange.

The identification of two different, ferromagnetic and antiferromagnetic coupled exchange Cu^{2+}-Cu^{2+} pairs in the one-dimensional coordination polymer [Cu4(L)2(μ1,1-OAc)2(μ1,3-OAc)4]n. The determining of the principal values of g-tensor and parameters of zero field splitting for the antiferromagnetic coupled dimers.

The observation of the multiline EPR spectrum of copper cluster 2x2 (tetramer) in the $C_{60}H_{60}Cu_4N_{24}O_4(NO_3)_4$ crystal polymer with self-assembled magnetic structure. The calculation of the spin level splitting for a single, flat-squared, with Cu^{2+} atoms in the corner tetramer. The theoretical calculation of both: position and intensity of resonance transition within the energy structure of tetramer used to describe the experimental results. The calculation of isotropic exchange integral between nearest neighboring copper ions. The description of the observed fine structure in the tetramer spectrum in terms of non-zero-symmetrical anisotropic exchange.

Determining that the main charge compensation mechanism is the creation of electronic defects (holes) in the solid solutions $(La_{1-x}Sr_x)(Ga_{1-y}Mn_y)O_3$ with overstechiometric strontium content ($x/y > 1$). The determining of local environment symmetry for Mn^{4+} ions in the crystal lattice, experimental estimation of the spin Hamiltonian parameters and theoretical description within the framework of superposition model. The observation of thermally activated narrowing of resonance lines in the EPR spectrum of Mn^{4+}, that was explained by the internal motion of the manganese ions associated with the holes delocalization effect.

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