

Załącznik nr 3

RESEARCH STATEMENT

Alina Gil, PhD

Jan Długosz University in Częstochowa
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Częstochowa 2015

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I. Name, Surname: Alina Gil

II. Education, Degrees¹:

1994 – Ph.D in Physics, Jagiellonian University in Cracow, Faculty of Mathematics and Physics;

Thesis topic: "Structural and magnetic properties of intermetallic compounds of RTX₂ type"

Work supervisor: prof. dr hab. Andrzej Szytuła

1988 – M.Sc. in Physics, Jagiellonian University in Cracow, Faculty of Mathematics and Physics

Specialization: Solid State Physics

Thesis topic: "Examination of the inorganic structures in biological systems"

Work supervisor: prof. dr hab. Andrzej Szytuła

1983 – Leaving Certificate of Secondary School, the Nicolaus Copernicus High School No. 2 in Mielec, a science oriented class (with extended curriculum in Mathematics and Physics)

III. Employment history:

1.10.1988÷20.02.1990	Trainee Assistant , Institute of Physics, Cracow University of Technology, (17.08.1989÷6.12.1989 maternity leave)
21.02.1990÷30.09.1990	Physicist Specialist - Tutor of physics laboratory, Institute of Physics, Cracow University of Technology,
1.10.1990÷30.09.1998	Assistant , Institute of Physics, Cracow University of Technology, (20.02.1995-9.09.1998 maternity and parental leave),
1.10.1998÷ to date	Assistant Professor , Institute of Technical Education and Safety, the Jan Dlugosz University of Czestochowa.

¹ 2015, December 6th at the Institute of Physics, University of Silesia in Katowice I had habilitation colloquium, the Council of the Institute of Physics, University of Silesia gave me a post-doctoral degree, which has not been approved by Central Commission for Academic Degrees and Titles

IV. Information on Published Scientific Papers and Creative Professional Work

Total number of publications: 66 (31 publications in journals classified in the JCR database), including:

- 48 publications in the field of physics (including 29 publications in the JCR database, 1 monograph, 2 chapters in books), 38 publications after obtaining a Ph.D. degree (including 23 publications classified in the JCR database:
 - Journal of Alloys and Compounds – 9 publications
 - Journal of Magnetism and Magnetic Materials – 6 publications
 - Journal of Solid State Physics – 2 publications
 - Journal of Physics: Condensed Matter – 1 publication
 - Physica B: Condensed Matter – 3 publications
 - Acta Physica Polonica A – 3 publications
 - Acta Physica Polonica B – 1 publication
 - Material Sciences – 1 publication);
- 18 publications outside the discipline represented (including 2 publications classified in the JCR database, 2 manuals for students, 4 chapters in books)

Hirsch Index acc. to the Web of Science database (WoS):7... (13.03.2015)

Total Impact Factor acc. to the Journal Citation Reports (JCR):

according to year of publication: ...**27,65**...

according to the IF for 2013:**49,53**....

Total citation number of publications classified acc. to the WoS database:..**140**..

without self-citations: ..**110**... (13.03.2015)

Participation in conferences: ...36 ...(26 international), including:

- 13 oral presentations (12 after obtaining Ph.D. degree, 6 in the field of Physics)
- 22 posters (18 after obtaining Ph.D. degree, 15 in the field of Physics)

Managing and Participation in National or International Research Projects

1. *Integrated infrastructure initiative for neutron scattering and muon spectroscopy* 7th Framework Programme INFRASTRUCTURES: CP-CSA_INFRA-2008-1.1.1. nr 226507-NMI3, **2009-2013**, research project funded by the European Commission – **participation (three times) in project that allows to perform the measurements in Helmholtz Zentrum Berlin:**
HZB Proposals:

-
- **2009** – PHY-01-2637, A. Gil, B. Penc, Neutron Diffraction Studys of RCr_xGe_2 (R = Tb, Dy, Ho, Er) compounds,
 - **2010** – PHY-01-2885, S. Baran, A. Gil, Investigation of magnetic structures in $\text{Tm}_3\text{Cu}_4\text{X}_4$ (X = Si, Ge, Sn) compounds,
 - **2011** – PHY-01-2977, A. Gil, S. Baran, Neutron diffraction studies of magnetic structures of RSnGe (R = Tb, Dy, Ho, Er) compounds,
2. *Evaluation toolkit on senior education to improve their quality of life (QEduSen)*, Lifelong Learning Programme nr: 518227-LLP-1-2011-1-ES-GRUNDTVIG-GMP, **2011-2014**, Multilateral Project funded by the European Commission, The coordinator: Universitat Jaume I Castellon (Spain); partners from 7 European countries: Spain, Italy, Finland, Latvia, Poland, Hungary, Bulgaria – **JDU Coordinator – managing the work of the Polish research team.**

V. Name an achievement meeting the requirements of Art. 16, section 2, of the Law on Academic Degrees and Title and Degrees and Title in the Arts Act of 14 March 2003 (Dz.U. (Official Journal of Laws) No. 65/2003, item 595, as amended)

a) Title of the scientific achievement (a series of 9 monothematic publications):

The influence of d- and p-electron elements on the magnetic structures of ternary intermetallic compounds of RT_xX_2 type with the crystal structure of $CeNiSi_2$ type

b) Publications included in the scientific achievement (IF given according to the year of publication, IF* given according to the year 2013):

- H1. A. Gil, B. Penc, S. Baran, J. Hernandez-Velasco, A. Szytuła, A. Zygmunt, **2003**, „*Magnetic structures of RNi_xSn_2 ($R = Tb, Ho$) compounds*”, **Journal of Alloys and Compounds** Vol. 361 pp. 32–35 (IF=1,08; IF*=2,726)
- H2. A. Gil, B. Penc, J. Hernandez-Velasco, A. Szytuła, A. Zygmunt, **2004**, “*Neutron diffraction studies of RNi_xSn_2 ($R=Tb, Dy, and Ho$) compounds*”, **Physica B – Condensed Matter**, 350, e119–e121 (IF=0,679, IF*=1,276)
- H3. A. Gil, B. Penc, E. Wawrzyńska, J. Hernandez-Velasco, A. Szytuła, A. Zygmunt, **2004**, „*Magnetic properties and magnetic structures of RCo_xSn_2 ($R=Gd-Er$) compounds*”, **Journal of Alloys and Compounds** Vol. 365, pp. 31–34 (IF=1,562; IF*=2,726)
- H4. A. Gil, D. Kaczorowski, J. Hernandez-Velasco, B. Penc, E. Wawrzyńska, A. Szytuła, **2004**, “*Magnetic structures of RCu_xGe_2 ($R = Ho, Er$) compounds*”, **Journal of Alloys and Compounds** Vol. 384, L4–L6 (IF=1,562; IF*=2,726)
- H5. A. Gil, D. Kaczorowski, B. Penc, A. Hoser, A. Szytuła, February **2011**, *Magnetic and transport properties of $RCr_{0.3}Ge_2$ ($R = Tb, Dy, Ho$ and Er) compounds*, **Journal of Solid State Chemistry**, Vol.: 184, Issue: 2, pp. 227–235 (IF=2,159; IF*=2,20)
- H6. A. Gil, B. Penc, S. Baran, A. Hoser, A. Szytuła, July **2011**, *Neutron Diffraction studies of $RSn_{1+x}Ge_{1-x}$ ($R=Tb - Er$) compounds*, **Journal of Solid State Chemistry**, Vol.: 184, Issue: 7, pp. 1631-1637 (IF=2,159; IF*=2,20)
- H7. A. Gil, A. Hoser, B. Penc, A. Szytuła, October **2013**, *Crystal and magnetic structure of $TbFe_{0.25}Ge_2$ compound*, **Journal of Magnetism and Magnetic Materials** Vol.: 344, pp 167-170 (IF=IF*=2,002)
- H8. A. Gil, **2006**, “*Magnetic interaction in RT_xX_2 ternary compounds*”, **Materials Science – Poland**, Vol. 24, no. 3, pp. 577–583 (IF=0,333, IF*=0,327);

H9. A.Gil, 2007, “Crystalline electric field parameters for RTX_2 compounds”, **Journal of Physics: Conference Series** 79, 012032, doi:10.1088/1742-6596/79/1/012032

Statements of the co-authors, specifying their individual contribution to the publications, are attached in the annex No. 4. The statement of doc. dr hab. Adam Zygmunt is not attached due to his death - his contribution is described by professor Szytula in his statement.

c) Discussion on the scientific/artistic objective of the aforementioned work/works as well as the results achieved, together with a discussion about their possible use

The objective of work

The subject of the research presented in this achievement were ternary intermetallic compounds with the RTX_2 composition, where R – rare earth element, T – *d*-electron element (transition metal), X – *p*-electron element.

Studies of rare earth compounds with transition metals are one of the dominant trends in modern magnetism and cover a wide range of research both basic and applicative nature. The impetus for this study was to obtain, among other things, the $Nd_2Fe_{14}B$ compound, which has become a new material for permanent magnets. The search for further compounds with better parameters encounters difficulties because of the lack of a complete theoretical description. Magnetism of rare-earth intermetallic compounds has been known for more than 60 years but still lacks a theory that would be sufficient to describe the experimental results. A systematic study of the magnetic properties of rare-earth compounds gives hope for full understanding of magnetism in these families of compounds. The main aim of the study of lanthanide compounds is to find answers to questions concerning mechanisms of interaction between the magnetic moments.

The aim of the present scientific achievement is to determine the arrangement of the magnetic moments and the influence of *d*- and *p*-electron elements on magnetic properties of the compounds of the orthorhombic $CeNiSi_2$ type crystal structure, described by the $Cmcm$ space group. On account of this, in addition to examine the nonstoichiometric RT_xX_2 compounds, I started studying the $RSn_{1+x}Ge_{1-x}$ ($x \approx 0.1$) compounds, which also crystallize in the orthorhombic $CeNiSi_2$ structure and they are interesting due to the replacement of the *d*-metal with the *p*-electron element.

