

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

Since April 2003 until now I am employed at the Institute of Physics, Polish Academy of Sciences in the Division of Physics of Magnetism

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*”

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

- H1. **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.
- H2. **P Aleshkevych**, M Baran, V Dyakonov, R Szymczak, H Szymczak, K Baberschke, J Lindner and K Lenz, “*Surface magnetic anisotropy of epitaxial $La_{0.7}Mn_{1.3}O_{2.84}$ thin films*”, Acta Physica Polonica A **110** (2006) 57.
- H3. **P Aleshkevych**, M Baran, V Dyakonov, R Szymczak, H Szymczak, K Baberschke, J Lindner, and K Lenz, “*Bulk and surface spin excitations in thin films of manganites*”, Physica Status Solidi (a) **203** (2006) 1586.
- H4. **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.

- H5. **P. Aleshkevych**, “*On the estimation of the magnetocaloric effect by means of microwave technique*”, AIP Advances **2** (2012) 042120.
- H6. 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.
- H7. 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.
- H8. **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 (La_{1-x}Sr_x)(Ga_{1-y}Mn_y)O₃ (x/y up to 8) supplemented by magnetic and optical spectroscopy measurements*”, J. Magn. Res. **255** (2015) 77.
- H9. 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.

2.4B Presentation of the scientific works and achieved results

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 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 studied materials

There were different single crystals used in the presented series of works:

- Thin manganites films $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_{2.84}$ with inhomogeneous surface [H2, H3].
- Superconducting single crystals $\text{FeTe}_{1-x}\text{Se}_x$ [H9].
- Cobaltites $\text{La}_{1-x}\text{A}_x\text{CoO}_3$ ($x=0.1-0.2$) and $\text{TbBaCo}_2\text{O}_{5.5}$ [H1].
- Exhibiting colossal magnetocaloric effect $\text{Gd}_5\text{Si}_2\text{Ge}_2$ and $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [H5].
- The Kagomé pseudo two-dimensional crystal structure $(\text{Mg}_{1-x}\text{Mn}_x)_3\text{V}_2\text{O}_8$ ($x = 0.01$) [H4].
- New copper-based coordination polymers [H6, H7].
- Solid solutions of $(\text{La}_{1-x}\text{Sr}_x)(\text{Ga}_{1-y}\text{Mn}_y)\text{O}_3$ [H8].

Experimental equipment

The main of presented here experimental results were obtained using the electron spin resonance spectrometers. The majority of the experimental results was 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. 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, SWR methods [H2, H3, H9], the results based on the non-resonance absorption [H1, H5] and the results derived by means of EPR technique [H4, H6, H7, H8].

The inhomogeneity of the magnetic structure was examined by means of the spin wave resonance technique in [H2]. This is a continuation and expansion of the $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_{2.84}$ epitaxial thin film studies started during Ph.D. studentship. At that time, it was the first observation of surface spin waves in the crystalline manganites films with excess manganese aside of the resonance modes associated with the bulk spin waves. The observation of the surface spin waves has a special interest in modern physics since resonance lines related to surface spin waves provide direct information concerning magnetic surfaces. The SWR spectra are extremely sensitive to any changes in magnetic structure of the films and in particular to changes of the magnetic structure on the surfaces of films. It was shown in paper [H2] that the microwave technique can be as valuable as inelastic neutron scattering in studying elementary magnetic excitations. In addition, it allows the study of such phenomena as stripe formation and volume or surface magnetic anisotropies. The analysis of the experimental data in [H2] was made within the framework of surface-inhomogeneity

(SI) model,¹ describing the influence of the bound (or pinning) conditions on the excitation of standing spin waves. In this way, using the SI model, it was found that the asymmetric boundary conditions are realized in the studied films, that is the SWR spectrum is determined by two different interfaces. While this conclusion seems to be apparent due to the natural difference at the two surfaces of the film, free surface and the interface connected with substrate, but this fact is in contrast to a majority of reports concerning SWR, where symmetrical boundary conditions are usually assumed and therefore the SWR spectrum is confined to the symmetrical waves only. Different surfaces allowed the observation of not only asymmetric spin waves in the [H2], but also allowed to identify the stripe structure formation on the free surface.

The well-resolved splitting of the resonance lines (into two lines) was observed at low temperature, when the film is ferromagnetically ordered. This “doublet structure” of SWR spectrum was comprehensively explained within the framework of the SI model and points for forming two magnetic sublattices (or stripes) on the surface. The surface anisotropy varies periodically on the free surface.

