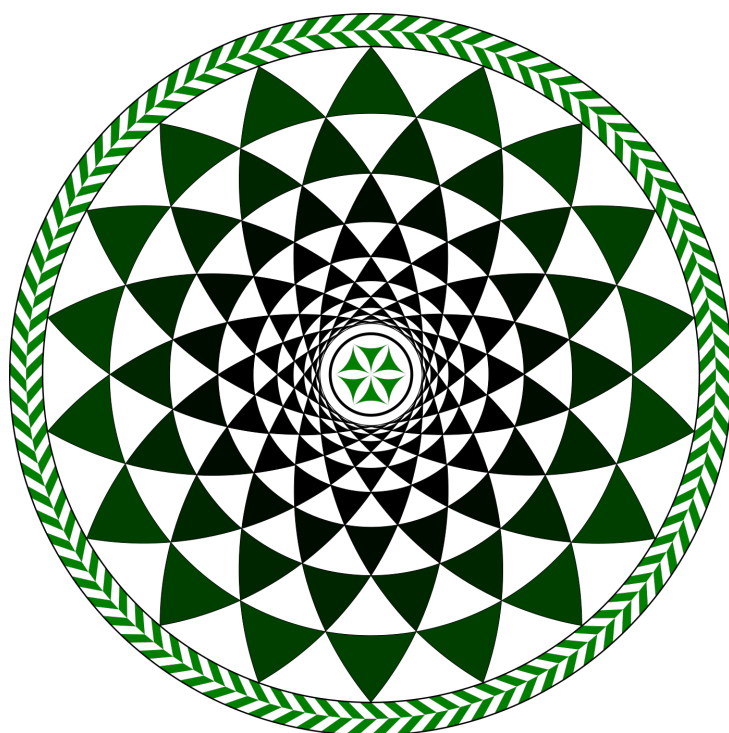


Multiscale phenomena in molecular matter

Monday 03 July 2017 - Thursday 06 July 2017



Book of Abstracts

Contents

The extraordinary mechanical properties of spider silk and its molecular foundation	1
Physics and chemistry in 2D materials: From 2D superconductors and magnets to hybrid molecular/2D heterostructures	3
Ultrafast photo-control of ferroelectric order in organic and inorganic strongly correlated matters: Role of hidden state	4
Manipulating magnetic domains at interfaces of coordination-polymer, nanosized heterostructures	5
Thin films of hexacyanometallates: towards tunable magnetic properties	7
Multi-scale investigation of MgO-based cements by NMR spectroscopy and relaxometry	8
Reentrant phenomenon and odd-even effect in homologous binary system of 4-alkyl-4'-cyanobiphenyl (<i>n</i> CB)	10
Helical structure of liquid crystals tested by spectroscopy methods	11
Scaling of the dielectric response of supercooled disordered phases	12
Cold crystallization and glass transitions in 4CFPB liquid crystal	13
Slippery interfaces - dynamics of director and helix rotations	15
Surface dynamics of polymers studied using low energy muons	16
Materials designed for electronics and IT technologies: porous silica thin films containing various functional units	17
Hydrothermally synthesized crystalline hydroxyapatite coatings on nanoporous titanium substrates for biomedical application	18
Highly ordered arrays of Fe ₆₀ Al ₄₀ nanomagnets embedded within flat paramagnetic matrix	19
Between single ion magnets and macromolecules: self-organizing, polymer-transition metal based macromolecular magnetic semi-solid solution	20

A homologous series of iron(II) spin-crossover complexes with bulky-decorated bipyridyl ligands	21
An Fe-azole based chemosensors for detection of gas- and vapor-phase analytes	22
Physical properties of new binary antiferroelectric liquid crystal mixtures	23
Critical behavior of magnetic materials studied with muon spectroscopy	25
Neutrons and atomistic simulations to study multiscale phenomena in molecular systems	26
Dielectric spectroscopy in bulk and at nanoscale	27
Using neutron techniques to explore the properties of thiophene-based polymers for organic electronics	29
Experimental evidence of „dead” magnetic outer shell in nanoparticle manganites RMnO_3 (R = Pr, Nd, Tb)	30
Organic solid state: accounts of co-crystals and of plastic crystal mesophases	31
Multiscale structure in amorphous carbohydrate matrices in relation to phase behavior, molecular packing and interaction with water	32
Polymorphism and isomerism in coordination compounds: The nemesis of crystal design	33
Positron annihilation in smectic E phase of 4 - alkyl - 4 – isothiocyanatobiphenyl (6TCB)	35
Physical properties and phase transitions of 3FmHPhF	36
Probing temperature changes in magnetocaloric molecular matter	37
Interplay of spin and spatial anisotropy in quasi-two-dimensional quantum magnets	38
Spatiotemporal observation and modelling of temperature scan rate effects on the thermal hysteresis and the dynamics of interface propagation in a spin-crossover single crystal	40
Ferromagnetism in two-dimensional Mott insulating compounds with strong electron correlations 21	41
Electrochemical reduction of NO on Pt(100): a combined DFT and KMC study	42
Challenges in the modelling of oxides	44
Spin transition of Fe(II) 1D triazole chains: hybrid materials and lattice dynamics	45
Structural phase transition in KFe_2As_2 from ab initio calculations	46

Hydrogen in AB ₂ and AB ₅ compounds	47
Spin-crossover phenomena of a Jahn-Teller active Mn(III) complex [Mn(taa)]	48
Functionalization of cyanido-bridged clusters by ligand decoration and metal ion embedment	49
Ln(III) Complexes as Single-Ion Magnets that light can disturb	50
Static and dynamic magnetic properties of the ferromagnetic quasi 1D Ising system [Co(NCS) ₂ pyridine ₂] _n	51
Study of water sorption into magnetic coordination networks	52
Investigation of the spatial anisotropy of exchange coupling in quasi-two-dimensional quantum magnets Cu(en)Cl ₂ and Cu(tn)Cl ₂	53
Studies of slow magnetic relaxations in monocrystalline of [Mn ^{III} F ₄ TPP][TCNE]* methanol	54
Magnonic excitations in low dimensional inhomogeneous nanostructures	55
Low temperature electronic state of β''-type organic conductors	56
Peculiar low-energy phonon excitations in organic crystal with strong charge fluctuations	57
Molecular dynamics in the smectic liquid crystal 4-n-butyloxybenzylidene-4'-n'-octylaniline (BBOA) in bulk and under confinement	58
Magnetic properties of new molecular compounds based on single cobalt (II) ion	59
Polymer dynamics and morphology in LDPE nanocomposites studied by NMR spectroscopy and relaxometry	60
Magnetic anisotropy and magnetization reversal mechanisms of nanoporous Co/Pd multilayers and CoPd alloy thin films	61
Physical properties of a new magnetic liquid crystal based on Co(II) ions.	62
Mesoporous silica thin films containing propyl-copper-phosphonate units inside vertically aligned pores as a novel material with tunable nonlinear optical (NLO) properties	63
Time scale effects in perception of acoustic signals	64
Formation of nanopatterned metal/oxide/metal multilayered structures using anodization process	65
Inducing exchange bias in Co/Au multilayers by oxygen ion implantation	66
Structural research of ternary nanoparticles for energy production	67

Mechanism of magnetisation reversal in thin L1 ₀ FePd nanopatterned layers . . .	68
Cyano-bridged bimetallic chains based on cyclam complexes of Ni(III) or Mn(III) and hexacyanometallates(III)	69
Photomagnetic Cu ^{II} -[Mo ^{IV} (CN) ₈] ⁴⁻ coordination polymers	70
Polymorphism and vibrational investigations (FT-IR and IINS) of glass-forming 2-phenylbutan-1-ol (BEP), 2-(trifluoromethyl)phenethyl alcohol (2TFMP) and 4-(trifluoromethyl)phenethyl alcohol (4TFMP)	71
Total transmission of elastic waves in solid-solid interface	72
Optimization of anodization parameters for nanoporous Al ₂ O ₃ templates fabrication	73
Nanoporous Al ₂ O ₃ templates: a route towards flexible humidity sensors with linear response	74
Ionic conductors based on metal-closo-borates	75
Phase diagram and molecular dynamics in the antiferroelectric liquid crystal (2S)-octano-2-yl-4'-(2-fluoro-4-{[5-(1,1,2,2,3,3,3 heptafluoropropoxy)pentyl]oxy}benzo-yloxy)-[1,1'-biphenyl]-4-carboxylate	76
How does the molecular structure of the bent-core molecules affects the occurrence of twist-bend nematic phase?: a mean-field study	77

Opening lecture**The extraordinary mechanical properties of spider silk and its molecular foundation****Author(s):** Prof. KREMER, Friedrich¹**Co-author(s):** Prof. PAPADOPOULOS, Periklis² ; Dr. FIGULI, Roxana³ ; Dr. KOSSACK, Wilhelm¹ ; Dr. ANTON, Markus¹¹ *Department of Molecular Physics, Leipzig University*² *Max Planck Institute for Polymer Research, Mainz, Germany*³ *Karlsruhe Institute of Technology, Germany***Corresponding Author(s):** kremer@physik.uni-leipzig.de

Spider silk is a high-performance fiber with unique mechanical properties which are currently not met by man-made materials. It consists essentially out of two proteins, major ampullate spidroin1 and spidroin2, having alanine-rich blocks interrupted by glycine-rich sequences. The former assembles to β -sheeted nanocrystals which are embedded in the amorphous chains of the latter and which are interlinked by a 10% fraction of *prestressed* chains. This causes within the fiber a negative inner pressure which is counterbalanced by the matrix surrounding the fibrils and by the outer skin. Wetting of the fiber results in a spontaneous “supercontraction” into the equilibrated state. In the talk a detailed description of this interplay between inner and outer constraints will be discussed based on a variety of complementary experimental methods like polarized, time-resolved FTIR spectroscopy, measurements of the mechanical modulus and micro-X-ray scattering. It enables one to deduce a *quantitative* model describing the macroscopic response in the dependence on the microscopic parameters.