Crystal structure

Compounds of the RT_xX_2 composition, where $1 \geq x > 0$, generally crystallize in nonstoichiometric RT_xX_2 composition and have orthorhombic $CeNiSi_2$ type crystal structure ($Cmcm$ space group) described by Bodak, Gladyshevsky¹. Each atom, i.e. Ce, Ni, Si_1 , Si_2 , occupies the 4(c) position with the coordinates $(0, y, \frac{1}{4})$, with different values of the *y* parameter. The characteristic feature of the structure is a coordination polyhedron formed of the transition metal atoms. Each of the atoms is located inside a slightly deformed square pyramid with the X atoms situated in its corners. The base of the pyramid is formed by X_2

¹ O.I. Bodak, E.I. Gladyshevsky, 1970, Sov. Phys. Cryst. 14, 859

atoms, and the top corner is occupied by an X_1 atom. Rare earth atoms occupy large holes in this framework having four X_1 , four T and four X_2 atoms as neighbors. The $CeNiSi_2$ crystal structure is of a layered type. Layers of the same atoms are arranged along the longest axis in the following order: R-T- X_2 -T-R- X_1 - X_1 -R-T- X_2 -T-R. The layered nature and anisotropy of the crystal structure ($a = 4.455$ (2) Å, $b = 17.374$ (4) Å, $c = 4.266$ (1) Å) affect the magnetic properties.

The problem of nonstoichiometry in this type of structure was examined in detail by M. Francois and colleagues². A characteristic feature of these compounds is the fact that along with decreasing radius of the rare earth ion, the number of vacancies in the 3d-element sublattice.

Experiment

The samples were prepared by arc melting the stoichiometric mixture of high-purity elements (99.9wt% in the case of rare earth and 99.99wt% in the case of other elements) in a purified argon atmosphere. Afterwards, to be homogenized, the samples were annealed in evacuated quartz ampoules at 800°C for one week.

An indispensable tool for studying properties of the magnetic crystals is the neutron diffraction method, used first in 1949 by Shull and Smart for research on magnetically ordered MnO polycrystal³. In 1994. The Nobel Prize in Physics was awarded to the pioneers of the experimental methods of neutron scattering: CG Shull and B.N. Brockhouse. Neutron diffraction method allows to determine the magnetic structures occurring in the studied compounds and I used it mainly in the implementation of my research. Neutron measurements were performed at the Helmholtz-Zentrum Berlin (previously Berlin Neutron Scattering Center) using the E6 instrument designed to study polycrystalline samples. The diffraction patterns were analyzed with the use of FULLPROF⁴, a Rietveld-type program⁵.

Other complementary methods to study the magnetic properties were used, such as measurements of magnetic susceptibility, magnetization, specific heat, electrical resistance (conducted mostly in Institute of Low Temperature and Structure Research, Polish Academy of Sciences in Wroclaw) and finally X-ray diffraction method, which was used basically to confirm the type of crystalline structure and to check the purity of the samples. Using the complementary experimental workshop allowed a deeper analysis of the properties of these compounds.

The applied models of interactions

The rare earths ions of intermetallic compounds are usually trivalent, except for Ce, Pr, Sm, Eu and Yb, among which the mixed valence states are possible. Lanthanides stand out among the other groups of elements, because of their interesting electron configuration, which can be generally described as a ... $4f^n 5s^2 5p^6$ where filling the f-shell varies from 0 for La^{3+} to 14 for Lu^{3+} . Unpaired electrons on a partially-filled 4f shell are the source of the

² M. Francois, G. Venturini, B. Malaman, B. Roques, 1990, J. Less-Common Met. 160, 197; 215

³ C.G Shull, 1995, Rev. Of Modern Physics, 67, 753

⁴ H.M. Rietveld, 1969, J. Appl. Cryst. 2, 65

⁵ J. Rodriguez-Carvajal, 1993, Physica B 192,55

magnetic moment of the rare earth ion. Distances between rare earth ions in these compounds are about 4 Å which excludes direct interaction. The uniqueness of a lanthanide is that the 4f electrons are highly localized and shielded by the external 5s and 5p shells. Hence, these compounds are good for application of the RKKY theory^{6 7 8}, which describes interaction of nuclear magnetic moments via the conduction electrons. The theory assumes that the localized magnetic moment of electrons causes nonlocal polarization of the conduction band, which has an oscillating character according to the function:

$$F_x = \frac{x \cos x - \sin x}{x^4}.$$

The Hamiltonian of this interaction assumes the form:

$$H = \sum_{i,j} J_{RKKY}(R_{ij}) \vec{S}_i \cdot \vec{S}_j,$$

where S_i, S_j – spins located at the i -th and j -th rare earth ion, J_{RKKY} - exchange integral:

$$J_{RKKY}(R_{ij}) = -\frac{9\pi}{8} n_c \frac{J_{sf}^2}{\varepsilon_F} \frac{x \cos x - \sin x}{x^4}, \text{ where } x = k_F R_{ij},$$

n_c – conduction electron density, ε_F – Fermi energy, k_F – the value of the wave vector at the Fermi level, R_{ij} – the distance between the interacting spins, J_{sf} – effective s - f exchange interaction due to the direct exchange and s - f mixing.

RKKY simplified model predicts that the paramagnetic Curie temperature θ_p or ferromagnetic Curie temperature T_C has the form:

$$\theta_p = -\frac{3\pi n^2}{k_B \varepsilon_F} J_{sf}^2 (g_J - 1)^2 J(J + 1) \sum_i F(2k_F R_{0i}),$$

where g_J – Lande factor, k_B – Boltzmann constant, θ_p is proportional to the molecular field acting on the central ion and derived from interaction with all its neighbors within R_{0i} .

In antiferromagnetic crystals there may be a different arrangement of the magnetic moment represented by the propagation vector $\mathbf{k} \neq 0$, therefore:

$$T_N = -\frac{3\pi n^2}{k_B \varepsilon_F} J_{sf}^2 (g_J - 1)^2 J(J + 1) \sum_i F(2k_F R_{0i}) \cos(k_0 R_{0i})^9.$$

RKKY model also shows that for isostructural rare-earth compounds the magnetic orderings temperature is proportional to the de Gennes factor¹⁰:

$$G = (g_J - 1)^2 J(J + 1).$$

RKKY model is often used to interpret the experimental results.

⁶ M.A. Ruderman, C. Kittel, 1954, Phys. Rev. 96, 99

⁷ T. Kasuya, 1956, Progr. Teor. Phys. 16, 45

⁸ K. Yosida, 1957, Phys. Rev. 106, 893

⁹ D.C. Mattis, 1965, The Theory of Magnetism, Harper & Row, New York

¹⁰ P.G. de Gennes, 1962, J. Phys. Radium 23, 510

In addition to the exchange interaction described by RKKY model, the magnetic ordering of intermetallic rare earths compounds is also influenced by crystal electric field (CEF). The electric field originating from the surrounding charge distribution affects 4f electrons of lanthanides. This effect partially or completely breaks the $(2J+1)$ -fold degeneration of the ground level. Fundamentals of crystalline field theory were developed by Bethe¹¹ but it was only the formalism of equivalent operators introduced by Stevens that greatly facilitated the interpretation of results.

The interaction of the CEF with the moments of rare-earth atom electrons is given by the Hamiltonian:

$$H_{CF} = \sum_{l,m} B_l^m O_l^m(J),$$

where B_l^m are the crystal field intensity parameters and O_l^m are called Stevens operators^{12 13}. The local symmetry of the lanthanide ion resets some crystal field parameters. For compounds with a field of orthorhombic mmm symmetry crystal field Hamiltonian is as follows:

$$H_{CF} = B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4 + B_6^0 O_6^0 + B_6^2 O_6^2 + B_6^4 O_6^4 + B_6^6 O_6^6.$$

Results

The magnetometric measurements of RNi_xSn_2 ($R = Gd-Er$) compounds showed that these compounds are antiferromagnets below the respective Néel temperatures: 27 K for $R = Gd$, 17.4 K for $R = Tb$, 8 K for $R = Dy$, 6.6 K for $R = Ho$ and 4 K for $R = Er$. The magnetization measurements in low magnetic fields showed behavior typical for the phase transition from an antiferro- to a paramagnetic state, while an inspection of the neutron diffraction patterns showed additional peaks of magnetic origin, which could be indexed with the propagation vector $\mathbf{k} = (0,0,1/2)$ for $TbNi_{0.26}Sn_2$, $\mathbf{k} = (1/2,1/2,0)$ for $HoNi_{0.16}Sn_2$ [H1] and $\mathbf{k} = (0,0,1/2)$ for $ErNi_{0.15}Sn_2$ ¹⁴. The first two compounds have the same magnetic ordering scheme described by the **A** (+ - - +)¹⁵ mode and the magnetic moment lies in the a - c plane. For the $R = Tb$ compound the magnetic moment of Tb is equal to $8.05(8) \mu_B$ and forms an angle of 33° with the c -axis (Fig. 1a) and for $R = Ho$ $\mu(Ho) = 7.46(13) \mu_B$ and forms an angle of 26° with the c -axis (Fig. 1b). In the $ErNi_{0.15}Sn_2$ compound the Er magnetic moments of $9.16(9) \mu_B$ form a structure of the **C** (+ + - -) type and they are parallel to the a -axis (Fig. 1c). The peaks of magnetic origin in the neutron diffraction pattern of $DyNi_{0.22}Sn_2$ in temperature 1.5 K were described by the propagation vector $\mathbf{k} = (0.361, 0, 0.343)$ [H2]. Analysis of magnetic peak intensities indicates a sine-wave modulated structure. The Dy magnetic moments equal to $9.2(3) \mu_B$ lie in the b - c plane and form an angle of 32° with the c -axis.

