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CENTRE OF NEW TECHNOLOGIES

THE UNIVERSITY OF WARSAW

Mariana Derzsi

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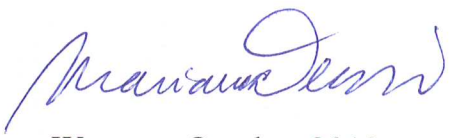

Warsaw, October 2013

I. Personal data

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Education

M.Sc. in physics – 2002
Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia.
Master theses: *Laser induced fluorescence and optical coherent tomography as tools for scanning of upper layers of skin*. Master's work carried at International Laser Centre SK.
Promoter: prof. Dušan Chorvát

Ph.D. in chemical physics – 2007
Institute of Inorganic Chemistry, Slovak Academy of Sciences (PhD degree awarded by Scientific Board of Faculty of Natural Sciences, Comenius University).
PhD thesis: *Structure and dynamics of selected hydrogen bonded molecules: inelastic neutron scattering, neutron diffraction and DFT study.*
Promoters: Dr. Ľubomír Smrčok and prof. Pavel Mach

Professional positions

2007-2009, scientific adjunct
Department of Theoretical Chemistry, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia.

2008, postdoctoral research associate
Institute of Nuclear Physics, Polish Academy of Sciences, Cracow.

2009-2012, postdoctoral research associate
Interdisciplinary Centre of Mathematical and Computational Modeling (ICM, 2009-2011) and Centre of New Technologies (CeNT, 2012), The Warsaw University (UW), Warsaw.

2012- , scientific adjunct
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Warsaw, 1 October 2013

II. Autopresentation – the course of scientific work

1. Prior to achieving Ph.D. degree

During my high school studies, I became increasingly interested in physics, foreign languages and international relations. My interests in physics have fully formed at the end of my high school studies when I became fascinated by atomic structure of matter. It was then when I realized that I wish to dedicate my life to uncovering mysteries of nature in its elemental form.

Mater studies (1996-2002)

I have connected my interests in physics and languages in interdisciplinary studies of physics and English language at Faculty of Mathematics, Physics and Informatics (FMPI) and Faculty of Philosophy at Comenius University (CU) in Bratislava, which I began in September 1996. These studies were adjusted for future teachers. Shortly after first semester, I have realized that I am much more attracted by physics than the languages and would like to study it on a more advanced level. Therefore, after two years of the interdisciplinary studies I have changed my major to physics. Because of the change, my studies have extended from five to six years. After the third year of my studies, I have chosen my specialization to be biophysics and molecular physics at Department of Biophysics and Molecular Physics (nowadays part of Department of Nuclear physics and Biophysics). My choice was influenced by two factors. First, the matter that fascinated me the most was the living matter. Second, the experimental techniques I wished to explore the most were the spectroscopic ones especially the laser techniques. Study of biophysics gave me the opportunity to merge both of my interests. At fourth year of my studies I started my master work at International Laser Centre (ILC) in Bratislava. The ILC is an interdisciplinary research organization formed to foster collaborative research in the areas of progressive methods and technologies of photonics and their application in industry and health care. My task was to get deeper insights into various laser techniques and especially into optical coherence tomography and its applications in study of living tissues and phenomenon of fluorescence. Some substances present in living cells have the ability to fluoresce thanks to which their noninvasive detection is possible. The subjects of my study were human pigment spots and their visualization by means of the optical coherence tomography. In the year 2002, I have defended my mater theses entitled "*Laser induced fluorescence and optical coherent tomography as tools for scanning of upper layers of skin*" under supervision of Professor Dušan Chorvát. I considered continuing my research in ILC centre but at the same time, I became attracted by theoretical tools to study

matter on the atomic scale introduced to me at final stage of my studies when taking a course on computer modeling of molecular structure. At the end of my studies, I stood in front of a dilemma which direction to choose, experimental or theoretical. Finally, Professor Pavel Mach helped me to salve my dilemma. He informed me about a possibility to do a PhD studies at the Department of Theoretical Chemistry at the Institute of Inorganic Chemistry (IICh) in Slovak Academy of Sciences (SAS), where, as it later turned out, I was given the opportunity to combine both experimental and theoretical tools to study matter.

Doctoral studies (2002-2006)

In fall 2002, I began the doctoral studies at Department of Theoretical Chemistry at the Institute IICh SAS. The Department of Theoretical Chemistry is engaged in three main research areas – (i) development of advanced computational methods for treating electron correlation in molecules and solids, (ii) studies of magnetic and electric properties of medium-sized systems including calculations of NMR and EPR parameters of organometallic, biologically and catalytically active substances and (iii) combining experimental methods (X-ray and neutron diffraction and neutron spectroscopy) with quantum-mechanical (QM) Density Functional Theory (DFT) calculations in the solid state. The third area became also area of my future research.

Topic of my PhD Thesis My task was to study structure and dynamics of selected systems with hydrogen bonds by means of neutron scattering techniques and DFT calculations under supervision of dr. Ľubomír Smrčok and Professor Pavel Mach. I found the topic of hydrogen bonds attractive because of the key role they play in biologically active substances. For example, they play an important role in determination and stabilization of structure of various macromolecules such as proteins and nucleic acids and are involved in important enzymatic catalytic reactions. The subjects of my studies included two molecular organic compounds $C_6O_5H_{10}$ (levoglucosan) and $C_4NO_3H_{11}$ (TRIS) and one inorganic coordination polymer NH_4VO_3. These systems were chosen in such a way as to fulfill very specific and important criteria. They should (i) cover variety of hydrogen bonds and crystal structures, (ii) form large high quality crystals stable at ambient (p,T) conditions, (iii) neutron scattering signal from other than hydrogen atoms was small and (iv) the size of the unit cell was within the reach of the available computational power. For all three systems, I have performed both molecular calculations and calculations in solid state. The molecular approach was used in study of the stable conformers of the systems in the gas phase and in study of the influence of intra-molecular hydrogen bonds on their geometries, dynamics and inelastic neutron spectra. The impact of the inter-molecular hydrogen bonds on crystal structure and lattice dynamics was studied by means of calculations in solid state. Additionally, molecular dynamics calculations in solid state were used to study the impact of temperature on dynamics of levoglucosan and on dynamics of the NH_4^+ cations in NH_4VO_3. All theoretical calculations were paralleled by and confronted with experimental observations. The structural models, which served as inputs

to the calculations, were based on data obtained from neutron diffraction experiments. The lattice dynamics was studied by inelastic and quasi-elastic neutron scattering. The neutron experiments were carried out at several neutron facilities: NFL in Studsvik (Sweden), ISIS Facility in Rutherford Appleton Laboratory (Great Britain), Hahn-Meitner Institute (HMI) in Berlin, Heinz Maier-Leibnitz Centrum in Munich (Germany) and Intense Pulsed Neutron Source (IPNS) in Argonne National Laboratory (USA). I took part in the experiments carries out in Studsvik, Berlin and Munich. The neutron scattering techniques were chosen because of their extreme sensitivity to hydrogen and additionally because of the fact that most studies involving hydrogen bonds were in those times carried out by means of X-ray diffraction and optical spectroscopy, methods with limited sensibility to hydrogen. Another reason for choosing the neutron techniques was to get better understanding of the techniques themselves, since their practical applications on atomic level were rather little known to the community of Slovak scientists. Finally, the QM calculations played important role in interpretation of the experimentally obtained neutron data.

The course of the PhD study Having no previous experience with the neutron scattering techniques or QM calculations in solid state, I found the subject of my study very challenging. On the first year of the study my task was to learn all necessary theoretical background and master the necessary computational tools required to start the research as well as to get hands on basic available diffraction techniques. The required theory included the following topics: neutron and X-ray scattering, crystallography, solid-state physics, QM methods both molecular and in solid state and selected topics from inorganic chemistry. The QM calculations required to master molecular packages GAUSSIAN and TURBOMOL and solid state package VASP. My practical training in experimental methods consisted of performing X-ray diffraction experiments on single crystals using Bragg's diffractometer and initial analysis of the diffraction images. At the second year of the study, one had to defend a so called "doctoral minimum", which authorized the PhD student to embark on a doctorate. The defense consists of passing exams from the required theory and of writing and defending a short dissertation thesis explaining the subject of the future PhD theses. Subject of my studies required passing exams at three independent scientific institution: from solid-state physics at IICh SAS, from QM methods at FMPI CU and from selected topics in inorganic chemistry and crystallography at Slovak Technical University (STU). During the course of my studies in year 2005, I have won participation in two certified courses focused on neutron scattering theory, techniques and instrumentation held in HMI Institute and in Oxford, and a participation in a summer school focused on scientific tools in study of condensed matter held in Zuoz, Switzerland. In order to get deeper insights into the computational tools to study solid-state matter, I took part in two international workshops in Grenoble (2004) and in Cracow (2004), held one foreign visit in Vienna (2006) and international internship in Cracow (2005). I have finished my four-year long doctoral studies in December 2006 and defended the doctoral thesis entitled *Structure and dynamics of selected hydrogen bonded molecules: inelastic neutron scattering, neutron diffraction and DFT study* in English language in September 2007. I was awarded the doctoral degree by scientific board of Faculty of Natural

Sciences at the Comenius University in Bratislava. The results of my research were published in six publications in international journals [B-01 – B-06]. I have additionally presented my results at three scientific competitions for young scientists (where I was awarded with 3rd price, 1st price and became Laureate), three international conferences, three international summer schools and one invited talk.

2. After achieving Ph.D. degree

Institute of Inorganic Chemistry IICh SAS in Bratislava: scientific adjunct (2007-2009)

Since January 2007 until December 2009, I was employed by the IICh Institute as scientific adjunct. After my doctoral studies, I continued to study of crystals with hydrogen bonds by means of the QM calculations. I have performed my research under the framework of the Slovak national program VEGA *Structure and dynamics of hydrogen bonds in solids by diffraction methods, quantum chemistry and inelastic neutron spectroscopy (INS)* and I have initiated cooperation with Professor Daniele Colognesi from Istituto dei Sistemi Complessi, Consiglio Nazionale delle Ricerche situated in Sesto Fiorentino in Italy. Our work focused on lattice dynamics of molecular crystal, potassium hydrogen phthalate $C_8H_5KO_4$, which exhibits one of the shortest intra-molecular O-H…O hydrogen bonds. He performed the experimental part of the study and I did the theoretical one. The results of our study were published in 2010 [B-07].

Institute of Nuclear Physics (INP) PAS in Cracow: postdoctoral associate (2008-2009)

Profile of the Department My first postdoctoral fellowship started in January 2008 and took place at the INP Institute PAS in Cracow at the Department of Material Research by Computers (DMRC), head of which was Professor Krzysztof Parliński. The main fields of studies conducted in DMRC include structural, electronic, and phonon properties, phase transitions, electron-phonon interaction, thermodynamic and elastic properties. The studies encompass a broad range of materials including bulk crystals, nanostructures, surfaces, and disordered systems.

Motivation Since my previous experience with QM calculations was limited to calculations of molecular and crystal structure and their dynamics, the postdoctoral fellowship in the DMRC Department presented a great opportunity to extend my knowledge to other areas of

the QM calculations in solids. The postdoctoral fellowship was connected with European geophysical project *c2c - Crust to Core: The Fate of Subducted Material* carried out in ten European laboratories in the framework of Marie Curie Research Training Network, in which I became awarded with a scholarship for early stage researcher. The task of the DMRC Department within the project was to perform the QM calculations for minerals present in the interiors of the Earth in order to understand their role in geophysical process taking place in the Earth's Crust. My task was to formulate and execute an individual scientific research that would meet with the Department's task within the project.

Olivine – Earth mantle mineral Given the unique opportunity to formulate my own research problem I decided to study iron silicate Fe_2SiO_4. Iron silicate is one end-member of $(Mg,Fe)_2SiO_4$ solid solution known as olivine. Olivine is known as the most abundant mineral in the Earth's upper mantle. It is therefore believed to play a key role in the geophysical processes such as thermodynamics of rock-forming minerals and mechanisms driving the plate tectonics. The second end-member of olivine, magnesium silicate Mg_2SiO_4, is already very thoroughly examined material by means of both experimental observations and theoretical QM calculations. The iron counterpart, on the other hand, was a much less characterized system. Theoretical studies concerning magnetic and crystal structure, mechanical, optical and dynamical properties as well as its thermodynamics were all mostly missing completely. My further motivation to study the iron silicate was the possibility it gave me to study magnetism and strong electron correlations in crystals. Iron silicate crystalizes in two phases, in orthorhombic known as fayalite and in high-pressure cubic spinel structure. The latter became the subject of my studies, which I have performed in two stages. First, I have focused on the study of the impact of magnetic and strong electron correlations on crystal and electronic structure and lattice dynamics of the spinel. Results of these studies revealed that both those factors have significant impact on the electronic ground states of the Fe_2SiO_4 spinel. The strong electron correlations stabilize the antiferromagnetic interactions, open the electronic band gap at the Fermi level and significantly modify the energies of phonons. Additionally, we have shown that the low Néel temperature $T_N \approx 12$ K, experimentally observed in Fe_2SiO_4 spinel, results due to geometric frustration of the magnetic moments on iron atoms. Results of these studies were published in Physical Review B in 2010 [A-01]. In the second stage, I focused on calculations of lattice dynamics of Fe_2SiO_4 spinel in function of external pressure and related with it its mechanical properties and thermodynamics. Results of this study were compared to those performed for the second end-member of olivine, Mg_2SiO_4 in the DMRC Department. This comparative study was published in Journal of Physics: Condensed Matter in 2010 [A-02]. They were subsequently used in study of impact of the iron concentration on the electronic and crystal structure and optical properties of $Mg_{2-x}Fe_xSiO_4$. The results of this study revealed that insertion of iron atoms into Mg_2SiO_4 results in appearance of electronic states at the Fermi energy and that strong electron correlations open a new band gap in these newly appeared states. In this way it was demonstrated how a band insulator Mg_2SiO_4 turns into a Mott insulator upon insertion of iron atoms. Additionally it was shown that the band gap decreases with increasing Fe

concentration due to increase of electron mobility upon Fe insertion as well as to the increase in external pressure. The results of this study were published in Physical Review B in 2010 [A-03]. During the course of my fellowship in 2008, I have presented the results of my calculations concerning Fe_2SiO_4 on three international conferences, namely in Finnish Saariselkä, Spanish Sevilla and Polish Cracow.