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Molecular Magnets / keynote lecture

Physics and chemistry in 2D materials: From 2D superconductors and magnets to hybrid molecular/2D heterostructures

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Superconductivity and ferromagnetism are two cooperative properties difficult to reach in the 2D limit. The discovery of graphene and other 2D materials has opened the possibility to check these phenomena in this limit. Here we show that, contrarily to the expectation, superconductivity of TaS₂ can be enhanced in the 2D limit [1]. As far as the 2D magnetic materials are concerned, we show that both solid state and coordination chemistries can provide examples of layered materials that can be exfoliated to afford 2D magnetic materials [2]. We also report the attempts we are making to measure the magnetism of these atomically-thin layers. Finally, we report some examples of hybrid heterostructures prepared by mixing functional molecules with 2D materials [3].

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Molecular Magnets / invited talk

Ultrafast photo-control of ferroelectric order in organic and inorganic strongly correlated matters: Role of hidden state

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In spite of various attractive natures of PIPT, the research is facing a difficult and essential problem, i.e. can we realize and identify a new phase of solid based on novel lattice structure which is unique for the photo-excited condition so called as a 'hidden phase'? This 'hidden phase' with electronic and structural order realized only by optical excitation is important merit of PIPT process for achieving ultrafast and sensitive phase control via pure photonic channel free from thermal effect. We have demonstrated that 'Hidden State' really plays an essential role in PIPT process based on realistic examples. The gigantic photo-induced spectral changes in $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ (NSMO) thin film has been attributed to the photo-induced formation of a new Charge-Orbital Ordered State based on the ps time-resolved X-ray diffraction (TR-XRD) combined with fs spectroscopic measurement [1]. We also demonstrated that such a hidden state also plays a key role in the gigantic photo-responses of organic [2,4] and inorganic [3] correlated systems. In case of $(\text{EDO-TTF})_2\text{PF}_6$ crystals, structural changes accompanied with the photo-induced conversion of Charge Ordered patten can be probed by fs time-resolved electron diffraction and IR measurements [2]. In the present study, we report the research on the role of photo-induced 'Hidden State' in exotic ferroelectric crystals utilizing linear (UV-IR region) and nonlinear spectroscopic techniques. In the case of proton- π electron coupled organic ferroelectric system, occurrence of photo-induced electronic-proton coupled structural change has been confirmed utilizing time-resolved IR spectroscopy. In addition, SHG intensity has been modulated about 30% within 100 fs after the photo-excitation. Similar large photo-modulation in nonlinear optical property has been also confirmed in inorganic Orbital-Lattice-Spin coupled system. We discuss the importance of structural dynamics of 'Hidden State' with short life-time for the development of a new class of photonic materials.

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Molecular Magnets / invited talk

Manipulating magnetic domains at interfaces of coordination-polymer, nanosized heterostructures

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In collaboration with Dan Talham and his group in UF Chemistry, the photocontrolled magnetic response of coordination polymer heterostructures has been extended up to 125 K [1], see Figures. Extensions to 200 K and higher are achievable if the photoinduced lattice distortions of the photo-active constituent of the heterostructure can be shifted to this temperature range. After reviewing the present understanding of the basic phenomenon, the presentation will focus on recent [2] and future investigations designed to probe the microscopic/mesoscopic thermal/photo induced changes at the interface. Specifically, the potential use of SANS (small angle neutron scattering) will be discussed. With the need to identify photo-active candidates whose lattice distortions persist to high temperatures (> 200 K), our recent research has focused on studies of spin crossover complexes on substrates. This direction was motivated by a report of the coexistence of high-spin and low-spin configurations of the second layer of a spin crossover complex on Au [3]. This direction of research employs STM (scanning tunneling microscopy) techniques and is receiving considerable attention [4]. A conjecture, which is now receiving experimental attention, will be described and provides an avenue for computational studies to guide the experimental directions.

Ultimately, independent of scale, most “spintronic” devices are heterostructures, and this work addresses fundamental aspects of the mesoscopic configurations and explores the possible route to photocontrolled applications.

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Acknowledgments

This work is part of an ongoing collaboration with Daniel R. Talham in UF Chemistry and involves an extended network of coworkers who are coauthors on our published work. Unpublished results involving SANS and STM investigations involve J. M. Cain and C. Averback (UF Chemistry: sample preparation and characterization), J. J. Hrudka and M. Shatruk (Florida State University Chemistry: sample preparation and characterization),

M. R. Fitzsimmons, L. Debeer-Schmitt, T. O. Farmer, D. M. Pajerowski, S. E. Nagler (Neutron Sciences Directorate, Oak Ridge National Lab: SANS), P. Maksymovich and J. Wang (Center for Nanophase Materials Science, Oak Ridge National Lab: STM), A. Feher, M. Orendáč, V. Komanický, T. Samuely, E. Čížmár (P. J. Šafárik University, Košice, Slovakia: STM and EPR). Aspects of this work were supported by the National Science Foundation (NSF) via DMR-1202033 (MWM) and DMR-1157490 (NHMFL).

Molecular Magnets / invited talk

Thin films of hexacyanometallates: towards tunable magnetic properties

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In the last few years, there has been a significant interest in the study of the molecular magnets in a form of thin films, that is motivated by the possibility of applying these materials as multifunctional sensors or in spintronic devices. One of the most important group of molecular magnets, which can be considered as relevant for such applications are cyanido-bridged coordination networks. A well-known example of that kind of compounds are Prussian blue analogues (PBA), a large family of cubic systems with face-centred crystal structure containing hexacyanometallates and transition metal ions. PBAs attract great attention due to interesting and tunable properties. The cyanido bridging ligands allow the effective magnetic coupling. Because of the highly symmetrical structure, the PBA's properties can be tuned by changing the transition metal ions involved in the cyano-bridging process.

Herein a study of a new dimensionally-reduced systems based on nickel hexacyanoferrate/chromate will be presented. Thin films were obtained with the "layer by layer" deposition technique, whereby the chemical composition was controlled by the dipping sequence. The primary aim of our work was to tune the physical properties of PBAs by adapting the strategy of incorporation of the three types of metal ions. A comprehensive analysis of magnetic, structural and spectroscopic properties of the resulting compound and the detailed investigation of the evolution of material's microstructure induced by the change in its chemical composition will be presented.

In addition we will present the first example of study on the magnetocaloric effect (MCE) in molecular magnet prepared in a form of thin film. Contrary to the compounds with magnetocrystalline anisotropy, anisotropic magnetic properties of PBA films are related almost only to shape anisotropy. The different magnetic response measured for sample oriented parallel and perpendicular to the direction of magnetic field has been explained by the geometry of a demagnetization factor. Besides the analysis of the magnetic entropy temperature dependence and its variation upon the rotating the sample from in- plane to out-of- plane orientation, we have studied the scaling behaviour of MCE for the sample in both positions.

Soft Matter / invited talk

Multi-scale investigation of MgO-based cements by NMR spectroscopy and relaxometry

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In the last years, MgO-based cementitious materials have attracted great interest as eco-sustainable alternatives to traditional Portland (CaO-based) cement, the dominant form of cement used worldwide. In particular, MgO-based formulations have been proposed with the aim of both reducing the environmental footprint associated with the production of Portland cement and developing cements to be used in the immobilization of nuclear or metal containing waste [1].

The binder phase of these cements is magnesium silicate hydrate (M-S-H), the amorphous phase that forms from the reaction of MgO with a source of silica (SiO₂) and water. Although a significant quantity of literature exists concerning the structure and nature of the M-S-H gel [2-8], a full comprehension of properties, such as hydration kinetics, the nature of the hydrated products and their multi-scale structure and organization, is still lacking. The investigation of these properties, as well as the research for new formulations with improved performances, is fundamental to achieve the industrial breakout of these materials.

In this work, novel MgO-based cements obtained by hydration of a 1:1 molar mixture of MgO and fumed silica (MgO/SiO₂) and mixed-formulations containing different amounts of MgO/SiO₂ and Portland cement were developed. The multi-scale structural properties and the hydration kinetics of these systems were investigated in detail by means of solid-state NMR spectroscopy (SSNMR) and relaxometry, which already proved to be very powerful for the study of traditional cement [9-12], with the support of complementary techniques such as X-Ray Diffraction, thermogravimetry, IR spectroscopy, Scanning Electron Microscopy, and Differential Scanning Calorimetry.

The nature and the structure at the sub-nanometric scale of the formed hydrated phases, as well as the kinetics of their formation, were investigated at different hydration times on freeze-dried samples by means of multi-nuclear high-resolution SSNMR experiments [13,14]. In particular, ²⁹Si MAS experiments allowed the different silicon sites, Q¹, Q² and Q³, characterized by different connectivity to -OSi, -OH, -OMg or -OCa groups, to be identified and quantified. In the case of mixed systems, it was also possible to distinguish between M-S-H and C-S-H (calcium silicate hydrate arising from hydration of alite and belite present in Portland cement) domains, and to study their properties and relative amounts as a function of composition and hydration time. The state of water and the evolution of the solid matrix during the hydration process were investigated as a function of time directly on the cement pastes by means of ¹H T₁ Fast Field-Cycling relaxometry and measurement of ¹H T₂ relaxation times at low magnetic field (proton Larmor frequency of 20 MHz) [15].

Acknowledgments

This work was financially supported by MIUR (FIR2013 Project RBFR132WSM).