At the time of publication [H2], it was known that in manganites with an excess of oxygen ($\text{LaMnO}_{3+\delta}$), as well as in $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_{2.84}$, the appearance of Mn ions in mixed valence states is a result of charge compensation caused by the enhanced defect structure. In general, in this crystal structure, there exist vacancies in both the cation and anion sublattices. Moreover, the defect chemistry can be described by a cluster model, where cation and anion vacancies may not only be randomly distributed, but also form more complex defects - mesoscopic cluster-type inhomogeneities. The surface chemical segregation phenomena were observed in rare-earth doped manganites also. It was found that the surface composition dramatically differs from its bulk counterpart, which strongly affects the magnetic properties of surface. The stripe formation in the $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_{2.84}$, observed in paper [H2], was explained by periodical ordering of oxygen vacancies in the vicinity of Mn ions with different valence.

Any type of oxygen vacancies cannot directly affect the resonance lines. However, oxygen vacancies that would assist the electronic ordering of the separation of the Mn ions could also assist charge ordering. By taking into account, that $\text{Mn}^{3+}/\text{Mn}^{4+}$ ratio is equal to 2:1 in the studied films, it was assumed that the stripe formation has a period of three lattice constant. The SWR has no splitting at low temperature where exchange interaction length is bigger than 3 lattice constant and two magnetic sublattices are effectively averaged. The splitting of the SWR lines starts at that temperature when exchange interaction length will decrease so much as it becomes comparable to or less than a stripe period.

For deeper insight the microscopic nature of surface magnetic interactions, the angular dependence of the surface anisotropy was measured and explained qualitatively. The anisotropy of each of the two interfaces was characterized by three microscopic parameters which are responsible for the strength of the exchange, dipolar magnetic and quadrupolar interactions, respectively. The contribution of each of this microscopic parameters to anisotropy was discussed.

The study of nonstoichiometry $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_{2.84}$ thin films by means of spin wave resonance technique was continued in the paper [H3]. Because the surface inhomogeneity as a stripe formation was

¹ H. Puzkarski, *Prog. Surf. Sci.* 9, 191 (1979)

associated with the oxygen vacancies ordering, the effect of thermal annealing on stripe structure was studied in this work, expecting that an annealing will have a big impact on surface (especially free surface) and consequently on the SWR spectrum. The legitimacy of such expectations stemmed from the knowledge that annealing in reducing or oxidizing atmospheres can be used to control the Mn^{3+}/Mn^{4+} ratio. Therefore, any significant modification of the SWR spectrum under the influence of annealing would corroborate the assumption of stripe formation by Mn^{3+} and Mn^{4+} ions on the free surface. The as-grown and annealed in oxygen atmosphere thin films was used previously in paper [H2]. A second annealing was carried out in the same conditions as the first post-preparation annealing in the paper [H3]. As was expected, the repeated annealing has not changed the magnetic properties in the film volume, since the value of the magnetic moment has remained the same as it was before, but this operation has strongly modified the free surface properties. Any traces of splitting disappeared in the SWR spectrum, recorded just after the additional annealing. As it turned out later, three months after the additional annealing, the SWR spectrum again starts to show the doublet structure.

Upon annealing, the surface accepts oxygen, changing the Mn^{3+}/Mn^{4+} ratio and averaging the magnetic interaction on the surface, that cause the disappearance of spitting in the spectrum. After the elapse of months the reverse process takes place, accompanied by the release of O_2 ions, followed by the free surface reconstruction with stripe formation and the splitting in the SWR spectrum is restored. In this way, it was confirmed a stripe formation of the charge-ordered manganese ions in $La_{0.7}Mn_{1.3}O_{2.84}$ films. It is a matter of course to assume, that each subsequent annealing will causes the same changes in the film. The application of this technique for observation of the stripes was possible because of the specific influence of the periodic boundary conditions on SWR spectra in the periodically inhomogeneous materials.

Additionally, the experimental dependence of the spin wave stiffness of temperature $D(T)$ was determined in [H3]. It was noted that the experimental $D(T)$ dependence deviates from the theoretical curve for $T > 150$ K, when the SWR spectrum begin to show splitting. It is known that $D(T)$ dependences have rather power-law behavior in manganites and appearing to collapse at temperatures approached to T_C . The observed deviation of $D(T)$ in opposite direction in the studied thin films was explained in paper [H3] by decreasing the effective length of exchange interaction, which mean that itinerant e_g electrons become localized and it is consistent with charge ordering and stripe formation of Mn ions.

The paper [H9] 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-stoichiometry. 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:

$$\frac{dP}{dH} = \frac{1}{2} \frac{d}{dH} (\chi_+'' + \chi_-''), \quad (1)$$

where P is the absorbed microwave power and χ_{\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 [H9] 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 $La_{1-x}A_xCoO_3$ ($x=0.1-0.2$, $A = Sr, Ca, \dots$) and $TbBaCo_2O_{5.5}$ were studied in paper [H1].