Mineral kanemite – molecular crystal Apart from the study of Fe_2SiO_4, I took part in a study of hydrated form of sodium silicate mineral $NaHSi_2O_5 \cdot 3H_2O$ known as kanemite, which was also encompassed by the European project *crust-2-core*. Kanemite is a naturally occurring mineral exhibiting high inner-crystalline reactivity due to which it can be easily modified. This makes kanemite a valuable staring material for synthesis of novel materials with technological applications. The crystal structure of kanemite is stabilized by extensive network of hydrogen bonds, which strongly dominate its physical properties. Since the neutron studies have not been performed for kanemite, the detailed and accurate information about the geometrical and dynamical properties of hydrogen bonds was in great part missing. Due to my experience with crystals with hydrogen bonds gained during my doctoral studies, my task was to perform the analysis of the theoretical results of crystal structure and lattice dynamics of kanemite obtained in the DMRC Department, which would explain the impact of hydrogen bonds on the crystal structure as well as on its lattice dynamics. The analysis revealed that the SiO_4 tetrahedra are linked by a short strong O-H…O hydrogen bond with a single asymmetric potential well at low temperatures. Two energetically equivalent sites were obtained for the position of the H atom. Apart from the hydrogen bonds reported in earlier studies, additional moderate O-H…O hydrogen bond was found to stabilize the hydrated Na layers within the silicate layers at low temperatures. Results of this study were published in Physical Revue B in 2009 [B-08]. I have additionally reported this study at an international conference in Tenerife in 2008.

ICM i CeNT UW in Warsaw: postdoctoral fellow (2009-2012)

Profile of the LTNMF laboratory In January 2009 I joined the Laboratory of Technology of Novel Functional Materials (LTNFM) in the Interdisciplinary Centre of Mathematical and Computational Modelling (ICM) at the University of Warsaw headed by dr. hab. Wojciech Grochala, prof. UW. Since 2012, the Laboratory is part of Centrum of New Technologies (CeNT) UW. The Laboratory focuses on complex study of physicochemical properties of mostly inorganic materials in solid state. The main objective of the studies is a search for novel functional materials including hydrogen storage materials, new families of superconductors, molecular memories, magnetic materials, strongly correlated systems and strong oxidizers. The research is carried out both by means of experimental measurements (which encompasses the synthesis and complex characterization of the physicochemical properties of the synthetized compounds) and by means of theoretical QM DFT calculations.

The objective of the calculations is to predict new functional materials as well as to support and help to analyze the experimental observations. The properties often calculated include electronic, magnetic and crystal structures, molecular and lattice dynamics, polymorphism, phase transitions and thermodynamics. The theoretical methods are additionally often used to build a suitable structural models needed in refinement of crystal structures from X-ray diffraction data.

Motivation The LTNFM Laboratory drew my attention by its comprehensive research profile as well as by the fact that all theoretical predictions are subject to continuous confrontation with the experiment performed on site. I was especially attracted by the opportunity to work on new materials synthesized in the Laboratory and to gain experience in predicting novel materials. In addition, collaboration with experimental chemists was for me as a theorist of particular interest. It offered the possibility to learn the chemical way of looking at the matter, which turned out later to be invaluable in predicting novel materials. My postdoctoral fellowship in the Laboratory was bonded to project TEAM entitled *Quest for superconductivity in crystal-engineered higher fluorides of silver* in which I became awarded with a scholarship. The project is a part of the TEAM Programme created by the Foundation for Polish Science to increase engagement of young scientists in research performed by the best scientific teams in Poland. The long-term aim of the project is to synthesize and characterize a high-temperature superconducting material (HTSC) based on fluorides of divalent silver or related compounds including oxides or chlorides. In the first step, potential precursors of the new family of superconductors were to be proposed and in the second step they were to be a subject to chemical doping in order to obtain the superconductivity.

My tasks My tasks in the TEAM project were to perform quantum mechanical calculations for crystals containing silver atoms and synthesized in the Laboratory, predict crystal structures for two unknown derivatives of silver, conduct training in the QM methods for master students taking part in the TEAM project and supervise their scientific research including their bachelor and master thesis. In order to understand the potential of the new compounds as precursors of superconductors, a very thorough characterization of their properties was desirable. In consequence, my calculations included calculations of crystal, electronic and magnetic structure, polymorphism, phase transitions, lattice dynamics and thermodynamics. I have additionally studied these properties in function of external and chemical pressures. Silver compounds are strongly electron-correlated systems; therefore, I have paid special attention to these correlations. Apart from the project TEAM, I took part in study of hydrogen storage materials. The results of my calculations performed in the LTNMF Laboratory enriched our knowledge of 21 inorganic solids including oxides, chlorides, sulfates and fluorosulfates of Ag^{2+} and their various derivatives, one aminoborate and one complex with Ni^{2+}. Within the framework of project TEAM, I supervised four students and I was a co-promoter of one engineering and one master thesis.

Ag^{2+}-F systems One of my first computational tasks was to perform high pressure calculations for a layered perovskite $K_2Ag^{2+}F_4$ (system d^9). Study of this compound was

motivated by its structural relation to La_2CuO_4, well-known precursor of oxocuprate HTSC. Within this study, I have predicted new layered forms of K_2AgF_4, one of which was later observed experimentally in the LTNFM Laboratory (doctoral theses of dr Dominik Kurzydłowski, Faculty of Chemistry UW, Warsaw 2013). I have next expanded this study to the entire family of ternary alkali-metal fluorides M_2XF_4, where M represents the Group 1 cation (Na, Li, K, Rb or Cs) and X is either Cu or Ag. Results of this study revealed an important role of the relative sizes of the M^{1+} and X^{2+} cations on the stability of the layered structure. We learned that the undesirable puckering of $[AgF_2]$ layers observed in K_2AgF_4 results due to insufficient size of the potassium cation and that it can be entirely suppressed by exchanging the potassium cation by rubidium or cesium. Equivalent alternative to the $K^+ \rightarrow Cs^+$ exchange turned out to be the exchange of Ag^{2+} cation by smaller Cu^{2+} one in structure of K_2AgF_4. On the other hand, the exchange of K^+ cation by much smaller Na^+ one resulted in both compounds, Na_2AgF_4 and Na_2CuF_4, in collapse of the layered structure into a one-dimensional post-perovskite structure. From this theoretical study as well as from experimental observations, we have learned that due to the mismatch of the size of the K^{1+} and Ag^{2+} cations in $K_2Ag^{2+}F_4$, the layered perovskite phase is a metastable phase, which transforms to energetically preferred one-dimensional post-perovskite structure of Na_2CuF_4 type. The results of this combined experimental and theoretical study of K_2AgF_4 were partly published in European Journal of Inorganic Chemistry in 2010 [A-04]. The impact of external pressure on the stability of the $[AgF_2]$ layers was found to be similar as the chemical one. It stabilizes layered structural forms of only those compounds, in which the sizes of the M^{1+} and X^{2+} cations are comparable. I have also obtained intriguing theoretical results, which point to two-dimensional antiferromagnetic structures stabilized at high external pressures. The study of the magnetism in these compounds is still in progress. In 2010, I have presented the above results at two international conferences, at European Symposium on Fluorine Chemistry in Ljubljana and at International Chemical Congress in Honolulu.

$AgSO_4$ While working on the ternary fluorides, I was simultaneously involved in study of unknown silver monosulfate $AgSO_4$. Transition-metal monosulfates form a large family of compounds, crystal structures of which are well known. Intriguingly, silver monosulfate was the only compound of the Group 11 monosulfates whose existence had not been reported. This founding was even more intriguing when considering that the cupper sulfate $CuSO_4$ is known to crystalize in five polymorphic forms and one of its hydrated from is a compulsory education material probably in every primary school. When I joined this research, the theoretical structure search of $AgSO_4$ was already initiated. It represented a subject of the master thesis of one of the students in the project, Eng. Krzysztof Dymowski (defended at Faculty of Chemistry, The University of Warsaw, 2009). While his task was to calculate dynamical stability of a series of crystal structures, my task was to propose suitable models for his calculations, supervise his master thesis and perform a more detailed study of the dynamically stable polymorphs. The first question needed to be answered was what would be the preferred oxidation state of silver cations (Ag^{2+} or mixed valence Ag^{1+}/Ag^{3+}) in this compound and what class of topologies (crystal network) would stabilize it. The results of this

study revealed that the preferred oxidation state of silver was Ag^{2+} (d^9) and that it would preferably form three-dimensional crystal networks while involving all oxygen atoms of the SO_4^{2-} anions in chemical bonding with Ag^{2+} cation (*d-p* hybridization). In 2009, I have presented these finding at two conferences, at Puszcza Piska and in Bucharest and our exhaustive study of polymorphism of $AgSO_4$ was subject to one publication [A-05]. Thanks to my freshly gained experience in predicting crystal structures from ab initio, in 2009 I was given the opportunity to give a lecture on this subject to master and doctoral students at international summer school in Białowieża.

In the course of the theoretical study of polymorphs of $AgSO_4$, the compound was successfully synthetized in the Laboratory. The black compound exhibited anomalously strong antiferromagnetic exchange constant J=-18 meV (by an order of magnitude larger than in the remaining metal sulfates), an unusually high temperature (the highest among metal sulfates), in which the magnetic order disappears (380K) because of thermal decomposition and narrow electronic band gap of 0.8 eV. There was however a serious problem with the crystal structure refinement. It was not possible to localize the positions of the light S and O atoms from the X-ray diffraction. Therefore, my next task was to propose a model that would fit the experimental diffraction pattern as well as to explain all other experimentally observed properties of the compound. In accord with the previous theoretical study of polymorphism of $AgSO_4$ [A-05], I have proposed a small triclinic *P*-1 (Z=2) cell, which represented a 3D crystal network of $Ag^{2+}SO_4$. This model was in agreement with all properties observed experimentally at ambient conditions including structural, spectroscopic, magnetic and electronic ones. It explained the character of the strong AFM super-exchange interactions, IR and Raman spectra, color of the compound and character of the narrow electronic band gap. The results of the theoretical calculations additionally revealed the key role of strong electron correlation in stabilization of both the AFM interactions and the electronic band gap. In addition, the knowledge of the details of the crystal network of the *P*-1 cell allowed us to rationalize the thermal decomposition of AgSO4 into $Ag^{1+}{}_2S_2O_7$. Immediately after finding of the small triclinic cell of $AgSO_4$, out further theoretical studies focused on the calculations of its properties in function of chemical and external pressure. The pressure-related properties of the *P*-1 cell became subject of master thesis of Juliusz Stasiewicz (defended at Faculty of Chemistry, The University of Warsaw, 2010). My responsibilities were connected with supervision of his master thesis and calculations of the impact of the chemical pressure on electronic properties of the triclinic cell. The results of these studies revealed that the *P*-1 cell is extremely resistant to metallization under external pressure and that its metallization would be obtained upon S→Cr exchange ($AgSO_4$ → $AgCrO_4$). The small triclinic cell along with the results of combined experimental and theoretical study of $AgSO_4$ was subject of four publications [A-06 – A-09].

The year 2012 gave an interesting twist to our study of $AgSO_4$ initiated by high-pressure X-ray diffraction study of the system. Our theoretically obtained results concerning the compressibility of $AgSO_4$ overestimated the experimental observations. Additionally, the calculations suggested several pressure-driven phase transitions, while no such phase transitions were observed experimentally. One interpretation of these discrepancies was that

the small triclinic *P*-1 cell was not a proper model for high-pressure behavior of $AgSO_4$. These new findings motivated me to re-analyze the theoretical results of $AgSO_4$ polymorphism [A-05]. In consequence, I have found that breaking of one symmetry element in the lowest-energy theoretically predicted tetragonal structure of AgO type further lowers the energy of the $AgSO_4$ system and results in large monoclinic *C*2/*c* (*Z*=16) cell. This new cell provided a better model for structural refinement, yielding a more stable and more accurate Rietveld fit than the former triclinic cell. The calculated pressure behavior of the large monoclinic cell was found to be in very good agreement with the experimental observations. It is important to note, that the large monoclinic cell is very closely related to the small triclinic one. The key difference between the two is in slight reorientation of the SO_4^{2-} tetrahedra. This change does not influence the character of the chemical bonds neither their topology, while preserving all important features including square planar coordination of Ag^{2+} cations, no terminal oxygen atoms and quasi-linear infinite Ag-O(SO_2)O- chains formed along one crystallographic direction. Therefore, the *P*-1 cell proved in the past as a very good minimal structural model for studying the ambient pressure properties of $AgSO_4$ [A-06, A-08, A-09]. The large monoclinic *C*2/*c* cell was published together with the combined experimental and theoretical high-pressure study in CrystEngComm in 2013 [A-10]. With this publication, my tasks in the study of $AgSO_4$ were fulfilled and the attention of the project has been shifted to attempts of doping of this system.

During the 4-years long period of my involvement with $AgSO_4$ system, I have gained a very detailed knowledge of the metal sulfates and found several important structural relations between the late-transition metal (LTM) monosulfates and respective monoxides. The structural analysis revealed that those LTM monoxides, which do not possess ideal NaCl-type lattice form tetragonally distorted NaCl-type lattices. Additionally, it revealed that PdO, CuO and AgO are metrically related and that the 4d and 5d LTM monosulfates are close to isostructural with their monoxides. Results of these analysis have been recently published [B-11].

Silver fluorosulfates and triflates We have found $AgSO_4$ to be a system with strongly structurally frustrated three-dimensional magnetic lattice with AFM interactions dominating along one crystallographic direction. The reason of this frustration lies in involvement of all oxygen atoms in strong *p-d* hybridization. One way to remove this frustration seemed to be replacement of one oxygen atom of the sulfate ion by an atom or a group of atoms that would be inactive in the *p-d* hybridization. Such replacement additionally offers at least a hypothetical possibility of obtaining a 2D AFM structure. This hypothesis became our motivation to study new derivatives of silver, namely fluorosulfates $Ag_x(SO_3\underline{F})_y$ (O→F substitution considered) and triflates $Ag_x(SO_3\underline{CF_3})_y$ (O→CF_3 substitution considered). Consequently, three distinct phases of silver fluorosulfate were synthesizes, including an intermediate-valence paramagnetic d^9 system $Ag^{2+}(SO_3F)_2$, a mixed-valence paramagnetic d^9/d^{10} system $Ag_3(SO_3F)_4$ and a diamagnetic d^{10} system $Ag^{1+}(SO_3F)$. In the same time, three phases from the family of silver triflates were synthetized, namely one paramagnetic form $Ag^{2+}(SO_3CF_3)_2$, one diamagnetic form $Ag^{1+}(SO_3CF_3)$ and one complex diamagnetic

derivative $Ag^{1+}S_2O_6CF_3$. My task in study of these compounds was to perform complex theoretical study of their physicochemical properties including crystal, electronic and magnetic structure, lattice dynamics and polymorphism. The results of magnetic calculations confirmed the hypothesis that that the O→F in silver sulfate leads to structurally and magnetically two-dimensional structure in case of $Ag^{2+}(SO_3F)_2$. However, the magnetic interactions within the $[Ag^{2+}(SO_3F)_2]$ layers were found to be ferromagnetic in nature and not antiferromagnetic as desired. A strong AFM interactions within the infinite $[AgSO_3F]$ chains, reminiscent of those in $AgSO_4$, were predicted for the second phase of silver fluorosulfate, $Ag_3(SO_3F)_4$. A 1D AFM character was confirmed theoretically also for triflate of Ag^{2+}, $Ag(SO_3CF_3)_2$ but with distinct character than the one confirmed theoretically in $Ag_3(SO_3F)_4$ or $AgSO_4$. The results of the combined experimental and theoretical study of the two fluorosulfates and the one triflate of Ag^{2+}, including calculations of their crystal, electronic and magnetic structure as well as lattice dynamics were subject of three publications published in 2011 [A-11 – A-13].