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Soft Matter / invited talk

Reentrant phenomenon and odd-even effect in homologous binary system of 4-alkyl-4'-cyanobiphenyl (n CB)

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A family of 4-alkyl-4'-cyanobiphenyl (n CB, n is the number of carbon atoms in the alkyl chain) is one of the most famous mesogenic series of calamitic molecules. The n CBs exhibit liquid crystalline phases, nematic (N) and smectic A_d (SmA_d , d means dimer) phases, below the isotropic liquid (IL) depending on the length n of the alkyl chain. Although a huge number of studies on both the n CBs and their mixtures (n CB/ m CB) have been done, only the normal sequence of long-range molecular order (IL-N- SmA_d on cooling) has been reported, in contrast to a structurally similar mesogenic series, 4-alkyloxy-4'-cyanobiphenyl (n OCB). 6OCB/8OCB mixture, for example, shows the reentrant phenomenon with the sequence of IL-N- SmA_d -reentrant N (RN) on cooling. Recently, we found the reentrant phenomenon showing the IL-N- SmA_d -RN sequence on cooling in n CB/ m CB ($n = 0-6$; $m = 8,9$) binary mixtures for the first time [1,2]. Interestingly, their phase diagram against an averaged length of alkyl-chain (n^*) showed four N(RN)- SmA_d phase boundary curves corresponding to four combinations of odd and even chains in n CB/ m CB systems: even/even, odd/even, even/odd, and odd/odd [2]. We successfully clarified the odd-even effect based on their molecular packing structure of the SmA_d phase. The reentrant phenomenon and the odd/even effect will be discussed.

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Soft Matter / invited talk

Helical structure of liquid crystals tested by spectroscopy methods

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Chiral liquid crystals form macroscopic helicoidal structure. It is characterized by two parameters: the value of helical pitch and the helical twist sense (handedness). Spectroscopy methods let measure both of these parameters. The helical pitch can be measured actually by different methods, but the most popular method uses UV-Vis-IRspectrophotometers. The idea of measurement is based on the selective reflection of the light from macroscopic structure. The handedness is measured by polarimetry technique. The used detector can be simply human eyes but more sophisticated method uses UV-Vis-IRspectrophotometers. In our laboratory liquid crystal compounds which show the change of helical twist sense upon temperature were found [1-3]. At lower temperature the macroscopic structure is right handed and helical pitch increases with temperature. At higher temperature the macroscopic structure is left handed and helical pitch decreases with temperature. In between the unwinding of the helicoidal structure is observed. This behavior can be confirmed by Electronic Circular Dichroic Spectrophotometry (ECD) as well as by Vibrational Circular Dichroic Spectrophotometry (VCD) [4]. The results of IR, ¹H NMR and ¹³C NMR will be also presented.

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Soft Matter / invited talk

Scaling of the dielectric response of supercooled disordered phases

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Spectrum of a dielectric permittivity for supercooled disordered phases most often is composed of two relaxation processes [1]: a main relaxation process (called α process) followed by resolved, unresolved (also called ‘excess wing phenomena’), or both secondary processes (β processes). Although there are many models describing dielectric relaxation [2-6] none of them describes the relaxation processes in supercooled disordered phases with a good precision, because of some simplifications introduced. Debye model [2] describes relaxation for non-interacting electric dipoles or electric dipoles in diluted non-polar medium whereas Debye-like models, i.e. Cole-Cole [3], Cole-Davidson [4], Havriliak-Negami [5], describe relaxation for non-interacting electric dipoles in viscous medium. Therefore, some scaling equations of the dielectric response were proposed [7-9] to describe molecular dynamics as a function of frequency of measuring field for various temperatures. However, they are limited to scaling of the imaginary part of dielectric permittivity only [7-9], and Nagel and co-authors model [7-8] refers in fact to systems with ‘special’ values of long-range and short-range correlation parameters of molecular interactions. Therefore, we have proposed a general form of scaling equation [10-11] that can be applied to the imaginary part of permittivity $\epsilon''(f)$ as well as to the real part of permittivity $\epsilon'(f) - \epsilon_\infty$. The proposed scaling of the dielectric response applied to supercooled disordered phases, i.e. supercooled isotropic liquid phase and supercooled plastic-crystal phase, shows that behavior of resolved and/or unresolved β relaxations strictly depends on the parameters of the main relaxation process. One can conclude that the main relaxation process and the secondary ones are not independent processes.

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Partial support by the 2014-2016 PAS-CNR bilateral project “Studies of phase polymorphism and dynamics in selected soft materials” and by the 2017-2019 PAS-CNR bilateral project “Multidisciplinary studies of structural and dynamic properties of glass-forming compounds” is acknowledged.

Soft Matter / invited talk

Cold crystallization and glass transitions in 4CFPB liquid crystal

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Presented research concerns the investigations of vitrification and crystallization processes in 4CFPB (4-cyano-3-fluorophenyl 4-butylbenzoate) liquid crystalline substance. Glass transition is important issue in new-day condensed matter physics. Additionally, cold crystallization phenomenon is also interesting case, especially in connection to glass formation tendency. Descriptions of both phenomena were performed using various methods like adiabatic calorimetry, differential scanning calorimetry (DSC), polarizing microscopy (POM) and broadband dielectric spectroscopy (BDS). Dielectric experiments of 4CFPB were performed at various pressure conditions like normal pressure, high pressure at isobaric and isothermal conditions. Additional measurements were conducted for confined sample in intersecting silica nanopores.

Polymorphism investigations of 4CFPB has shown two liquid phases: isotropic and nematic, and three solid states like two crystalline phases (C II and C I) and glass of nematic with partial long range order of molecules. Additionally, during high pressure measurements liquid-like SmA phase was induced. Temperature-pressure phase diagram upon cooling and heating was constructed.

Investigated substance shows ease tendency to vitrify. Glass transition temperature was determined for various pressure conditions. In addition to calorimetric and dielectric methods, diminishing of number of cracks in glass around T_g were observed on heating by polarizing microscopy [1]. On further heating two types of mechanisms of CII crystallization were found. For slow heating (up to 5K/min) strong dependence of heating rate on temperature of full crystallization and half time of crystallization were identified. These facts indicates that diffusion controlled mechanism with the energy barrier 57 kJ/mol took place. For faster heating thermodynamic mechanism characterized by energy barrier 180 kJ/mol and small effect of heating rate on temperature of full crystallization and half time of crystallization was found [2].

Molecular dynamics studies have shown bimodal structural relaxations connected with flip-flop motions and precession of molecules were found in all pressure conditions. Secondary relaxation, positively tested as Johari-Goldstein type, was observed in nematic glass. In nanopores complexity of dynamics is quite different. New relaxation processes were found, connected with reptation and collective motions of molecules. The crystallization process of 4CFPB was not observed under confinement, only the molecular arrangement along pore walls was observed.

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Surfaces & Interfaces / invited talk

Slippery interfaces - dynamics of director and helix rotations

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We have invented the principle of slippery interfaces and design low voltage driven fast switching liquid crystal display cell. The anchoring force on the glass surfaces of the cell diminishes to lubricate the rotational motion of LC molecules. We have succeeded to demonstrate the large reduction of driving voltage in DH-FLC mode of SmC* keeping the fast switching response. The slippery interfaces can be realized by the spin coated swollen azo-LC gel films on the glass substrates. Under UV irradiation, trans-cis isomerization of the azo-dye co-polymerized in the azo-LC gel film, induces the slippery interfaces by the disordering effect. Since the co-polymerized azo-dye cannot be dissolved into LC, the disordering effect is completely localized in the interface between swollen azo-LC gel and bulk SmC* material.

By lubrication of the motion of the C-director rotation on the slippery interface, two types of C-director rotation modes appear. Relaxation frequencies of both mode are strongly dependent on the applied electric field. One is the intra helix motion which is quite fast, (~ 50 micro sec), but it requires rather large driving voltage (> 1.5 V/micro meter) and induces small transmitted light intensity ($\Delta I/I < 0.5$). Interhelix motion can be enhanced by the slippery interfaces, which is rather slow response (> 1 ms), but it is easy to be excited by the low driving voltage (< 1.0 V/micro meter) and creates the large transmitted light intensity ($\Delta I/I > 0.75$). Then, the inter helix mode is quite effective to reduce the driving voltage of DH-FLC mode.

Surfaces & Interfaces / invited talk**Surface dynamics of polymers studied using low energy muons**Dr. PRATT, Francis¹¹ *STFC***Corresponding Author(s):** francis.pratt@stfc.ac.uk

Intensive studies of the properties of polymer thin films have followed the discovery of significant suppression of the glass transition temperature T_g for freestanding films of nanoscale thickness (reviewed in [1]). A local T_g that depends on distance from a free surface has often been invoked to explain these results, but there has previously been a lack of experimental techniques able to measure directly such dependence in an individual sample. Low energy muons (LEM) can be used to clarify this issue by making depth-resolved measurements of the local T_g near the surface of a polymer, which can be used to identify the mechanisms responsible for reducing T_g . LEM data obtained for polybutadiene (PBD) and polystyrene (PS) across a range of molecular weights have been analysed against possible models for the transition between surface and bulk behaviour and a consistent picture emerges [2] in which the transition is governed by a mechanism of diffusing conformational kinks first proposed by de Gennes [3]. This diffusive mechanism operates over a length scale determined by the size of the polymer chain, crossing over at longer distances to a capillary wave mechanism first proposed by Herminghaus [4]. A detailed study of the characteristic length scale against molecular weight for PBD shows good agreement with random coil length scales at low molecular weight but a crossover in the behaviour is seen around 50 kDa, suggesting breakdown of the random coil assumption for larger molecules [2]. In addition, when the muon implantation depth is increased beyond 100 nm we find evidence for a buried region containing inhomogeneous nanostructure [5], most likely nanopores formed as the solvent is evacuated in the spin coating process. Studies on the polymer polydimethylsiloxane (PDMS) have also been made, showing some basic similarities as well as some clear differences with the PBD/PS results [5].