¹¹ H.A. Bethe, 1929, Ann. Phys. 3, 133

¹² K.W.H. Stevens, 1953, Proc. Phys. Soc., London, A218, 553

¹³ M.T. Hutchings, 1964 in F. Seitz, D.Turnbull, ed. Solid State Physics, vol. 16, 227, Academic Press, New York

¹⁴ B. Penc, E. Wawrzyńska, A. Szytuła, A. Gil, J. Hernandez-Velasco, A. Zygmunt, 2004, J. Alloys Comp., 375, L1

¹⁵ E.F. Bertaut, 1968, Acta Crystallogr. A 24, 217

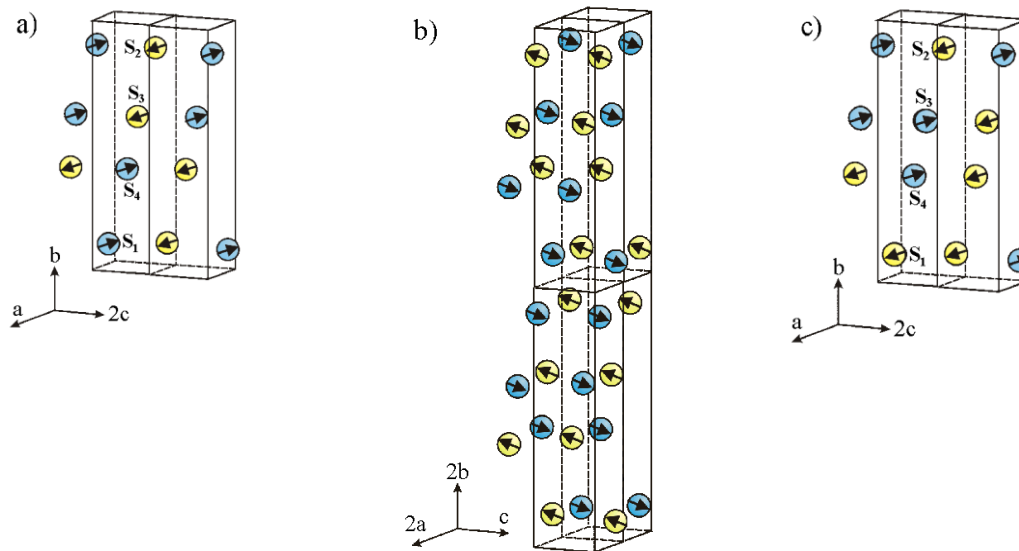


Fig. 1. Magnetic structures: a) $\text{TbNi}_{0.26}\text{Sn}_2$, b) $\text{HoNi}_{0.16}\text{Sn}_2$ [H1] and c) $\text{ErNi}_{0.15}\text{Sn}_2$ ¹⁴

The magnetization measurements of RCo_xSn_2 ($R = \text{Gd-Er}$) compounds¹⁶ showed, that all that of these compounds are antiferromagnets at low temperatures, and the suitable Néel temperatures are as follows: 16.5 K (for $R = \text{Gd}$), 18.8 K ($R = \text{Tb}$), 7 K ($R = \text{Dy}$), 5.6 K ($R = \text{Ho}$) and 4.5 K ($R = \text{Er}$). An increased magnetization, below 4 K, was observed for the compounds with Tb, Ho and Er.

The results of neutron diffraction measurements carried out on the RCo_xSn_2 compounds with $R = \text{Tb}$ and Ho [H3] showed presence of collinear antiferromagnetic **A**-type structures with additional magnetic peaks, which were successfully indexed by the propagation $\mathbf{k} = (0,0,1/2)$ for $\text{TbCo}_{0.25}\text{Sn}_2$ and $\mathbf{k} = (1/2,1/2,0)$ for $\text{HoCo}_{0.23}\text{Sn}_2$. The Tb magnetic moment equals $7.14(8) \mu_B$, and the Ho is equal to $6.79(23) \mu_B$, and they both lie in the a - c plane, forming angles 20.4° (Tb) and 19.8° (Ho) with the c -axis, respectively. Whereas, the Er magnetic moments in $\text{ErCo}_{0.24}\text{Sn}_2$ ¹⁴ compound, equal to $6.15(13) \mu_B$, form a **C**-type magnetic structure and they are parallel to the a -axis. The determined magnetic structures of RCo_xSn_2 ($R = \text{Tb, Ho}$) are similar to those observed in the isostructural RNi_xSn_2 .

Neutron diffraction measurements of the $\text{TbCu}_{0.4}\text{Ge}_2$ compound indicate presence of collinear magnetic structures of the G_z model with the Tb magnetic moments equal to $8.82(5) \mu_B$ ¹⁷. A similar **G** – type structure I has been observed in $\text{HoCu}_{0.33}\text{Ge}_2$ and $\text{ErCu}_{0.25}\text{Ge}_2$, but the directions of the magnetic moments are different. The Ho magnetic moments equal to $8.18(21) \mu_B$ are parallel to the c -axis, while the Er moments equal to $7.89(15) \mu_B$ are parallel to the a -axis [H4].

The X-ray diffraction as well as the neutron diffraction data recorded for intermetallic $\text{RCr}_{0.3}\text{Ge}_2$ compounds ($R = \text{Tb, Dy, Ho}$ and Er) [H5] in paramagnetic state confirmed that the investigated compounds crystallize in the orthorhombic CeNiSi_2 -type crystal structure.

¹⁶ S. Baran, F.Henkel, D. Kaczorowski, J. Hernandez-Velasco, B. Penc, N. Stuser, A. Szytuła, E. Wawrzyńska, 2006, J. Alloys Comp. 415, 1

¹⁷ P. Schobinger-Papamentellos, K.H.J. Buschow, 1992, J. Alloys Comp. 187, 73

The results of magnetic measurements indicate antiferromagnetic ordering below the respective Néel temperature – 18,5 K (Tb), 11,8 K (Dy), 5,8 K (Ho), 3,4 K (Er). Neutron diffraction measurements allowed to determine the magnetic structures, and thus:

- for $\text{TbCr}_{0.3}\text{Ge}_2$ and $\text{DyCr}_{0.3}\text{Ge}_2$ compounds magnetic ordering at low temperatures can be described by using two propagation vectors, respectively: $\mathbf{k}_1 = (\frac{1}{2}, 0, 0)$ and $\mathbf{k}_2 = (\frac{1}{4}, 0, \frac{1}{4})$ for $R = \text{Tb}$ (Fig. 2), and $\mathbf{k}_1 = (\frac{1}{2}, 0, 0)$ and $\mathbf{k}_2 = (\frac{1}{2}, 0, \frac{1}{2})$ for $R = \text{Dy}$ (Fig. 3);

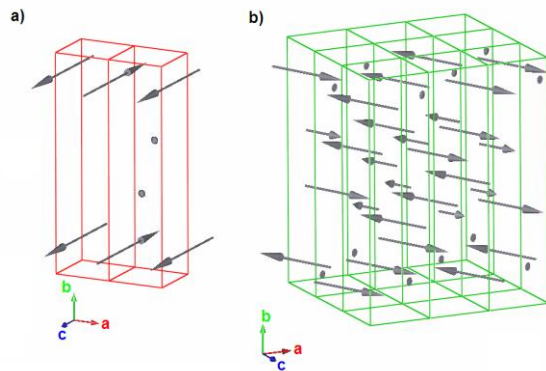


Fig. 2. Magnetic structure of $\text{TbCr}_{0.3}\text{Ge}_2$ at the temperature of 1.5 K described by two wave vectors $\mathbf{k}=(\frac{1}{2}, 0, 0)$ (a) and $\mathbf{k}=(\frac{1}{4}, 0, \frac{1}{4})$ (b) [H5]

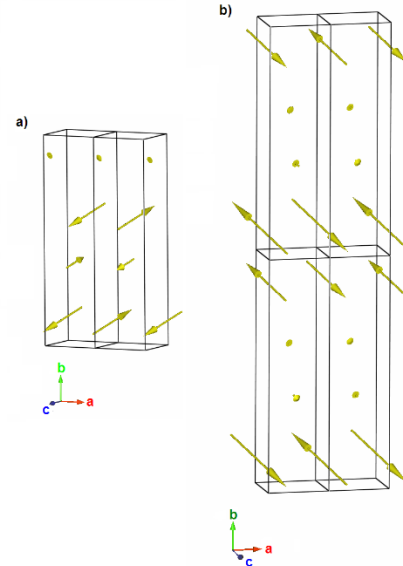


Fig.3. Magnetic structure of $\text{DyCr}_{0.3}\text{Ge}_2$ at the temperature of 1.5 K described by two wave vectors $\mathbf{k}=(\frac{1}{2}, 0, 0)$ (a) and $\mathbf{k}=(\frac{1}{2}, 0, \frac{1}{2})$ (b) [H5]

- for $\text{HoCr}_{0.3}\text{Ge}_2$ and $\text{ErCr}_{0.3}\text{Ge}_2$ magnetic ordering at low temperatures is described by one propagation vector, respectively: $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ for $R = \text{Ho}$ and $\mathbf{k} = (0, 0, 0.4187(2))$ for $R = \text{Er}$ (figures of structures are in ref. H5);
- for $\text{DyCr}_{0.3}\text{Ge}_2$ an additional phase transition in $T_t = 5.1$ K is observed. In the temperature range of T_t to T_N the magnetic ordering is described by the propagation vector $\mathbf{k} = (\frac{1}{2}, 0, 0)$;
- $\text{YCr}_{0.3}\text{Ge}_2$ is a Pauli paramagnet down to 1.72 K, which suggests that in the entire $\text{RCr}_{0.3}\text{Ge}_2$ series the Cr atoms do not carry any magnetic moments.

All the studied compounds exhibit metallic character of the electrical resistivity, whereas temperature dependencies of the lattice parameters reveal strong magnetostriction effect at the respective Néel temperatures.