In case of Ag^{1+} derivatives of the above systems, the theoretical calculations were focused mainly on their polymorphism and lattice dynamics. The normal-mode analysis (assignment of IR and Raman active normal modes) was crucial in distinguishing the Ag^{1+} derivatives from the Ag^{2+} ones, in the vibrational spectra, since the latter thermally decompose to the former. The results of the theoretical study of polymorphism have revealed that the experimentally observed phase of $AgSO_3F$ is a metastable one and that a lower energy of $AgSO_3CF_3$-type should exist. This theoretical phase now awaits its experimental confirmation in the Laboratory. The results of the combined experimental and theoretical study of Ag^{1+} systems became subjects of two publications [A-15–16].

AgO and $AgCl_2$ In 2010 two new students from the Warsaw Technical University (WTU) joined the theoretical section of the TEAM project. My task was to conduct training in the QM methods in solid state for them, after which they were to perform calculations for two distinct systems of Ag^{2+} under my supervision. The task of one of the students, Izabela Włodarska, was to perform high-pressure calculations of mixed-valance Ag^{1+}/Ag^{3+} silver monoxide AgO in order to examine the possibility of its metallization. The task of the second student, Paweł Kondratiuk, was to search for dynamically stable structural models for yet unknown system of Ag^{2+}, namely $AgCl_2$ in solid state.

Silver oxide crystallizes in two phases, monoclinic and tetragonal. The results obtained from the high-pressure calculations of crystal, electronic and fonon structure and mechanical properties of the two phases became the subject of Ms. Włodarska's engineering thesis (defended at Faculty of Physics, Warsaw Technical University, 2011) and master thesis (defense planned in 2013), under supervision of dr. Krzysztof Zberecki from WTU and mine. Results of her calculations revealed new high-pressure mixed-valence forms of AgO. I am now continuation the study of AgO, by calculating the impact of magnetic interactions on stability of hypothetical intermediate-valence $Ag^{2+}O$ structures at high pressures relative to the high-pressure mixed valence ones.

Concerning the study of yet unknown $AgCl_2$, Mr. Kondratiuk obtained several dynamically stable crystal structures during his one-year long contract in the TEAM project. He performed a very fast structure screening on LDA level of DFT theory. I am now continuing the study of polymorphism in $AgCl_2$ on higher level of theory (hybrid DFT), while in the same time examining the electronic structure, magnetism and effect of strong correlations in the dynamically stable structures. Our temporary theoretical results revealed a rich polymorphism of $AgCl_2$ with diverse electronic structures and magnetism. Within the lowest energy forms obtained on hybrid DFT level a metallic form was obtained. I have presented these results on two conferences (Lisbon 2012 and Warsaw 2013) and at one invited seminar at Faculty of Physics UW in 2013.

Pyrazine compounds One of the first goals of the experimental section of the LTNFM Laboratory concerning the TEAM project, was to synthetize a pyrazine complex of Ag^{2+} - $Ag(C_4H_4N_2)_2](S_2O_8)$. This compound was synthetized for the first time in 1971 but its crystal structure was unknown. However, its cupper sibling $Cu(C_4H_4N_2)_2](S_2O_8)$ is known to crystalize in a layered structure with 2D AFM interactions mediated within the layers, formed by Cu^{2+} and pyrazine molecules $C_4H_4N_2$. In consequence, the knowledge of the crystal and magnetic structure of the silver complex was highly desirable. If isostructural with the respective Cu^{2+} complex, it would represent the first 2D AFM compound of Ag^{2+}. My task in this study was to examine the nature of magnetic interactions in the Ag^{2+} complex, once the crystal structure was refined from X-day diffraction data. In the course of this study in 2009, a competing US team has published the crystal structure as well as electronic and magnetic properties of the Ag^{2+} pyrazine complex, confirming the presence of the 2D AFM layers [J. AM. CHEM. SOC. 2009, 131, 4590–4591]. They have also reported a theoretical study of the AFM interactions considering a dimer model within molecular approach. The results of my periodic calculations confirmed the 2D nature of the AFM interactions and additionally revealed that the AFM super-exchange between neighboring Ag^{2+} cations is being mediated by four atoms of carbon and two atoms of nitrogen. These results were published in 2012 [A-14, ESI]. Attempts of doping of the Ag^{2+} complex have been later initiated in the LTNFM Laboratory.

In the course of the study concerning pyrazine derivatives, a potential candidate for ferroelectric material, a novel molecular crystal of $(C_4H_4N_2)_2H^+HSO^-_4$, was synthetized in two polymorphs, α and β, in the LTNFM Laboratory. I have performed QM calculations for both of its forms, first to analyze the geometry of hydrogen atoms, since the crystal structures were refined from X-ray diffraction data insensible to hydrogen content. Next, I have performed QM calculations for both of its forms in order to examine its potential as ferroelectric theoretically. The results of these calculations indicated a possible existence of a hypothetical polar *P*1 form of the β polymorph (β') with an unusually high dipole moment of 0.19 C m^{-2} present already without presence of external electric field. In the same time a low barrier is expected for the β→β' phase transition. The results of this study were published in 2010 [B-09].

Hydrogen storage material Apart from the project TEAM, I took part in study of hydrogen storage material, also carried out in the LTNFM Laboratory. My role was to examine the crystal and electronic structure and lattice dynamics in $Na[Li(AB)_2]$ and *high spin-low spin* magnetic transition in a molecular complex of Ni^{2+} - tetrafluoroborane of Ni^{2+} by means of theoretical QM calculations. $Na[Li(AB)_2]$ is a new compound exhibiting hydrogen storage capacity of 11 tw% and belonging to group of intensively studied aminoborate compounds. The results of my calculations of crystal structure and lattice dynamics were in very good agreement with the experimental observations. Additionally, they revealed that $Na[Li(AB)_2]$ is a charge-transfer insulator. These results were published in in 2011 [B-10]. Results of the molecular calculations and calculations in solid state performed for the complex of Ni^{2+} has helped us to understand the relationship between reversible incorporation of two water molecules into its crystal structure and its 'chemoswitching' properties. The results of these calculations were published 2012 [A-17].

Teaching activity The experience that I have gained during my 10-years long study of solids has motivated me to deliver a new course on solid state for students of the University of Warsaw. The interactive coarse entitled "Ciało stale prosto i po raz pierwszy w 3D" (free translation: Simple approach to solid-state matter with 3D projections) is a general course at the University of Warsaw since fall 2012. The goal of the course is to present the subject in a manner accessible to wide range of students, especially those from interdisciplinary fields. It also provides introduction to the subject for students of physics and solid-state chemistry. During the course, students are being thought the relationships between crystal structures and their physicochemical properties, while special attention is paid to visual illustrations of various examples. The course takes advantage of freelance programs for 3D crystal structure visualization, which are accessible to all students of the course.

3. Present scientific activity

Since November 2012, after completion of the project TEAM, I have been employed as scientific adjunct in CeNT UW. The knowledge gained during my engagement in the TEAM project has motivated me to further exploration of novel compounds of Ag^{2+} as well as to broaden our knowledge of late-transition metal compounds. Apart from my participation in the ongoing research of AgO and $AgCl_2$ and layered perovskites M_2XF_4 (M from Group 1 and X from Group 11) as described above, systems of my current scientific interests encompass binary transition-metal (TM) oxides and fluorides and new stoichiometries stabilizing layered structures with Ag^{2+}. The theoretical study of the TM oxides is realized in cooperation with Dr. Hab. Przemysław Piekarz from Institute of Nuclear Physics PAS in Cracow. Here, we focus on Jahn-Teller effects in late-TM monoxides and with it related polymorphism observed

in this group of compounds. Its goal is to explain the instability of the ideal rock salt lattice in these compounds as well as mechanisms of its collapse to the experimentally observed structures. The goal in the study of TM binary fluorides is to perform a systematic study of their magnetism by means of QM calculations. This study is motivated by previous reports of anomalously large AFM interactions in AgF_2 [J. Phys. Cond. Matt. 19(12): 116206-1, 2007] and $KAgF_3$ [Chem. Commun. 49(56): 6262, 2013]. Finally, based on the experience with Ag^{2+} compounds gained during the project TEAM, we have proposed new oxides of Ag^{2+} containing either lanthanum or strontium cations with a potential to host 2D AFM. These studies are carried out in cooperation with Dr. Krzysztof Zberecki from Warsaw Technical University.

Warsaw, 1 October 2013

III. Series of 17 monographic works selected for purpose of habilitation procedure

In accordance with the art. Paragraph 16.2 of the Act from 14 March 2003 on scientific degrees and scientific title and degrees and title in arts (Journal of Laws No. 65, item. 595, as amended.), I am presenting as my scientific achievement Series of 17 [A-01 - A-17] monographic works entitled

Electronic, magnetic and crystal structure and lattice dynamics of selected systems of late transition metals.

1. Introduction

The Series of publications [A-01 – A-17] entitled *Electronic, magnetic and crystal structure and lattice dynamics of selected systems of transition metals* is dedicated to inorganic crystalline strongly electron correlated compounds with iron, nickel and silver belonging to families of silicates, fluorides and interrelated compounds. While the iron-rich silicates presented in this Series are naturally occurring magnetic minerals, forming an important component of the Earth's Mantle, the presented Ni- and Ag-based materials represent novel functional compounds such as ferro- and antiferromagnets and extremely strong electron-withdrawing systems (Ag^{2+} compounds), charge-density wave (mixed-valence Ag^{1+}/Ag^{2+} compound) and spin-crossover system (Ni^{2+} complex).

The first three publications within the presented Series [A-01 – A-03] are dedicated to iron-rich silicate minerals: $(Mg,Fe)_2SiO_4$ solid solution and its end-members, Mg_2SiO_4 and Fe_2SiO_4. These publications present results of purely theoretical studies. They encompass QM DFT(+U) calculations in solid state of electronic, magnetic, crystal and phonon structure, mechanical and optical properties and thermodynamics of the minerals in their high-pressure cubic (spinel) form. Purpose of this study was to provide a complex theoretical characterization of the solid solution and its end-members in their high-pressure cubic spinel structure, while special attention was paid to role of iron content, impact of the magnetic interactions, strong electron correlations and external pressure. This study was carried out in Department of Material Research by Computers in INF PAN in Cracow.

Publications dedicated to novel functional Ag- and Ni-based material [A-04 – A-17] present results of comprehensive theoretical and experimental studies. The theoretical studies encompass QM calculations in solid state on DFT(+U) and hybrid DFT level of theory. Apart from the properties studied in the iron-rich silicates, the calculations were performed here

additionally to study structural polymorphism and phase transitions and in one case in prediction of crystal structure of an unknown compound. The experimental techniques used included X-ray powder diffractometry, infrared and Raman spectroscopy, electron spin-resonance spectroscopy (ESR), mass spectroscopy, thermal gravimetry (TGA), differential scanning calometry (DSC) and magnetometry. The TGA, DSC and spectroscopic stools were used to identify products of synthesis. For all crystalline products, crystal structure was refined from X-ray diffraction data and magnetic susceptibility was measured. These comprehensive studies aimed to enrich the family of Ag^{2+} and Ni^{2+} compounds and our knowledge of their physicochemical properties, while special attention was paid to examination of their potential to form 2D AFM structures. The theoretical studies were carried out at the LTNFM Laboratory UW in Warsaw while taking advantage of the supercomputers in ICM UW. The experimental studies were performed in collaboration of the Laboratory with several national as well as with international partners.

My contribution to publications presented in this Series is in performing most of the QM calculations and their analysis. Concerning the study of iron-rich silicates, I performed all calculations for the Fe_2SiO_4 system and took part in the analysis of the results obtained for $Mg_{2-x}Fe_xSiO_4$. In case of the Ag- and Ni-based compounds, I was responsible for all theoretical studies. In two publications dedicated to silver sulfate, part of the calculations were additionally done by two master students, Krzysztof Dymkowski [A-05] and Juliusz Stasiewicz [A-09], under my supervision. Apart from the theoretical studies, I took part in interpretation of experimental data obtained for Ag-based systems including X-ray diffractions, IR and Raman spectra and crystal structures.

2. List of publications

The numbers in parentheses stand for impact factor and number of citations as listed by Web of Science.

A-01 M. Derzsi, P. Piekarz, P. T. Jochym, J. Łażewski, M. Sternik, A. M. Oleś, and K. Parliński, *Effects of Coulomb interaction on the electronic structure and lattice dynamics of the Mott insulator Fe_2SiO_4 spinel*, PHYS. REV. B 79(20), 205105 (2009), (3,475; 8).

My contribution: I proposed the subject of study, performed all DFT(+U) calculations for the title compound, which included calculations of crystal, electronic, magnetic and phonon structure and performed analysis of their results. I wrote the manuscript and was the corresponding author. My contribution: 60%.

A-02 M. Derzsi, P. Piekarz, K. Tokar, P. T. Jochym, J. Łażewski, M. Sternik and K. Parliński, *Comparative ab initio study of lattice dynamics and thermodynamics of*

Fe_2SiO_4 and Mg_2SiO_4 spinels, J PHYS: COND MAT 23(10), 105401 (2010), (2,546; 3).

My contribution: I proposed the subject of study, performed all DFT(+U) calculations for Fe_2SiO_4, which included calculations of lattice dynamics in function of pressure and thermodynamic functions and performed analysis of their results. I wrote the manuscript and was the corresponding author. My contribution: 50%.

A-03 K. Tokar, P. Piekarz, M. Derzsi, P. T. Jochym, J. Łażewski, M. Sternik, A. M. Oleś and K. Parliński, *Electronic and optical properties of $Mg_{2-x}Fe_xSiO4$ spinel: From band insulator to Mott insulator*. PHYS REV B 82(19), 195116 (2010), (3,475; 3).

My contribution: I performed all high-pressure DFT(+U) calculations for Fe_2SiO_4 and analysis of their results, performed analysis of calculations concerning impact of iron concentration on crystal structure of $(Mg,Fe)_2SiO_4$, took part in construction of the manuscript (fragments of text, figure and table) and edited the manuscript. My contribution: 20%.

A-04 D. Kurzydłowski, M. Derzsi, A. Budzianowski, Z. Jagličić, W. Koźminski, Z. Mazej, W. Grochala, *Polymorphism of Fluoroargentates(II): Facile Collapse of a Layered Network of α–K_2AgF_4 Due to Insufficient Size of Potassium Cation*, EUR J INORG CHEM (19), 2919-2925 (2010), (3,049; 2).