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Surfaces & Interfaces / invited talk

Materials designed for electronics and IT technologies: porous silica thin films containing various functional units

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The present work is devoted to novel classes of nanomaterials: mesoporous silica thin films containing vertically aligned channels containing functional units or crystalline structures. Such a functionalization makes the materials highly applicative in electronics or IT technologies. We consider three types of silica based materials, containing various functional units inside pores. Porous silica films containing single molecular magnets in pores bottom can play a role of a layout of independent, bistable magnetic units. Such a material can be used as molecular neurons. Similar material containing permanent magnetic specimen inside pores can be use for fabrication of super-dense magnetic memory. Thin silica films with channels arranged perpendicular to the substrate and containing strongly dipolar units (copper phosphonate) have strong non-linear optical (NLO) response. Moreover, NLO susceptibility can be tune by means of functional groups concentration variation. All materials quoted above have strong applicative potential.

Surfaces & Interfaces / invited talk

Hydrothermally synthesized crystalline hydroxyapatite coatings on nanoporous titanium substrates for biomedical application

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High requirements for dental and orthopedic implants have pushed the research towards complex and intelligent biomaterials. To overcome the disadvantages of a single phase implant, such as low biocompatibility for metals and poor mechanical properties for ceramics, significant amount of research has focused on the development of their combination, i.e. covering load-bearing metallic implants with thin bioactive hydroxyapatite [HAp, Ca₅(PO₄)₃(OH)₂] films.

Titanium and its alloys, with excellent mechanical properties and high corrosion resistance, have been widely used as leading materials for hard tissue replacement. However, because of their lack of bioactivity, they cannot bond with surrounding tissues directly nor promote new bone formation on their surface at the early stage after implantation. Self-organized TiO₂ nanotube arrays, fabricated by electrochemical anodic oxidation, have been reported to increase significantly the titanium surface area and enhance the formation of HAp and the bond strength between the substrate and the coating.

Herein, we investigate the effect of the nanoporous TiO₂ substrate on the morphology and uniformity of hydrothermally precipitated hydroxyapatite coatings. Nanotubular TiO₂ substrates were synthesized on a titanium plate by anodic oxidation and subsequently annealed at 500°C or 600°C to create the crystalline anatase and/or rutile forms of TiO₂. The substrates were further used for HAp growth under hydrothermal conditions. The hydrothermal method is based on a chemical precipitation from aqueous solution containing calcium and phosphate source, carried out in an autoclave at elevated temperature and high vapor pressure. The samples were then characterized with the XRD, Raman and SEM techniques. The results show that hydrothermal synthesis leads to formation of needle-like coating layer of HAp particles. The diameter and length of HAp crystals decrease with increasing annealing temperature of TiO₂ nanotubular arrays. Furthermore, we demonstrate that nanostructured surface of titanium oxide has beneficial influence on the HAp nucleation and coverage.

Surfaces & Interfaces / contributed talk

Highly ordered arrays of Fe₆₀Al₄₀ nanomagnets embedded within flat paramagnetic matrix

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Large-scale periodic arrays of trigonal ferromagnetic islands embedded in a paramagnetic matrix have been fabricated by ion irradiation of 40 nm thick B2-Fe₆₀Al₄₀ thin films through the mask of polystyrene nanospheres with size of 200 nm, 400 nm and 800 nm. The irradiation was performed with 20 keV Ne⁺ ions at 6 x 10¹⁴ cm⁻² fluence, which induced chemical disorder and thus a ferromagnetic phase in the uncovered Fe₆₀Al₄₀. Using SQUID and Kerr magnetometry, changes in coercive field, saturation magnetization, and magnetic anisotropy constant have been determined in a temperature range of 5 K – 350 K and correlated with the radiation damage distribution obtained from simulations of the ion stopping and range. The domain shapes and sizes together with the switching behaviour were studied by scanning magnetoresistive microscopy in variable external field. The results demonstrated that the proposed approach can be effectively used to produce large-area magnetic arrays embedded within a topographically flat surface with magnetic properties tuneable by temperature and patterning period.

Acknowledgments

This work was supported by The German Academic Exchange Service (DAAD) with contract No. PPP-PL 57214850.

Multifunctional Materials I / contributed talk

Between single ion magnets and macromolecules: self-organizing, polymer-transition metal based macromolecular magnetic semi-solid solution**Author(s):** Dr. MAJCHER, Anna¹**Co-author(s):** Mr. DĄBCZYŃSKI, Paweł¹ ; Dr. MARZEC, Mateusz M.² ; Ms. CEGLARSKA, Magdalena¹ ; Dr. RYSZ, Jakub¹ ; Dr. BERNASIK, Andrzej³ ; Prof. OHKOSHI, Shin-ichi⁴ ; Dr. STEFAŃCZYK, Olaf⁴¹ *Institute of Physics, Jagiellonian University, prof. Stanisława Łojasiewicza 11, 30-348 Kraków, Poland*² *Academic Centre for Materials and Nanotechnology, AGH University of Science and Technology, al. Mickiewicza 30, 30-049 Kraków, Poland*³ *Faculty of Physics and Applied Computer Science, AGH University of Science and Technology, al. Mickiewicza 30, 30-049 Kraków, Poland*⁴ *Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan***Corresponding Author(s):** anna.majcher@uj.edu.pl

We present a new approach to obtain functional magnetic materials: one that combines the qualities of polymers that are widely used to produce thin films, and Single Ion Magnets that exhibit magnetic relaxations.^[1] By reactions of pyridine and 4-vinylpyridine with CoBr₂, we obtained two SIMs, showing field-induced relaxations of magnetization with energy barriers of 28(2) and 35(3) K, and τ_0 values of $8 \cdot 10^{-10}$ s and $1 \cdot 10^{-11}$ s, respectively. Next, resulting from a reaction of poly(4-vinylpyridine) (P4VP), with its structural units identical to the ligands used to form the SIMs, with CoBr₂, a new material was formed with CoBr₂ bound to the pyridines within the polymer chains, forming a cross-linked macromolecular matrix. Field-induced relaxations of magnetization are preserved and dependent on the Co:P4VP structural units molar ratio, making it an amorphous semi-solid solution. Thin magnetic films were obtained by immersion of P4VP spin-cast films in CoBr₂ orthogonal solution. Atomic Force Microscopy (see figure, middle), Secondary Ion Mass Spectrometry and X-ray Photoelectron Spectroscopy confirm the binding of cobalt salts within the layer. AC magnetic measurements confirm the preservation of magnetic relaxations in the film. We believe that our research opens a new path that combines two fields of material research and is extremely promising regarding future applications of molecular magnets – as self-organizing macromolecular magnetic materials.

Acknowledgments

This research was financed by the Polish National Science Centre within the SONATA Project UMO-2015/19/D/ST5/01936.

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Multifunctional Materials I / contributed talk

A homologous series of iron(II) spin-crossover complexes with bulky-decorated bipyridyl ligands**Author(s):** Dr. XUE, Shufang¹**Co-author(s):** Dr. GUO, Yunnan¹; Dr. DIRTU, Marinela M.¹; Dr. ROBEYNS, Koen¹; Prof. ROTARU, Aurelian²; Prof. GARCIA, yann¹¹ *Université catholique de Louvain*² *“Stefan cel Mare” University***Corresponding Author(s):** shufang.xue@uclouvain.be

Molecules with switchable magnetic moment such as Fe(II) complexes of pseudo-octahedral geometry, are interesting and promising candidate materials for the ultra-high-density memory, devices, sensors, electronics and spintronics in nanoscience [1]. Such outstanding and useful physical property is due to the switchable bistable state of the central Fe(II) ion from a diamagnetic low-spin state to a thermally populated paramagnetic high-spin state under various external stimuli (temperature, pressure, light, magnetic ligand and chemical decoration). The temperature and cooperativity characters are strongly dependent on ligand field and intermolecular interactions. The important strategy of modification the ligand is to tune σ -donor or π -acceptor characters to tune the ligand field strength to crossover range [2].

Bipyridine(bipy) ligand is a classical representative of imine ligands for SCO systems [3]. Aiming, herein, at shedding light on the influence of ligand field to SCO, we reported a series of bulky substituted bipy-related iron(II) compounds. The skeleton of FeN₆ is similar to the previous structure [3]. All the compounds exhibit thermal-dependent SCO which occur over different temperature ranges. Of particular interest is compound 4 which display a complete spin transition at $T_{1/2} = 195$ K. Structural-property relationship reveals that the different transition temperature can be attributed to the effects of a change in bipyridyl ligand conformation. These results obtained have been proposed as potential building blocks for constructing novel SCO frameworks (SCOFs).

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Multifunctional Materials I / contributed talk**An Fe-azole based chemosensors for detection of gas- and vapor-phase analytes****Author(s):** Dr. GUO, Yunnan¹**Co-author(s):** Dr. DIRTU, Marinela M. ¹ ; Prof. GARCIA, yann ¹¹ *Université catholique de Louvain***Corresponding Author(s):** yunnan.guo@uclouvain.be

There is currently a huge appeal for “chemosensors” based on metal–organic frameworks (MOFs) for the sensitive and selective detection of gas- and vapor-phase analytes for a range of applications including chemical threat alerts, medical diagnostics, and environmental monitoring. Here, We have developed a simple colorimetric molecular sensor that detects a wide range of volatile analytes and then applied it to the detection of toxic gases. The sensor consists of a mononuclear complex, $[\text{Fe}(\text{trz-tet})_2(\text{H}_2\text{O})_4]\cdot 2\text{H}_2\text{O}$, with a FeN_2O_4 chromophore with monodentate triazole coordination that can be changed by diverse chemical interactions with analytes. The colour change for the sensor is a unique molecular fingerprint. Clear differentiation among 6 different chemicals, including 4 toxic industrial chemicals (TICs) within two minutes of exposure under vapor diffusion.

