Summary of Professional Accomplishments

PhD Eng. Dominika Jendrzejczyk-Handzlik

AGH University of Science and Technology
Faculty of Non-Ferrous Metals

1. Name and Surname:

Dominika Jendrzejczyk-Handzlik

2. Diplomas and scientific degrees - with the name, place and year of obtaining them, the title of doctoral dissertation and the names of persons who acted as supervisors and reviewers

PhD in Technical Sciences

Subject: Metallurgy
Title of PhD dissertation: “Determination of thermodynamic properties of liquid Ag-In-Sb and Ag-In-Sn solutions by electrochemical method”
Date of defense: 25.07.2008
Place: AGH University of Science and Technology in Krakow, Faculty of Non-Ferrous Metals
Supervisor: Prof. Dr. Hab. Eng. Krzysztof Fitzner
Reviewers: Prof. Dr. Hab. Eng. Jan Botor,
Prof. Dr. Hab. Lidia Burzyńska

Master of Science

Subject: Materials Science
Title of MSc dissertation: “Determination of the rate of corrosion of titanium using polarization measurements”
Date of defense: 01.07.2003
Place: AGH University of Science and Technology in Krakow, Faculty of Non-Ferrous Metals
Supervisor: Prof. Dr. Hab. Eng. Krzysztof Fitzner

3. Information on current employment in scientific institutions

Assistant Professor
AGH University of Science and Technology in Krakow, Faculty of Non-Ferrous Metals
Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals
01.01.2009 – until now

Assistant
AGH University of Science and Technology in Krakow, Faculty of Non-Ferrous Metals
Department of Physical Chemistry and Electrochemistry
01.01.2007-31.12.2008

Senior technical consultant
AGH University of Science and Technology in Krakow, Faculty of Non-Ferrous Metals
Department of Physical Chemistry and Electrochemistry
02.02.2004-31.12.2006

4. Description of scientific achievement obtained after receiving a doctoral degree, declared as a significant contribution to the development of the discipline of Metallurgy in accordance with Article 16 paragraph 2 of the Act of 14 March 2003 on the Academic Degrees and the Academic Title and on the Degrees and the Title in the Arts

a. The title of the scientific achievement

Thermodynamic properties and phase equilibria in systems with gallium

b. List of scientific papers documenting the scientific achievement (s) justifying the request to open the habilitation proceedings is enclosed at the end of this document

A.1. **D. Jendrzejczyk-Handzlik**, K. Fitzner, 2011, *Thermodynamic properties of liquid silver-gallium alloys determined from e.m.f. and calorimetric measurements*, Journal of Chemical Thermodynamics 43, 392-398.
(Impact Factor: 2.422) (List of Ministry of Science and Higher Education: 35)

My contribution to this work consisted in performing electrochemical and calorimetric measurements. I carried out an analysis of the obtained results. I wrote part of the work, made all the drawings and tables, and made a manuscript correction after the reviews. I estimate my contribution as **80%**.

A.2. W. Gierlotka, **D. Jendrzejczyk-Handzlik**, 2011, *Thermodynamic description of the binary Ag-Ga system*, Journal of Alloys and Compounds 509, 38-42.
(Impact Factor: 2.289) (List of Ministry of Science and Higher Education: 35)

My contribution to of this work consisted in creating a thermodynamic data base for the liquid phase used to calculation the Ag-Ga system. I estimate my contribution as **30%**.

A.3. **D. Jendrzejczyk-Handzlik**, P. Handzlik, K. Fitzner, 2014, *Enthalpies of mixing of liquid Ag–Ga, Cu–Ga and Ag–Cu–Ga alloys*, Calphad 44, 39-47.
(Impact Factor: 1.370) (List of Ministry of Science and Higher Education: 25)

My contribution to this work consisted in developing a research concept. I carried out calorimetric measurements and analyzed the obtained results. I wrote the content of the publication, I made almost all the figures and tables, and made a manuscript correction after the reviews. I estimate my contribution as **80%**.

A.4. **D. Jendrzejczyk-Handzlik**, K. Fitzner, W. Gierlotka, 2015, *On the Cu – Ga system: Electromotive force measurement and thermodynamic reoptimization,* Journal of Alloys and Compounds 621, 287–294.
(Impact Factor: 3.014) (List of Ministry of Science and Higher Education: 35)

My contribution to this work consisted in performing electrochemical measurements and analyzing the obtained results. I wrote part of the work, I made some figures and tables. I made the correction of the manuscript after the reviews. I estimate my contribution as **45%**.

A.5. **D. Jendrzejczyk-Handzlik**, K. Fitzner, 2015, *Thermodynamic stability of copper gallates determined from the E.M.F.method,* Journal of Solid State Chemistry 232, 207–212.
(Impact Factor: 2.265) (List of Ministry of Science and Higher Education: 30)

My contribution to the creation of this work consisted in performing electrochemical measurements and then analyzing the obtained results. I wrote part of the work, I made all the figures and tables. I made the correction of the manuscript after the reviews. I estimate my contribution as **60%**.

A.6. W. Gierlotka, **D. Jendrzejczyk-Handzlik**, K. Fitzner, P. Handzlik, 2015, *On the ternary Ag - Cu - Ga system: Electromotive force measurement and thermodynamic modeling,* Journal of Alloys and Compounds 646, 1023-1031.
(Impact Factor: 3.014) (List of Ministry of Science and Higher Education: 35)

My contribution to the creation of this work consisted in performing electrochemical measurements and then analyzing the obtained results. I wrote part of the work, I made some figures and tables. I made the correction of the manuscript after the reviews. I estimate my contribution as **40%**.

A.7. **D. Jendrzejczyk-Handzlik**, 2017, *Enthalpies of mixing of liquid Ag–Ga, Au–Ga and Ag–Au–Ga alloys,* The Journal of Chemical Thermodynamics, 107, 114-125.
(Impact Factor: 2.784) (List of Ministry of Science and Higher Education: 30)

My participation in the publication **100%**.

A.8. **D. Jendrzejczyk-Handzlik**, 2017, *Thermodynamic Study and Re-optimization of the Au-Ga Binary System,* Journal of Phase Equilibria and Diffusion 38, 305-318.
(Impact Factor: 0.748) (List of Ministry of Science and Higher Education: 15)

My participation in the publication **100%**.

A.9. **D. Jendrzejczyk-Handzlik**, 2017, *Phase Equilibria in the Ternary Ag-Au-Ga System: Isothermal Sections at 250°C and 450°C*, Journal of Mining and Metallurgy, Section B: Metallurgy 53 (3) B, 215-222.
(Impact Factor: 0.807) (List of Ministry of Science and Higher Education: 30)

My participation in the publication **100%**.

A.10. **D. Jendrzejczyk-Handzlik**, 2018, *Thermodynamic properties of liquid silver-gold–gallium alloys determined from EMF measurements with solid YSZ electrolyte*, Thermochimica Acta, 622, 126-134.
(Impact Factor: 2.545) (List of Ministry of Science and Higher Education: 30)

My participation in the publication **100%**.

c. Scientific objective of the study/studies and the results achieved including a discussion of their possible use

" Thermodynaimc properties and phase equilibria in systems with gallium"

Noble metals such as gold, silver, platinum and palladium are recovered in Poland during the production of copper and silver by KGHM Polska Miedź S.A. Then, these metals are usually sold as pure metals. The jewelry industry is strongly associated with noble metals. Different colors of gold, which is used in the production of jewelry items, are created by the formation of gold-based alloys in which the type and amount of used additives determine the color of the material obtained. Currently, the most commonly used gold alloys for jewelry are: green gold (Ag-Au alloy), red gold (Au-Cu alloy), white gold (Au-Cu-Ni-Zn alloy or Ag-Au-Pd) and yellow gold (Ag-Au-Cu alloy). A separate group consists of special gold colors such as purple, blue, brown and black *(K. Wongpreedee et al., Proceedings Gold 2009 - The 5th international conference on gold science, technology and its applications, Heidelberg, Germany 2009, 366 oraz K. Masubuchi et al., Proceedings Gold 2009 - The 5th international conference on gold science, technology and its applications, Heidelberg, Germany 2009, 256)*. There are two ways of obtaining this type of gold color: one by surface change of the color, and the other through the preparation of a specific alloy based on gold.

The purple and blue color of gold is obtained by alloying gold with indium, gallium and aluminum, where the basis is the occurrence of intermetallic phases with a fixed AuX_2 stoichiometry (X = Al, Ga, In). The purple gold corresponds to $AuAl_2$ phase in which exhibit good optical properties (*S. Supansombon, A. Maaroof, M.B. Cortie, Gold Bull. 41, 2008, 296*). Dark blue gold corresponds to $AuIn_2$ and light blue to $AuGa_2$.