Magnetic structures observed in $\text{RCr}_{0.3}\text{Ge}_2$ compounds, excluding $R = \text{Er}$, are commensurate with the crystalline structure. The rare-earth moments are parallel to the c -axis for $\text{TbCr}_{0.3}\text{Ge}_2$ and $\text{HoCr}_{0.3}\text{Ge}_2$, and for $\text{DyCr}_{0.3}\text{Ge}_2$ they are slightly inclined from this direction. For $\text{ErCr}_{0.3}\text{Ge}_2$, magnetic moment is parallel to the a -axis. These results indicate that the crystal field (CEF) plays an important role. Changing the direction of the magnetic moments may be related to sign changes of the Stevens α_J coefficient from negative for $R = \text{Tb-Ho}$ to positive for $R = \text{Er, Tm}$. The metallic character of the temperature

dependencies of the electrical resistivity is in good agreement with the high density of states on the Fermi level reported for $\text{YFe}_{0.25}\text{Ge}_2$ ¹⁸.

The next investigated compound was $\text{TbFe}_{0.25}\text{Ge}_2$ [H7] as a complement to the research on this family of compounds made earlier by my colleagues^{19 20 21}. The X-ray and neutron diffraction data confirmed the orthorhombic CeNiSi_2 -type crystal structure (space group Cmcm). The magnetic measurements showed that this compound is an antiferromagnet below $T_N = 19.5$ K. The neutron diffraction data allowed to determine the magnetic structure which can be described as a complex consisting of two components: a collinear \mathbf{G} -type component with Tb magnetic moment equal to $4.05(10) \mu_B$ and parallel to the c -axis, and sine-wave modulated component, described by the propagation vector $\mathbf{k} = (0.460(8), 0, 0.305(1))$ with the Tb magnetic moment equal to $7.82(8) \mu_B$ situated in the b - c plane and forming an $\theta = 24(2)^\circ$ angle with the c -axis (Fig. 4). The collinear component decreases to zero at 22.6 K while the modulated one at 19.8 K.

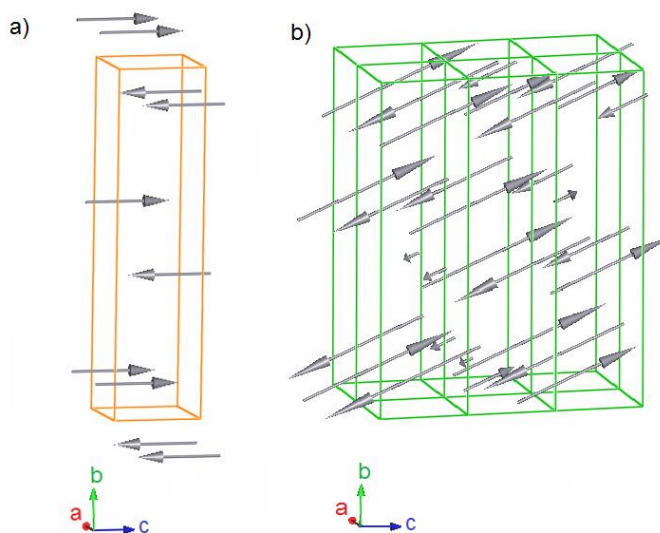


Fig. 4. Magnetic structure of $\text{TbFe}_{0.25}\text{Ge}_2$: (a) collinear, (b) sine-modulated [H7]

The $\text{RSn}_{1+x}\text{Ge}_{1-x}$ compounds ($\text{R} = \text{Tb-Er}$)²², which also have the CeNiSi_2 -type crystal structure, seemed interesting because of the possibility to compare the results with those of RT_xX_2 ($\text{X} = \text{Ge, Sn}$) in order to determine the influence of other elements (T, Ge, Sn) on magnetic ordering in rare earths sublattice.

Magnetic structures of $\text{RSn}_{1+x}\text{Ge}_{1-x}$ compounds ($\text{R} = \text{Tb, Dy, Ho}$ and Er , $x \approx 0.15$) [H6] were determined on the basis of neutron diffraction measurements of polycrystalline samples. The data showed that all these compounds are antiferromagnets at low temperatures. Magnetic ordering in $\text{TbSn}_{1.12}\text{Ge}_{0.88}$ is sine-modulated, described by the propagation vector $\mathbf{k} = (0.4257(2), 0, 0.5880(3))$. The Tb magnetic moment at 1.5 K

¹⁸ M. A. Zhuravleva, D. Bilc, R. J. Pcionek, S. D. Mahantl, M. G. Kanatzidis, 2005, *Inorg. Chem.* 44, 2177

¹⁹ S. Baran, Ł. Gondek, J. Hernandez-Velasco, D. Kaczorowski, A. Szytuła, 2005, *J. Magn. Magn. Mater.* 285, 188

²⁰ A. Szytuła, D. Kaczorowski, unpublished results

²¹ S. Baran, D. Kaczorowski, B. Penc, D. Sheptyakov, A. Szytuła, 2010, *J. Magn. Magn. Mater.* 322, 2198

²² P.H. Tobash, J.J. Mayers, G. DiFilippo, S. Bobev, F. Ronning, J.D. Thompson, J.L.Sarrao, 2008, *Chem. Mater.* 20, 2151

temperature equals $9.1(2) \mu_B$, lies in the b - c plane and forms an angle of $\theta = 17.4(2)^\circ$ with the c -axis. This structure is stable up to the Néel temperature equal to 31 K. Magnetic structures of $\text{R}\text{Sn}_{1+x}\text{Ge}_{1-x}$, where $\text{R} = \text{Dy}$, Ho and Er at $T = 1.5$ K are described by propagation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$. For $\text{Dy}\text{Sn}_{1.09}\text{Ge}_{0.91}$ and $\text{Ho}\text{Sn}_{1.1}\text{Ge}_{0.9}$ magnetic moments are equal to $7.25(15) \mu_B$ and $8.60(6) \mu_B$ respectively and they are parallel to the c -axis. For Ho compound this ordering is stable up to $T_N = 10.7$ K while for Er compound at $T_t = 3.5$ K sine-modulated structure described by propagation vector $\mathbf{k} = (0.496(1), 0.446(4), 0)$ appears. For $\text{Er}\text{Sn}_{1.08}\text{Ge}_{0.92}$, magnetic moment equals to $7.76(7) \mu_B$ at $T = 1.5$ K and is parallel to the b -axis, while in the modulated phase it lies in the b - c plane and forms an angle of $48(3)^\circ$ with the c -axis. In compounds with $\text{R} = \text{Tb}$, Ho and Er the magnetostriction effect at the Néel temperature is observed. The determined magnetic structures are presented in Figure 5.

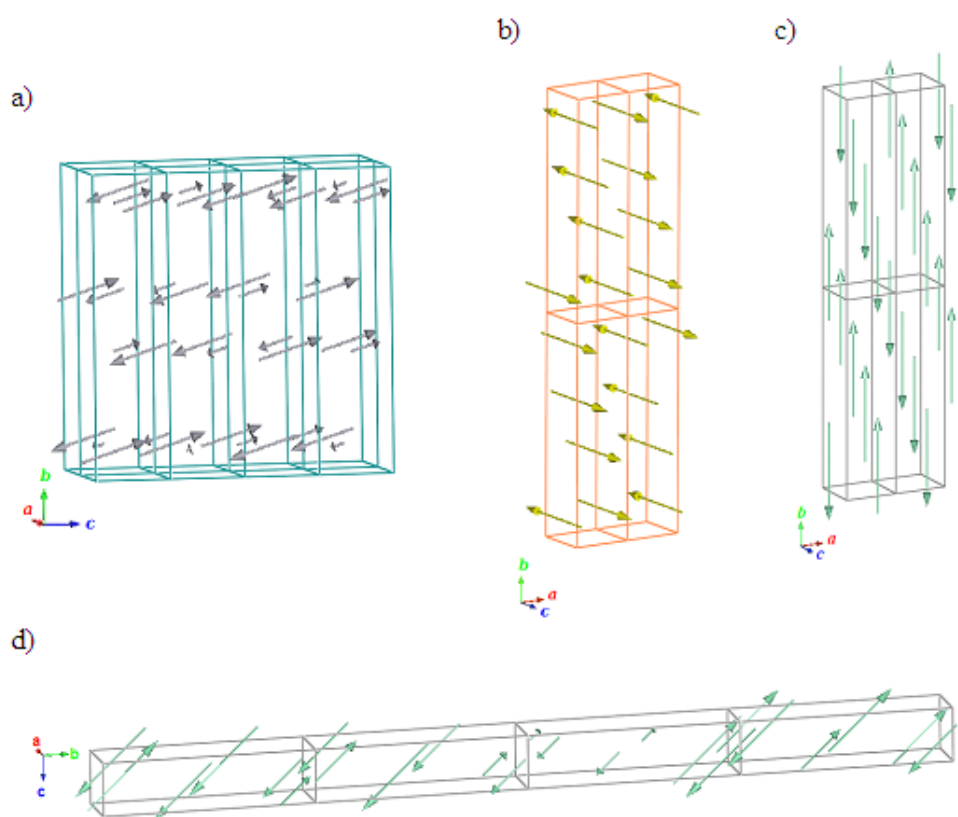


Fig. 5. Magnetic structures of $\text{R}\text{Sn}_{1+x}\text{Ge}_{1-x}$: $\text{R}=\text{Tb}$ (a), Dy (b), Ho (c), Er (d) [H6]

Conclusions

The results presented above were analyzed taking into consideration the additional literature data about other types of ternary RT_xX_2 compounds.

The measurements have shown that the RT_xX_2 compounds of the CeNiSi_2 -type structure with germanium and tin form defected arrangements on the transition metal sublattice, which is conditioned by the size of X element atoms and filling of the d-electron's shell of the transition metal T. Among the compounds with germanium and tin, there exist families

which crystallize as stoichiometric systems, for example $RNiSn_2^{23}$ or $RTGe_2^{24}$, where $T = Ir, Pd, Pt$, but they have a different crystal structure although they are orthorhombic too, and associated with the $CeNiSi_2$ structure.