My contribution: I performed all DFT(+U) calculations including crystal, electronic and magnetic structure, calculations of polymorphism and analysis of the their results. I took part in writing the manuscript (providing fragments of text concerning the theoretical results including figures/graphs and material to ESI), and edited the manuscript. My contribution: 25%.

A-05 M. Derzsi, K. Dymkowski, W. Grochala, *The Theoretical Quest for Sulfate of Ag^{2+}: Genuine $Ag(II)SO_4$, Diamagnetic $Ag(I)_2S_2O_8$ or Rather Mixed-Valence $Ag(I)[Ag(III)(SO_4)_2]$?* INORG CHEM 49(6), 2735–2742 (2010), (4,601; 8).

My contribution: I supervised the DFT (LDA) calculations of Mr. Krzysztof Dymkowski – prediction of dynamically stable polymorphs of the title compound. For all theoretically predicted dynamically stable structures, I performed more precise calculations on DFT(GGA) level and analysis of their results, concerning crystal structures, polymorphism, oxidation state of silver and relative stabilities. I wrote the manuscript and was the corresponding author. My contribution: 50%.

A-06 P.J. Malinowski, M. Derzsi, Z. Mazej, Z. Jagličić, B. Gaweł, W. Łasocha, and W. Grochala, *$Ag^{II}SO_4$: A Genuine Sulfate of Divalent Silver with Anomalously Strong One-Dimensional Antiferromagnetic Interactions*, ANGEW CHEM INT ED ENGL 49(9), 1683–1686 (2010), (13,455; 19).

My contribution: I took part in the crystal structure refinement of the title compound (proposing small *P*-1 cell, which was used in interpretation of all experimental data). I performed all DFT(+U) calculations of $AgSO_4$ in the *P*-1 cell including crystal, electronic and magnetic structure and analysis of their results. I took part in constructing the manuscript (providing fragments of text concerning the results of calculations including figure and graphs to both article and to ESI) and in editing of the manuscript. My contribution: 20%.

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A-07 M. Derzsi, P. J. Malinowski, Z. Mazej, W. Grochala, *Phonon spectra and phonon–dependent properties of $AgSO_4$, an unusual sulfate of divalent silver*, VIBR SPECTR 57(2), 334–337 (2011), (1,65; 4).

My contribution: I performed all DFT calculations of the title compound: phonon spectra and thermodynamic parameters, took part in construction of the manuscript and its editing and I was the corresponding author. My contribution: 65%.

A-08 P. J. Malinowski, M. Derzsi, A. Budzianowski, P. J. Leszczyński, B. Gaweł, Z. Mazej, Grochala W, *Unusual thermal decomposition of $Ag(II)SO_4$ yielding $Ag(I)_2S_2O_7$: bending the Hammond's rule*, CHEM EUR J 17(38), 10524-10527 (2011), (5,925; 5).

My contribution: I performed all DFT calculations concerning polymorphism of $Ag_2S_2O_7$ and analysis of their results (predicting HP form of $Ag_2S_2O_7$). I also preformed analysis of structural aspects of the thermal decomposition of $AgSO_4$ to $Ag_2S_2O_7$, took part in constructing the manuscript (providing figures and tables also to ESI) and edited the manuscript. My contribution: 20%.

A-09 M. Derzsi, J. Stasiewicz, W. Grochala, *Crystal and electronic structure and high-pressure behaviour of $AgSO_4$, a unique narrow band gap semiconductor. LDA(+U) picture*, J MOL MODEL 17(9), 2259-2264 (2011), (1,797; 5).

My contribution: I supervised the high-pressure DFT (LDA) calculations of $AgSO_4$ of Mr. Juliusz Stasiewicz, performed the calculations of electronic and magnetic structure of $AgSO_4$, $AgSeO_4$ and $AgCrO_4$ and analysis of their results. I took part in writing the manuscript, provided some of the graphics (figures, graphs), edited the manuscript and was the corresponding author. My contribution: 60%.

A-10 M. Derzsi, A. Budzianowski, V. V. Struzhkin, P. J. Malinowski, P. J. Leszczyński, Mazej Z, Grochala W, *Redetermination of crystal structure of $Ag(II)SO_4$ and its high pressure behavior up to 30 GPa*, CRYSTENGCOMM 15(1), 192–198 (2013), (3,842; 1).

My contribution: I took part in the interpretation of the high-pressure X-ray diffraction data of $AgSO_4$ proposing a large monoclinic cell, which was used in interpretation of the experimental data. I performed high-pressure DFT(+U) calculations of the crystal and magnetic structure of $AgSO_4$ in the new monoclinic cell and polymorphism of $Ag_2S_2O_7$ (high-pressure decomposition product of $AgSO_4$) and performed analysis of their results. I took part constructing the manuscript and ESI (providing fragments of text and graphics), edited the manuscript, was the corresponding author. My contribution: 25%.

A-11 P. J. Malinowski, M. Derzsi, Z. Mazej, Z. Jagličić, P. J. Leszczyński, T. Michałowski, W. Grochala, *$Ag(SO_3F)_2$, silver(II) fluorosulfate – a thermally fragile ferromagnetic derivative of divalent silver in oxa- ligand environment*, EUR J INORG CHEM (16), 2499–2507 (2011), (3,049; 8).

My contribution: I performed all DFT(+U) calculations of the title compound including crystal, electronic, magnetic and phonon structure and performed analysis of their results. I took part in interpretation of measured vibrational spectra (assignment of all IR and Raman active modes) and in

construction of the manuscript, providing text and graphics concerning the results of the calculations and material to ESI. I edited the manuscript. My contribution: 20%.

A-12 T. Michałowski, P. Malinowski, M. Derzsi, Z. Mazej, Z. Jagličić, P. J. Leszczyński, W. Grochala, *$Ag_3(SO_3F)_4$ – a rare example of mixed valence Ag(I)/Ag(II) compound showing 1D Antiferromagnetism*, EUR J INORG CHEM (16), 2508–2516 (2011), (3,049; 8).

My contribution: I performed all DFT(+U) calculations of the title compound including crystal, electronic and magnetic structure and performed analysis of their results. I took part in construction of the manuscript, providing text and graphics concerning the results of the calculations. I edited the manuscript. My contribution: 15%.

A-13 P. J. Malinowski, Z. Mazej, M. Derzsi, Z. Jagličić, J. Szydłowska, T. Gilewski, W. Grochala, *Silver (II) triflate with one dimensional $[Ag(II)(SO_3CF_3)_{4/2}]_\infty$ chains hosting antiferromagnetism*, CRYSTENGCOMM 13(22), 6871-6879 (2011), (3,842; 4).

My contribution: I performed all DFT(+U) calculations of the title compound including crystal, electronic, magnetic and phonon structure and performed analysis of their results. I took part in interpretation of measured vibrational spectra (assignment of all IR and Raman active modes) and in construction of the manuscript, providing text and graphics concerning the results of the calculations and material to ESI. I edited the manuscript. My contribution: 20%.

A-14 P. J. Leszczyński, A. Budzianowski, M. Derzsi, Ł. Dobrzycki, M. K. Cyrański, W. Grochala, *Thermal and chemical decomposition of di(pyrazine)silver(II) peroxydisulfate and unusual crystal structure of a Ag(I) by-product*, DALTON TRANS 41(2), 396-402 (2012), (3,838; 2).

My contribution: I performed all DFT+U calculations of magnetic structure of the title Ag(II) complex and performed analysis of their results. I took part in writing the manuscript (section concerning the Ag(II) complex) also providing text and graphics concerning the results of the calculations (ESI). My contribution: 30%.

A-15 W. Grochala, M. K. Cyrański, M. Derzsi, T. Michałowski, P. J. Malinowski, Z. Mazej, D. Kurzydłowski, W. Koźminski, A. Budzianowski, P. J. Leszczyński, *Crystal and electronic structure, lattice dynamics and thermal properties of $Ag(I)(SO_3)R$ (R=F, CF_3) Lewis acids in the solid state*, DALTON TRANS 41(7), 2034-2047 (2012), (3,838; 4).

My contribution: I performed all DFT calculations of the title compounds including crystal, electronic and phonon structure and polymorphism and performed analysis of their results. I took part in interpretation of the disordered crystal structure of $Ag(I)SO_3F$ (also predicting its meta-stability) and of measured vibrational spectra (assignment of all IR and Raman active modes) and in construction of the manuscript, providing text and graphics concerning the results of the calculations (also to ESI). I edited the manuscript. My contribution: 25%.

A-16 P. J. Malinowski, M. Derzsi, W. Grochala, *Ag(I)$S_2O_6CF_3$: the first trifluoromethyldisulphate(VI)*, in press, DALTON TRANS 42 (29), 10417-10423 2013, (3,838; 0).

My contribution: I performed all DFT calculations of lattice dynamics of the title compound and performed analysis of their results. I took part in interpretation of vibrational spectra (assignment of all IR and Raman active modes). My contribution: 30%.

A-17 A. J. Churchard, M. Derzsi, Z. Jagličić, A. Remhof, W. Grochala, *Chemo-switched chromatic, structural and magnetic changes with retention of molecular crystallinity, Ni(II)(12aneS4)(BF_4)$_2$*, DALTON TRANS 41(17): 5172-5176 (2012), (3,838; 1).

My contribution: I took part in the interpretation of the crystal structure of the hydrated form of the Ni(II) complex, performed DFT+U calculations in solid state of its crystal structure (of hydrated and dehydrated form) and HS-LS electronic transition and performed the analysis of the results of the calculations. My contribution: 35%.

3. The main results

$(Mg,Fe)_2SiO_4$ spinel and its end-members Fe_2SiO_4 and Mg_2SiO_4

Prior to the resented studies, the least studied system among the three title silicates was the Fe_2SiO_4 spinel while the Mg_2SiO_4 one was well characterized both experimentally and theoretically. Therefore we have first concentrated on detailed characterization of the Fe-end member and then on role of iron concentration in $(Mg,Fe)_2SiO_4$. The calculations of the Mg-end member were performed mostly for comparative purposes. Since spinel is a high-pressure from of all three title silicates all calculations were performed at elevated pressures.

Based in the DFT (GGA+U) calculations, we have first determined the electronic (magnetic) ground state of Fe_2SiO_4 spinel at 20 GPa. Our results strongly suggest that the Fe_2SiO_4 spinel is an AFM insulator with Mott-Hubbard band gap and tetragonally distorted crystal structure, which permits symmetry breaking in a system with frustrated antiferromagnetic interactions. We have demonstrated that this solution is both electronically and dynamically stable and that the strong Coulomb interactions are crucial for stabilization of both the AFM interaction as well as opening of the electronic band gap and play important role in modulating of phonon energies [A-01]. Next, impact of the cation Mg→Fe exchange on the lattice dynamics and thermodynamics of the spinel was determined taking the advantage of the DFT calculation at GGA level. The modes with the larges sensitivity to this exchange were detected to be the lowest energy inactive A_{2u} and the lowest IR-active T_{1u} modes [A-02]. Finally, we have calculated the electronic structure and optical properties of the $Mg_{2-x}Fe_xSiO_4$ spinel in function of iron concentration on GGA+U level and described the

details of the transition of the *p*-band insulator Mg_2SiO_4 into the Mott-Hubbard Fe_2SiO_4 insulator. We have demonstrated that the transition is connected with appearance of strongly correlated Fe *d* bands in the band *p* gap of Mg_2SiO_4, appearance of additional optical $t_{2g} \rightarrow e_g$ transitions visible in the *p* band gap, and decrease of the newly formed *d*-band gap due to the enhanced electron mobility and the increasing width of t_{2g} band. Our further calculations revealed that the same effect of the band gap decrease in Fe_2SiO_4 is induced by external pressure [A-03].

Finally, we have provided an exhaustive description of $(Mg,Fe)_2SiO_4$ spinel as a unique combination of properties of its two distinct end-members, a magnetically frustrated AFM and strongly correlated Mott-type insulator Fe_2SiO_4 and nonmagnetic *p*-band insulator Mg_2SiO_4.

Novel Ag-based compounds

In this section, 12 novel Ag-based compounds are presented including fluorides, sulfates, and modified sulfates, in which one oxygen atom of the SO_4 group was replaced by fluorine atom or CF_3 group, or additional molecules were incorporated into the crystal structure. Within these systems, silver atoms can be found in Ag^{1+} (d^{10}) and/or in Ag^{2+} (d^9) oxidation state. The Ag^{2+} cation is extremely reactive (unstable) because of its strong oxidation power and only the most electronegative species such as fluorine or sulfate anion can form stable compound with it. Therefore, we have paid the largest attention to the systems containing Ag^{2+} cations, while the Ag^{1+} compounds in this Series represent in a great part products of their spontaneous thermal decomposition. Prior to these studies, the family of Ag^{2+} compounds was limited mainly to fluorides. Our studies have broadened this group by sulfates ($-SO_4$), fluorosulfates ($-SO_3F$) and triflates ($-SO_3CF_3$).

i) Compounds with Ag^{2+} and mixed-valence Ag^{1+}/Ag^{2+}

The first Ag^{2+} system studied within this Series is a post-perovskite (Na_2CuF_4-type) structure of K_2AgF_4 [A-04]. The post-perovskite structure was a newly discovered form of K_2AgF_4, while previously only a layered-perovskite type was known. Our theoretical DFT+U study of K_2AgF_4 revealed that the post-perovskite structure is a FM insulator and that it is energetically favored over the layered-perovskite one. They thus confirmed that the layered-perovskite structure is a metastable form of K_2AgF_4.

The most studied Ag-based system within this Series was $AgSO_4$, while six publications were dedicated only to this inorganic solid [A-05 – 10]. Our understating of this compound is result of an exhaustive four-year long study, in which the theory and experiment gave course to each other. Prior to its synthesis, we have performed an exhaustive theoretical DFT search of its dynamically stable structures [A-05]. We have learned from this study that $AgSO_4$ will

most probably form a 3D crystal network with all oxygen atoms incorporated into chemical bonding with silver (*d-p* hybridization) and that it should be an intermediate-valence compound with Ag^{2+} cations and not mixed-valence $Ag^{1+}Ag^{3+}(SO)_4$ or $Ag^{1+}{}_2S_2O_8$ one, which were also found to be dynamically stable configurations. Base on this information and using the clue about magnetic structure dimensionality obtained from the magnetic susceptibility measurements of synthetized $AgSO_4$, I was later able to propose a small triclinic cell *P*-1 (Z=2) which fitted well the X-ray diffraction pattern, and provided a valuable structural model for calculation of electronic, magnetic and phonon structure of $AgSO_4$. Considering this model in electronic and magnetic structure DFT (GGA+U) calculations, the model justified the interpretations of magnetic susceptibility data (1D AFM) and optical measurements together with its its black color (insulator with electronic gap < 1 eV) [A-06]. The theoretical normal-mode analysis performed on DFT (LDA and GGA) level for the small P-*1* cell provided interpretations for all experimentally observed IR and Raman active modes of $AgSO_4$ [A-07]. Finally, the model helped us to understand structural links between $AgSO_4$ and product of its thermal decomposition $Ag_2S_2O_7$ [A-08]. However, the small *P*-1 cell turned out to be insufficient in interpretation of the high-pressure behavior of the sulfate measured in the range 0-30 GPa. The purely theoretical high-pressure study of the small *P*-1 cell, performed on LDA level prior to the high-pressure experiment, suggested number of phase transitions [A-09], while no such behavior was later observed experimentally. Therefore, I have returned to our initial theoretical study of the dynamically stable polymorph and performed further structural analysis. The predicted lowest-energy polymorph with slight additional monoclinic distortions (resulting into large monoclinic *C*2/*c* cell with *Z*=16) proved to be an excellent model for the interpretation of the high-pressure X-ray diffraction data in the entire measured range 0–30 GPa, while in the same type preserving all the important properties of the *P*-1 model. Additionally, results of the magnetic high-pressure calculations (GGA+U) of the large *C*2/*c* cell suggest a strong resistivity of the 1D AFM in this structure to external pressure [A-10].