In recent years, an interest in the use of gallium and its compounds has increased. Gallium is a metal with unparalleled properties among other metals. It occurs in a liquid state in a wide temperature range because its melting point is close to room temperature and is equal to 29 °C, while the boiling point is 2400 °C. Therefore, the introduction of gallium into multi-component alloys should bring down their melting temperature. This effect can be used in the amalgam bonding process. This is a very interesting process, but not yet well known, and has been described so far only by MacKey (*C.A. MacKay IEEE Micro, 13, 1993, 46*) and Schmid-Fetzer (*R. Schmid-Fetzer, Fundamentals of bonding by isothermal solidification for high temperature semiconductor applications, in: R.Y. Lin, Y.A. Chang, R.G. Reddy, C.T. Liu (Eds.*), *Design fundamentals of high temperature composites, intermetallics and metal-ceramic system, Proceedings of the 125th TMS Annual Meeting; Anaheim, CA, USA 4 -8 Feb 1996, The Minerals, Metals & Materials Society, Warrendale, PA (USA) 1996 75-98*). In this method the joint is made at a low temperature, close to room temperature. In this process, low-melting metal is a solvent. It seems that gallium is the most suitable candidate for such a technology. Gallium has also found application as a component in Ga-Mn-Ni alloys. They are shape memory alloys which exhibit a magneto-mechanical effect. This effect allows the development of materials whose properties can be controlled by a magnetic field (*A.A. Likhachev, K. Ullakko, Phys. Lett. A 275, 2000, 142 and V.V. Khovailo, V. Novosad, T. Takagi, D.A. Filippov, R.Z. Levitin , A.N. Vasilev, Phys. Rev. B 70, 2004, 174413-1-7*). The discovery of recent years are CIGS materials (Cu-In-Ga-Se alloy), which have found application as materials for solar cells. In the years 2010-2012, the *HiPOCIGS (New concepts for high efficiency and lowcost in – line manufactured flexible CIGS solar cells)*, project was carried out as part of the European Union funds. The CIGS alloys were investigated in the field of CIGS solar cells.

In turn, among the gallium compounds, Ga_2O_3, GaAs, GaP, and GaN deserve attention. They have found application in optoelectronics (β-Ga_2O_3) and electronics. Also, the compound of gallium oxide with lanthanum oxide ($LaGaO_3$-perovskite) is considered as a potential solid electrolyte in high-temperature fuel cells (*W. Kuncewicz-Kucprzyk, D. Kobertz, M. Miller, C. Chatillon, L. Singheiser, K. Hilpert, J Am. Ceram. Soc., 85, 2002, 2299*). This information about gallium and its compounds indicates that interest in its application is growing. One can therefore wonder where and how one may try to introduce gallium, e.g. in ternary alloys into use. Gallium is a metal accompanying aluminum and zinc ores, and its world production reaches about 1000 tons per year. Considering the small scale of world production, it is obvious that in order to achieve profit, such a product must have a high value. There are two areas in which this aim can be achieved. One of them is density, where the new dental fillings in which gallium is a component, are used (*F.M. Blair, J.M. Whitworth,* *J.F. McCabe, Dental Materials, 11, 1995, 277 and H. Hero, C.J. Simensen, R.B. Jorgensen, Biomaterial, 17, 1996, 1321*). However, without working together with the "medical world" it is difficult to develop compositions of such a new alloy. The second area of research seems to be the use of noble metals in combination with gallium as new materials for the production in jewelry industry.

In the world literature, one cannot find numerous data about systems with gallium. So far, the literature provides phase equilibria and transformation temperatures in the following systems: Ag-Ga-Bi (phase equilibrium at 473 K, the course of liquidus line and temperature of phase transitions determined by thermal analysis), Ag-Ga-Sn (phase equilibrium at 373 K, the course of liquidus line and temperature of phase transformations determined by means of thermal analysis as well as enthalpy of mixing at 803 K), Ag-Ga-Tb (phase equilibrium at 873 K), Au-Ga-In (phase equilibrium at 553 K and identification of Au_2GaIn_2 ternary phase at 667 K), Au-Ga-Sb (phase equilibrium at 298 K, the course of liquidus line and phase transition temperatures determined by thermal analysis), Cu-Ga-Bi (phase equilibrium at 473 K, the course of liquidus line and temperature of phase transitions determined by thermal analysis) and Cu-Ga-In (phase equilibrium at 623 K and temperature phase transformations determined by means of thermal analysis). With the exception of the Ag-Ga-Sn system, there is no information about the thermodynamic properties of these ternary systems. **Therefore, the scientific aim of my work was to determine the thermodynamic properties and to provide information on the topology of phase equilibria in the ternary Ag-Cu-Ga and Ag-Au-Ga systems.**

The research scope of this scientific aim is closely related to the realization of the research project [II.J.4] "Thermodynamic properties and phase equilibria in the Cu-Ag-Ga system" and the "Iuventus Plus" project [II.J.6] “Thermodynamic properties and phase equilibria in the Ag-Au-Ga system" carried out at the Faculty of Non-Ferrous Metals, AGH University of Science and Technology in Krakow.

The thermodynamic properties of liquid gallium-containing metal solutions can be determined with the electrochemical method using a cell with a solid electrolyte, and using a calorimetric method. Information on the course of the liquidus line can be obtained by applying differential thermal analysis, DTA. In turn, information on the topology of the system describing phase equilibrium in selected alloys can be obtained as a result of isothermal expriments on the basis of which the analysis of chemical composition of phases (using SEM method with EDS) and phase composition (using XRD method)can be derived. To carry out the experiments mentioned above, I used the following methods:

a) Electrochemical method: cells with solid electrolyte

The electrochemical method is considered to be the most accurate method for the determination of the component's activity in metallic multi-component systems. In the electrochemical cell, the quantity of isothermal-isobaric work necessary to transfer 1 mole of the selected element with valency z from the pure state to the solution corresponds to the transferring the change $Q = (zF)$ and is related to Gibbs free energy change by the equation:

$\Delta G_r = -zFE$ (1)

where E is the electromotive force produced by the cell and F is the Faraday constant equal to 96 487 [C·mol-1].

For the cell to work properly, the following requirements must be met:

- the choice of the proper electrolyte,
- proper identification of electrode processes,
- no side reactions taking place in the cell.

I got acquainted with the electrochemical method doing my PhD thesis and through the development of a chapter in the book on the principles of cells construction and the basics of this method [II.E.2]. To determine the thermodynamic properties of liquid solutions with gallium a high-temperature electrochemical cell with a solid zirconium oxide stabilized yttrium oxide electrolyte, was used. Measurements of this type are widely used in the world. Therefore, the methodology of these measurements and cell construction as well as the properties of the electrolyte itself are well described in the literature (*E.C. Subbarao: Solid Electrolytes and Their Applications. Plenum Press, New York, 1980 and K. Kiukkola, C. Wagner: J. Electrochem. Soc., 104, 1957, 308*).

The electrochemical method with the solid zirconium electrolyte was used in my research to determine gallium activity in the following systems: Ag-Ga, Au-Ga, Cu-Ga, Ag-Cu-Ga and Ag-Au-Ga.

b) Calorimetric method

The calorimetric method consists in measurements of thermal effects accompanying the dissolution of the component in the metallic bath of the selected composition and mass. The quantity determined on the basis of this experiment is the recorded thermal effect ΔH, which involves heating, melting and dissolving the sample in a metal bath:

$\Delta H = \int_{T_1}^{T_2} C_p \, dT + \Delta H_{\text{transformation}} + \Delta H_{\text{dissolution}}$ (2)

where ΔH is the total thermal effect recorded during the measurement, C_p is the heat capacity of the metal to be added, $\Delta H_{\text{transformation}}$ is the heat accompanying the possible phase transformation occurring in the added metal, $\Delta H_{\text{dissolution}}$ is the heat of dissolution of the added metal.

The colorimetric method has been used in my work to determine the enthalpy of mixing in the following binary systems: Ag-Ga, Cu-Ga, Au-Ga (to improve the description of the liquid phase in these metallic systems and to determine the values of the enthalpy of mixing needed to determine later the enthalpy of mixing in ternary systems Ag-Ga-*X* where *X* is Au or Cu, respectively) and in ternary Ag-Cu-Ga and Ag-Au-Ga systems (to provide new information on the liquid phase in these metallic systems). I have gained the knowledge and experience in performing measurements using the calorimetric method in the laboratories leading in this research method in Europe. In 2005, I cooperated with prof. G. Borzone during a one month stay at the Universiteti degli Studi di Genoa in Italy, in 2006 during a two-month scholarship, I cooperated with Prof. J.C. Gachon at Université Henri Poincaré in

Nancy, France, and in 2008 I cooperated with prof. H. Ipser and prof. H. Flandorfer during the monthly stay at the Universität Wien in Austria. In connection with the purchase of the MHTC96, Setaram calorimeter for our laboratory, I had one week of training conducted by Setaram Company in Lyon [III.Q.a.1].

c) Differential thermal analysis DTA/DSC, SEM and XRF methods

In my work, thermal analysis has been applied to determine the temperature of changes taking place in systems. The differential thermal analysis (DTA) was used to describe the Au-Ga system and to determine the course of the liquidus line in the Ag-Cu-Ga ternary system. I gained experience in doing this kind of research in 2010 due to cooperation with prof. H. Ipser, during one month stay at the Universität Wien in Austria. In 2011 I took individual training in the use of thermal analysis techniques carried out by NETZSCH company, as well as during trainings in the use of research techniques used in thermal analysis that took place in 2010-2017 in Krakow [III.Q.a.3, III.Q.a.6, III.Q.a.9].

Scanning electron microscopy (SEM) is one of the basic methods of studying a solid materials in a microscale and a nanoscale. The ability to achieve high resolution up to 1 µm as well as a short response time of the device gives great opportunities to analyze a wide range of materials. In my work the SEM-EDS method was used to determine the chemical composition of the equilibrated phases in the studied ternary Ag-Cu-Ga and Ag-Au-Ga systems. Then, using the X-ray diffraction method (XRD), the phase composition was determined in the above-mentioned ternary systems. On the basis of the obtained results, I determined the phase equilibria: in the Ag-Cu-Ga system at 723 K, and in the Ag-Au-Ga system at 523 and 723 K.