It turns out that in most of the investigated compounds, and in all presented in the achievement, the antiferromagnetic ordering is observed at low temperatures and lots of variants of magnetic structures ranging from simple collinear (**G**, **A**, **C** according to the Bertaut Symbolism²⁵) to the sine-modulated structures with commensurate or incommensurate propagation vector.

In all these ternaries the magnetic ordering is the result of the competitive long-range interactions of the RKKY-type between the rare-earth magnetic moments (distance between adjacent atoms of the rare earth is about 4 Å) additionally influenced by crystal electric field (CEF) and probably also by small quadrupole–quadrupole interactions. The transition metal atoms do not have localized magnetic moments (except manganese atoms in the stoichiometric compounds²⁶). The electronic structure studies of the $CeCo_{0.86}Ge_2^{27}$ compound carried out by XPS method indicate hybridization of cerium 4f states with transition metal 3d and germanium 4p states, and that the cobalt 3d band is below the Fermi level, which explains the absence of a localized magnetic moment on the transition metal atom. Similarly, the XPS spectra analysis conducted for $NdCo_{0.82}Ge_2$ and $PrCo_{0.85}Ge_2^{28}$ showed hybridization 4f electrons of the rare earth with conduction band, indicating good shielding of the f-shell of these compounds. Specific hybridization energy values are similar to those for the $CeCo_{0.86}Ge_2$ compound.

In references H8 and H9, I carried out the analysis of magnetic interactions (including the exchange integrals) according to the RKKY and CEF model, and I made an attempt to estimate the crystal field parameters using the so-called point-charge model²⁹.

According to the RKKY model, critical temperatures of magnetic ordering should be proportional to the de Gennes factor: $G = (g-1)^2 J(J+1)$. With reference to the de Gennes scaling, T_N should reach a maximum for compounds with gadolinium. The T_N shifting from $R = Gd$ compounds to $R = Tb$ compounds observed in the compounds I studied may result from the crystalline electric field effect [H8]. The following facts confirm the crystal electric field effect on the ordering of magnetic moments:

- in all series of compounds a decrease in the magnitude of magnetic moments in the ordered state compared to the free ion R^{3+} values is observed, while the effective magnetic moments in the paramagnetic state are comparable to the free ion values;
- determined magnetic structures for compounds with tin are different than for those with germanium. In the compounds with Ge we have generally a simple antiferromagnetic structure of the **G** (+ – + –) type and the magnetic moment is along

²³ L.P. Komarowskaya, L.G. Akselrud, 1988, Izv. Akad. Nauk. SSSR, Neorg. Mater. 24, 1490

²⁴ P. Salamaka, O. Sologub, J.K. Yakintosh, Ch.D. Routs, 1998, J. Alloys Comp. 267, 192

²⁵ E.F. Bertaut, op. cit.

²⁶ B. Malaman, G. Venturini, L. Pontonnier, D. Fruchart, 1990, J. Magn. Mater. 86, 349

²⁷ A. Gil, 2004, Magnetic ordering in the rare earth intermetallic compounds of RTX_2 -type, JDU Publishing House, Czestochowa, s. 108

²⁸ A. Szytuła, B. Penc, D. Kaczorowski, A. Arulraj, S. Baran, N. Stusser, K. Tomala, 2008, J. Alloys Comp. 460, 120

²⁹ M.T. Hutchings, op. cit.

the c -axis, whereas for compounds with tin the magnetic moment of the rare earth forms an angle with the c -axis.

These results indicate that changing the p -electron element X from Ge to Sn influences magnetic interactions and leads to changes in the direction of the magnetic moments..

The calculations of CEF parameters of RT_xX_2 [H8, H9] suggest that the preferred direction of magnetic moment occurs in the plane (010) as well as that the B_2^0 , B_2^2 and B_4^0 parameter play an important role in the CEF Hamiltonian and the assumption about the leading contribution of B_2^0 parameter would be an error.

Analysis of the magnetic properties of $RSn_{1+x}Ge_{1-x}$ compounds shows similarity to the RT_xX_2 compounds. The Néel temperatures for both series of compounds are also similar. The neutron diffraction data show that the magnetic moment is localized on the rare earth atoms. Large distances between R-R atoms, as well as the metallic nature of electrical resistivity suggest that the interaction between the magnetic moments is performed via conduction electrons (model RKKY).

The data of magnetic structures types, critical temperatures, values and orientation of the magnetic moments for $RSn_{1+x}Ge_{1-x}$, RSn_2 , RT_xSn_2 and RT_xGe_2 compounds were collected in Tables 1, 2 and 3 (see pp. 18÷20). In addition to our own research results, the results of other authors are included to give a full knowledge of magnetic properties of these compounds. The observed ordering is associated with magnetic moments localized on the rare earth atoms. Except five magnetic structure types proposed for by Venturini et al.^{30 31} for tin compounds I added five additional types for germanides.

In $RSn_{1+x}Ge_{1-x}$ compounds (R=Dy, Ho, Er) magnetic ordering at temperature $T=1.5$ K can be described by the propagation vector $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)$ – AF2, as in most compounds with holmium, germanium and tin, e.g.: $HoCr_{0.33}Ge_2$ [H5], $HoCo_{0.4}Ge_2$ ³², $HoSn_2$ ³¹, $HoFe_{0.14}Sn_2$ ³⁰, $HoCo_{0.23}Sn_2$ [H3], $HoNi_{0.16}Sn_2$ [H1] – it is the most frequently occurring type of structure. The other most frequently occurring type of structure is AF1, which can be described by the wave vector $\mathbf{k} = (0, 0, \frac{1}{2})$.

The role of the T-element in interactions between the magnetic moments of the investigated compounds is insignificant, considering that its content in the compounds is small. The results show that it does not have a localized magnetic moment. Incorporation additional T atoms into the crystal lattice results in increased lattice constants and thus also in increased distance between the rare earth atoms. This results in reduction of Néel temperature - you can compare the values for RT_xSn_2 and RSn_2 compounds (Table 2). Another effect is stabilization of the collinear magnetic structures. In the RT_xSn_2 compounds collinear structures are stable up to T_N , while in RSn_2 transition to non-collinear modulated structures is observed near the T_N . Such behavior is observed in many rare earth intermetallic compounds, and is associated with competition between the RKKY-type interactions and

³⁰ B. Malaman, G. Venturini, 2010, J. Alloys Comp. 494, 44

³¹ G. Venturini, P. Lemoine, B. Malaman, B. Ouladdiaf, 2010, J. Alloys Comp. 505, 404

³² S. Baran, F. Henkel, D. Kaczorowski, J. Hernandez-Velasco, B. Penc, N. Stuser, A. Szytuła, E. Wawrzyńska, 2006, J. Alloys Comp. 415, 1

crystalline electric field³³. A small role of d-electron element was also confirmed by the investigations of $R\text{Sn}_{1+x}\text{Ge}_{1-x}$ compounds which have structures similar to the magnetic structures of RT_xSn_2 compounds.

The role of p-electron element is difficult to determine. For example, the AF2 type structure is observed in all compounds except HoT_xGe_2 where $T = \text{Ni, Cu}$. The role of individual elements is more evident in the analysis of the magnetic moments direction. In the RSn_2 compounds magnetic moments for $R = \text{Tb-Ho}$ are parallel to the c -axis, while for $R = \text{Er}$ they are parallel to the a -axis. This is in agreement with the change of the sign of Stevens α_J constant. Incorporation of d-electron element causes the magnetic moments lie in the b - c or a - c plane (Table 3). This shows that d-electron elements significantly affect altering of the parameters of the crystal electric field. It is also surprising that in TbCo_xGe_2 and DyCo_xGe_2 compounds there is no magnetic ordering, whereas for compounds with Ho and Er the magnetic ordering is observed. This fact demonstrates the complexity of magnetic interactions in this family of compounds and is difficult to explain.

Summary

The results shown in my habilitation achievement allow to:

- systematize macroscopic properties (type of arrangement, the critical temperatures of magnetic orderings) and microscopic (type of arrangement and values of the rare earth magnetic moments, no magnetic moment localized on the d-element atoms) for the studied group of compounds,
- systematize designated magnetic structures, allowing to draw conclusions about the mechanisms of interaction between the magnetic moments and the impact of the d- and p-electron elements on stabilization determined structures.

Perhaps the experimental estimation of the crystal electric field parameters for these families of compounds, determination of the anisotropy of Fermi surface and repeating neutron diffraction measurements on single-crystals would give more complete information of the impact on the mechanism of magnetic ordering.