In the course of the exhaustive experimental and theoretical study of $AgSO_4$ we learned that its structurally frustrated magnetic lattice with strong 1D AFM interactions cannot be modified into a desirable 2D antiferromagnet or metallized neither by external pressure or temperature (in both decomposition to Ag^{1+} products takes over). Therefore, we turned our attention to role of chemical substitution. Results of our theoretical study of anion substitution in $AgSO_4$ suggest that replacement of the SO_4^{2-} by chemically comparable CrO_4^{2-} one lead to ferrimagnetic metal $Ag^{2+}CrO_4$ [A-09]. Further Ag^{2+} systems examined both experimentally and theoretically were fluorosulfates [Ag–SO_3F] and triflates [Ag-SO_3CF_3]. In consequence, this Series is completed by three publications dedicated to $Ag^{2+}(SO_3F)_2$ [A-11], mixed-valance $Ag^{2+}Ag^{1+}{}_2(SO_3F)_4$ [A-12] and $Ag^{2+}(SO_3CF_3)_2$ [A-13]. In all three cases, the magnetic, electron and phonon structure were revealed by theoretical DFT(+U) calculations. The last Ag^{2+} system studied was a $Ag(C_4H_4N_2)_2(S_2O_8)$ complex [A-14]. This system turned to be the first 2D AFM compound with Ag^{2+}. In the theoretical DFT+U study of this compound we have turned our attention to the character of the magnetic interactions.

Results of my calculations revealed, that all the Ag^{2+} (d9) systems presented within this Series are magnetic (spin-1/2) insulators with calculated electronic band gap in the range ~0.8 – 1.6 eV. The magnetic interactions and strong electron correlations were found to play an important role in stabilizing the band gap, which was often found to be intermediate between the Mott-type and charge-transfer type one. Calculations of the magnetic spin density revealed that the unpaired electron resides always on the $d(x^2-y^2)$ orbital, which strongly hybridizes with the p_x and p_y orbitals of the ligands. In consequence, the Ag^{2+} cations are in them always found in a close to square-planar coordination. The strong *d-p* hybridization observed in the calculated electronic densities of states suggests a substantial covalent character of the four bonds (Ag-O in oxo-compounds, Ag-F in fluorides, Ag-N in the Ag complex) in the first coordination sphere of silver and is responsible for considerable smearing of the magnetic moment over the coordinating atoms (X = O, F or N). The calculated magnetic moment per one such X side is usually found to be in the range 0.04-0.088μ_B per O or N atom while it takes even higher values (~0.1μ_B) for fluorine atoms. The magnetic moments per one Ag side takes values within the range 0.335-0.506μ_B, which shows that in some cases more than half of the magnetic density is distributed over the ligands. This hybridization was found to be crucial for mediation of the magnetic interactions in these systems. The calculations of the magnetic spin density revealed that the magnetic interactions between Ag^{2+} centers are mediated usually by more than one atom. This is the case of all sulfate-related compounds (magnetic superexchange mediated by 2 to 4 O atoms) and the Ag complex (magnetic superexchange mediated 2 N and 4 C atoms). Considering the substantial smearing of magnetic density and the long magnetic links in these systems, the AFM superexchange interactions observed in them should be considered as strong (J is found between -4.6 and -19 meV). The sigh of the superexchange was found to be strongly dependent on the geometry of chemical bonds and dimensionally of the crystal network. The 2D antiferromagnetism was observed, and confirmed theoretically, only in the Ag complex, which exhibits layered crystal structure with Ag^{2+} cations imbedded in a square lattice. Puckering of the layers was found responsible for suppression of 2D AFM interactions and onset of 2D FM interactions in the Ag^{2+} fluorosulfate. The large triflate anion in $Ag(SO_3CF_3)_2$ caused further delusion of the magnetic network by weakening the *d-p* hybridization in one direction within the layers, and a 1D AFM chains weakly ferromagnetically coupled resulted. Similar effect was caused by excess of the Ag^{1+} cations in the mixed-valence Ag^{1+}/Ag^{2+} fluorosulfate. Finally, $AgSO_4$ represent a strongly frustrated 3D magnetic lattice due involvement of all oxygen atoms of the tetrahedral SO_4^{2-} anion in the substantial *d-p* hybridization.

ii) **Ag^{1+} compounds**

This section is dedicated to three Ag^{1+} products of spontaneous thermal decomposition of the Ag^{2+} sulfate, fluorosulfate and triflate and a related system $Ag^{1+}S_2O_6CF_4$.

First, $Ag^{2+}SO_4$ was found to decompose to $Ag^{1+}{}_2S_2O_7$. Two of its possible crystal structures were checked by DFT calculations $Na_2S_2O_7$ and $K_2S_2O_7$. Both were predicted to be possible structures of $Ag_2S_2O_7$, while the sodium one was predicted to be the lower-pressure type and the potassium one a higher-pressure one. Both of these predictions were confirmed experimentally. The potassium type was observed as high-pressure decomposition product of $AgSO_4$ [A-09, A-10].

The Ag^{2+} fluorosulfate $Ag(SO_3F)_2$ was found to decompose to $Ag^{1+}SO_3F$. This Ag^{1+} system turned out to have complex crystal structure with structural disorder of fluorine and oxygen atoms. Results of the DFT calculations suggest that there is no strong preference for any particular ordering, while negligible energy differences were obtained between all tested ordered models. The calculations further suggest that the experimentally observed disordered structure is a metastable form of $AgSO_3F$, while an hypothetical Ag^{1+}-triflate type structure was found to be favored by ~10.6 meV/FU and dynamically stable [A-15].

For Ag^{1+} fluorosulfate, Ag^{1+} triflate and the related $Ag^{1+}S_2O_6CF_4$ compound IR and Raman active modes were calculated by means of DFT calculations, based on which their experimental vibrational spectra were successfully assigned [A-15, A-16]. Theoretical calculations of the normal modes in both, Ag^{2+} and Ag^{1+} compounds, helped to us in their identification in the experimental vibrational spectra of partially decomposed samples.

iii) Ni^{2+} complex

The only Ni^{2+} compound presented in this Series enriches the vast family of Ni^{2+} complexes by unique molecular crystal $Ni(II)(12aneS_4)(BF_4)_2$. It exhibits reversible ability to absorb vapor, while in the same time changing its chromatic and magnetic properties and crystal structure. The DFT calculations in solid state proved that the complex can incorporate two water molecules into its crystal network, while modifying the properties of the complex. The theoretical calculations, both molecular and in solid state, has confirmed that these changes are connected with Ni^{2+} *high spin-low spin* electronic transition and provided details of this transition [A-17].

4. Short summary of each publication

A-01 M. Derzsi, P. Piekarz, P. T. Jochym, J. Łażewski, M. Sternik, A. M. Oleś, and K. Parliński, Effects of Coulomb interaction on the electronic structure and lattice dynamics of the Mott insulator Fe2SiO4 spinel, PHYS. REV. B 79(20), 205105 (2009), (3,475; 6).

This work presents the first theoretical DFT (GGA+U) study of the electronic, magnetic, crystal and phonon structure of Fe_2SiO_4 spinel at 20 GPa. The main objective of this study was to find the electronic (magnetic) ground state of Fe_2SiO_4 spinel and to understand the effect of strong electron correlations of the 3d electrons at Fe ions on its properties. The spinel was found to be a AFM Mott-Hubbard insulator with electronic band gap of ~2.25 eV at the realistic value of U = 4.5 eV. The AFM interactions reduce the cubic symmetry to tetragonal one with vanishing impact on the crystal structure. A metal-insulator transition was calculated at U = 2 eV. Below this value, both FM and AFM solutions were found to be metallic with FM solution being the ground state. Above this transition, the electronic band gap opens in the t_{2g} states for both FM and AFM solution, while larger gap is obtained for the AFM one at all values of U considered. The cell volume and magnetic moments on Fe atoms increase with U. The changes are small with a discontinuity observed at the metal-insulator border. The GGA (with no U) approach favors the FM over the AFM solution by 50 meV/atom. With increasing U, the enthalpy difference between the two states decreases and at U=4.5 eV the AFM solution is favored only by 6 meV/atom. Using the Heisenberg model the magnetic interatomic-exchange constant was calculated to be J=1.72 meV resulting to the Curie-Weiss temperature Θ_{CW} = 340 K, which largely deviates from its experimentally obtained Néel temperature T_N=11.8 K. These results indicate a strongly frustrated magnetic ground state, which arises from the conflict between the spinel crystal structure and the exchange interactions, which favor the AFM order. The small value of the Néel temperature is thus consequence of the magnetic frustration. Independently of U, dynamically stable phonon structure was obtained only for the AFM solution. In case of the AFM solution, the Coulomb correlations cause the upshift of energy of all phonons. The largest change, ΔE = +10.4 meV, was obtained for the optic mode with the T_{1u} symmetry. These changes are mainly associated with the metal-insulator transition.

A-02 M. Derzsi, P. Piekarz, K. Tokar, P. T. Jochym, J. Łażewski, M. Sternik and K. Parliński, *Comparative ab initio study of lattice dynamics and thermodynamics of Fe_2SiO_4 and Mg_2SiO_4 spinels*, J PHYS: COND MAT 23(10), 105401 (2010), (2,546; 2).

In this work, we present the results of the DFT (GGA) calculations of the lattice dynamics, mechanical properties and thermodynamic functions of the AFM Fe_2SiO_4 spinel in function of external pressure up to 20 GPa. The obtained results were thoroughly confronted with those obtained for the magnesium end-member and were found to be in very good agreement with the accessible experimental data. The study has shown that Mg → Fe exchange in the Mg_2SiO_4 spinel results in the lowering of energy of all atomic vibrations. The largest energy changes have been found for the lowest inactive A_{2u} (ΔE = 50.2 meV) and the lowest IR T_{1u} mode (ΔE = 24.9 meV). The predicted increase of the lattice constant, upon the Mg → Fe exchange, is close to 2% at all considered pressures and temperatures up to 500 K. The modifications of the low energy phonon DOS caused by the Mg → Fe exchange result in pronounced changes in the temperature dependence of the bulk modulus and significant enhancement of the entropy and heat capacity. The following results were obtained considering the pressure of 10 GPa in which both end-members coexist. While at low temperatures both end members have comparable bulk moduli, B (B~220 GPa for T<50K), at higher temperatures the Fe-end member becomes softer (at 800 K: $B_{Fe\text{-}end}$ = 180 GPa and $B_{Mg\text{-}end}$ = 208 GPa) and in the broad range of temperatures exhibits higher heat capacity than the magnesium one. At lower temperatures, the heat capacity of the iron end-member is additionally enhanced by magnetic interactions. The entropy of the iron end-member grows faster thanks to higher contribution of the phonon density of states at low temperatures.

A-03 K. Tokar, P. Piekarz, M. Derzsi, P. T. Jochym, J. Łażewski, M. Sternik, A. M. Oleś and K. Parliński, *Electronic and optical properties of $Mg_{2-x}Fe_xSiO4$ spinel: From band insulator to Mott insulator*. PHYS REV B 82(19), 195116 (2010), (3,475; 2).

This work presents results of the first theoretical (DFT+U) study, which reveals the impact of the iron concentration on the electronic and crystal structure and on optical properties of $Mg_{2-x}Fe_xSiO_4$ in the wide range of Fe concentration. It was shown, that the lattice constant increase linearly with Fe concentration x from a=7.88 Å to 8.05Å in agreement with the Vegard's law. The total enthalpy also changes linearly with x, decreasing in this case with increasing x. This result shows that the Fe doping stabilizes the spinel structure at a considered pressure. The calculated AFM magnetic moments on Fe cations exhibits a monotonous increase with increasing Fe concentration x from the value of 3.65μ_B at x=1.25 to 3.69μ_B at x=2 (for Hubbard U=4.5 eV), while they become saturated for x>1.5. The changes in the moments are small as expected in presence of large Coulomb interactions, which almost localize 3d electrons. The results of the electron structure calculations of $Mg_{2-x}Fe_xSiO_4$ revealed that insertion of the iron atoms into Mg_2SiO_4 results in appearance of new electronic states on the Fermi level and due to strong electron correlations on the iron atoms a new Mott-Hubbard electronic band gap is being formed within the newly-appeared

states. The magnitude of the band gap in $Mg_{2-x}Fe_xSiO_4$ jumps first from the impurity value of 5.8 eV at x=0 to 3.3 eV at x=0.125, and then exhibits a monotonous decrease to 1.46 eV at x=2 (in calculations with U=4.5 eV). Finally, the absorption spectra as function of Fe concentration x were calculated. The calculated absorption edge for x=0 is close to 6 eV in accordance with the value of band gap of Mg_2SiO_4. Insertion of iron atoms induces additional optical transitions visible in the band gap of Mg_2SiO_4. For small iron concentrations (x=0.125), the calculated energies of the $t_{2g} \rightarrow e_g$ are equal to 1.57 eV and 1.98 eV (for U=4.5 eV) in good agreement with experimental values.

A-04 D. Kurzydłowski, M. Derzsi, A. Budzianowski, Z. Jagličić, W. Koźminski, Z. Mazej, W. Grochala, *Polymorphism of Fluoroargentates(II): Facile Collapse of a Layered Network of α–K_2AgF_4 Due to Insufficient Size of Potassium Cation*, EUR J INORG CHEM (19), 2919-2925 (2010), (3,049; 2).