I gained the knowledge and the experience in performing research using SEM and XRD methods in 2011 during participation in a week's training in materials analysis techniques at the University of Surrey [III.Q.a.5] and in the course of independent work on the scanning electron microscope (Hitachi SU-70) and on the XRF spectrometer (Rigaku, Mini Flex II), which are available at our Faculty.

d) CALPHAD method

The name CALPHAD is originally an abbreviation of CALculation of PHAse Diagrams, but was later expanded to include Computer Coupling of Phase Diagrams and Thermochemistry. The CALPHAD method collects and evaluates all available experimental and theoretical information on phase equilibrium and thermochemical properties in the system under consideration. The thermodynamic properties of each phase are then described by the Gibbs free energy, using a mathematical model containing adjustable parameters. These parameters are evaluated by optimizing the fit of the model to all assessed experimental information, also involving the co-existing phases. Next, one can recalculate the thermodynamic properties of all phases of the entire system and the phase diagram. The philosophy of the CALPHAD method is to obtain a consistent description of the phase diagram and thermodynamic properties. In CALPHAD method, information about lower order systems is used to calculate higher order systems. This is a very helpful method in topics related to the modeling of phase transformations.

In my work CALPHAD method was used to calculate the following systems: Ag-Ga, Au-Ga, Cu-Ga, Cu-Ag-Ga and Ag-Au-Ga. Calculation of phase diagrams using the CALPHAD method I began under the supervision of dr inż. Wojciech Gierlotka. In the years 2003-2010 we cooperated within one research team headed by prof. Krzysztof Fitzner. Doctor Gierlotka introduced me to the CALPHAD method, models used to determine Gibbs free energy of phases in multicomponent systems and specialized software used for this type of calculations i.e. Pandat and ThermoCalc softwares. During our cooperation we have calculated the following phase systems: Pb-Te, Cu-Sb, Ag-Ga, Cu-Ga [II.A.5, II.A.6, and papers: A2, A4]. At the same time, I developed my skills in performing calculations on my own and participated in trainings in the years 2015-2017 in ThermoCalc program organized by the software producer [III.Q.a.7, III.Q.a.8].

The aim of my research, in combination with the acceptance of CALPHAD methods for the description of the phase diagrams, has forced me to organize my work in the following way. First, I studied the two-component systems, and then I could start the investigations and description of the ternary systems. Consequently, the main stages of my work were data analysis and experimental work on the following gallium systems:

1. Ag-Ga system
2. Cu-Ga system
3. Ag-Cu-Ga system
4. Au-Ga system
5. Au-Ag-Ga system

Data of the two binary Ag-Cu and Ag-Au systems, which are necessary for the interpretation of ternary systems, are taken from the literature. The Ag-Cu and Ag-Au systems are well known and described in the literature. Thus in my work, their descriptions were adopted on the basis of the COST 531 database (*A. T. Dinsdale, A. Watson, A. Kroup, A. Zemanov, J. Vrestal, J. Vizdal, COST 531 Thermodynamic Database, Version 3.0, 2008*).

Ad. 1 Ag-Ga system

The literature review showed that in the case of the Ag-Ga system, various measurements in the solid and the liquid phase were performed from which thermodynamic properties of this binary system were derived. As far as the information about the solid phase is not in doubt, the situation is slightly different in the case of results obtained for the liquid phase. Analysis of these data showed that there are some contradictions between the results obtained for the liquid phase. The mixing enthalpy determined experimentally for the liquid Ag-Ga system showed a temperature dependence, however the results reported in three available works are not consistent *(R. Beja, M. Laffitte, C.R. Acad. Sci., C. Fr. 267, 1968, 123; B. Predel, D.W. Stein, Acta Metall. 20, 1972, 515; K. Itagaki, A. Yazawa, J. Japan Inst. Metals 32, 1968, 1294).* The activity of gallium and silver in the liquid phase was determined on the basis of the experimental data presented in four works, in which the mass spectrometry and the electrochemical method with solid and liquid electrolyte were used. Unfortunately, the work in which the electrochemical method with solid electrolyte was used (which is a method dedicated to the determination of gallium activity in the liquid Ag-Ga system) has not been available to me *(K. Kameda, Doctor Thesis, Tohoku University, 1986)*. Gallium activity data determined on the basis of the results obtained by mass spectrometry presented in the work of Qi *(G. Qi, M. Hino, T. Azaki, Mater Trans., JIM 30, 8, 1989, 575)* were compared with the results obtained by Kameda, but it was only mentioned in this work that these data are different from each other. Additionally, it is difficult to assume that the results obtained by Danilin and Yatsenko (*V.N. Danilin, S.P. Yatsenko, Izv. AN SSSR, Metall. 3, 1958, 224*) are reliable since they used molten salts during their measurements, and there is no certainty about the degree of gallium oxidation (I or III). This information is crucial in the calculation of gallium activity on the basis of e.m.f. measurements. In this work, data of the enthalpy of mixing determined from emf's were also shown, which in this situation are not reliable. Predel and Schallner *(B. Predel, U. Schallner, Z. Metallkd. 63, 1972, 341)* in their experimental work on the Ag-Ga system used also an electrochemical method with the liquid electrolyte (molten salts). On the basis of the results obtained by them, gallium activity in liquid Ag-Ga can be determined. As in the case of Danilin and Yastenko's work similar doubts arise as to the reliability of the data thus obtained. All the above-mentioned results were used in the calculation of Ag-Ga system by Li *et al. (Y. Zhang, J.K. Liang, J.B. Li, Q.L. Liu, Y.G. Xiao, Q. Zhang, G.H. Gao, J. Alloys Comp. 429, 2007, 184),* in which the associates model was used to describe the liquid phase. The compound energy model consisting of two sublattice Ag and Ga was used for the description of the phase ζ', assuming that the Ga sublattice may be occupied by Ga or Ag atoms (the authors adopted such a model based on their own research, whose results are different from the available literature data *(E. Gunnes, O.B. Karlsen, A. Olsen, O.T. Zagerski, J. Alloys Comp. 297, 200, 144).*

Due to ambiguities regarding information about the liquid phase in the Ag-Ga system, I decided to carry out measurements by using both calorimetric and electrochemical methods to provide new information on this binary solution. The new data will help to explain inconsistencies between the activity of gallium and enthalpy of mixing data in liquid Ag-Ga system.

The electrochemical method was used to determined the activity of gallium in liquid Ag-Ga solutions. Measurements were carried out by using cell of the type:

W, $Ag_xGa_{(1-x)}$,Ga_2O_3 //ZrO_2 + Y_2O_3// FeO, Fe, W (I)

in the temperature range from 1098 to 1273 K , and in the range of gallium mole fraction from 0.1 to 0.9. As a result of my measurements for each of the tested alloys, I determined the linear dependence of the electromotive force as a function of temperature. Then, using on these linear relationships, I determined gallium activity in the liquid Ag-Ga phase. The gallium and silver activity obtained in this way showed a negative deviation from Raoult's law.

Next, I used the calorimetric method to determine the enthalpy of mixing in the liquid phase Ag-Ga. I carried out the measurements by using the high temperature calorimeter MHTC 96 from Setaram at two chosen temperatures 923 and 1123 K, in the range of gallium mole fraction X_{Ga} from 0.948 to 0.429. At each temperature, two experimental series were carried out, and the obtained results were reproducible. Experimental data obtained at two selected temperatures showed negative values of the enthalpy of mixing in the whole range of gallium composition X_{Ga}. The results obtained by myself confirmed the temperature dependence of the enthalpy of mixing in the Ag-Ga system.

This new information I obtained on the thermodynamic properties of liquid Ag-Ga solutions was used to recalculate the binary system using CALPHAD method. In the calculations of Ag-Ga system I did in the cooperation with dr W. Gierlotka, a substitutional model was used to describe the liquid phase. It is a right model for describing the mixing enthalpy for the liquid phase that occurs in the Ag-Ga system. The intermetallic phase Ag_3Ga_2 has been described as a linear stoichiometric compound. The compound energy model consisting of two sublattice Ag and Ga was used for the description of the ζ' phase, in which the Ga sublattice can be occupied by Ga, Ag atoms or vacancies with the general formula $(Ag)_2$:(Ga, Ag, Va$)_1$. The selected model for describing this phase was adopted on the basis of the data taken from the work of Gunnes et al. *(E. Gunnes, O. B. Karlsen, A. Olsen, O.T. Zagerski, J. Alloys Comp. 297,200, 144)*. Based on the calculation of the Ag-Ga system, a very good agreement of the calculated phase diagram and the thermodynamic functions with the experimental data was obtained. It is better than in the case of the previous calculation of this binary system made by the above-mentioned authors. The calculation of the phase diagram was carried out using a specialized ThermoCalc v.r software.

Obtained results of measurements and calculation of the Ag-Ga system were published in papers [A1, A2] in journals from the JCR list and were presented at international conferences [II.L.2, III.B.2].