³³ D. Gignoux, D. Schmitt, 1993, Phys. Rev. B 48, 12682

Table 1. Magnetic structures observed in RT_xX_2 , $RSn_{1+x}Ge_{1-x}$ and RSn_2 compounds

R	$RSn_{1+x}Ge_{1-x}$	RSn_2	RFe_xSn_2	RCo_xSn_2	RNi_xSn_2	RCr_xGe_2	RFe_xGe_2	RCo_xGe_2	RNi_xGe_2	RCu_xGe_2
Tb	SM1	AF1→SM1	AF1	AF1	AF1	AF4→AF7	AF6→SM1	-	AF6	AF6
Dy	AF2	AF3→SM1	AF1	-	SM1	AF4→AF2	-	-	-	-
Ho	AF2	AF2→SM1	AF2	AF2	AF2	AF2	AF2	AF2	AF6	AF6
Er	AF2→SM4	AF1→SM1	AF2	AF1	AF1	SM3	SM2	SM4	AF6	AF6

AF – antiferromagnetic structure; SM – sine-modulated structure

AF1 – $\mathbf{k} = (0, 0, \frac{1}{2})^*$; AF2 – $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, 0)^*$; AF3 – $\mathbf{k} = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})^*$; AF4 – $\mathbf{k} = (\frac{1}{2}, 0, 0)$; AF5 – $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$; AF6 – $\mathbf{k} = (0, 0, 0)$; AF7 – $\mathbf{k} = (\frac{1}{4}, 0, \frac{1}{4})$, SM1 – $\mathbf{k} = (k_x, 0, k_z)^*$; SM2 – $\mathbf{k} = (0, k_y, k_z)^*$; SM3 – $\mathbf{k} = (0, 0, k_z)$; SM4 – $\mathbf{k} = (k_x, k_y, 0)$

* The marks according to Ref.: *G. Venturini, P. Lemoine, B. Malaman, B. Ouladdiaf, 2010, J. Alloys Comp. 505, 404*

Table 2. Néel temperatures T_N [K] for presented compounds

R	$R\text{Sn}_{1+x}\text{Ge}_{1-x}$	$R\text{Sn}_2$	$R\text{Fe}_x\text{Sn}_2$	$R\text{Co}_x\text{Sn}_2$	$R\text{Ni}_x\text{Sn}_2$	$R\text{Cr}_x\text{Ge}_2$	$R\text{Fe}_x\text{Ge}_2$	$R\text{Co}_x\text{Ge}_2$	$R\text{Ni}_x\text{Ge}_2$	$R\text{Cu}_x\text{Ge}_2$
Tb	31 ³⁵ , 29 ³⁶	26.7 ³⁷	18.4 ³⁸	18.8 ³⁹	17.4 ⁴⁰	18.5 ⁴³	20 ⁴⁴ , 22.6 ⁴⁵	-	16 ⁴⁹ , 31 ⁵⁰ , 38 ⁵⁰	39 ⁴⁹
Dy	16 ³⁶	17.2 ³⁷	6.9 ³⁸	7 ³⁹	8 ⁴¹	11.8 ⁴³	-	10 ⁴⁸	-	-
Ho	10.7 ³⁵ , 10 ³⁶	7.8 ³⁷	5.9 ³⁸	5.6 ³⁹	6.6 ⁴⁰	5.8 ⁴³	8 ⁴⁶	8 ⁴⁸	11 ⁵¹	8 ⁵²
Er	4.8 ³⁵ , 4 ³⁶	4.5 ³⁷	5.5 ³⁸	4.5 ³⁹	4 ⁴²	3.4 ⁴³	2.5 ⁴⁷	~1.5 ⁴⁸	2.3 ⁴⁷	4.5 ⁵²

³⁵ A. Gil, B. Penc, S. Baran, A. Hoser, A. Szytuła, 2011, *Journal of Solid State Chemistry*, 184, Issue: 7, 1631

³⁶ P.H. Tobash, J.J. Meyers, G. DiFilippo, S. Bobev, F. Ronning, J.D. Thompson, J.L. Sarrao, 2008, *Chem. Mater.* 20, 2151

³⁷ G. Venturini, P. Lemoine, B. Malaman, B. Ouladdiaf, 2010, *J. Alloys Comp.* 505, 404

³⁸ B. Malaman, G. Venturini, 2010, *J. Alloys Comp.* 494, 44

³⁹ A. Gil, B. Penc, E. Wawrzyńska, J. Hernandez-Velasco, A. Szytuła, A. Zygmunt, 2004, *Journal of Alloys and Compounds* 365, 31

⁴⁰ A. Gil, B. Penc, S. Baran, J. Hernandez-Velasco, A. Szytuła, A. Zygmunt, 2003, *Journal of Alloys and Compounds* 361, 32

⁴¹ A. Gil, B. Penc, S. Baran, E. Wawrzyńska, A. Szytuła, J. Hernandez-Velasco, A. Zygmunt, 2003, *Neutron Scattering and Complementary Methods in Investigations of Condensed Phase, Vol.1, University of Podlasie Publishing House © Monograph No. 45, p. 103*

⁴² B. Penc, E. Wawrzyńska, A. Szytuła, A. Gil, J. Hernandez-Velasco, A. Zygmunt, 2004, *Journal of Alloys and Compounds*, 375, L1

⁴³ A. Gil, D. Kaczorowski, B. Penc, A. Hoser, A. Szytuła, February 2011, *Journal of Solid State Chemistry, Vol.: 184, Issue: 2, p. 227*

⁴⁴ M.A. Zhuravieva, D. Bilc, R.J. Pcionek, S.D. Mahanti, M.G. Kamatzidis, 2005, *Inorg. Chem.* 44, 2177

⁴⁵ A. Gil, A. Hoser, B. Penc, A. Szytuła, October 2013, *Journal of Magnetism and Magnetic Materials Volume: 344, p. 167*

⁴⁶ S. Baran, Ł. Gondek, J. Hernandez-Velasco, D. Kaczorowski, A. Szytuła, 2005, *J. Magn. Magn. Matter.* 285, 188

⁴⁷ B. Penc, A. Arulraj, D. Kaczorowski, A. Szytuła, E. Wawrzyńska, 2010, *Acta Physica Polonica A* 117, 595

⁴⁸ S. Baran, F. Henkel, D. Kaczorowski, J. Hernandez-Velasco, B. Penc, N. Stuser, E. Wawrzyńska, 2006, *J. Alloys Comp.* 415, 1

⁴⁹ P. Schobinger-Papamentellos, K.H.J. Buschow, 1992, *J. Alloys Comp.* 187, 73

⁵⁰ P. Schobinger-Papamentellos, K.H.J. Buschow, C. Ritter, 1999, *J. Alloys Comp.* 287, 51

⁵¹ W. Bażela, J. Leciejewicz, K. Małetka, A. Szytuła, 1992, *J. Magn. Magn. Mater.* 109, 305

⁵² A. Gil, D. Kaczorowski, J. Hernandez-Velasco, B. Penc, E. Wawrzyńska, A. Szytuła, 2004, *Journal of Alloys and Compounds* 384, L4

Table 3. Magnetic moments in ordered state (μ_s [μ_B]) and the directions of rare earth magnetic moments

R	$RSn_{1+x}Ge_{1-x}$	RSn_2	RFe_xSn_2	RCo_xSn_2	RNi_xSn_2	RCr_xGe_2	RFe_xGe_2	RCo_xGe_2	RNi_xGe_2	RCu_xGe_2
Tb	9.0, (<i>b-c</i>)	8.8, $\parallel c$	8.1, (<i>b-c</i>)	7.14, (<i>a-c</i>)	8.05, (<i>a-c</i>)	7.6, $\parallel c \rightarrow 4.52$, (<i>a-c</i>)	3.81, $\parallel c \rightarrow 7.75$, (<i>b-c</i>)	-	5.6, 8.9, 8.7, $\parallel c$	8.82, $\parallel c$
Dy	7.25, $\parallel c$	4.2, $\parallel c$	5.5, (<i>b-c</i>)	-	9.2, (<i>b-c</i>)	4.46 \rightarrow 7.18, (<i>a-c</i>)	-	3.55*	-	-
Ho	8.6, $\parallel c$	7.4, $\parallel c$	6.6, (<i>b-c</i>)	6.79, (<i>a-c</i>)	7.46, (<i>a-c</i>)	6.99, $\parallel c$	5.4, $\parallel c$	8.0, <i>a-c</i>	6.7, $\parallel c$	8.18, $\parallel c$
Er	7.76, $\parallel b$	2.07, $\parallel a$	7.3, $\parallel a$	6.15, $\parallel a$	9.16, $\parallel a$	8.32, $\parallel a$	5.9, $\parallel a$	3.3, $\parallel c$	2.9, $\parallel a$	7.89, $\parallel a$

* the result comes from the magnetic measurements

Other results are quoted according to the same references as in Table 2.

VI. Other achievements of scientific research

I am a graduate of Physics, specialization: Solid State Physics, at the Faculty of Mathematics and Physics of the Jagiellonian University in Cracow. I defended my Master's thesis prepared under the supervision of prof. dr. hab. Andrzej Szytuła “*The study of inorganic structures in biological systems*” in June 1988.

In the context of my work, the arterial mineral products (mainly aortic) were studied with the use of the X-ray diffraction to determine which chemical components are precipitated during the aging process. The main mineral component found in the aortas was a hydroxyapatite, a compound with hexagonal structure consisting mainly of calcium and phosphorus. The results were so interesting that they were included in the joint publication: E. Rokita, T. Cichocki, D. Heck, L. Jarczyk, A. Miłoś (now A. Gil), J. Ryczek, A. Strzałkowski, A. Szytuła, „*Physicochemical characterization of the inorganic phases in the aortic wall of young individuals*”. *Pathologica* 84 (1992) 489–502.

a) Scientific work before obtaining a Ph.D. Degree

After graduation, in October 1988, I started working at the Institute of Physics of the Cracow University of Technology as an assistant-trainee, continuing the scientific cooperation with professor Szytuła (Institute of Physics Jagiellonian University). I started a study of structural and magnetic properties of ternary intermetallic compounds with rare earth, transition metal and silicon or germanium.

My attention was initially concentrated on a group of intermetallic compounds of RTX_2 type, wherein R – rare earth metal, T – 3d metal (mostly Ni, Mn) and X = Si, Ge. The X-ray diffraction studies of polycrystalline samples confirmed the $CeNiSi_2$ type crystal structure of these compounds. On the basis of the magnetometric results (magnetic susceptibility, magnetization – conducted in IFUJ and INTiBS in Wrocław) and neutron diffraction data (conducted in Świerk with the help of professor Janusz Leciejewicz), I described the magnetic properties including determination of the magnetic structure of the aforementioned family of compounds.