This work presents results of a complex experimental and theoretical study of a new post-perovskite phase (β phase) of $K_2Ag^{II}F_4$ (d^9, spin-½ system). The experimental part includes details of the synthesis, measurements of the crystal structure and magnetic susceptibility. In theoretical (DFT+U) study targeted the details of the crystal, electronic and magnetic structure and the role of strong electron correlations. It was shown that the new β phase forms a 1D crystal and electronic structure. It is paramagnetic above 20 K with low Curie temperature (T_C<5K). It was confirmed both experimentally and theoretically that the new β phase is thermodynamically favored over the earlier discovered layered perovskite phase α. The higher thermodynamic stability of the new β phase is governed by the size of the potassium cation, which turned out to be too small to stabilize the layered α form. The results of the DFT+U calculations have shown that the β phase is a ferromagnetic insulator with electronic band gap of ~1,65 eV. They additionally revealed distinct mechanisms governing the opening of the band gap in both forms. In the β phase, the band gap is opened by ferromagnetic interactions and the strong electron correlations play an enhancement role. In the α phase, on the other hand, magnetic interactions are not sufficient to open the band gap. Here the strong electron correlations pay a crucial role in the gap opening. Results of the magnetic spin density calculations showed that the unpaired electrons reside preferable on the $d(x^2-y^2)$ orbitals.

A-05 M. Derzsi, K. Dymkowski, W. Grochala, *The Theoretical Quest for Sulfate of Ag^{2+}: Genuine Ag(II)SO_4, Diamagnetic Ag(I)$_2S_2O_8$ or Rather Mixed-Valence Ag(I)[Ag(III)$(SO_4)_2$]?* INORG CHEM 49(6), 2735–2742 (2010), (4,601; 7).

The work present the results of an extensive theoretical (DFT) search of dynamically stable polymorphs of unknown $AgSO_4$. Metal sulfates form a large family of

compounds which crystal structures are already known. Silver was the only metal of the Group 11 (Cu, Ag, Au), monosulfate of which was unknown. The non-existence of $AgSO_4$ presented therefore an intriguing problem. The results of the study revealed seventeen dynamically stable crystal structures. In most of them silver occurs on the 2nd oxideation state (d^9 system) and the $Ag^{2+}SO_4$ stoichiometry turned out to be energetically favored over the other two possible ones – $Ag^{1+}Ag^{3+}(SO_4)_2$ (mixed valance d^8/d^{10} system) or $Ag^{1+}{}_2S_2O_8$ (d^{10} system with O-O chemical bond). In the lowest energy structures, four oxygen atoms coordinate silver cations in a square planar coordination and the structures form three-dimensional crystal networks. In later studies, the lowest energy form (with small additional monoclinic distortion) turned out to be observed experimentally [A-10].

A-06 P. J. Malinowski, M. Derzsi, Z. Mazej, Z. Jagličić, B. Gaweł, W. Łasocha, and W. Grochala, *$Ag^{II}SO_4$: A Genuine Sulfate of Divalent Silver with Anomalously Strong One-Dimensional Antiferromagnetic Interactions*, ANGEW CHEM INT ED ENGL 49(9), 1683–1686 (2010), (13,455; 17).

This work presents the results of a combined experimental and theoretical (DFT+U) study, which was focused on search for possible synthesis routs of $AgSO_4$ and on characterization of physicochemical properties of the silver sulfate. Two synthesis routs were found to lead to $AgSO_4$ product. Based on the X-tay diffraction results and our previous theoretical study of $AgSO_4$ polymorphism [A-05] a small triclinic *P*-1 (Z=2) cell was proposed. The electronic structure calculations revealed that $AgSO_4$ is semiconductor with a small band gap, which explained the observed black color. The calculated AFM super-exchange J was found to be in good agreement with the value obtained from the magnetic susceptibility measurements, which turned out to be anomalously large J=-18 meV. This value is an order of the magnitude larger in comparison the other known metal sulfates. $AgSO_4$ also exhibits uniquely high temperature in which the magnetic ordering disappears (>380K). The theoretical calculations additionally revealed a key role of the strong electron correlations in stabilization of the AFM interactions as well as in opening of the electronic band gap at the Fermi level.

A-07 M. Derzsi, P. J. Malinowski, Z. Mazej, W. Grochala, *Phonon spectra and phonon–dependent properties of $AgSO_4$, an unusual sulfate of divalent silver*, VIBR SPECTR 57(2), 334–337 (2011), (1,65; 4).

In this work we have focused on the details of lattice dynamics in $AgSO_4$ by means of experimental measurements (IR and Raman spectra) and theoretical DFT (GGA and LDA) calculations of dispersion curves and thermodynamical parameters of previously proposed triclinic *P*-1 cell [A-06]. It turned out that the previously published optical

spectra [A-06] were strongly contaminated by unknown substances. Here we presented optical spectra of highly pure $AgSO_4$ samples. The assignment of the peaks was done on the basis of the theoretically calculated IR and Raman active optical modes. The LDA calculated normal modes were in better agreement with the experimental observations in contrary to the GGA ones (the correlation factor = 1.05). They LDA results were used to calculated the standard absolute vibrational entropy (=118 kJ mol^{-1} K^{-1}), heat capacity (=99.1 kJ mol^{-1} K^{-1}), zero-point energy (=48.3 kJ mol^{-1}) and Debye temperature (=1606 K).

A-08 P. J. Malinowski, M. Derzsi, A. Budzianowski, P. J. Leszczyński, B. Gaweł, Z. Mazej, Grochala W, *Unusual thermal decomposition of Ag(II)SO_4 yielding Ag(I)$_2S_2O_7$: bending the Hammond's rule*, CHEM EUR J 17(38), 10524-10527 (2011), (5,925; 1).

This work presents results of the study of thermal decomposition of $AgSO_4$, analysis of crystal structure of its decomposition product $Ag_2S_2O_7$ and results of theoretical DFT calculations of possible polymorphic forms of the latter compound. $AgSO_4$ was found to be thermally unstable in ambient conditions. The thermal decomposition process, during which Ag^{2+} is reduced to Ag^{1+} and molecular oxygen is evolved, turned out to be unique among the metal sulfates. In the other metal sulfates, the decomposition process involves evolution of SO_3 gas. Additionally the temperature of decomposition, T_{dec}=380K, turned out to be the lowest among the metal sulfates. The analysis of the diffraction data of the decomposition products revealed that it crystalizes in $Na_2S_2O_7$-type structure. The results of DFT calculations suggests also the existence of a $K_2S_2O_7$-type. The calculated DFT energies of both phases are comparable. Within the DFT-LDA approach, the potassium form is favored over the sodium one by 3.3 kJ/mol. Within the DFT-GGA approach on the other hand, the sodium phase is favored by 10.7 kJ/mol. The further analysis involving the volumes of both phases (the potassium form havening lower volume by 1.4 to 3.2%), suggests that the potassium form should be formed at higher pressures. This theoretical prediction was confirmed by experimental observations in later high pressure studies [A-10].

A-09 M. Derzsi, J. Stasiewicz, W. Grochala, *Crystal and electronic structure and high-pressure behaviour of $AgSO_4$, a unique narrow band gap semiconductor. LDA(+U) picture*, J MOL MODEL 17(9), 2259-2264 (2011), (1,797; 4).

This work presents our theoretical (LDA+U) search for evidence of metallization of $AgSO_4$ under external or chemical pressure. These results revealed that the small triclinic *P*-1 $AgSO_4$ cell, proposed in the previous study [A-06], is very resistant to metallization under high pressures and several other polymorphs were found to be

energetically preferred at elevated pressures. Considering the chemical pressure, a metallic state was obtained under S→Cr exchange in $Ag^{2+}SO_4$.

A-10 M. Derzsi, A. Budzianowski, V. V. Struzhkin, P. J. Malinowski, P. J. Leszczyński, Mazej Z, Grochala W, *Redetermination of crystal structure of Ag(II)SO_4 and its high pressure behavior up to 30 GPa*, CRYSTENGCOMM 15(1), 192–198 (2013), (3,842; 0).

This work presents combined experimental and theoretical (DFT) high-pressure study of $AgSO_4$. The work for the first time presents $AgSO_4$ in a large monoclinic *C*2/*c* (Z=16) crystal structure, results of a high pressure X-ray diffraction measurements of $AgSO_4$ carried out in a diamond anvil cell and theoretical calculations of crystal and magnetic structure of $AgSO_4$ as function of pressure. The previously published small triclinic *P*-1 (Z=2) cell of $AgSO_4$ [A-06] was proved to be an insufficient model to interpret the high-pressure data. The new larger monoclinic cell was proposed based on a re-analysis of the structures obtained previously in the theoretical study of polymorphism of $AgSO_4$ [A-05] and additional calculations. The new results have revealed that breaking of one symmetry elements in the lowest energy polymorph of AgO-type $I4_1/a$ (Z=16) reported in [A-05] leads to further lowering of energy of the system and also to lowering of the tetragonal symmetry to the large *C*2/*c* (Z=16) cell. The results of the high-pressure DFT calculations performed on the large *C*2/*c* reproduced very well the experimentally observed evolution of the cell parameters with pressure. Excellent agreement between the theoretical and measured bulk modulus was obtained (B_0^{exp}=36.9 GPa and B_0^{DFT}=39.5 GPa). It is important to note that the large *C*2/*c* cell contains all the key features of the small *P*-1 that were published previously, which that encompass: square planar coordination of Ag^{2+}, lack of terminal oxygen atoms, electronic and magnetic structure with strong 1D AFM interactions. Additionally, both the high-pressure data as well as the theoretical calculations revealed that $AgSO_4$ sluggishly decomposes under pressure to a high-pressure form of $Ag_2S_2O_7$. The theoretical calculations proved that the high-pressure form of $Ag_2S_2O_7$ is of $K_2S_2O_7$ type as for the first time predicted in [A-08]. The high-pressure magnetic calculations performed for the $AgSO_4$ C2/c cell that in both 0GPa and 30 GPa (the higher pressure measured) the magnetic interactions are dominated by 1D AFM interactions. Among all of the models studied, a triclinic *P*-1 magnetic model was found to be the ground state at 0 PGa and a monoclinic $P2_1/c$ at 30 GPa.

A-11 P. J. Malinowski, M. Derzsi, Z. Mazej, Z. Jagličić, P. J. Leszczyński, T. Michałowski, W. Grochala, *$Ag(SO_3F)_2$, silver(II) fluorosulfate – a thermally fragile ferromagnetic*

derivative of divalent silver in oxa- ligand environment, EUR J INORG CHEM (16), 2499–2507 (2011), (3,049; 7).

This study presents for the first time the crystal structure and results of thorough physicochemical characterization of $Ag(SO_3F)_2$ compound based on the experimental observations and theoretical DFT+U calculations. Analysis of the diffraction data revealed that the title compound crystalizes in a layered structure. The results of magnetic susceptibility measurements showed that it is a soft ferromagnetic with Curie temperature T_C=24.8 K and small magnetic exchange constant =1 meV. The electronic structure calculations revealed that $Ag(SO_3F)_2$ is a two-dimensional ferromagnetic insulator with FM intra-layer interactions (J_{intra}=1,05 meV) and weaker AFM inter-layer ones (J_{inter}= -0.3 meV). The FM ordering results due to strong puckering of the $Ag(SO_3F)_2$ layers. These results correlate very well with the experimental observations. The magnetic moment resides mostly on Ag2+ (d^9) cations (0.5μ_B) but it is also considerably smeared over the oxygen atoms (~0.09μ_B). This smearing is partly responsible for thermal decomposition of $Ag(SO_3F)_2$ in room temperature. The electronic band structure calculations revealed that an indirect charge-transfer type electronic band gap opens at the Fermi level between the α and β states due to FM ordering. The strong electron correlations considerably enhance the band gap (from 0.25 eV to 1.05 eV). The optical (IR and Raman) spectra were measured and the assignments were done based on the DFT calculated normal (IR and Raman active) modes. A very good agreement between the theoretical and experimental frequencies was obtained. Both, the experimental spectra as well as the theoretical calculations confirmed the strong covalent character of the Ag-O bonds.

A-12 T. Michałowski, P. Malinowski, M. Derzsi, Z. Mazej, Z. Jagličić, P. J. Leszczyński, W. Grochala, *$Ag_3(SO_3F)_4$ – a rare example of mixed valence Ag(I)/Ag(II) compound showing 1D Antiferromagnetism*, EUR J INORG CHEM (16), 2508–2516 (2011), (3,049; 6).

This study present the results of a complex combined experimental and theoretical (DFT+U) study of crystal, electronic and magnetic structure and lattice dynamics of $Ag_3(SO_3F)_4$, a system from a very rare group of compounds containing silver cations in two oxidation states Ag^{2+}(electronic configuration d^9) and Ag^{1+} (electronic configuration d^{10}). Refinement of the crystal structure from the X-ray diffraction measurements, magnetic measurements, as well as the theoretical DFT+U calculations, confirmed occurrence of the Ag^{2+} and Ag^{1+} cations in the compound. The Ag^{2+} and Ag^{1+} cations were found to reside in separate layers with ABAB stacking. The Ag^{2+} are interconnected with SO_3F^- cations into infinite one-dimensional chains. The theoretical calculations revealed antiferromagnetic (AFM) interactions within these chains and much weaker (by 2 order of magnitudes) ferromagnetic (FM) inter-

chains interactions in agreement with the experimental observations. The measured magnetic exchange constant (J_{exp} = -15 meV) was found to be extremely large when considering that the magnetic exchange is mediated by super-exchange through two 2p orbitals of non-chemically bonded oxygen atoms. The character of the exchange was confirmed by calculations of the magnetic spin density. The calculated magnetic moments on the atoms involved in the AFM super-exchange are $m_{Ag2+}\uparrow/\downarrow$=+0.49/-0,49$\mu_B$ and $m_O\uparrow/\downarrow$+0.01/-0.08 μ_B. The considerable smearing of the spin density on the oxygen atoms is partly responsible for the observed thermal decomposition of the title compound at room temperature. The electronic structure calculations revealed that $Ag_3(SO_3F)_4$ is a Mott insulator and that the strong electron correlations play a role of strong enhancement of the opening of the electronic band gap at Fermi level. Comparable calculated values of 0.6 eV and 0.5 eV were obtained for the direct and indirect band gap in the electronic band structure calculations. Vibrational spectra (IR and Raman) were measured and the assignment of the modes was based on the results of theoretical DFT calculations while a very good agreement between the experiment and theory was reached.

A-13 P. J. Malinowski, Z. Mazej, M. Derzsi, Z. Jagličić, J. Szydłowska, T. Gilewski, W. Grochala, *Silver (II) triflate with one dimensional [Ag(II)$(SO_3CF_3)_{4/2}]\infty$ chains hosting antiferromagnetism*, CRYSTENGCOMM 13(22), 6871-6879 (2011), (3,842; 2).