Ad. 2 Cu-Ga system

A review of the literature showed that there are two papers *(J.C. Gachon, M. Notin, C. Cunat, J. Hertz, J.C. Parlebas, G. Moraitis, B. Stupefl, F. Gautier, Acta Metall. 28, 1980, 489 and B. Predel, U. Schallner, Mater. Sci. Eng. 10, 1972, 249)* containing contradictory information about gallium activity in the solid α phase existing in this binary system. In addition, the enthalpy of mixing in liquid Cu-Ga was determined only at one temperature (at 1423 K) by Predel and Stein (*B. Predel, D. W. Stein, Acta Metall. 20, 1962, 1183*). Therefore, the dependence of this thermodynamic function on the temperature is unknown. Data taken from these two works were used by Li et all. to describe the Cu-Ga system (*J.B. Li, L.N. Ji, J.K. Liang, Y. Zhang, J. Luo, R.C. Li, G.H. Rao, Calphad, 32, 2008, 447*). However, the application of this thermodynamic description of this particular binary system to calculate ternary Cu-Ga-Me systems using CALPHAD method did not bring satisfactory results.

Due to ambiguities regarding the information about the solid phase in the Cu-Ga system, I decided to carry out measurements using electrochemical method with a solid zirconium electrolyte. Gallium activity was determined in α phase, in γ_0 phase, and in the liquid phase (to confirm consistency with available information on the liquid phase and thus confirming the results obtained in my work).

Measurements were carried out in temperature range from 948 to 1173 K by using cell of the type:

W, $Cu_xGa_{(1-x)}$,Ga_2O_3 //ZrO_2 + Y_2O_3// FeO, Fe, W (II)

for three chosen alloy compositions representing the following phases in the Cu-Ga system: Cu0.25Ga0.75-liquid phase, Cu0.68Ga0.32-γ_0 phase and Cu0.9Ga0.1-α phase. On the basis of obtained results, I determined the linear dependence of the electromotive force as a function of temperature for the investigated alloys. Then, using these equations, I determined gallium activity in selected phases in the Cu-Ga system. On the basis of a comparison of my data on gallium activity in the α phase with the literature data, the results of Predel and Schallner were rejected, whereas the results obtained by me and by Gachon *et al.* gave a consistent description of α phase.

Using the calorimetric method, I decided to carry out measurements that would explain whether there is a mixing enthalpy dependence on temperature in the liquid Cu-Ga. I carried out the measurements using the high-temperature calorimeter MHTC 96 from Setaram at three chosen temperatures 1128, 1273 and 1423 K in the range of gallium mole fraction X_{Ga} from 0.188 to 0.921. At each temperature two measurement series were carried out, and the obtained results were reproducible. Experimental data obtained at three selected temperatures indicated negative values of enthalpy of mixing in the whole composition range X_{Ga}, in which the measurements were carried out. The minimum value of the enthalpy of mixing in each experiment was found in the range of gallium mole fraction X_{Ga} from 0.25 to 0.35. Mine results at 1423 K are consistent with Predel and Stein data, who determined the enthalpy of mixing liquid Cu-Ga solutions at the same temperature. Based on these results and the literature data, it can be concluded that the enthalpy of mixing in liquid Cu-Ga depends on temperature.

Next, the data obtained for gallium activity and mixing enthalpy for Cu-Ga alloys were used to recalculate this binary system using CALPHAD method. It was done in cooperation with dr W. Gierlotka. Calculating this phase diagram, the compound energy model of three sublattice $(Cu)_6$:(Cu, Ga)$_6$:(Ga) was used to describe the gamma phase. The $CuGa_2$ intermetallic phase has been described as a linear stoichiometric compound. The remaining phases, including the liquid phase, have been described with the substitutional model. The phase description used is identical to that used by Li *et al*. On the basis of the performed calculations, a very good agreement for the Cu-Ga phase diagram described as well as thermodynamic functions with the experimental data was obtained. The thermodynamic description of this binary system has changed. The calculated thermodynamic functions such as enthalpy of mixing and gallium activity in the liquid phase and gallium activity in the solid phases are now in better agreement with the literature data compared to that given by Li *et al*. It should be emphasized that the correct description of the binary system is necessary if one wants to use it to calculate higher order systems using CALPHAD method. The calculation of the phase diagram was carried out using ThermoCalc v. 3.1 software.

Obtained results of measurements and calculation of the Cu-Ga system were published in papers [A3, A4] in Journals from the JCR list (and were presented at international conferences [II.L.10, II.L.11, III.B.10, III.B.11].

Ad. 3 Au-Ga system

Analysis of the existing information about the Au-Ga system has raised some doubts as to the reliability of the information about the liquid phase in this binary system. It turned out that while the enthalpy of mixing in liquid Au-Ga solutions was studied in a wide range of temperatures (from 774 to 1661 K), the analysis of the results did not give a definite answer regarding the temperature dependence of the enthalpy of mixing in this binary system. In addition, the published data are inconsistent (*data from K. Itagaki and A. Yazawa, Trans. JIM 16, 1975, 979 and B. Predel and D. W. Stein, Acta Metall. 20, 1972, 515 are less negative than other literature data*). Also, the data for gallium activity in liquid Au-Ga solutions are not certain. There were two works in which gallium activity was determined. Bergman et al. (*C. Bergman, J.P. Bros, M. Carbonel, M. Gambino, and M. Laffitte, Rev. Int. Hautes Temp Refract., 8, 1971, 205*) determined a_{Ga} at 1400 K using the mass spectrometry method. Kameda and Azaki (*K. Kameda and T. Azaki, J. Jpn. Inst. Met., 40, 1976, 1087*) determined a_{Ga} at two temperatures at 973 and 1073 K using electrochemical cell with liquid electrolyte. This experimental method in the case of gallium alloys is not the best choice due to the possibility of reaction between the investigated alloy and liquid electrolyte. Consequently, there is no certainty about the degree of gallium oxidation (I or III) while this information is crucial in the calculation of the activity. Comparison of the data taken from these two works indicated that they differ significantly, and additionally gallium activity determined by Kameda and Azakami does not show temperature dependence, which is a strange trend in this thermodynamic function. In the literature there are two different interpretations of thermodynamic properties of the Au-Ga system that have been used to calculate this binary system. Liu et al. (*J. Liu, C. Guo, C. Li, Z. Du, J Alloys Comp. 58, 2011, 62*) performed a thermodynamic description of this system assuming no temperature dependence for the enthalpy mixing in liquid Au-Ga alloys. In addition, they did not verify the literature data and, without considering their mutual exclusion, used all of them to calculate the Au-Ga system. Then, Wang et al. (*J. Wang, YJ Liu, LB Liu, HY Zhou, ZP Jin, Calphad, 35, 2011, 242*) performed the Au-Ga system calculations and adopted the temperature dependence for the enthalpy of mixing in the liquid phase, while rejecting the Itagaki and Yazawa data as well as Predel and

Stein. In the case of both works, a substitutional model was used to describe the liquid phase in the Au-Ga system.

Due to such a different interpretation of the enthalpy of mixing and the few data on gallium activity in this system, I decided to carry out measurements on liquid solutions of this binary system using electrochemical method and calorimetric method.

The electrochemical cell with the solid YSZ electrolyte was used to determine gallium activity in liquid Au-Ga solutions. The measurements were carried out using a cell with the following scheme:

W, $Au_xGa_{(1-x)}$,Ga_2O_3 //ZrO_2 + Y_2O_3// FeO, Fe, W (III)

in the temperature range from 1050 to 1273 K, and in range of gallium mole fraction X_{Ga} from 0.2 to 0.8. As a result of my measurements for each of the tested alloys I determined the linear dependence of the electromotive force as a function of temperature. Then, based on these linear dependences and dependences for pure gallium, I determined gallium activity in the Ag-Ga liquid solutions. The results of gallium activity obtained by me indicated a negative deviation from Raoult's law, and together with Bergman *et al.* data created a consistent description of this thermodynamic function.

I also used calorimetric method to determine the enthalpy of mixing in the Au-Ga liquid phase. I carried out the measurements using high temperature calorimeter MHTC 96, Setaram at two chosen temperatures at 1223 and 1323 K, and in the range of gold mole fraction X_{Au} from 0.03 to 0.64. The experimental data obtained at two selected temperatures indicated the negative values of the enthalpy of mixing in the whole range of gallium compositions X_{Ga}. A minimum heat of mixing value was found in the range of gallium mole fractions X_{Ga} from 0.4 to 0.5. These results confirmed the lack of temperature dependence of the enthalpy of mixing in the Au-Ga system, and together with the literature data (without considering the Itagaki and Yazawa, and Predel and Stein data, which were considered inappropriate) created a consistent description of this thermodynamic function.

In addition, I performed differential thermal analysis (DTA) measurements on three selected Au-Ga alloys with the following compositions: Au0.85Ga0.15, Au0.75Ga25 and Au0.6Ga0.4. The tests were carried out in the temperature range from 473 to 1300 K using the NETZSCH DTA 404 apparatus. Two heating and cooling cycles at 5 and 2 K/min were carried out for each of the tested samples to verify the transition temperatures and the temperature of the liquidus line for selected alloys. The obtained results created a consistent description with available literature data.