I did not observe any magnetic moment on nickel atoms. In compounds with light rare earths (Nd, Pr) ferromagnetic ordering at low temperatures was observed, whereas in those with heavy rare earths (Tb, Dy, Ho, Er) the arrangement was of anti-ferromagnetic nature⁵³. Therefore, it seemed interesting to examine the mixed systems $Tb_{1-x}Nd_xNiGe_2$ ^{55,56}, where the transition from antiferro- to ferromagnetic ordering for $x > 0.65$ neodymium content was observed. The results were published in worldwide journals and became the basis for the

⁵³ A. Gil, A. Szytuła, Z. Tomkowicz, K. Wojciechowski, A. Zygmunt, 1994, *J. Magn. Magn. Mater.*, 129, 271-278

⁵⁴ A. Gil, J. Leciejewicz, K. Małetka, A. Szytuła, Z. Tomkowicz, K. Wojciechowski, 1994, *J. Magn. Magn. Mater.*, 129, L155-L159

⁵⁵ A. Gil, J. Leciejewicz, K. Małetka, A. Szytuła, A. Zygmunt, 1994, *J. Magn. Magn. Mater.*, 131, 217–223

⁵⁶ A. Gil, J. Leciejewicz, A. Szytuła, Z. Tomkowicz, A. Zygmunt, 1995, *J. Magn. Magn. Mater.* 140-144, 927–928

development of a doctoral dissertation written under the supervision of professor Szytuła: *Structural and magnetic properties of intermetallic compounds RTX₂-type*. In the dissertation, I presented my experimental results and, additionally, I conducted an analysis of magnetic interactions for this group of compounds based on existing theories, ie. RKKY model and the crystalline electric field model (CEF).

The change in arrangement of magnetic moments observed in Tb_{1-x}Nd_xNiGe₂ compounds can be explained based on the RKKY theory, but the Néel temperature dependence as a function of de Gennes factor for RNiX₂ compounds with heavy rare earths can be explained when the CEF terms are added to the exchange Hamiltonian.

Defense of the Dissertation took place in 1994 at the Faculty of Mathematics and Physics of the Jagiellonian University.

b) Scientific work after obtaining a Ph.D. Degree

In 1995-1998 due to maternity and child care there was a break in my research work. At that time, I moved to Czestochowa and after parental leave ie. 1st October 1998, I started working at the Institute of Technical Education at Jan Długosz University of Czestochowa and continued research topics and scientific collaboration with professor Szytuła's research group expanding research themes for other families of intermetallic compounds.

The compounds of the RTX₂ composition remained within the range of my main interests, but in a much wider range of constituent elements. I undertook studies of magnetic properties, including magnetic structures of compounds with germanium and tin, which usually crystallize in nonstoichiometric RT_xX₂ composition, but all have the same orthorhombic CeNiSi₂ type crystal structure (space group Cmcm).

Neutron diffraction measurements of RMn_xGe₂⁵⁷ compounds, carried out before my Ph.D degree, showed that the compounds are antiferromagnets at 4.2 K with a simple collinear magnetic structure of the **G** (+ - + -) type and magnetic moments lie along the c-axis⁵⁸. Neutron diffraction studies of TbMn_{0.33}Ge₂ were repeated with the use of the E6 diffractometer in Berlin Neutron Scattering Center, which offered better resolution and was equipped with multichannel detectors. Magnetic structure of TbMn_{0.33}Ge₂ determined at 1.5 K proved to be more complex than the ones reported earlier⁵⁹. The Tb magnetic moment was consisted of two components: collinear antiferromagnetic G_z-type equal to 6.95(10) μ_B and sine-modulated with wave vector **k** = (0.6885, 0.0660, 0.1701), equal to 4.5(2) μ_B and parallel to the *a*-axis. The total Tb magnetic moment of 8.2(2) μ_B was close to the free Tb³⁺ ion value.

Similarly to the earlier performed neutron diffraction measurements of the Tb_{0.4}Nd_{0.6}NiGe₂ compound, which demarcates the ferro- and antiferromagnetic Tb_{1-x}Nd_xNiGe₂ compounds, the repeated studies confirmed existence of the G_z type

⁵⁷ A. Gil, J. Leciejewicz, K. Małetka, A. Szytuła, Z. Tomkowicz, K. Wojciechowski, 1994, J. Magn. Mater. 129, L155–L159

⁵⁸ E.F. Bertaut, op. cit.

⁵⁹ A. Gil, M. Hofmann, B. Penc, A. Szytuła, 2001, J. Alloys Comp. 320, 29

antiferromagnetic structure at the temperature below 11 K, and at the same time revealed a complex magnetic structure below 6 K⁶⁰.

Analysis of the neutron-diffraction patterns measured at temperatures 1.5 and 6 K showed that the positions of the magnetic reflections are the same, while the intensities are different, which indicates that the magnetic ordering changes. In the low-temperature patterns at 1.5 K two sets of magnetic reflections are observed. The analysis of their intensities gives a complex magnetic ordering with:

- an antiferromagnetic component corresponding to the **G**-mode with the magnetic moment equal to 2.35(14) μ_B situated in the *b*-*c* ($\mu_b = 1.44(37) \mu_B$ and $\mu_c = 1.86(16) \mu_B$) plane, and
- a ferromagnetic component with *m* equal to 2.82(27) μ_B and parallel to the *c*-axis.

The additional small intensity peak at $2\theta = 13.6^\circ$ indicates the existence of modulated ordering described by the propagation vector $\mathbf{k} = (0, 0.428, 0)$. A similar modulated structure is observed in isostructural, nonstoichiometric TbNi_xGe₂ compounds⁶¹.

Neutron diffraction studies of CeCu_{0.86}Ge₂ compound⁶² showed the collinear antiferromagnetic ordering corresponding to the **C** (+ + - -) mode. At 1.5 K the magnetic moment of Ce is 1.85(4) μ_B and at 5 K – 1.83(4) μ_B and it is parallel to the *c*-axis.

The symmetry analysis of the magnetic phase transition from the paramagnetic phase of PrMn_{0.5}Sn_{1.83} compound⁶³, with the Pr atoms in the 4(*c*) positions, to the magnetic state with propagation vector $\mathbf{k} = (0, 0, 0)$ led to the conclusion that the magnetic structure of this compound consists of ferromagnetic layers of Pr magnetic moments lined along the *b*-axis according to the (+ - + -) sequence. The Pr magnetic moments equal to 3.09(8) μ_B are parallel to the *c*-axis. This value is close to the free ion Pr³⁺ (3.27 μ_B). No ordering in the Mn sublattice was detected.

There were also magnetometric and neutron diffraction measurements performed for RNi_xSn₂, RCo_xSn₂ and RCu_xGe₂ – they are described in details in the discussion on the habilitation achievement.

I also took on studies of stoichiometric compounds with germanium of RTGe₂ type, where R = Gd–Er, T = Ir, Pt, which also have an orthorhombic structure, but of the YIrGe₂ type (space group Immm), in order to determine how the change of the crystal structure affects the arrangement of magnetic moments.

The results of the studies indicated that at high temperatures magnetic susceptibility for both RT_xX₂ and RTGe₂ series of compounds obey the Curie–Weiss law and the effective magnetic moments are close to the free R³⁺ ions values. Thus, the magnetic properties of these compounds correspond to rare earth elements. At low temperature (liquid helium), most of the compounds become antiferromagnets and, at the same time, a large variety of magnetic structures can be observed.

The mechanism of interaction in the RTGe₂ compounds (T = Pd, Pt, Ir) is more complex than in RT_xX₂. The rare earth atoms are distributed over two distinct sublattices 4(*i*) and 4(*h*)

⁶⁰ A. Gil, B. Penc, N. Stusser, A. Szytuła, 2004, Physica B, 350, e327–e329

⁶¹ P. Schobinger-Papamentellos, K.H.J. Buschow, C. Ritter, 1999, J. Alloys Comp. 287, 51

⁶² A. Gil, B. Penc, Ł. Gondek, A. Szytuła, J. Hernandez-Velasco, 2002, J. Alloys Comp. 346, 43–46

⁶³ A. Gil, A. Oleś, W. Sikora, A. Szytuła, 2003, J. Alloys Comp. 360, 21–23

sites with different atomic coordination. All the investigated compounds have antiferromagnetic ordering of magnetic moments at low temperatures. In some compounds the magnetic ordering in the different sublattices occurs independently at different temperatures. In most compounds the critical temperatures for the $4(i)$ sublattice were higher than the one for the $4(h)$ sublattice. The Néel temperatures T_N do not satisfy the de Gennes scaling. Rare earth atoms in the $4(i)$ sublattice have the same atomic scheme as in the CeNiSi₂ type structure. The results of neutron diffraction studies have shown that magnetic moments in this sublattice form collinear antiferromagnetic structures. Magnetic moments in the $4(h)$ sublattice, where the rare earth atoms have different atomic scheme, form other order, mainly modulated. This result indicates that differences in the atomic scheme influence the type of magnetic moment arrangements in these systems.

The investigation of RTGe₂ compounds (T = Pt, Pd) carried out almost simultaneously by Papathanassiou et al.^{64 65} and Schmitt et al.⁶⁶ led the authors to similar conclusions: the magnetic moments of $4(i)$ and $4(h)$ sublattices order independently at different temperatures and give rise to collinear and modulated structures. Magnetic moments on different sublattices lie along different crystallographic directions. This reflects the high magnetocrystalline anisotropy.

Results of the studies mentioned above were published in journals included in the JCR database, as well as in national publications and were also used to prepare and publish a Monograph entitled: *Magnetic ordering in rare earth intermetallic compounds RTX₂ type*⁶⁷.

In this monograph I analyzed and sorted my results together with the data found in literature for such compounds. I conducted a discussion on the role of nonstoichiometry, magnetic interactions and crystal electric field in these systems, and how these factors affect e.g. the size of the magnetic moment. I also analyzed properties of the CeT_xGe₂ compounds, where T – 3d-metal (Fe, Co, Ni, Cu). When the number of d-electrons increase we observed the change from lack of magnetic ordering in compounds with Fe and Co to appearance of magnetic order in those with Ni and Cu at low temperatures. These changes can be associated with the change of the Sommerfeld constant γ and with the related density of states at the Fermi level.

Till 2005, I published a total of 21 publications (including 15 after obtaining the Ph.D. degree) in journals in the JCR database and 10 articles in national publications, of which 3 were review articles published in the Scientific Issues of Pedagogical University in Czestochowa and 1 article was a chapter in the Monograph No. 45 University of Podlasie Publishing House © 2003.