$\text{La}_{1-x}\text{A}_x\text{CoO}_3$ 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 [H1] 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 $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ 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 $S_{\text{eff}} = 1/2$. 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 ($t_{2g}^5 e_g^1$, $S=1$) 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 [H1], 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 $\text{La}_{0.9}\text{Ca}_{0.1}\text{CoO}_3$ was investigated in the paper [H1]. 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 $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ 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 $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$, 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 [H1], 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 $\text{TbBaCo}_2\text{O}_{5.5}$ cobaltite were studied in the second part of paper [H1] 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 $\text{TbBaCo}_2\text{O}_{5.5}$ was connected with the presence of magnetic domain structure. There was no theoretical approach, up to the moment of publishing the paper [H1], 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 [H1] 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 $\text{Gd}_5\text{Si}_2\text{Ge}_2$ compound and b) single crystal of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ 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 $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ or structural phase separation as in $\text{Gd}_5\text{Si}_2\text{Ge}_2$. 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.

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

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 $(\text{Mg}_{1-x}\text{Mn}_x)_3\text{V}_2\text{O}_8$ ($x=0.01$) single crystals were studied in the paper [H4] by means of EPR technique. The single crystal has buckled 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 field 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 [H6, H7] 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 [H6, H7] presents the results of measurements in polymer crystals. Additionally, the powdered sample in [H6] was also studied by means of EPR technique.

The one dimensional coordination polymer $[\text{Cu}_4(\text{L})_2(\mu_1,1\text{-OAc})_2(\mu_1,3\text{-OAc})_4]_n$ was studied in paper [H6]. 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 $\text{C}_{60}\text{H}_{60}\text{Cu}_4\text{N}_{24}\text{O}_4(\text{NO}_3)_4$ 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 [H7]. 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 [H7]. 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:

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

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 [H7] 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 \tilde{J} can be reduced to the single parameter $J_{ij} = J_{ji} (i \leftrightarrow j) = D$ 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 $(\text{La}_{1-x}\text{Sr}_x)(\text{Ga}_{1-y}\text{Mn}_y)\text{O}_3$ solid solutions (LSGM) was studied in paper [H8]. The ratio $x(\text{Sr})/y(\text{Mn})$ 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 $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$. 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 [H8] was complemented by magnetic susceptibility and optical studies.

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

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 Mn⁴⁺ resonance, is observed. There were no signs of easily detectable spectra of Mn²⁺ 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 Mn⁴⁺ up to the Mn³⁺.

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 Mn⁴⁺ ions, that has been associated with the vibrations within the MnO₆ complex induced by the dynamic valence change Mn⁴⁺ \leftrightarrow Mn³⁺. 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 Mn⁴⁺ ($S = 3/2$) 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 observation of charge ordering in the form of periodic strip formation of nanoscopic size at the surface of La_{0.7}Mn_{1.3}O_{2.84} manganites thin film. The proposition of a qualitative explanation of the microscopic nature of the surface magnetic anisotropy within the framework of surface heterogeneity model. The observation of the time-reversible surface reconstruction upon the film annealing in an oxygen atmosphere.

Showing that in the case of thin films, inelastic neutron scattering, as well as, Brillouin light scattering experiments can be successfully replaced by microwave technique for studying of spin dynamics.

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 Fe₇Se₈ embedded in a host matrix and a crystalline precipitate of Fe₃O₄ 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_xCoO₃ ($x = 0.1, 0.2$).

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 cobalites: $\text{La}_{0.8}\text{Ca}_{0.2}\text{CoO}_3$ and $\text{TbBaCo}_2\text{O}_{5.5}$. 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 $(\text{Mg}_{1-x}\text{Mn}_x)_3\text{V}_2\text{O}_8$ ($x=0.01$) by means of electron paramagnetic resonance. The observation of microwave absorption from exchange coupled $\text{Mn}^{2+} - \text{Mn}^{2+}$ pairs, and estimating the values of both: isotropic and biquadratic exchange.

The identification of two different, ferromagnetic and antiferromagnetic coupled exchange $\text{Cu}^{2+} - \text{Cu}^{2+}$ pairs in the one-dimensional coordination polymer $[\text{Cu}_4(\text{L})_2(\mu_1,1\text{-OAc})_2(\mu_1,3\text{-OAc})_4]_n$. 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 2×2 (tetramer) in the $\text{C}_{60}\text{H}_{60}\text{Cu}_4\text{N}_{24}\text{O}_4(\text{NO}_3)_4$ 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 $(\text{La}_{1-x}\text{Sr}_x)(\text{Ga}_{1-y}\text{Mn}_y)\text{O}_3$ with overstoichiometric 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.

Pavlo Aleshkevych

Warsaw, October 5, 2015