All data obtained by me: activity gallium and enthalpy of mixing in the liquid phase Au-Ga, and the data from the differential analysis were used to recalculate the Au-Ga by CALPHAD method. I completed thermodynamic description of the Au-Ga system myself. To describe the liquid phase, as in previous reports (Liu *et al*. and Wang *et al*.) I used substitutional model. Solid phases: fcc_A1, D024 and Orthorombic_Ga are also described with substitutional model, and the remaining five phases: AuGa, Au2Ga, β-Au7Ga2, β'-Au7Ga2 and γ-Au7Ga3 have been described as stoichiometric compounds (the same description applied in his work Wang et al). On the basis of these calculations very good agreement of the thermodynamic functions and phase diagram with the experimental data was obtained. The calculation of the phase diagram was carried out using the ThermoCalc v. 3.1 software.

Obtained experimental results and calculation of the Au-Ga binary system were published in papers [A7, A8] in Journals from the JCR list and were presented at international conferences [III.Q.b.1, III.Q.b.3].

Ad. 4 Ag-Cu-Ga system

The description of three binary Ag-Ga, Cu-Ga and Ag-Cu (data base COST 531) made it possible to deal with the ternary system. A review of the literature on the Ag-Cu-Ga system showed that there are only a few data on this ternary system. In the elaboration of Petzow and Effenberg in 1989 (*G. Petzow, G. Effenberg, A Ternary Alloys, Comprehensive Compendium of Evaluated Constitutional Data and Phase Diagrams, Verlag Chemie, Weinheim, 1988*), there is no information on the Ag-Cu-Ga system. Similarly, in the study of Villars et al. (*P. Villars, A. Prience, H. Okamoto, Handbook of Ternary Alloy Phase Diagrams, ASM International, Metals Park, Ohio, 1995*), there is also no data on the phase equilibria in this ternary system. In the literature there is only one work done by Markiv et al. (*V.J. Markiv, V.M. Mayorenko, N.N. Beliavin, Metally 6, 1989, 198*), who carried out phase equilibria measurements for one isothermal section at 723 K. Having a cross-section of the system in only one selected temperature it is difficult to think about the phase equilibrium evolution with the change of temperature.

Therefore, I decided to carry out measurements that will provide new information on the liquid phase and solid phases in the Ag-Cu-Ga system under consideration, necessary to determine thermodynamic properties and phase equilibria. The investigations were carried out using the following techniques: to determine the thermodynamic properties of the liquid phase, I used the electrochemical method and a calorimetric method. On the other hand, the results obtained from thermal analysis, and analyzes performed by scanning microscopy (SEM) and X-ray diffractometry were used to determine isothermal phase equilibria in the Ag-Cu-Ga system.

I started my work on the Ag-Cu-Ga system from calorimetric measurements to determine the enthalpy of mixing in liquid solutions of this ternary system. The measurements were carried out using high-temperature calorimeter MHTC 96 along two cross-sections, where X_{Ag}/X_{Ga}=1: 1, and X_{Cu}/X_{Ga}=1:1, and at two temperatures 1128 and 1273 K. Two series of measurements were carried out at each temperature, and obtained results were repeatable. The experimental data obtained along cross-section X_{Ag}/X_{Ga}=1:1 at two selected temperatures indicated the negative values of enthalpy of mixing in the whole concentration range X_{Cu}, with the minimum value for the alloy composition X_{Cu} = 0.5. The mixing enthalpy obtained for the second cross-section along which the calorimetric measurements were carried out, i.e. for X_{Cu}/X_{Ga}=1:1, did not show a minimum value. Based on the conducted measurements, it can be concluded that the enthalpy of mixing in liquid

Ag-Cu-Ga solutions does not depend on the temperature. The results obtained by me were the first results describing the enthalpy of mixing in this ternary system and were published in 2014 in paper [A3].

Then, I carried out investigation by using the electrochemical cell with YSZ solid electrolyte to determine gallium activity in liquid Ag-Cu-Ga solutions.

The first question that must be asked is about the selection of the compositions that the working electrode may have. I assumed that it should be an Ag-Cu-Ga alloy with a selected composition and gallium (III) oxide Ga_2O_3. Literature analysis showed that there is a possibility of additional side reactions during the experiment (under conditions of equilibrium pressure p_{O_2} and at temperatures above 973 K), which may result in the formation of a $CuGaO_2$ or $CuGa_2O_4$ compounds. In this situation, it would be a mistake to use Ga_2O_3 oxide as a component of the working electrode to carry out measurements and to attempt a determination of gallium activity in liquid Ag-Cu-Ga solutions. Therefore, additional measurements were performed using electrochemical method to determine the standard Gibbs free energy of formation reactions of these compounds.

I carried out these measurements in the temperature range from 1048 to 1223 K. They included preparation of $CuGa_2O_4$ and $CuGa_2O_4$ compounds. For the following reactions of formation of these two compounds: $CuO + Ga_2O = CuGa_2O_4$ and $1/2Cu_2O+1/2Ga_2O_3 = CuGaO_2$ I determined the standard Gibbs free energy change, which I described by the following temperature relationships:

$$\Delta G^0_{CuGa_2O_4} = 21642 - 26.1 * T(J * mol^{-1}) \tag{3}$$
$$\Delta G^0_{CuGaO_2} = -12879 + 6.28 * T(J * mol^{-1}) \tag{4}$$

These obtained results were used to calculate the oxygen potential and, consequently, to determine the stability range of the compounds present in the Cu-Ga-O system at temperatures 773 and 1273 K. The obtained results ruled out the possibility of formation of $CuGa_2O_4$ and $CuGa_2O_4$ under the conditions of the experiments while using the electrochemical method for selected compositions of the Ag-Cu-Ga system. The results obtained by me were published in 2015 in paper [A5] in journal from the JCR list.

Then, I measured gallium chemical potential in the liquid Ag-Cu-Ga solutions using an electrochemical cells with the solid YSZ electrolyte. The cells had the following scheme:

W, $Au_xCu_yGa_{(1-x-y)}$,Ga_2O_3 //ZrO_2 + Y_2O_3// FeO, Fe, W
(IV)

Experiments were run along two cross-sections with X_{Ag}/X_{Cu}=3:1, and 1:1. The measurements were carried out in the temperature range from 1023 to 1323 K, and for X_{Ga} from 0.8 to 0.3. The range of compositions was selected on the basis of the data on the Ag-Cu-Ga system obtained on the basis of respective binary systems. Another limitation of the used method was the selection of electrical contacts with the working electrode, which was Ag-Cu-Ga alloy (of selected composition) with gallium (III) oxide. The most suitable electric contact was tungsten wire, however, analysis of the literature data showed that a reaction copper with tungsten oxides is possible, and these appear in small amounts during this measurement. Therefore, it was impossible (using this electrical contact) to use the electrochemical method on this ternary system on the copper side.

As a result of my investigations for each of the tested alloys, I determined the linear dependence of the electromotive force as a function of temperature for each alloy. Then, based on these linear relationships, I determined gallium activity in the Ag-Cu-Ga liquid phase. Gallium activity shows a negative deviation from Raoult's law in the studied range of compositions. The results obtained by me were published in 2015 in paper [A6] in journal from the JCR list .

In addition to the determination of the enthalpy of mixing and gallium activity in liquid Ag-Cu-Ga solutions, I conducted experiments based on which I determined the course of the liquidus line using the differential thermal analysis (DTA) method. The measurements were carried out along two cross sections where X_{Ag}/X_{Cu}=1:1 (for X_{Ga} from 0.1 to 0.8 and X_{Ag}/X_{Ga}=1:1 (for X_{Cu} from 0.1 to 0.8). The experiments were carried out with the rate 10 K/min in two heating and cooling cycles using a high-temperature multi-calorimeter (model Pegasus 404, Netzsch). As a result of these measurements, I determined the course of the liquidus line along two selected cross-sections in the Ag-Cu-Ga system. The results obtained by me are the first to represent the course of the liquidus line in the ternary system studied. These results have been presented in paper [A6] in the journal from the JCR list.

Results obtained on the basis of electrochemical method (negative deviation from Raoult's Law for gallium activity) and calorimetric method (negative values of the enthalpy of mixing, including a clear minimum on one of the cross-sections) may indicate a tendency to form a ternary phase in the Ag-Cu-Ga system. Therefore, I additionally carried out investigations of phase equilibria for isothermal section of the Ag-Cu-Ga system at the selected temperature 723 K. The samples after isothermal equilibrium were analyzed using scanning electron microscopy (to establish chemical composition), and then by using the X-ray diffraction method (to establish phase composition). On the basis of the obtained results I suggested a phase equilibrium diagram at T=723 K. The obtained results did not confirm the formation of the ternary phase at this temperature. Comparison of the results obtained in my work with Markiva's *et al*. data at 723 K showed some differences. I did not confirm the solubility of Ag, Cu or Ga in the gamma_ordered phase, whereas the solubility of Ag in this phase was identified by Markiva *et al.*. The results obtained by me have been presented in paper [A6] in the journal from the JCR list.

Based on all experimental results obtained in my work, this ternary system was calculated using the CALPHAD method. In the calculation of the Ag-Cu-Ga system, a description of the Ag-Ga and Cu-Ga systems was used, which was done in cooperation with dr W. Gierlotka [A2, A4]. In the Ag-Cu-Ga system, the substitutional model was used to describe the liquid phase and the solid phases: FCC_A1 (Ag) and FCC_A1 (Cu), HCP_A3 and BCC_A2. The HCP phase is described by the compound energy model of two sublattice with the scheme Ag_2:(Ga, Ag, Va)$_1$ and the gamma phase is the compound energy model of three sublattice (Cu)$_6$:(Cu, Ga)$_6$:(Ga), Ag_3Ga_2 intermetallic phases and $CuGa_2$ have been described as stoichiometric compounds. The calculated Ag-Cu-Ga showed very good agreement with the experimental data. The calculation of the phase diagram was done using the ThermoCalc v. 4.1 software. The calculation of this phase diagram has been published in paper [A6] in the journal from the JCR list. All the above-mentioned data obtained by me for the Ag-Cu-Ga system and the calculation of this system using the CALPHAD method were presented at international conferences [II.L.9, II.L.10, III.B.9, III.B.10].