Before 2005, I participated in 3 international conferences: 2nd European Conference on Neutron Scattering (ECNS) – Budapest 1999, European Spallation Source (ESS) – European Conference – Bonn 2002, and 3rd ECNS - Montpellier 2003, and 8 national conferences and I presented my results in the form of oral presentations or posters.

⁶⁴ G. Papathanassiou., P.A. Kostanidis, J.K. Yakinthos, 1998, Zeitschr. Kristallogr. 213, 28

⁶⁵ G. Papathanassiou., P.A. Kostanidis, J.K. Yakinthos, W. Schäfer, 1999, J. Alloys Comp. 290, 17

⁶⁶ D. Schmitt, B. Ouladdiaf, Ch.D. Routsis, J.K. Yakinthos, H. Gamari-Seale, 1999, J. Alloys Comp. 292, 21

⁶⁷ A. Gil, 2004, Magnetic ordering in the rare earth intermetallic compounds of RTX₂-type, JDU Publishing House, Czestochowa

I had 4 oral presentations:

- in Bonn – *Crystal and magnetic structure of CeCu_{0.86}Ge₂* in 2002,
- in Chlewiska
 - a) *Magnetic properties and magnetic structure of RIrGe₂ compounds (R = Gd-Er)* in 2001,
 - b) *Magnetic structure of RT_xSn₂ compounds (R=Tb, Ho; T=Ni, Co)* in 2003,
- in Kule – *New magnetic structure of TbMn_{0.33}Ge₂ compound* in 2001,

and I presented 8 posters. During the 9th International Seminar on Physics and Chemistry of Solids in Zloty Potok in 2003. I was awarded the Best Poster Prize.

With the above achievements I entered the habilitation colloquium, which took place on 6 December 2005 before the Scientific Council of the Institute of Physics at the Faculty of Mathematics, Physics and Chemistry of the University of Silesia in Katowice. All three reviewers appointed by the Council of the Institute of Physics, sent positive reviews and supported the request of the Council for granting me the postdoctoral degree.

By decision of the Scientific Council of the Institute of Physics the postdoctoral degree has been granted to me and, in accordance to the applicable rules, my documentation was submitted to the Central Commission for the Academic Degrees and Titles (CC) for approval habilitation. Unfortunately, a “super reviewer” appointed by the CC expressed a negative opinion and in spite of appointment of another reviewer, whose opinion was positive, the verdict of the CC was unfavorable for me and in October 2006, I received a negative decision regarding the approval of my postdoctoral degree.

Unable to accept the allegations of the “super reviewer” No 1 and decision of the Central Commission I applied to the Council of the Institute of Physics of the University of Silesia for a joint appeal against the CC decision, which the Council did.

Regrettably, in October 2008. (After almost three years after the colloquium) after two additional reviews commissioned by the CC and both positive, I was astonished to receive another refusal to recognize my habilitation.

In 2009, I took the new study of intermetallic compounds of the RCr_{0.3}Ge₂ (R = Tb, Dy, Ho and Er) and RSn_{1+x}Ge_{1-x} (R = Tb-Er) families, which have CeNiSi₂ type crystal structure. It seemed interesting to compare the results with those for RT_xX₂ (X = Ge, Sn) to determine the influence of p- and d-electron elements on the magnetic ordering in rare earth sublattice - the results of these studies are described in the section of habilitation achievement.

After obtaining the Ph.D. degree I have examined the total of approx. 40 rare earth intermetallic compounds and I have determined their magnetic properties and magnetic structures.

I have recently undertaken the theoretical research in order to clarify the nature of the magnetic behavior of the compounds studied by me. I started with theoretical calculations of magnetic and electronic properties of RCrGe₂ and RCr_{0.3}Ge₂ (R = Tb, Dy, Ho and Er) compounds applying plane-wave DFT/PBE⁶⁸ methodology. The computational investigations were performed for the stoichiometric and nonstoichiometric crystal structure

⁶⁸ A. Gil, M. Makowska-Janusik, 2015, Acta Physica Polonica A, Vol. 127, No 2, 385

with the Cmcm space group. The theoretical predictions were compared to the experimentally obtained results. The results lead to the following conclusions: the diverse magnetic behavior originates from the competition of interactions between the R atoms, which are arranged in double-layer slabs stacked perpendicularly to the *b*-axis. In the Cr reached structures the d-electrons on the Cr atoms contribute little to the magnetic properties of crystals. The stoichiometry of the rare-earth chromium germanide compounds has significant effect on their electronic properties. These findings correlate well with the experimentally obtained results. In the near future I plan to undertake a similar study of theoretical relationships with manganese and cobalt.

c) Other works outside the discipline represented

Due to my employment in the Institute of Technical Education at the Jan Długosz University and because of the need to teach not only physics but also other subjects such as information technology I focused my research interests on the information technology and its wide applications, which resulted in publishing articles about the use of the interactive whiteboard in teaching⁶⁹, the use of a virtual laboratory for teaching^{70 71}, the role of social networks⁷². At the time when I was the Director of the Institute, we started a new course of study called "Safety Engineering". Due to the change in the education profile and the need to shift the scope of scientific interest in the Institute to the safety engineering direction, I concentrated on security problems of information and communication technologies, which resulted in publishing the articles about analysis of means and methods of protection the operating systems⁷³, cybercrime⁷⁴, conditions copyright protection for computer programs⁷⁵ and the protection of personal data⁷⁶.

Social transformations and technological developments (including new communication technologies and IT), as well as globalization, have led to a substantially easier access to knowledge, mass application of IT (including the Internet), and the need for continuous improvement and adaptation. Therefore, in 2011, I joined the European project QEdUSen (<http://www.edusenior.eu/>), the aim of which was to create a toolkit for evaluating

⁶⁹ T. Prauzner, A. Gil, 2008, "Zastosowanie nowoczesnych środków dydaktycznych w nauczaniu przedmiotów technicznych", [w:] Informatyka w kształceniu, red. K. Lenik, G. Borowski, Lubelskie Towarzystwo Naukowe, tom II, s. 31-37

⁷⁰ A. Gil, M. Drabik, 2009, *Wirtualne laboratorium pomiarowe*, [w:] Postępy nauki i techniki nr 3, s. 96-103

⁷¹ M. Drabik, A. Gil, U. Nowacka, *Virtual laboratory in the engineering education*, [in:] Rural Environment. Education. Personality, Proceedings of the International Scientific Conference, No. 6, ISSN 2255-808X., 2013, Jelgava, Latvia, p. 317-323

⁷² A. Gil, 2011, *Portale społecznościowe sposobem na społeczny problem samotności*, Zeszyty Naukowe Uniwersytetu Szczecińskiego Nr 656 „Studia Informatica" nr 28, s.239-252

⁷³ A. Gil, T. Karoń, 2012, *Analiza Środków i Metod Ochrony Systemów Operacyjnych*, Postępy nauki i techniki nr 12, s. 149-168

⁷⁴ A. Gil, U. Nowacka, 2012, *Cyberprzestępczość, klasyfikacja, zwalczanie, zapobieganie*, [w:] Monografii: Inżynieria bezpieczeństwa a zagrożenia cywilizacyjne, tom I, red. A. Gil, U. Nowacka, M. Chmiel, Częstochowa, s. 309-323

⁷⁵ U. Nowacka, A. Gil, 2010, *Uwarunkowania prawnoautorskiej ochrony programów komputerowych*, Postępy nauki i techniki nr 4, s. 5-11

⁷⁶ A. Gil, K. Nowotna, 2014, *Ochrona danych osobowych na przykładzie wybranego Urzędu Miasta*, [w:] Prace naukowe Akademii im. Jana Długosza w Częstochowie Technika, Informatyka, Inżynieria bezpieczeństwa", red. M. Sosnowski, tom II, s. 69-80

educational institutions that are currently offering courses and activities aimed at senior learners or would like to introduce learning activity for this group. In the Multilateral LLP project, implemented from 1.11.2011 to 01.31.2014 by 7 European countries (Spain, Italy, Finland, Latvia, Poland, Bulgaria, Hungary), 75% of which was financed by the European Commission (project value EUR 393,799). a guide *Education and quality of life of senior citizens* and *Evaluation toolkit for educational institutions; increasing impact on Senior learners' quality of life* were developed. They will be useful as well as innovative for educational institutions in shaping the education of the elderly. During the project I coordinated the work of the Polish group of researchers. I participated in 5 coordination meetings of project's partners (in Czestochowa, Jurmala, Budapest, Sofia, Barcelona) and in conferences, where I promoted the project's idea. Apart from a significant contribution to the development of the project's products, published in English and translated into all languages of the partners I was also a co-author of a few articles concerning education of the seniors^{77 78 79}.

A list of all published works together with a specification of my individual contribution can be found in Annex 4.

Ahina Gil

⁷⁷ A. Gil, U. Nowacka, L. Ochoa, 2012, *Analysis of selected areas of educational activity of senior citizens*, [w:] Society, Integration, Education. Proceedings of the International Scientifical Conference, Rezekne Vol. 1, p. 490-496, ISSN 1691-5887

⁷⁸ A. Kozerska, E. Napora, M. Piasecka, A. Gil, J. Górna, U. Nowacka, L.S. Ochoa, 2014, *Psycho-educational context of supporting seniors in Poland, using tools from the Edusenior project*, [w:] Society, Integration, education, Proceedings of International Scientifical Conference, Rezekne, part II, p.124-138, ISSN 1691-5887, ISBN 978-9984-44-141-2

⁷⁹ U. Nowacka, A. Gil, L. Ochoa, 2014, „*Uczyć się aby być*” w aspekcie aktywności edukacyjnej seniorów, [w:] Monografii „Podstawy Edukacji. Trendy Cywilizacyjne Wobec Wiedzy, Innego Człowieka, Społeczeństwa”, Wydawnictwo Impuls, Kraków, s. 345-360, ISBN 978-83-7850-693-5