Multifunctional Materials I / contributed talk

Physical properties of new binary antiferroelectric liquid crystal mixtures**Author(s):** Mr. FITAS, Jakub¹**Co-author(s):** Ms. SZYMKOWIAK, Marta¹; Dr. JAWORSKA-GOŁĄB, Teresa¹; DEPTUCH, Aleksandra¹; Dr. TYKARSKA, Marzena²; Ms. KURP, Katarzyna²; Dr. ŻUROWSKA, Magdalena²; Dr. MARZEC, MONIKA¹¹ *Institute of Physics, Jagiellonian University*² *Military University of Technology***Corresponding Author(s):** monika.marzec@uj.edu.pl

Liquid crystal displays (LCDs) remain in frequent use since the construction of the first nematic-based display. From that time, their importance as an image display technology is steadily growing. This occurs because of the constant development of both new liquid crystalline materials and new approaches to their application. The antiferroelectric liquid crystal (AFLC) exhibiting tilt angle ca. 45° are called orthoconic antiferroelectric liquid crystals (OAFLC) and they are very attractive materials for use in new kind of LCD. Ferroelectric as well as antiferroelectric liquid crystals are also promising as similar improvements in other optoelectronic devices. [1,2] The development of this field requires constant search for new liquid crystals both pure compounds and mixtures, as well as valuation of their properties relevant to use in various optoelectronic switches. In particular, the mutual miscibility of many pure compounds is a greatly valuable method to design new liquid crystals exhibiting desired qualities. [3]

The aim of this work was to study the physical properties of three new ferroelectric mixtures for purpose of their potential application in optoelectronic devices. The studied mixtures consist of two chiral compounds 6F2OBi and 3F7HBM6(S) mixed in proportions 3:1, 1:1 and 1:3 and denoted as W-331-1, W-331-2 and W-331-3, respectively. Both ingredients were studied by us earlier [4,5]. One of the ingredients (6F2OBi) is ferroelectric liquid crystal while 3F7HBM6(S) is antiferroelectric one exhibiting antiferroelectric SmC_A* phase next to ferroelectric SmC*.

Properties of chosen mixtures were studied by complementary methods such as dielectric, electrooptic, calorimetric and XRD. It was found that addition of 3F7HBM6(S) to 6F2OBi increases both melting and clearing points. Moreover, the tilted smectic overcools easily and is stabilised in low temperatures by electric field. So, the switching is observed down to 10÷15°C, what means that it exists in the broad temperature range (ca. 100 degree), covered room temperature. The maximum value of spontaneous polarization was determined between 45 and 160 nC/cm², depending on the mixture while the tilt angle achieves saturation close to 45°, what means that these mixtures belong to OAFLC. Additionally, the switching time is short, below 1 ms, for all studied mixtures. Therefore it may be concluded that W-331 mixtures are promising materials for the composition of the multicomponent mixtures based on the same or similar chemical compounds.

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Multifunctional Materials I / contributed talk

Critical behavior of magnetic materials studied with muon spectroscopyDr. ZIELIŃSKI, Piotr M.¹¹ *The Henryk Niewodniczański Institute of Nuclear Physics, Polish Academy of Sciences***Corresponding Author(s):** pm.zielinski@ifj.edu.pl

Usefulness of the muon spin research (μ SR) [1] in study of critical properties of molecule-based magnets, will be presented on the example of cyano-bridged molecular networks. μ SR spectroscopy makes use of implanted muons to probe properties of matter at the microscopic level. The implanted muons remain in a sample until the time of their natural decay. A careful analysis of the decay positrons provides information about the interaction between spins of the implanted muons and the sample.

The $[M(CN)_8]^{n-}$ complexes [2], are universal building blocks for a molecule based magnets, leading to various spatial structures, depending on the surrounding ligands and the choice of the metal ions. With these complexes many novel, functional magnetic compounds of different network dimensionality and unique physical properties have been recently developed [3]. The μ SR experimental method allows to study magnetic properties of such materials in zero applied field. Therefore it is perfectly suited to study magnetic fluctuations and spin dynamics in the vicinity of phase transition, capable to provide a set of static and dynamic critical exponents. Examples of results obtained for several molecular magnets, based on $[M(CN)_8]^{n-}$ building blocks ($M = W^V, Mo^V, Nb^{IV}$) and d -electron spin centers such as $Cu^{II}, Mn^{II}, Fe^{II}$ will be shown [4,5].

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Spectroscopy & Neutron Research / keynote lecture

Neutrons and atomistic simulations to study multiscale phenomena in molecular systems

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Neutron techniques cover many orders of magnitude in time and length scales, which can be extended even further by combining real time and space with reciprocal time and space techniques - neutrons are therefore perfectly suited to studying multiscale phenomena. Since neutrons are scattered primarily by nuclei, the data can be directly compared with atomistic simulations, in particular those based on empirical force fields, which treat electrons implicitly and cover the widest range in time and length scales. A range of examples will be shown on energy and bio-related materials to illustrate how neutrons and atomistic simulations give critical insight into multiscale phenomena in molecular systems.

Spectroscopy & Neutron Research / invited talk

Dielectric spectroscopy in bulk and at nanoscale

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Glass-forming systems are characterized by complex relaxation dynamics involving a wide range of time and length scales. Broadband Dielectric Spectroscopy (BDS) is able to study the orientational response of molecular dipoles to external electric fields, covering more than 16 decades (0.1 mHz - 1 THz) [1]. Thus it is a suitable method to study the relaxation processes in glass-forming systems since, in contrast with proper frequencies of resonant phenomena, their timescales are highly temperature-dependent, varying over 13-15 orders of magnitude between the glass temperature and the normal melting temperature. Polymers, in particular, show a rich scenario originating at short times from local motions and from side chain groups (β -type), followed by segmental (α -) cooperative relaxation related to the glass transition, and by chain motions (i.e. sub-Rouse and Rouse type) at larger time and length scales. In the present study we will show recent results on the dynamics polymeric systems (polyethers and derivatives of polylactic acids) where chain, segmental and secondary relaxations can be revealed by BDS. In particular, it can be shown that normal-mode process can be used as a “molecular ruler” to investigate the length scale of the glass transition.

The length scale over which dynamical processes are active is of paramount importance for nano-confined systems, such as ultrathin polymer films (thicknesses < 200 nm) or close to interfaces, like in polymer nanocomposites or at the free interface. When the physical dimension of a film or the spacing between nanoparticles in a composite is comparable to the characteristic length scale of a physical process, such as the characteristic length scale of relaxation processes, the related properties can be truly different with respect to the bulk behavior. A comprehension of the intriguing phenomena connected to these changes is required in order to design polymeric nanodevices. An increasing number of experimental works based on BDS have recently dealt with the influence of the substrate interactions on the properties of the polymer layers at the very interface with it [2, 3] or in extreme nano-confinement [4]. Actually, quite rare in literature are studies enabling an assessment of the dielectric relaxation properties at the nanoscale with a high spatial resolution, that is of strong interest in the study of nanostructured materials or polymer blends. To answer to this challenge, local dielectric spectroscopy (LDS) has been recently implemented [5, 6]: by measuring electric force between a polarized tip and a conducting substrate supporting a thin polymeric film, the dielectric relaxation dynamics of a small volume of material can be investigated over a size of tens nanometer, releasing the need of continuous and uniform ultrathin polymer films to avoiding short circuits between the substrate and the upper electrode. A strong effect at the interface of polymers with embedded nanoparticles will be shown, as well as a recent technical development [7], allowing LDS to span more than 7 decades.

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Spectroscopy & Neutron Research / invited talk

Using neutron techniques to explore the properties of thiophene-based polymers for organic electronics

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In this talk I will showcase how the use of neutrons is helpful to gain information on the behaviour of polythiophene-fullerene systems for organic electronic applications. I will concentrate on two areas. First, nanoscale control of the structural organisation and as a result the dynamical behaviour, is paramount to boost their performance. Quasi-elastic scattering has been used to probe the effect of fullerenes on polymer dynamics. In addition, neutron reflectivity shows that the intercalation of the fullerene molecules between the side-chains can be tuned by simply controlling the degree of self-organization of the polymer. Second, we use neutrons in a slightly different way, not by scattering but by irradiation. I will present results of the first study of the neutron radiation tolerance of two polythiophenes showing that crystallinity plays an important role.

Spectroscopy & Neutron Research / contributed talk

Experimental evidence of „dead” magnetic outer shell in nanoparticle manganites RMnO_3 (R = Pr, Nd, Tb)

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The results of magnetic measurements for the $\text{La}_{0.667}\text{Ca}_{0.333}\text{MnO}_3$ nano samples indicate an existence of not magnetically ordered outer shell [1].

In order to investigate this phenomenon magnetic and neutron diffraction measurements for RMnO_3 (R = Pr, Nd, Tb) nano manganites have been performed. The samples were obtained by a sol-gel technique and afterwards annealed at different temperatures between 800 and 900 °C. The crystal structure and the grain size were determined by the XRD method. The compounds crystallize in orthorhombic crystal structure (SG *Pnma*). Magnetic measurements were performed with the use of VSM and ACMS options of the Quantum Design PPMS platform. The neutron diffractograms were obtained in temperature range 1.5 – 50 K using the E6 diffractometer installed at the BERII reactor. Ac magnetic data indicate spin glass properties for the RMnO_3 (R = Pr, Nd) nano samples. Neutron diffraction data confirm spin glass properties for the PrMnO_3 sample annealed at 800 °C while for those annealed at 850 and 900 °C as well as for Nd samples a magnetic order, similar to that observed in poly-samples, is observed with lower values of the magnetic moments.