Ad. 6 Ag-Au-Ga system

Similarly to the Ag-Cu-Ga system, also for the Ag-Au-Ga system (*G. Petzow, G. Effenberg, A Ternary Alloys, Comprehensive Review of Evaluated Constitutional Data and Phase Diagrams, Verlag Chemie, Weinheim , 1988* and *P. Villars, A. Prience, H. Okamoto, Handbook of Ternary Alloy Phase Diagrams, ASM International, Metals Park, Ohio, 1995*), there is no information on phase equilibria in this system. In the literature there is only one work regarding the wettability tests of Ag-Au-Ga thin films reported by Andronov *et al.* (*V.M. Andronov, I. P. Grebennik, S.V. Dukarov, Funct. Mater., 4, 1997, 387*).

Due to the lack of data on the Ag-Au-Ga system, I decided to carry out investigations that provide information on the liquid phase and solid phases, and then use the results to determine thermodynamic properties and phase equilibria. The measurements were carried out using the following techniques: to determine the thermodynamic properties in the liquid phase, I used the electrochemical method and the calorimetric method. In the same time, the results obtained from thermal analysis and analyzes performed on scanning microscopy and X-ray diffractometry were used to determine the phase equilibria in the Ag-Au-Ga system.

I started my measurements on the Ag-Au-Ga system by measuring the enthalpy of mixing of liquid solutions. The measurements were carried out using a high-temperature calorimeter MHTC 96 by Setaram, along two cross-sections X_{Ag}/X_{Ga}=1:1, and X_{Au}/X_{Ga}=1:1 and two temperatures at 1223 K and 1323 K. Two series of measurements were carried out at each temperature, and the results obtained were reproducible. Experimental data obtained for the cross-section X_{Ag}/X_{Ga}=1:1 at two selected temperatures indicated negative enthalpy mixing in the whole concentration range of X_{Au}, with the minimum value for the composition X_{Au}=0.5. The results for the enthalpy of mixing obtained along the second cross-section where X_{Au}/X_{Ga}=1:1, did not show the minimum value. On the basis of the performed measurements, it can be concluded that the enthalpy of mixing in the liquid Ag-Au-Ga solutions does not depend on the temperature. These results obtained by me were the first data for the liquid phase of the Ag-Au-Ga system and were published in 2017 in paper [A7].

Next, I carried out investigations of the Ag-Au-Ga system using an electrochemical method. The measurements were carried out using a cell with the following scheme:

$$\mathrm{W,\ Ag_xAu_yGa_{(1-x-y)},Ga_2O_3\ //ZrO_2 + Y_2O_3//\ FeO,\ Fe,\ W} \qquad \text{(V)}$$

The gallium activity was measured along three cross-sections: X_{Ag}/X_{Au}=2:1, 1:1 and 1:2 for X_{Ga} from 0.1 to 0.8 and in the temperature range from 1023 to 1348 K. I determined a linear dependence of the electromotive force on the temperature for investigated ternary alloys. Using these relationships, I have determined the a_{Ga}, which in this system shows a negative deviation from Raoult's law. Then, using the mixing enthalpy data and gallium activity obtained for the Ag-Au-Ga liquid phase, I completed a liquid phase description using CALPHAD method. The liquid phase in the Ag-Au-Ga system has been described with the substitutional model using ThermoCalc v. 2015b software. As a result of these calculations I obtained a consistent description of the experimental data. The obtained results were published in 2018 in paper [A10] in the journal from the JCR list.

The results obtained by electrochemical method (negative deviation from Raoult's law for gallium activity) and calorimetric method (negative values of enthalpy of mixing including the clear minimum along one cross-section along which the measurements were carried out) may indicate a tendency to the formation of a ternary phase in the Ag-Au-Ga system.

Taking above into account, the next stage of research concerning the Ag-Au-Ga system was focused on phase equilibria for selected isothermal sections at two temperatures 523 and 723 K. After isothermal equilibration, I analyzed 22 samples with selected compositions. The samples were analyzed by me using scanning electron microscop (the chemical composition of the phases was determined) and then using the X-Ray diffraction method (the phase composition was determined). Based on the results obtained after conducting the above-mentioned analyzes, I determined the phase equilibria at two selected temperatures. The obtained results did not confirm the formation of the ternary phase in this temperature range, i.e. between 523 and 723 K. To display the phase equilibria in the ternary system I used a specialized PanDat 8.1 software. These results have been published in paper [A9] the journal from the JCR list.

The results obtained for the Ag-Au-Ga system were presented at international conference [III.Q.b.1].

The presented scientific achievement includes the results of research conducted using several experimental methods: electrochemical method, calorimetric method, differential thermal analysis (DTA/DSC) and identyfication of phase equilibria based on the results obtained from scanning microscopy and X-ray diffraction analyzes. In addition to the measurements carried out with the described experimental methods, calculations of phase equilibria using CALPHAD method were carried out For Ag-Ga, Cu-Ga, Au-Ga, Ag-Cu-Ga and Ag-Au-Ga systems.

Summarazing, it can be stated that:

- Using the electrochemical method I determined the activity of gallium in three binary systems: Ag-Ga, Au-Ga and Cu-Ga and in two ternary systems Ag-Cu-Ga and Ag-Au-Ga. It is characterized by the negative deviations from Raoult's law. The results obtained for binary systems were used to verify and to enlarge the information about them. Gallium activity data obtained on the basis of the experiments for liquid solutions Ag-Cu-Ga and Ag-Au-Ga are the only available in the literature.

- I determined the enthalpy of mixing for the liquid alloys containing gallium using a calorimetric method in two binary systems: Ag-Ga and Au-Ga and in two ternary systems: Ag-Cu-Ga and Ag-Au-Ga. The results obtained for binary systems were used to verify and to enlarge the information about them. Experimental results for the enthalpy of mixing in liquid Ag-Cu-Ga and Ag-Au-Ga solutions are the only available in the literature and are characterized by negative deviations from the behavior of ideal solutions,
- I determined the course of the liquidus line in the Ag-Cu-Ga system using the DTA method. The obtained results are reported first time in the literature,
- I determined phase equilibria at selected temperatures in Ag-Cu-Ga and Ag-Au-Ga systems using the results of analysis obtained from scanning microscopy analysis and X-ray diffraction method. In the case of the Ag-Cu-Ga system, the obtained results complemented and verified the earlier description available in the literature. However, the results obtained for the Ag-Au-Ga system are reported first time in the literature,
- on the basis of the obtained results, the Ag-Cu-Ga system was calculated using the CALPHAD method. This is the first description of this ternary system available in the literature,
- I independently calculated the Au-Ga system using CALPHAD method,
- I independently calculated the liquid phase in the Ag-Au-Ga system using CALPHAD method,
- obtained description of the phase diagrams by CALPHAD method allows one to follow the evolution of the phase equilibrium with temperature during crystallization of alloys (using e.g. the Scheil method).

5. Discussion of other scientific and research achievements of the applicant proving the important contribution of his/her scientific activity

5.1. General information

I am a graduate of the Faculty of Non-Ferrous Metals (major: Metallurgy) of the AGH University of Science and Technology in Krakow. I graduated in 2003 with a master's degree in Engineering. My master's thesis entitled "Determination of the rate of corrosion of titanium using polarization technique" was carried out under the supervision of prof. dr hab. Eng. Krzysztof Fitzner.

In the years 2003-2008 I attended doctoral studies at the Faculty of Non-Ferrous Metals AGH. During my doctoral studies I completed a six-month pedagogical course at the Pedagogical College of the AGH University of Science and Technology, raising my didactic qualifications. From January 2004 I became an employee of the Non-Ferrous Metals Faculty at the AGH University of Science and Technology in Krakow. In May 2008, I obtained PhD degree in technical sciences, for a thesis entitled "Determination of thermodynamic properties of liquid Ag-In-Sb and Ag-In-Sn solutions by electrochemical method". The supervisor of this doctoral dissertation was prof. dr hab. Eng. Krzysztof Fitzner and reviewers of this work were prof. dr hab. Lidia Burzyńska (AGH University of Science and Technology in Krakow, Faculty of Non-Ferrous Metals) and prof. dr hab. Eng. Jan Botor (Institute of Non-Ferrous Metals in Gliwice).