This study presents for the first time the crystal structure and results of a combined experimental and theoretical (DFT+U) study of the crystal, electronic and magnetic structure and lattice dynamics of $Ag(SO_3CF_3)_2$ d^9-system. The analysis of the X-ray diffraction data revealed a layered structure with van der Waals inter-layer contacts between the $-CF_3$ fragments of SO_3CF_3 groups. The neighboring Ag^{2+} cations are doubly bridged by two $-SO_3R$ ($R=CF_3$) ions into infinite chains. The theoretical calculations revealed antiferromagnetic (AFM) super-exchange interactions within these chains and weak ferromagnetic (FM) inter-chain interactions ($J_{intra}/J_{inter}\sim10^{-2}$-$10^{-3}$). The AFM interaction are mediated by four 2p O orbitals (two distinct O...O magnetic links) between two neighboring Ag centers. In this way, 1D AFM character of the compound was confirmed. The measured magnetic exchange constant J is equal to -9 meV. The calculated magnetic moments of the atoms taking part in the magnetic interactions are: $m(\uparrow/\downarrow)$ = +0.51/-0.51μ_B and $m_O(\uparrow/\downarrow)$ = +0.07/-0.07μ_B. The DFT-GGA electronic structure calculations revealed that $Ag(SO_3CF_3)_2$ is a charge-transfer type semiconductor with a direct band gap of ~0.3 eV. The strong electron corelations enhance the band gap to 1.1 V and they change the character of the bag from direct to indirect. The optical (IR and Raman) spectra were measured and normal modes calculated. A very good agreement between the two allowed for assignment of all modes.

A-14 P. J. Leszczyński, A. Budzianowski, M. Derzsi, Ł. Dobrzycki, M. K. Cyrański, W. Grochala, *Thermal and chemical decomposition of di(pyrazine)silver(II) peroxydisulfate and unusual crystal structure of a Ag(I) by-product*, DALTON TRANS 41(2), 396-402 (2012), (3,838; 1).

The study presents new synthetic routs towards a 2D AFM complex of Ag^{2+} (in which the silver cations form a square net interconnected by $C_4H_4N_2$ molecules) and the crystal structure of its decomposition product $[(Ag(I)(pyz)]_5(H_2O)_2(HSO_4)_2(H(SO_4)_2)$ in presence of water. Theoretical DFT+U calculations were additionally carried out in order to examine the magnetic structure of the Ag^{2+} complex. They confirmed the 2D AFM character of the compound in agreement with the experiment. The super-exchange is mediated by two atoms of nitrogen and four atoms of carbon (of the $C_4H_4N_2$ molecule) which is confirmed by calculated magnetic moments on these atoms ($m_N(\uparrow/\downarrow)$ = +0.08/-008 μ_B and $m_C(\uparrow/\downarrow)$ = +0.06/-0.06 μ_B). The theoretically obtained magnetic super-exchange constant is 6-times larger than the measured one (J_{calc}=-29.6 meV and J_{exp}=-4.6 meV). This discrepancy is due to performing the calculations on a frozen crystal structure (atomic and lattice parameters were frozen to experimental values), which was forced by large dimensions of the magnetic cell.

A-15 W. Grochala, M. K. Cyrański, M. Derzsi, T. Michałowski, P. J. Malinowski, Z. Mazej, D. Kurzydłowski, W. Koźminski, A. Budzianowski, P. J. Leszczyński, *Crystal and electronic structure, lattice dynamics and thermal properties of Ag(I)(SO_3)R (R=F, CF_3) Lewis acids in the solid state*, DALTON TRANS 41(7), 2034-2047 (2012), (3,838; 2).

This work presents for the first time crystal structures of two derivatives of Ag^{1+} (0-spin, electronic configuration d^{10}) - $Ag(SO_3)F$ i $Ag(SO_3)CF_3$. Both of these compounds we subject to extensive study of their physicochemical properties. ^{109}Ag MAS NMR, the oscillation IR and Raman spectra, as well as their thermal decomposition process, were analyzed. The theoretical DFT calculations were carried out for both of the compounds in order to analyze the character of chemical bonds, phase transitions, polymorphism, electronic structure and lattice dynamics. Analysis of the diffraction data revealed that $Ag(SO_3)CF_3$ crystalizes in hexagonal *R*-3 space group forming layered structure with van der Waals gaps between the CF_3 groups. Ag(I)(SO_3)F on the other crystallizes in a monoclinic $P2_1/m$ space group forming a complex three-dimensional crystal network. The layered Ag(I)(SO_3)CF_3 was found to undergo two temperature-driven phase transitions (at ~280°C i ~320°C). In case of the Ag(I)(SO_3)F, a structure disorder was observed on fluorine and oxygen atoms. The results of the theoretical calculations showed that the structural disorder results while no strong preference exists for any specific ordered structure – the energy difference between the theoretical ordered forms studied was less than ~2 meV per formula unit.

They additionally suggest that the experimentally observed monoclinic disordered phase of $Ag(I)(SO_3)F$ is a metastable one. The system may lower its energy by as much as 10.6 meV per formula unit when adopting a hexagonal structure of the $Ag(I)(SO_3)CF_3$ type (in which CF_3 → F). The calculations of phonon dispersion curves revealed that the hypothetical hexagonal form is dynamically stable and it is expected to exists in ambient conditions. Electronic structure calculated for the experimentally observed crystal structures revealed that both compounds are insulators and that the interactions between Ag^{1+} and oxygen atoms in their first coordination sphere in these compounds are mostly of ionic nature. The calculated DFT+U values of the band gaps are 2.4 eV (in $Ag(I)(SO_3)F$) and 2.9 eV (in $Ag(I)(SO_3)CF_3$). The normal mode analysis revealed a good agreement between the theory and experiment (IR and Raman spectra). Therefore, all modes could be assigned in vibrational spectra of both compounds.

A-16 P. J. Malinowski, M. Derzsi, W. Grochala, *$Ag(I)S_2O_6CF_3$: the first trifluoromethyldisulphate(VI)*, in press, DALTON TRANS 42 (29), 10417-10423 2013, (3,838; 0).

This work presents for the first time crystal structure and vibrational (IR and Raman) spectra of $Ag(I)S_2O_6CF_3$, a Ag^{1+} (0-spin, electronic configuration d^{10}) compound of a new class of trifluoromethyldisulphates (VI). The analysis of the diffraction data revealed a monoclinic $P2_1/c$ cell with layered crystal structure and with van der Waals gaps formed between oppositely oriented CF_3 groups. The theoretical DFT calculations confirmed the details of the crystal structure. A very good agreement between theory and experiment allowed for full assignment of the measured IR and Raman vibrational spectra.

A-17 A. J. Churchard, M. Derzsi, Z. Jagličić, A. Remhof, W. Grochala, *Chemo-switched chromatic, structural and magnetic changes with retention of molecular crystallinity, $Ni(II)(12aneS4)(BF_4)_2$*, DALTON TRANS 41(17): 5172-5176 (2012), (3,838; 0).

This work presents for the first time an unusual molecular complex of tetrafluoroborate of Ni^{2+}, which has the ability to reversibly absorb and release water vapor. This ability was shown to be linked with broad range of its physicochemical properties. Crystal structure of both the dehydrated and hydrated form of the complex was refined from diffraction data. The results of the DFT calculations confirmed that the complex can incorporate two water molecules into its crystal network and provided the details of the hydrogen bond network. This incorporation influences its optical properties and crystal and magnetic structure. The color changes from light blue to violet, the square planar coordination of nickel is enriched by two oxygen atoms (from

the water molecules each), and the magnetic susceptibility increases. The theoretical calculations, both molecular and in solid state, has confirmed that these changes are connected with Ni^{2+} *high spin-low spin* electronic transition and provided details of this transition.

Warsaw, 1 October 2013

IV. Other achievements in science and scientific research

1. Publications featured in Journal Citation Reports (JCR)

The numbers in parentheses stand for:
- impact factor
- number of citations according to Web of Science and Scopus.

a) Works published prior to obtaining a doctoral degree

B-01 V. Langer, M. Soóš, D. Gyepesová, M. Sládkovičová, J. Lustoň and J. Kronek, *Three isomeric forms of hydroxyphenyl-2-oxazoline: 2-(2-hydroxyphenyl)-2-oxazoline, 2-(3-hydroxuphenyl)-2-oxazoline and 2-(4-hydroxyphenyl)-2-oxazoline*, ACTA CRYST C 61, o602-o606 (2005), (0,782; 8).

My contribution: I performed QM DFT calculations of crystal structure of the three isomeric forms of the title compound and performed analysis of geometry of hydrogen bonds in the calculated structures. My contribution: 5%.

B-02 Ľ. Smrčok, M. Sládkovičová, V. Langer, C. C. Wilson and M. Kóš, *On hydrogen bonding in 1,6-anhydro-β -D-glucopyranose (levoglucosan): X-ray and neutron diffraction and DFT study*, ACTA CRYST B 62, 912-918 (2006), (1,801; 9).

My contribution: I took part in measurement of neutron diffraction data and in analysis of crystal structure, performed QM molecular calculations and calculations in solid state (DFT), took part in analysis of the theoretically obtained results and in constructing the manuscript providing tables and figures. My contribution: 25%.

B-03 Ľ. Smrčok, P. M. Briggs Piccoli, M. Sládkovičová, P. Mach, *On hydrogen bonding in 2-amino-3-hydroxymethyl-1,3-propane diol (Tris) – variable temperature neutron single crystal and DFT study*, Z KRISTALLOGR 222(10), 555-565 (2007), (0,95; 2).

My contribution: I performed part of QM molecular calculations and all calculations in solid state (DFT), took part in analysis of the theoretically obtained results and in construction of the manuscript, providing tables and figures. My contribution: 30%.

B-04 M. Sládkovičová, P. Mach, Ľ. Smrčok, H. Rundlöf, *DFT and neutron diffraction study of 1,6-anhydro-β-D-glucopyranose (levoglucosan)*, CENT EUR J CHEM 5(1), 55-70 (2007), (1,07; 7).

My contribution: I took part in measurement of the neutron diffraction data, in performing QM molecular calculations and carried out all calculations in solid state (DFT), performed analysis of the theoretically obtained results and took part in preparing the manuscript by providing tables and figures and writing text concerning the theoretically obtained results. I was the corresponding author. My contribution: 50%.

B-05 M. Sládkovičová, Ľ. Smrčok, P. Mach, D. Tunega, A. Kolesnikov, *Inelastic Neutron Scattering and DFT Study of 2-amino-3-hydroxymethyl-1,3-propane diol*, CHEM PHYS 340(1-3), 245-259 (2007), (1,896; 3).

My contribution: I took part in QM molecular calculations and their interpretation, performed all DFT calculations in solid state and their analysis, performed assignment of measured INS spectrum and wrote the manuscript. I was the corresponding author. My contribution: 60 %.

B-06 M. Sládkovičová, Ľ. Smrčok, P. Mach, D. Tunega, A. J. Ramírez Cuesta, *Inelastic Neutron Scattering and DFT Study of 1,6-anhydro-β-D-glucopyranose (levoglucosan)*, J MOL STRUCTURE 874 (1-3), 108-120 (2008), (1,634; 8).

My contribution: I took part in QM molecular calculations and calculations of molecular dynamics (DFT) and in interpretation of their results. I performed all other theoretical DFT calculations in solid state, assignment of the measured INS spectrum and wrote the manuscript. I was the corresponding author. My contribution: 60%.

b) Papers published after obtaining a doctoral degree

B-07 M. Derzsi, D. Colognesi, *Inelastic neutron scattering and DFT study of potassium hydrogen phthalate*, J MOL STRUCT 967(1-3), 89-93 (2010), (1,634; 0).

My contribution: I performed QM DFT calculations in solid state, analysis of their results and interpretation of the measured INS spectrum. I wrote the manuscript and was the corresponding author. My contribution: 70%.

B-08 P. Piekarz, M. Derzsi, P. T. Jochym, J. Łażewski, M. Sternik, K. Parliński, and E. M. Serwicka, *Crystal structure, hydrogen bonds, and lattice dynamics in kanemite from first-principles calculations*, PHYS REV B 79(13), 134105 (2009), (3,475; 0).

My contribution: I performed the analysis of hydrogen bonds and their dynamics and took part in assignments of the experimental oscillation spectra and in construction of the manuscript by providing figures and text. My contribution: 20%.

Derzsi

B-09 A. Budzianowski, M. Derzsi, P. J. Leszczyński, M. K. Cyrański, W. Grochala, *Structural polymorphism of pyrazinium hydrogen sulphate: extending chemistry of pyrazinium salts with small anions*, ACTA CRYST B 66(4), 451-457 (2010), (2,286; 3).

My contribution: I performed QM DFT calculations in solid state and analysis of their results. My contribution: 10%.

B-10 K. J. Fijałkowski, R. V. Genova, Y. Filinchuk, A. Budzianowski, M. Derzsi, T. Jaroń, P. J. Leszczyński, W. Grochala, *$Na[Li(NH_2BH_3)_2]$ – the first mixed-cation amidoborane with unusual crystal structure*, DALTON TRANS 40(17), 4407-4413 (2011), (3,838; 30).

My contribution: I performed QM DFT calculations in solid state and analysis of their results. My contribution: 10%.

B-11 M. Derzsi, A. Hermann, R. Hoffmann, W. Grochala, *The Close Relationships between the Crystal Structures of MO and MSO_4 (M = Group 10, 11, or 12 Metal), and the Predicted Structures of AuO and $PtSO_4$*, EUR. J. INORG. CHEM (29), 5095-5102 (2013), (3,049; 0).

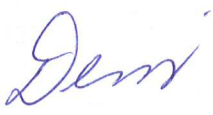
My contribution: I performed structural analysis, took part in the QM DFT calculations in solid state and wrote the manuscript. My contribution: 60%.

2. Other publications

a) Works published prior to obtaining the Ph.D. degree

C-01 M. Derzsi, *Hydrogen Bonding in TRIS: INS Spectroscopy and Quantum Chemistry Methods*, Materials Structure in Chemistry, Biology, Physics and Technology 13(3), 135 (May 2006).

I performed all DFT calculations in solid state and their analysis and performed assignment of measured INS spectrum.



b) Papers published after obtaining the Ph.D. degree

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3. Patents, expertise, other documentation

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4. Visits and internships

1. Institute of Nuclear Physics, Polish Academy of Sciences, Department of Materials Research by Computers, Cracow, 2004 (5 weeks).
2. Institute of Nuclear Physics, Polish Academy of Sciences, Department of Materials Research by Computers, Cracow, 2008 (1 year).
3. Interdisciplinary Centre for Mathematical and Computational Modelling, The University of Warsaw, Laboratory of Technology of Novel Functional Materials, 2009-2012 (4 years).