The dc magnetic data for TbMnO_3 indicate that the Néel temperatures for nanosamples (7.1 – 7.4 K) are lower than that of poly sample (9.2 K). Neutron diffraction data for nanosamples indicate that the peaks of magnetic origin of are broad and the determined values of magnetic moments are lower than the one found for the poly sample.

A thickness (t) of nonmagnetic shell may be determined from the formula $t = 1/2d[1 - (\mu_n/\mu_p)^{1/3}]$ where d is a grain size while μ_n and μ_p refer to magnetic moment in nano and poly samples, respectively.

Presented results are in good agreement with those presented in Ref. [1]. The values of thickness t found from magnetization and neutron diffraction data indicate that the external magnetic field causes a decrease of magnetically dead layer.

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Structure Research / invited talk

Organic solid state: accounts of co-crystals and of plastic crystal mesophases

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The investigation of solid forms of organic compounds and its structural characterization is an area of active research. It is particularly relevant in what concerns active pharmaceutical ingredients [1, 2], but also in all other domains where differences in the solid-state form may impact the material properties [3, 4]. Polymorphs of the pure compound, solvates, salts, co-crystals and their polymorphs, are different types of solid forms of organic compounds that may be considered, which may have different physicochemical properties. Nevertheless, the design and reproducible preparation of particular solid forms is far to be predictable and each compound represents a new challenge. From the combined efforts of the scientific community, contributions to understand and, if possible, to control the solid state chemistry of a target compound may be expected.

This communication will focus on two aspects of the research on the solid state of organic compounds that is been carried out in our laboratory. Results will be presented on the investigation of co-crystals, including some that exhibit liquid crystalline mesophases. The second topic to be addressed, concerns an investigation on the polymorphism of cyclohexanediol derivatives and on their different ability to give rise to plastic crystal mesophases.

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Structure Research / invited talk**Multiscale structure in amorphous carbohydrate matrices in relation to phase behavior, molecular packing and interaction with water****Author(s):** Prof. UBBINK, Job¹**Co-author(s):** Dr. TEDESCHI, Concetta² ; Dr. LEUENBERGER, Bruno² ; Dr. BADOLATO, Gabriela² ; Dr. MARTINI, Francesca³ ; Dr. GEPPI, Marco³ ; Prof. ALAM, Ashraf⁴ ; Dr. HUGHES, David⁴¹ *California Polytechnic State University*² *DSM Nutritional Products AG, Research Center Formulation & Application, P.O. Box 2676, 4002 Basel, Switzerland*³ *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, Italy*⁴ *H. H. Wills Physics Laboratory, University of Bristol, Tyndall Avenue, Bristol, BS8 1TL, UK***Corresponding Author(s):** job.ubbink@themill.ch

Glassy matrices for the encapsulation and stabilization of bioactive compounds often consist of molecularly miscible blends of a carbohydrate of higher molecular weight and a low molecular weight carbohydrate or polyol. Typical examples of such blends are maltodextrin/sucrose and trehalose/glycerol. The optimization of the barrier properties of such matrices depends in a subtle way on the balance between the plasticization and antiplasticization of the high molecular weight carbohydrate by the low molecular weight compound [1]. Here, we report on the phase behavior of encapsulation matrices consisting of blends of a hydrophobically-modified starch and sucrose. By differential scanning calorimetry (DSC), it is shown that the blends exhibit two glass transitions, with the specific heat and the temperatures of the transitions varying in a systematic way with the blend composition [2]. This hints at a limited degree of phase separation of the matrix into two amorphous phases. We present a model to calculate the degree of phase separation of the blends and the composition of the phases from the dependence of the glass transition temperatures of the blends on the sucrose content. The antiplasticization of the starch-rich phase by sucrose is confirmed by the decrease in molecular hole size with increasing sucrose content as determined by positron annihilation lifetime spectroscopy (PALS) [3] and the stiffening of the starch chains solid state NMR by the addition of sucrose to the matrix. We conclude the lecture by discussing the advantages and disadvantages of the two-phase system for its use in encapsulation systems.

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Structure Research / invited talk

Polymorphism and isomerism in coordination compounds: The nemesis of crystal design

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Investigations on the development of strategies for a more rational synthesis of new materials with desired physical properties is still a major field in modern chemistry. This approach, called “crystal engineering”, includes systematic investigations on the structure property relationships of compounds as well as ideas how a given structure can specifically be prepared. In this context, coordination compounds are of special importance, because based on simple considerations concerning the nature of the metal cations and the coordination properties of the ligands, their coordination networks can be predefined to some extent. This is of extraordinary importance, because if one have control over the structure one have also no control over the properties of the compounds. Following these ideas, an increasing number of new coordination compounds with interesting physical properties were recently reported.

However, for any further application or for any characterization of the properties of a material, large and pure amounts are required, which even for coordination compounds is sometimes difficult to achieve. In most cases their synthesis is performed in solution where different species will be in equilibria and therefore, crystallization can lead to mixtures of different compounds, which also will include polymorphic modifications or isomers. Moreover, several of such compounds or modifications will be thermodynamically metastable and thus, can be easily overlooked if the synthesis conditions are not investigated in detail. Finally, because the energy differences between different modifications are usually very small, structure prediction is frequently more difficult than expected and any conclusion on the stability of a compound only on the basis of structural parameters should not be drawn.

This lecture will give a brief introduction into this topic, which includes some basics on the thermodynamic and kinetic aspects of polymorphism and the transition behaviour of polymorphic modifications. Several examples are shown, where different metastable compounds, isomers or polymorphic modifications of “simple” coordination compounds were synthesized, which indicates that this is a widespread phenomenon.¹⁻⁶ It is shown how metastable coordination compounds can be obtained by, e.g., kinetic control or by thermal decomposition of suitable precursor compounds, where sometimes some structural relationships are observed between the structure of the precursor and that of the final product. In a few cases, the reactivity of such compounds can also be influenced by mixed crystal formation of compounds that exhibits a different crystal structure. Unfortunately, because coordination compounds and polymers do not melt and usually decompose before they transform into a different modification, the experimental possibilities for their investigations are limited. Nevertheless, some examples will be presented that show how to prove which of the different forms are thermodynamically stable or metastable at a given temperature and how these forms can be transformed into each other. However, even if all these phenomena can limit a “structure design” they also can be useful for the investigation of structure property relationships. In the case where the chemical composition is identical, all changes in the physical properties can directly be correlated with the different arrangement of the building blocks in the crystal, with the different connectivity of the coordination networks or with the different coordination at the metal centre. Representative examples supporting these facts will be also given.

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Structure Research / contributed talk

Positron annihilation in smectic E phase of 4 - alkyl - 4 - isothiocyanatobiphenyl (6TCB)

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Positron annihilation lifetime spectroscopy (PALS) has been employed for characterization of the local structure in molecular substances such as polymers or liquid crystals. When a positron enters an insulator solid it can form a bound state with an electron called positronium (Ps). Ps is located in low electron density regions like local free volume holes. Ps can be formed in two spin states: para-Ps (*p*-Ps) and ortho-Ps (*o*-Ps) due to possible positron and electron spin alignment, i.e., antiparallel and parallel, respectively. In vacuum, the self-annihilation lifetime of *o*-Ps is 142 ns and it decays into three quanta while the *p*-Ps lifetime is much shorter, i.e., 125 ps with decay into two quanta. The relative abundance of these two spin states is 1:3. In molecular solids, due its to relatively long lifetime, *o*-Ps interacts with the electrons of surrounding molecules. Its lifetime is determined mainly by the annihilations of the positron with one of these external electrons. This process is called *pick-off* annihilation. It causes shortening of the *o*-Ps lifetime to several nanoseconds. The lifetime of *o*-Ps annihilating in the pick-off process is connected to the free volume hole radius and it is a basis of broadly understood positron porosimetry.

In case of liquid crystals not only local microstructure but also molecular dynamics can influence the Ps lifetime as it was demonstrated in our studies of supercooled smectic E (SmE) phase of 4TCB [1,2]. The obtained value of *o*-Ps for 4TCB can be explained by formation of Ps bubbles due to a liquid-like state of the butyl chains molecules in the SmE phase and the lamellar structure with nano-segregation of alkyl chains and other parts of molecules proposed by Saito et al. [3].

The present studies were performed for the other member of the nTCB homologous series, i.e. 6TCB. The obtained temperature dependencies of the *o*-Ps lifetime and its intensity for the supercooled SmE phase indicate two processes taking place during heating of the sample. Softening of the glass phase and cold crystallization occurring simultaneously cannot be resolved in positron lifetime measurements as it was in the case of 4TCB thanks to difficult and lengthy crystallization of the latter. The proposed explanation of the obtained dependencies may shed light on the results of previous positron lifetime studies of supercooled liquid crystals reported in the literature.

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Structure Research / contributed talk

Physical properties and phase transitions of 3FmH-PhF

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Liquid crystalline compounds belonging to 3FmHPhF homologous series ($m = 2, 4, 5, 6, 7$) have been studied by complementary methods such as differential scanning calorimetry (DSC), polarizing optical microscopy (POM), electrooptic methods, frequency domain dielectric spectroscopy (FDDS) and X-ray diffraction (XRD). All studied compounds exhibit ferroelectric smectic C* and antiferroelectric smectic C_A* phases, therefore they are interesting from application point of view in liquid crystal displays (LCDs). Additionally, paraelectric smectic A phase is present in homologues with $m = 5, 6, 7$ [1].