In my doctoral thesis I presented the results of high-temperature measurements of thermodynamic properties of liquid alloys containing indium: Ag-In, Ag-In-Sb and Ag-In-Sn. The conducted research was related to the implementation of a special project [II.J.1] pt. "New materials and technologies for lead-free soldering, European Cooperation in the field of Scientific and Technical Research (COST). Action 531- Lead-free soldering materials" carried out as a part of the international COST 531-Lead-free Solder Materials project. This project was carried out as a part of the search for new ecological lead free solder alloys. In addition, as part of the COST 531 project, I investigated the liquid Cu-In-Sn solutions in the temperature range from 973 to 1223 K using the electrochemical method. On the basis of the obtained results, indium activity in the liquid phase was determined, which showed a variable deviation from Raoult's law. Participation in the COST 531 project gave me the opportunity to complete my first foreign internship in 2005 (Universiti degli Studi di Genova, cooperation with Prof. G. Borzone in Italy, 1 month). During my stay at the University of Genoa, I began to study the calorimetric method. As part of my stay in Genoa, I carried out calorimetric measurements, on the basis of which I determined the enthalpy of mixing of liquid Cu-In solutions at two selected temperatures: 998 and 1025 K. The obtained data did not show the temperature dependence of the enthalpy of mixing in the liquid phase. All experimental data obtained by me was used to calculate the Cu-In-Sn phase system. The obtained research results were presented at an international conference [II.L.4, III.B.4] as well as were published in the journal from the JCR list [II.A.4].

The research of Ag-In, Ag-In-Sb and Ag-In-Sn systems performed as a part of my doctoral thesis presented various degrees of difficulty requiring the use of several research techniques. In the case of Ag-In and Ag-In-Sb systems, measurements were carried out using an electrochemical method using a cell with a solid zirconium electrolyte. In the case of the Ag-In-Sn system, in addition to the electrochemical method, it was necessary to experimentally determine the equilibrium conditions between the liquid phase and the solid oxide solution. In addition, work on the Ag-In-Sn system has been supported with calorimetric studies.

During my doctoral studies in 2006, I became a scholarship holder of the French Government, which enabled me to complete a two-month internship at Université Henri Poincaré in Nancy, France. In the course of this stay, I continued my study of performing the research by calorimetric method. During my stay in France, I cooperated with Prof. J.C. Gachon, one of the best specialists in the field of calorimetry in Europe. During my two-month stay I performed calorimetric measurements of the enthalpy of mixing in liquid Ag-In-Sn solutions at the selected temperature at 1003 K. The results of these measurements are presented in my doctoral thesis. On the basis of the results obtained by me, thermodynamic properties of liquid solutions Ag-In, Ag-In-Sb (indium activity, partial enthalpy of indium and partial entropy of indium) and Ag-In-Sn (indium activity, partial enthalpy of indium and partial entropy of indium and mixing enthalpy) were determined. Then, this data were used in the calculation of the Ag-In, Ag-In-Sb and Ag-In-Sn phase diagrams. The results I obtained were presented at international conferences [II.L.1, II.L.2, II.L.3, III.B.1, III.B.2, III.B.3] as well as were published in journals from the JCR list [II.A.1, II.A.2, II.A.3].

As a part of international cooperation established under the COST 531 Action, I am the co-author of the publication, which was created in a cooperation with a research team from Univerzitet in Beograd in Bor directed by Prof. D. Zivkovic. This work refers to the analysis of phase equilibrium in the vicinity of a ternary eutectic point in the Ag-In-Sb system. I participated in the development of the thermodynamic description of Ag-In-Sb alloys [II.E.1].

All results obtained by me in connection with the realization of the project "New materials and technologies for lead-free soldering, European Cooperation in the Field of Scientific and Technical Research Action COST 531- Lead-free soldering materials" [II.J.1] regarding the systems: Ag-In, Ag-In-Sb, Ag-In-Sn and Cu-In-Sn were used in the thermodynamic COST 531 database *A. Dinsdale, A. Watson, A. Kroupa, A. Zemanova, J. Vrestal, J. Vizdal, COST 531 Thermodynamic Database, Version 3.0, 2008*. This database, in addition to numerous publications that appeared due to the realization of this project is the direct result of the cooperation of many researchers in Europe who participated in this project.

Thanks to the cooperation with dr Eng. Wojciech Gierlotka, during my doctoral studies, I began to study the calculation of phase diagrams using CALPHAD method with the aid of specialistic softwares ThermoCalc and Pandat. During the entire period of my doctoral studies, Dr Eng. Wojciech Gierlotka gave me advice and help in performing this type of calculations.

5.2 Scientific-research and expert activity

Since 2009, I have been employed as an adjunct at the Faculty of Non-Ferrous Metals at the AGH University of Science and Technology St. Staszica in Krakow. During this time I continued research using cells with solid zirconium electrolyte, I studied better and better use of the calorimetric method and I expanded my skills with research using DTA /DSC thermal analysis. In addition, I started to learn how to analyze materials using scanning microscopy and X-ray diffraction methods.

After obtaining my PhD degree, I continued research on lead-free alloys in connection with the project implemented in years 2008-2012 [II.J.2]. Thermodynamic properties of liquid phases and phase relations in Cu-Sb-Sn, Ag-Sb-Sn and Au-Sn-Sb systems" as a part of the international COST MP0602 Advanced Solder Materials for High Temperature Application (HISOLD). As a part of my participation in the realization of the above-mentioned project, I carried out measurements on liquid Cu-Sb-Sn and Au-Sb-Sn solutions using the electrochemical method. On the basis of the obtained data, tin activity was determined in the measured ternary alloys. In the case of the Cu-Sb-Sn system, the measurements were carried out along three selected cross-sections where $X_{\mathrm{Cu}}/X_{\mathrm{Sb}}$=1:3, 1:1 and 3:1 in the temperature range from 998 to 1223 K, and the determined tin activity showed slight negative deviations from Raoult's law. For the Au-Sb-Sn system, the studies were carried out along two selected cross-sections where $X_{\mathrm{Au}}/X_{\mathrm{Sb}}$=1:2 and 2:1 in the temperature range from 973 to 1273 K. The determined tin activity showed a negative deviation from Raoult's law. I also determined the enthalpy of mixing of liquid solutions of Au-Sn and Au-Sn-Sb along three selected cross-sections where $X_{\mathrm{Au}}/X_{\mathrm{Sb}}$=1:2, 1:1 and 2:1 at two temperatures 923 and 1078 K. As a result of my research it turned out that in liquid Au-Sb-Sn solutions the enthalpy of mixing has negative values over the entire X_{Sn} shift range with a clear minimum value for X_{Sn} between 0.45 and 0.6. On the basis of the obtained results, it can be concluded that the enthalpy of mixing in the liquid Au-Sb-Sn alloys does not have a temperature dependence.

Then, on the basis of the data obtained by me from the electrochemical and calorimetric methods, a description of the liquid phase with CALPHAD method was done, in which a substitutional model was used to describe the liquid phase. The results obtained were presented at an international conference and published in journals from the JCR list [II.A.6, II.A.8, II.A.9, II.A.11].

Participation in the international COST MP0602 project has enabled me to hold two more internships abroad. In 2008 I completed a one month internship at the Universität Wien during which I cooperated with prof. H. Ipser and prof. H. Flandorfere. As part of the internship, I developed my skills and broadened my knowledge in the field of conducting measurements using the calorimetric method. I performed calorimetric measurements on the basis of which I determined the enthalpy of mixing liquid Cu-Sb-Sn solutions along two cross-sections $X_{\mathrm{Cu}}/X_{\mathrm{Sb}}$=1:1 and $X_{\mathrm{Sn}}/X_{\mathrm{Sb}}$=3:1 in the selected temperature at 1100 K. The result of my cooperation with prof. Ipserem and prof. Flanorfer is a publication on the enthalpy of mixing in liquid Cu-Sb-Sn solutions, which was published in the journal from the JCR list [II.A.7]. The results from the conducted research were also presented at the international conference [II.L.5, III.B.5].

In addition, in 2008 I participated in a week-long training in Lyon in France organized by the Institut de Recherches sur la Catalyse et l'Environnement de Lyon and the company Setaram (a global producer of calorimeters) [III.Q.a.1]. During this week's training various research techniques used in the calorimetric method were presented, discussed and practiced.

In 2010 at the Universität Wien I took another internship, under which I cooperated with prof. H. Ipser. During my monthly stay, I expanded my knowledge and skills in conducting research using thermal analysis. During the internship, I determined the course of the liquidus line in the Au-Sb-Sn system using differential thermal analysis of DTA along two selected cuts characterized by the mole ratio X_{Au}/X_{Sn}=1:1 and X_{Au}/X_{Sb}=1:1.

The results obtained for me for ternary Cu-Sb-Sn and Au-Sb-Sn systems were used in the calculation of phase diagrams of these systems. They were presented at international conferences [II.L.5, II.L.6. II.L.8, III.B.5, III.B.6, III.B.8] as well as were published in journals from the JCR list [II.A.6, II.A.7, II.A.8, II.A.9, II.A.11].

As a result of the implementation of the international project COST MP0602 [II.J.2], a book appeared in which all the results obtained during the project were collected. I am a co-author of one of the chapters in which I have presented the data I obtained for the Cu-Sb-Sn and Au-Sb-Sn systems [III.E.3].

In addition, in 2010 I took a weekly training in spectroscopic ellipsometry [III.Q.a.2]. In 2011 I took part in individual training on the use of thermal analysis methods at Netzsch [III.Q.a.4]. I have also been trained in the field of material analysis using scanning microscopy - a week-long training in scanning microscopy at the University of Surrey in England in 2011 [III.Q.a.5]. I continued to learn the calculation of phase diagrams based on the CALPHAD method using the PanDat and ThermoCalc softwares. In addition, I took two trainings in the field of ThermoCalc application [III.Q.a.7, III.Q.a.8].