5. Conferences and seminars

a) Invited talks

1. *Vibrational spectroscopy with neutrons of molecular systems*, Summer School on Neutron Scattering, Hotel Rysy, Tatranská Štrba, High Tatras, Slovakia (2007)
2. *Molekulová spektroskopia s neutrónmi* (trans.: "Neutron spectroscopy as a tool to study molecular systems"), Department of Biophysics Seminar, Faculty of Mathematics, Physics and Informatics, Comenius University, Bratislava, Slovakia (2007)

3. *The theoretical quest for $AgCl_2$ in solid state: unique polymorphism and electronic structure*, Theory and Modeling of Nanostructures Seminars, Faculty of Physics, The University of Warsaw, Warsaw (2013)

4. *Nieelastyczna neutronowa spektroskopia* (Trans.: Inelastic neutron spectroscopy), A series of meetings "Mam Ochotę na Chemię" organized by students' scientific association of chemists of The University of Warsaw "Fulleren", Warsaw (2013)

b) Oral contributions

Before obtaining the Ph.D. degree

5. *Hydrogen bonding in Tris*, 9th Oxford School on Neutron Scattering, Oxford, Great Britain (2005).

6. *Hydrogen Bonding in Tris(hydroxymethyl)-aminomethane: INS spectroscopy and Quantum Chemistry Methods*, Contest for Young Scientists, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia (2005).

7. *Hydrogen Bonding in TRIS: INS Spectroscopy and Quantum Chemistry Methods*, Synchrotron Radiation and Neutron Scattering, Institute Laue-Langevin, Grenoble, France (2006).

8. *INS and DFT study of hydrogen bonding in levoglucosan*, International Workshop on Dynamics of Molecules and Materials, Institute Laue-Langevin, Grenoble, France (2007).

9. *The dynamics of NH_4^+ in the NH_4VO_3: inelastic neutron scattering (INS) and DFT study*, Competition for young scientists, Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava, Slovakia (2007).

10. *Neutron diffraction, inelastic neutron scattering (INS) and DFT study of levoglucosan (1,6-anhydro-β-D-glucopyranose)*, 24th European Crystallographic Meeting, Marrakech, Morocco (2007).

After obtaining the Ph.D. degree

11. *Crystal structure, hydrogen bonds, and lattice dynamics in kanemite from first principles calculations*, 3rd Meeting of the Marie Curie Research Training Network c2c in Adeje, Tenerife, Spain (2008).

12. *Structural and dynamical properties of Fe_2SiO_4-spinel at 20 GPa: DFT study*, Workshop on ab initio calculations in geosciences, Cracow, Poland (2008).

13. *Theoretical investigation of polymorphism and stability of Ag(II) sulfate, an as-yet unknown compound*, ICM users meeting, Puszcza Piska, Poland (2009).

14. *A simple structure screening algorithm for prediction of crystal structure of functional materials: Case of Ag(II) sulfate*, XX International School on Physics and Chemistry of Condensed Matter: Structural Investigation of Functional Materials, Białowieża, Poland (2009).

15. *The realm of unusual compounds of Ag^{2+}: Prediction of crystal structure, magnetism and stability of $Ag(II)SO_4$, a hypothetical superconductor precursor*, 6th Japanese-Mediterranean Workshop on Applied Electromagnetic Engineering for Magnetic, Superconducting and Nanomaterials, Bucharest, Romania (2009).

16. *Lighter balls kicking heavier ones: what can we learn from neutron's impact on H-rich materials?*, Hydrogen for the future, Marie Curie Research Training Network 'Hydrogen', The 3rd Research Training Network Meeting, Warsaw (2009).

17. *Theoretical modeling of crystal and electronic structures and phonon spectra of fluoroargentates(II) and related compounds*, 16th European Symposium on Fluorine Chemistry, Ljubljana, Slovenia (2010).

18. *$[AgF_2]$ layers: Excursion to positive and negative pressure regimes*, The International Chemical Congress of Pacific Basin Societies, Honolulu, Hawaii (2010).

19. *The theoretical quest for $AgCl_2$ in solid state: unique p-metal and not magnetic insulator...!*, 18th International Conference on Solid Compounds of Transition Elements, Lisbon (2012).

20. *Modelowanie $AgCl_2$ w fazie stałej z pierwszych zasad* (trans.: 'Modeling $AgCl_2$ from ab initio'), Conference inaugurating the Centre MODEL (ICM UW, CePT), Warsaw, Poland (2013).

c) Posters

21. *Hydrogen bonding in Tris*, 4th Zuoz Summer School on Condensed Matter Research: Spectroscopy/Microscopy, Zuoz, Switzerland (2005).

22. *Electronic and magnetic properties and lattice dynamics of Fe_2SiO_4-spinel: ground state and the effect of pressure*, The 13th International Symposium on Deep Seismic Profiling of the Continents and Their Margins, Saariselkä, Finland (2008).

23. *First principles study of the electronic structure and lattice dynamics in the Mott insulator Fe_2SiO_4 spinel*, 4rd Meeting of the Marie Curie Research Training Network c2c, Sevilla, Spain (2009).

24. *Electronic structure and magnetism of $AgSO_4$, an unusual 1D antiferromagnet – insights from DFT*, Modeling and Design of Molecular Materials, Wrocław, Poland (2010).

d) Seminars

25. Three seminars concerning $(Fe,Mg)_2SiO_4$ solid solution, Seminars of the Department of Materials Research by Computers, Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland (2008).

26. *Struktura krystaliczna, elektronowa i magnetyczna oraz dynamika sieci w Fe_2SiO_4-spinel* (trans.: Crystal, electronic and magnetic structure and lattice dynamics of Fe_2SiO_4 spinel), Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland (2008).

27. *Kryształy molekularne: metody rozpraszania neutronowego i obliczenia DFT* (trans.: Molecular crystals: methods of neutron scattering and DFT calculations), Seminars of the Laboratory of Technology of Novel Functional Materials, Interdisciplinary Centre for Mathematical and Computational Modelling, The University of Warsaw, (2009).

28. *Strong correlations in transition-metal salts*, seminars of the Laboratory of Technology of Novel Functional Materials, Interdisciplinary Centre for Mathematical and Computational Modelling, The University of Warsaw, (2010).

29. *Polymorphism in layered perovskites of fluorides*, seminars of the Laboratory of Technology of Novel Functional Materials, Interdisciplinary Centre for Mathematical and Computational Modelling, The University of Warsaw, (2010).

30. *Excursion to positive and negative pressure regimes*, seminars of the Laboratory of Technology of Novel Functional Materials, Interdisciplinary Centre for Mathematical and Computational Modelling, The University of Warsaw, (2011).

6. Participation in organizing conferences

1. Structure Solution from Powder Diffraction Data, Stara Lesna, High Tatras, Slovakia (2003). My role: preparation of the conference material, first contact with the participants of the conference, care of the participants during the conference.
2. Workshop on ab initio calculations in geosciences, Cracow, Poland (2008). My role: preparation of the Workshop material, first contact with the participants of the Workshop, care of the participants.

7. Participation in scientific organizations, committees and research councils

1. Slovak Chemical Society: participant (2003-2007)
2. American Chemical Association: participant (2010)

8. Editorial experiences

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9. Scientific projects

1. *Structure and dynamics of hydrogen bonds in solids by diffraction methods, quantum chemistry and inelastic neutron spectroscopy (INS)*, Slovak Grant Agency VEGA nr 2/6178/26 (2007-2009), **executor**.

2. *Structure and dynamics of hydrogen bonds in solids by diffraction methods, quantum chemistry and inelastic neutron spectroscopy (INS)*, Slovak Grant Agency VEGA nr 2/0150/09 (2009-2011), **executor**.

3. *C2c Crust to core: the fate of subducted material*, Marie Curie RTN, FP6-MOBILITY nr 35957 (2007-2012), **executor**.

4. *Quest for superconductivity in crystal–engineered higher fluorides of silver*, Foundation for Polish Science, project 'TEAM' co-financed by EU European Regional Development Fund, nr TEAM/2008-1/3 (2008-2012), **executor**.

5. *AgCENT: novel unique magnetic and electronic materials based on the compounds of divalent silver,* NCN UMO-2011/01/B/ST5/06673 (2012-2014), **executor**.

6. *HP. Użycie wysokich ciśnień do modyfikacji stechiometrii, struktury krystalicznej, elektronowej i magnetyzmu związków funkcjonalnych* (trans.: The use of high pressures to modify the stoichiometry, crystal, electronic and magnetic structure of functional compounds), NCN UMO-2012/06/M/ST5/00344 (2013-2016), **executor**.

10. Reviews of scientific works

1. ANGEWANDTE CHEMIE INT. ED. – 1
   Co-reviewer with prof. Dr. Hab. Wojciech Grochala

11. Teaching experiences and supervision of students

1. *Ciało stale prosto i po raz pierwszy w 3D* (trans.: Simple approach to solid-state matter with 3D projections) – **general course** of the University of Warsaw, Poland.

2. **Co-promoter of the engineer work** of Ms. Izabela C. Włodarska, student of The Warsaw University of Technology (the alma mater promoter being Dr. Krzysztof Zberecki) defended in 2012.
   The title Eng. thesis: *Modelowanie struktury krystalicznej i własności mechanicznych materiału tlenkowego AgO pod ciśnieniem* (trans.: Calculations of crystal structure and mechanical properties of AgO under pressure).

3. **Co-promoter of the mater work** of Eng. Izabela C. Włodarska, student of The Warsaw University of technology (the alma mater promoter being Dr. Krzysztof Zberecki). Defense planned in 2013.
   The title of the work: *Modelowanie struktury elektronowej i magnetycznej oraz dynamiki sieci krystalicznej tlenku srebra AgO pod wysokim ciśnieniem z użyciem Teorii Funkcjonału Gęstości* (trans.: DFT calculations of electronic and magnetic structure and lattice dynamics of AgO under pressure).

4. Teaching responsibilities within the project TEAM (Foundation for Polish Science):

   - **Supervision of scientific research** of master students (Mr. Krzysztof Dymkowski, Mr. Juliusz Stasiewicz from The university of Warsaw, Collegium MISMaP, and Mr. Paweł Kondratiuk and Ms. Izabela Włodarska from the Warsaw Technical University, Faculty of Physics).

   - **Conducting training** in the QM methods in solid state for students of The Warsaw University of Technology, from the Faculty of Physics (Mr. Paweł Kondratiuk and Ms. Izabela Włodarska).

5. **Lectures** for undergraduate and graduate students during **Summer Schools**:

   - *Summer school on neutron scattering*, Hotel Rysy, Tatranská Štrba, High Tatras, Slovakia (2007).

   - *XX International School on Physics and Chemistry of Condensed Matter: Structural Investigation of Functional Materials*, Białowieża, Poland (2009).

12. Promoting science

1. **Open Days of the Institute of Inorganic Chemistry**, Slovak Academy of Sciences organized between the years 2003-2007. Promoting the theoretical section of the Institute.

2. **Festival of Science**: experimental chemistry site of the Interdisciplinary Centre for Mathematical and Computational Modelling, The University of Warsaw, Poland (2010). Performing demonstrations of chemical experiments.

3. **Promotion of neutron spectroscopy** by giving lecture *Nieelastyczna neutronowa spektroskopia* (trans.: Inelastic neutron spectroscopy). A series of meetings "Mam Ochotę na Chemię" organized by students' scientific association of chemists of The University of Warsaw "Fulleren", Warsaw (2013).

4. *Ciało stale prosto a po raz pierwszy w 3D* (trans.: Simple approach to solid-state matter with 3D projections) – general course of the University of Warsaw, Poland (school years 2011/12r. and 2012/13r.) **Course prepared for students of various scientific fields.** Apart from the students of physics and chemistry, the course was attended by students from various other specializations such as biophysics, biology, informatics, geology, philosophy and economics.

5. **Promotion in the press** of the most interesting scientific accomplishments (2009 - 2013):
   - The magazine of the University of Warsaw "Pismo Uczelni UW": contribution to 5 articles.
   - Bulletin of the Jožef Stefan Institute, Ljubljana, Slovenia: contribution to 2 articles.
   - Slovenian daily magazine DELO: contribution to 1 article.
   - Contributed to promotion the scientific work and discoveries of the Laboratory of Technology of the Novel Functional Materials – mediated by various internet portals.

13. Distinctions and Awards

1. **Third place** in *Competition for Young Scientists*, Award of the Institute of Inorganic Chemistry of the Slovak Academy of Sciences (2005).

2. **First place** in *Competition for Young Scientists*, Award of the Institute of Inorganic Chemistry of the Slovak Academy of Sciences (2007).

3. **Laureate** of *Competition for Young Scientists* in the category *Living nature and Chemical Sciences*, Award of the Slovak Academy of Sciences (2008).

4. **Marie Curie Fellowship** for young scientists (Early Stage Researcher) (2008).

5. **Fellowship of Foundation for Polish Science** in the framework of project TEAM (2009-2012).

6. **Best speaker**, Award of the conference *Hydrogen for the future*, Marie Curie Research Training Network 'Hydrogen', The 3rd RTN Meeting, Warszawa (2009).

7. Co-author of a publication [A-06] featured as **VIP paper** in ANGEW CHEM INT ED ENGL entitled *$AgIISO_4$: genuine sulfate of divalent silver with anomalously strong 1D antiferromagnetic interactions* (2010).

8. Co-author of publication [A-14] featured as **HOT paper** in DALTON TRANS entitled *Thermal and chemical decomposition of di(pyrazine)silver(II) peroxydisulfate and unusual crystal structure of a Ag(I) by-product* (2012).

9. Co-author of several publications [A-06, A-08, A-14, A-17] featured on **front or back covers of journals** from the Philadelphia list: ANGEW CHEM INT ED ENGL, CHEM EUR J, DALTON TRANS (2010-2013).

10. Co-author of a publication [A-06] exposed in a ***Highlight*** **article** (Jürgen Köhler, ANGEW CHEM INT ED 49, 3114-3115 (2010)).

Warsaw, 1 October 2013

V. Statistics

1. Publications

1. Total number of publications in the journals from the Web of Science and Scopus citation reports: **28**.
   - number of publications prior to obtaining a doctoral degree: **6**.
   - number of publications after obtaining a doctoral degree: **22**.

2. Total number of other publications: **1**.
   - number of publications prior to obtaining a doctoral degree: **1**.
   - number of publications after obtaining a doctoral degree: **0**.

3. Total impact factor: **91.52**.
4. Total number of citations according to Web of Science and Scopus: **155**.
5. Total number of citations without auto-citations according to Web of Science and Scopus: **100**.
6. Hirsch Index (h-index) according to Web of Science and Scopus: **7**.
7. Total number of publications selected for the purpose of habilitation procedure: **17**.
8. Total number of citations of the publications selected for the purpose of habilitation procedure according to Web of Science and Scopus: **85**.
9. Total impact factor of the publications on basis of which the applicant is applying for the degree of Doctor of Sciences (D.Sc.): **69.11**.

2. Conferences

1. Total number of presentations on conferences: **21**.
2. Total number of invited talks: **1**.
3. Total number of oral presentations: **16**.
4. Total number of posters: **4**.

3. Reviews of scientific works

1. Total number of reviews of scientific works: **1**.

Warsaw, 1 October 2013