DSC measurements with different heating/cooling rates were performed to obtain temperatures and enthalpy changes related to the phase transitions. Electrooptic methods based on POM allowed to measure the temperature dependence of spontaneous polarization, switching time and optical tilt angle, while FDDS measurements gave information about the relaxation times and activation energies of the processes existing in the smectic phases. Relaxation processes in the SmA, SmC* and SmC_A* phases were interpreted based on the results obtained by fitting the Cole-Cole equation to the experimental data.

XRD patterns were used to determine the values of structural parameters characterizing the studied compounds, namely the average distance between the molecules and the correlation length of the short-range order within the smectic layers, the layer thickness and the value of geometrical tilt angle (the latter incorporates the results of molecular modelling in HyperChem). The maximum values of an optical tilt angle in all compounds are close to 45° which means that they are orthoconic antiferroelectric liquid crystals (OAFLCs) – very perspective materials for display applications. The discrepancy between optical and geometrical tilt angle has been explained.

Two lower homologues ($m = 2, 4$) crystallize during cooling while compounds with $m = 5, 6, 7$ undergo a glass transition and their cold crystallization is visible during heating. The Vogel-Fulcher-Tammann equation has been fitted to FDDS results of α dielectric relaxation times related to a glass transition and a fragility parameter was calculated from FDDS and DSC results. The connection between short range order in smectic layers and the glass transition is discussed as well.

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Molecular Magnets & Conductors / keynote lecture

Probing temperature changes in magnetocaloric molecular matter

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Many molecular materials have been proposed for low-temperature magnetic refrigeration, due to the high magnetic degeneracies that can be built in by the appropriate choice of the metal ion and a favourable exchange coupling scheme. Almost all these studies have relied on calculating the magnetocaloric effect (MCE) from magnetization and/or heat capacity experimental data, which are analysed to predict some maximum magnetic entropy change for a maximum field change. Such indirect measurements of the MCE can give impressive headline figures but are blind to the structure and true beauty of the isentropes that are a function of the magnetic interactions. Recently, we have developed an experimental method to measure directly the MCE by following the temperature evolution induced by continuous field variations over magnetization-demagnetization cycles under controlled quasiadiabatic conditions, down to sub-Kelvin temperatures [1,2,3]. Our results show that it is possible to design the cooling properties of molecular materials by choosing an appropriate topology of magnetic couplings between the interacting spins, hence exploiting the great control of the latter given by molecular coordination chemistry.

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Molecular Magnets & Conductors / invited talk**Interplay of spin and spatial anisotropy in quasi-two-dimensional quantum magnets****Author(s):** Dr. ORENDÁČOVÁ, Alžbeta¹**Co-author(s):** Ms. LEDEROVÁ, Lívia¹; Dr. CHOVAN, Jaroslav²; Dr. STREČKA, Jozef¹; Dr. TARASENKO, Robert¹; Dr. LEGUT, Dominik³; Dr. ČÍŽMÁR, Erik¹; Prof. ORENDÁČ, Martin¹; Prof. FEHER, Alexander¹¹ *P. J. Šafárik University, Košice, Slovakia*² *M. Bel University, B. Bystrica, Slovakia*³ *Technical University of Ostrava, Ostrava, Czech Rep.***Corresponding Author(s):** alzbeta.orendacova@upjs.sk

The model of a spin 1/2 Heisenberg antiferromagnet (HAF) on the square lattice with nearest-neighbor coupling, J , represents an important paradigm of a two-dimensional (2D) magnetism. It represents a limiting case of more complicated 2D systems with the spatial anisotropy, R . The simplest example is a model of a rectangular lattice comprising of a 2D array of chains coupled by the inter-chain coupling J' . While the properties of the spatially isotropic square lattice ($R = J'/J = 1$) have been intensively investigated, the aforementioned spatially anisotropic analog with $R < 1$ has not received so much attention. The lack of corresponding theoretical predictions and difficulties with preparation of such materials did not allow finding proper experimental realizations of the HAF square lattice with $R < 1$.

Our work is focused at the theoretical and experimental investigation of spin and exchange anisotropy in $\text{Cu(en)SO}_4(\text{H}_2\text{O})_2$ (CUEN). This quasi-2D quantum magnet with spin 1/2 was previously identified as a representative of a spin 1/2 HAF on the spatially anisotropic triangular lattice with the Neel ground state [1]. First-principle calculations of exchange interactions in CUEN revealed that the system can be treated as a 2D array of zig-zag chains forming a zig-zag square lattice. To confirm this expectation, using quantum Monte Carlo (QMC) simulations, the behavior of the model at finite temperatures was investigated. In parallel, single-crystal experimental studies were performed involving specific heat, susceptibility and magnetization measurements. The analysis of the data revealed excellent agreement with the QMC predictions; the 2D correlations in CUEN approximate those of spin HAF zig-zag square lattice with $R = 0.35$. While a spin anisotropy of the order $10^{-3}J$ has a negligible effect on the finite-temperature properties of 2D lattice, the onset of long-range order set at 0.93 K is highly sensitive to the presence of the weak spin anisotropy. A symmetry constraints within the magnetic layer expected only symmetric exchange anisotropy with an easy-axis breaking symmetry within the easy plane. Correspondingly, a spin flop (SF) within the easy plane should occur in the field applied along the easy axis. The expectation was confirmed by magnetization studies at 0.5 K which revealed the SF in the field 200 mT. It was shown that sufficiently strong magnetic field can overcome the intrinsic spin anisotropy and the field can introduce an easy-plane anisotropy with the easy plane perpendicular to the magnetic field direction. Finally, the magnetic phase transitions in the applied field show universal behavior independent of the field orientation, mimicking the scenario of the field-induced Berezinskii-Kosterlitz-Thouless phase transition [2].

Acknowledgments

Projects VEGA 1/0269/17, DS-2016-0046, APVV-14-0078 and APVV-14-0073 are acknowledged.

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Molecular Magnets & Conductors / invited talk

Spatiotemporal observation and modelling of temperature scan rate effects on the thermal hysteresis and the dynamics of interface propagation in a spin-crossover single crystal

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The direct observation by optical microscopy of the thermally-induced spin transition [1] and the subsequent low-spin high-spin interface propagation inside the thermal hysteresis is a fascinating problem. The kinetic aspects of the spin crossover (SCO) transition investigated under various scan rates was studied so far on powder sample which then average the kinetic effects of the thermal hysteresis. This problem is studied here on the robust spin-crossover single crystal $[\{\text{Fe}(\text{NCSe})(\text{py})_2\}_2(\text{m-bpypz})]$ for which we followed the dynamics of the thermal hysteresis at several controlled temperature scan rates [2]. In addition to the expected shifts of the switching temperatures, sizable change in the velocity of the high-spin (HS) low-spin (LS) interface dynamics are observed for the first time. Theoretical developments based on a spatiotemporal description of the SCO phenomenon using reaction diffusion equations including the heat balance between the crystal and its immediate environment. We identified the competition between the heat transfer between the crystal and the thermal bath with the temperature scan rate kinetics as key parameter governing the interface velocity, at the origin of the kinetic features of the hysteresis. The experimental data are modelled using a reaction diffusion equation allowing to fairly reproduce the essential features of the spatiotemporal properties of the spin transition.

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Molecular Magnets & Conductors / contributed talk

Ferromagnetism in two-dimensional Mott insulating compounds with strong electron correlations**Author(s):** Prof. NAKAZAWA, Yasuhiro¹**Co-author(s):** Mr. YOSHIMOTO, Ryo¹; Dr. YAMASHITA, Satoshi¹; Dr. AKUTSU, Hiroki¹; Dr. KUSAMOTO, Tetsuro²; Prof. YAMAMOTO, Hiroshi M.³; Prof. KATO, Reizo⁴¹ *Dept. of Chem., Graduate School of Science, Osaka University*² *Dept. of Chem., Graduate School of Science, the Univ. of Tokyo*³ *Institute for Molecular Science*⁴ *Condensed Molecular Materials Lab. RIKEN***Corresponding Author(s):** y.naka.thermo@gmail.com

The Mott insulating state of organic charge transfer complexes with layered structures usually has strong antiferromagnetic interactions in two dimensional characters. They induce various novel electronic phases such as unconventional superconductivity, spin liquids, and anomalous conductivities in π -electrons. It is well understood that not only spins but also charge and lattice degrees of freedom are coupled to each other and therefore organic π -electrons systems give interesting crossover or quantum mechanical proximity at low temperature region. As a further variation of molecule-based Mott-insulating state, we focused on the multi-layers dimer-Mott system, in which the counter ions have dipole-moments and aligned in one direction to form net-polarization to the organic donor/acceptor layers. Depending on the direction and magnitude of the net polarization, different molecular packing and physical properties appears in alternative layers. We report systematic experimental results of low-temperature heat capacity measurements as well as the magnetization, and transport measurements for the multi-layer dimer-Mott compounds of $X[\text{Ni}(\text{dmit})_2]_2$ ($X = \text{ethyl-4-bromothiazolium (Et-4BrT)}$, $\text{ethyl-2-iodo-5-bromopyridinium (Et-2I-5BrP)}$, and $\text{ethyl-2-iodo-5-bromopyridinium (Et-2,5-DBrP)}$), where dmit is 1,3-dithiole-2-thione-4,5-dithiolate. The order of the magnitude of net polarization was evaluated as $\text{Et-4BrT} > \text{Et-2I-5BrP} > \text{Et-2,5-DBrP}$ in them.