In the years 2008-2011 I participated in the implementation of the research project "Determination of tellurium recovery parameters from semi-finished products and materials accompanying the copper production process at Głogów smelter", [II.J.3] which was carried out at the Department of Physical Chemistry and Metallurgy of Non-Ferrous Matals at AGH in Krakow. The subject of the project was related to the recovery of the tellurium accompanying the copper production process at the Głogów smelter. As a part of my participation in this work, together with dr inż. Wojciech Gierlotka I carried out, calculation of the Pb-Te phase system. The description of the Pb-Te system presented by us assumed the change of the substitutional model used so far when calculating this binary system for an ionic liquid model. The description of the Pb-Te system we proposed was published in the journal from the JCR list [II.A.5].

In 2011, INTECH published a book entitled "Electromotive Force and Measurement in Several Systems", which is one of the largest publishing house in the "open access" in the field of technical sciences and medicine. In this book a chapter was published, "Electromotive Force Measurements in High-Temperature Systems" which I co-authored with prof. dr hab.eng. Krzysztof Fitzner. This chapter describes the electrochemical method using different types of cells (with liquid and solid electrolyte) for measurements at high temperatures. Specific examples have been described in which these cells were used to carry out measurements and to determine thermodynamic functions. From the very beginning, this chapter has been popular with scientists from around the world, as evidenced by annual reports informing about the interest in this chapter [II.E.2].

In 2012, I received the I Individual Award of the Rector of AGH University of Science and Technology St. Staszica in Krakow for series of monothematic publications.

In the years 2010-2013 I participated in the implementation of the research project "Theoretical foundations of a new technology for the recovery of copper from slags" [II.J.5] whose research topic was concerned with a new technology for the recovery of copper from slags. As part of my work in this project, I participated in the development of the thermodynamic description of Cu-Pb-Fe alloys. Therefore, binary Cu-Fe and Cu-Pb systems were recalculated, which were then used to calculate the Cu-Pb-Fe ternary system using a substitutional model and using CALPHAD method. The calculated phase equilibrium lines and thermodynamic functions in the Cu-Pb-Fe system were compared with the available experimental data. The proposed description of the Cu-Pb-Fe system has been published in the journal from the JCR list [II.A.10].

In the years 2012-2015, I was one of the performers of the PBS project entitled "Diagnostics of early recognition of the PCL phenomenon in lead batteries in order to increase the reliability of back-up power systems". As part of my participation, I participated in the implementation of the task at the AGH University of Science and Technology in Krakow in 2013-2014 "Determination of physicochemical parameters and analysis of the interface properties of the current collector - active mass - electrolyte". I performed measurements in which I determined the morphology and chemical composition of negative and positive battery plates using SEM scanning microscopy together with the analysis of the chemical composition of EDS. I also dealt with the determination of the morphology and chemical composition of the negative and positive battery plates with the detected PCL effect using SEM scanning microscopy together with the analysis of the chemical composition of EDS [II.J.7].

In the years 2013-2016 I was one of the performers of the INNOTECH project entitled "Development of methods for the recovery of metals from electronic scrap". As part of my participation in this project, I carried out research on the determination of phase composition by X-ray diffraction (XRD) of cathodic deposits resulting from Sn electrolysis from solutions after leaching of electronic scrap granules. In this project, I cooperated with P.P.H.U. PolBlume [II.J.8].

In the years 2013-2016 I was the manager of the research project obtained as part of the "Iuventus Plus" program [II.J.9]. The subject of the project was concerned with the determination of thermodynamic properties of liquid solutions Bi_2O_3-Sb_2O_3. I determined the oxygen activity coefficient and oxygen diffusion coefficient in liquid diluted Bi-O, Sb-O and Bi-Sb-O solutions (*obtained results are presented in the form of D. Jendrzejczyk-Handzlik, P. Handzlik and K. Fitzner, Activity and Diffusion of Oxygen in the Liquid Dilute BixSb1-x Solutions, J. Min. Metall. Sect. B-Metall.B, submitted in March 2018*) and I determined change of Gibbs free energy of formation of a solid $BiSbO_4$. The results obtained supplemented the existing state of knowledge about liquid solutions of Bi_2O_3-Sb_2O_3 and created a consistent description with literature data. Obtained results were presented at two international conferences [III.B.poster 1, III.Q.b.2].

In the years 2016-2017, I was one of the performer of the GEKON project (Generator of Ecological Concepts) [II.J.10]. The aim of this project was the recovery of precious metals in the process of recycling electronic scrap. As part of my research, I dealt with the determination of the effect of pressure on the process of removing zinc from solid brass being an electronic scrap. A special system was built to carry out the tests, enabling measurements to be made under strict control of the vacuum level. As a result of the tests, the degree of zinc extraction and zinc evaporation rate were determined depending on the pressure set in the system, i.e. 10 or 100 Pa. During this project, I cooperated with TDM Electronics S.A.

In addition to my research work, I also conducted expert work for industrial units - I am the contractor for three research projects for the Fenix Metals Sp. z o. o. and KGHM Polska Miedź S.A. companies [III.M.1-4].

I am a member of international organizations: from 2009 *The Minerals, Metals and Materials Society* (*TMS*) and from 2013 *Associated Phase Diagram and Thermodynamics Committee* (*APDTC*) [III.H.1-2].

Since 2010, at the request of the editors, I have been a reviewer of 13 manuscripts submitted to journals from the Journal Citation Reports list, the full list of which is in [III.P.1-10].

In 2011 and 2012, I was twice the winner of the MNiSW "Iuventus plus" competition (1st and 2nd edition). According to the regulations of this competition, in addition to the content-related appraisal, the project's decision-making factor is the publication of the project manager in the journals from JCR list with a high Impact Factor [II.J.6, II.J.9].

I am an auxiliary supervisor of the PhD thesis of Mrs. Sylwia Drzewowska entitled "Phase equilibria in thermoelectric materials Ag-Bi-Te" at the Faculty of Non-Ferrous Metals at the AGH University of Science and Technology in Krakow [III.K.1].

To sum up, until now I have been a co-author of 22 published scientific papers [I.B.1-10, II.A.1-11, II.E.1], 21 works have been published in journals from the JCR list, 18 of which were published after obtaining the doctoral degree. I took an active part in the realisation of 10 research and development projects [III.J.1-10] as well as in 3 works commissioned by domestic industrial enterprises [III.M.1-4]. I am also a co-author of the chapter in the book "Electromotive Force and Measurement in Several Systems" published by INTECH publishing house which is one of the largest publishing houses in the "open access" system [II.E.2]. Data on the number of citations, the Hirsch index and the total Impact Factor of the publications are summarized in the table below:

State of: 14.05.2018	Web of Science
Citations	102
Without self citations	63
Hirsch index	7
Total Impact Factor:	37.397
The sum of MNiSW points:	561

5.3. Organizational activity

Since 2003, I have been rebuilding my interests and skills in the study of multicomponent metallic systems. In the years 2004-2014, together with prof. dr hab. Eng. Krzysztof Fitzner, I was responsible for retrofitting the high-temperature laboratory at the Department of Physical Chemistry and Metallurgy of Non-Ferrous Metals. As a part of my activity I participated in the purchase of the following equipment: high temperature calorimeter company Setaram, high temperature operating furnaces, high temperature elements for the construction of tubular furnaces, precise scales Sartorius, cutters company Struers and specialized ThermoCalc, Pandat and HSC software. As a result, a very well-equipped laboratory was created which allows investigations using a calorimetric and electrochemical method. At the same time, having specialist ThermoCalc and PanDat softwares enabled calculation of phase diagrams using CALPHAD method at the global level. Since 2012, I have been the supervisor of the "High Temperature Research Laboratory". As part of the team's work under the direction of prof. dr hab. Eng. Krzysztof Fitzner, which includes myself: dr Eng. Wojciech Gierlotka (until 2010) and since 2008 dr hab. Eng. Boguslaw Onderka, prof. AGH, research and computational work on multicomponent metal and oxide systems is being carried out.

In the years 2009-2011 I was a member of the Faculty recruitment commission at the Faculty of Non-Ferrous Metals AGH. From 2017, I am the deputy chairman of the Faculty Recruitment Commission at the Faculty of Non-Ferrous Metals AGH.

As part of the popularization of science, I took part in the "Night of Researchers" project in 2016 as part of which I gave a lecture entitled "Terrible effects of charge flow".

5.4. Teaching activity

During my work at the Faculty of Non-Ferrous Metals AGH I conducted teaching in several subjects for full-time students. They were:

1. Chemistry of metals - lecture
2. Heat and chemical treatment of metallic materials - lecture
3. Physical chemistry - auditorium exercises
4. Theory of metallurgical processes - auditorium exercises
5. General chemistry - laboratories
6. Chemistry - laboratories
7. Chemistry of metals-computer laboratories (classes implemented using the MathCad program from which I received training)
8. Computation of phase equilibria - computer laboratories (classes carried out using the MathCad and Pandat softwares)
9. Computer aided design AutoCad -a computer labs (I have a three-level certificate from the AutoCad training)
10. Computer support in science and technology Matlab - computer labs (I have a certificate from the MatLab training)

The learning was and still is performed with a full-time teaching load (in some years was over a teaching-load). I was the creator of materials and didactic studies (laboratory stands, programs for subjects in the Sylabus system).

As a part of my educational activity I was a supervisor of 5 master theses and 5 engineering dissertations [III.J.a.1-5, III.J.b.1-5].

Dominika Jendrzejczyk-Handzlik

Signature of the Applicant