We succeeded to detected distinct peak structures in the temperature dependences of heat capacity which are in association with long-range ordering of π -electron spins around 1 K. The large transition entropy of 20-40% of $R \ln 2$ in these compounds is suggesting that long-range ordering occurs in bulk feature. From the heat capacity measurements under magnetic fields, we observed an upward shift of the peak structure in $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$, which indicates that the ferromagnetic behavior occurs as a bulk feature. $(\text{Et-2I-5BrP})[\text{Ni}(\text{dmit})_2]_2$ and $(\text{Et-2,5-DBrP})[\text{Ni}(\text{dmit})_2]_2$ showed small magnetic field dependence which indicates paramagnetic like and anti-ferromagnetic behavior, respectively. The variation of the magnetic states can be understood as a kind of doping between layers. Furthermore, we detected that the application of pressure up to 1.0 GPa for $(\text{Et-4BrT})[\text{Ni}(\text{dmit})_2]_2$, the ground state changes to metallic state where the electronic heat capacity coefficient γ is nearly 2-3 times rather than usual metallic compound. The ferromagnetic fluctuations in the metallic states are expected in these multi-layer compounds. Systematic variation of the magnetic and conductive states will be discussed.

Computational Physics / invited talk

Electrochemical reduction of NO on Pt(100): a combined DFT and KMC study

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Electrocatalytic denitrification is a promising technology for the removal of NO_x species in groundwater. However, a lack of understanding of molecular reaction pathways that control the overpotential and product distribution have limited the advancement of NO chemistry to the same level of well-understood electrocatalytic processes like oxygen reduction reaction. Nitrate and nitrite electroreduction can produce a variety of different products but adsorbed NO has been considered a selectivity-determining species in the process. Experimentally, NO electroreduction has been studied under a variety of reaction conditions and the reaction demonstrates a rich chemistry with several possible reaction steps and intermediates. Thermodynamically, N₂ is the most favorable product but other products such as NH₄⁺ and N₂O are usually observed. Cyclic voltammetry experiments on Pt(100) demonstrate that NH₄⁺ is the only product in acid electrolyte and the onset potential of the reaction is 0.25 VSHE. Furthermore, NO reduction was proposed to proceed via the HNO intermediate together with the facile formation of ammonia after chemical N-O dissociation.

The DFT calculations were performed with the VASP code to address the thermodynamic and kinetic aspects for various possible elementary steps of NO electrochemical conversion to ammonia, nitrogen gas, and nitrous oxide both at low and saturated NO coverage on Pt(100). DFT results suggest that at low coverage a HNO intermediate dominates, while at experimentally observed NO coverages there is a significant thermodynamic and kinetic competition between two pathways proceeding either via NOH or HNO intermediates. Our kMC program employs the first reaction algorithm⁴ together with periodic boundary conditions, and takes the needed input parameters, which are reaction barriers and equilibrium constants for included elementary steps, directly from DFT calculations. Furthermore, we permit the formation of other products than NH₄⁺ in kMC but they were not observed during simulations. The potential-dependent kinetic Monte Carlo calculations were performed to simulate NO stripping experiments. We demonstrate how these profiles change as a function of the initial NO coverage dosed on Pt(100) and the calculated electrochemical NO stripping curve agrees well the measured one. Furthermore, simulations provide a mechanistic interpretation for observed peaks: high voltage results from NOH formation and conversion in simulations and the second peak originates from the coverage-dependent activation energy for NOH formation. Based on the large number of analyzed reaction pathways from kMC simulations and the calculated Tafel slope, we are able to identify a reaction mechanism, which consists of two consecutive proton electron steps which takes place after the initial NO adsorption. Along the most probable reaction pathway, NOH protonates to HNOH, which undergoes a combined dissociation and protonation step forming NH and water. Finally, NH transfers to NH₃, which spontaneously forms NH₄⁺.

To conclude, the synergic DFT+kMC strategy provides detailed microscopic information to future development of denitrification technologies and it also offers a template to investigate and analyze other electrochemical transformations.

The reduction of NO has been identified as a key step in the electrochemical denitrification of nitrites and nitrates. We combine density functional theory calculations and kinetic Monte Carlo simulations to study the reduction reaction on Pt(100). This approach

describes the effects of coverage-dependent adsorbate-adsorbate interaction, reaction thermodynamics, water-mediated protonation kinetics, and transient potential sweeps on product rates and selectivities. We are able to predict electrochemical NO stripping curves in nice agreement with experiments and provide an elementary mechanistic interpretation of observed current peaks. The combined methodology provides a full reaction profile and reveals the sensitive balance between thermodynamics and kinetics in NO reduction. However, the computational approach is sufficiently general to be applicable to other electrocatalytic processes on metal catalysts that are technologically and environmentally important.

Computational Physics / invited talk

Challenges in the modelling of oxides

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Oxides are active materials for multiple applications including catalysis and particularly for energy purposes. However, many properties are still not fully understood and fundamental questions regarding the structure are far from being known. In the present talk, I will give a description of key structural issues that might affect the properties of these materials. Oxides constitute a class of active catalytic materials in chemical transformations some of them aimed at providing new energy vectors. Even the most fundamental questions regarding the nature, stoichiometry and structure of the surface of some oxide are intriguing. For ceria, a material widely employed as catalytic support, we have found that the termination of open, polar surfaces will be completely controlled by configurational entropy. This observation opens a wide new concept in the way we understand the properties of this class of materials.

Computational Physics / invited talk

Spin transition of Fe(II) 1D triazole chains: hybrid materials and lattice dynamics

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Iron(II) spin crossover (SCO) complexes continue to attract a great deal of interest [1,2], due to their potential technological applications, for instance in pressure sensors [3]. SCO nanomaterials have emerged as an appealing class of materials considering nanostructuring processes and size reduction effects. Although sophisticated techniques can be used for the preparation of SCO nanoparticles, we have introduced a botanic biomembrane as a soft and green support for deposition of SCO micro and nanocrystals, which were used for printing on various supports [4]. More recently, we investigated the SCO properties of a hybrid nanomaterial [5], based on a metal organic framework embedding $[\text{Fe}(\text{HB}(\text{pz})_3)_2]$. We have also studied the composite material made of MCM-41 and 1D Fe(II) 1,2,4-triazole coordination polymers [6]. This later class of SCO materials, which were shown to present the LIESST effect [2,7], afforded the first 1D chain with 1,2,4-triazole ligands displaying a thermally induced two-step spin conversion [8]. A non solvated 1D SCO chain switching at room temperature with a wide reversible bistability domain of 60 K, has been recently discovered [9].

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Computational Physics / invited talk

Structural phase transition in KFe_2As_2 from ab initio calculations

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KFe_2As_2 belonging to the most investigated family of iron-based superconductors, AFe_2As_2 (A = alkali metal or alkali earth metal) is the first self-doped iron pnictide compound that does not need chemical substitutions or imposing of pressure to superconduct. However, the superconducting transition temperature, 3.8 K, is rather low [1]. It rises with partial substitution of Sr or Ba atoms for K atoms to 37 K [1] or 38 K [2], respectively. In contrast to other AFe_2As_2 (A=Ca,Ba,Eu,Sr) compounds that exhibit a structural phase transition from a high-temperature tetragonal to a low-temperature orthorhombic phase, followed by an antiferromagnetic spin density-wave transition the crystal structure of KFe_2As_2 remains tetragonal down to lowest temperatures. Also, no magnetic order develops in that material. Under pressure, the tetragonal phase transforms to the collapsed tetragonal (cT) phase with the same symmetry but with strong and extremely anisotropic changes of the lattice parameters [3]. The cT phase of KFe_2As_2 is superconducting with $T_c=12$ K.

To obtain a deeper insight in the mechanism of the phase transition in KFe_2As_2 the structural, electronic and dynamical (phonon) properties of the crystal under pressure have been studied using the first-principles calculations. The crystal structure optimization under various pressures were performed using the projector augmented-wave formalism of the Kohn-Sham density functional theory (DFT) within the generalized gradient approximation (GGA) approach in PAW-PBE form, implemented in the Vienna ab initio simulation package (VASP). It has been shown that the source of this transformation is the formation of the As-As bonds between initially non-bonded As-As atoms caused by the overlap of $4p_z$ orbitals being a result of imposed pressure.

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Computational Physics / invited talk

Hydrogen in AB₂ and AB₅ compounds

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Hydrogen is seen as one of the important energy carriers of this century and is indicated as a fuel of future. Research problem of physical properties of metal hydrides is strongly connected with very actual topical issues of the hydrogen storage. Especially interesting and promising are hydrides of intermetallic compounds. Among widely studied RT₂H_x systems (R a rare earth or alkaline metal, T – transition metal like Fe, Co, Ni and Mn), the hydrides RMn₂H_x present very interesting physical properties. It comes from the fact that already alone RT₂ compounds exhibit a complex interaction of two sublattices: the R- and 3d-metal sublattice. The first one can be described with the localized 4f magnetic moments, while the other is regarded as essentially an itinerant electron system. The RMn₂ compounds can absorb very easily large amount of hydrogen, which locates inside of characteristic tetrahedrons build of R and Mn atoms. The systematic investigation (XRD, ND and magnetic measurements) of the RMn₂H_x hydrides with R = Y, Nd, Sm, Gd, Tb, Dy, Ho and Er allowed to observe the role of rare earth metal in hydrogen induced structural and magnetic transformations. Hydrogen absorption in RMn₂ compounds leads to magnetic and structural changes: an increase of the magnetic ordering temperature – from below 100 K up to (200 ÷ 400) K depending on the hydrogen concentration, structure transformations and an increase of the cell volume (even up to 30 %). The role of the host structures (Laves phases of the C14 and C15 type) in formation of hydrides and their magnetic properties is presented – on the base of obtained results the universal structural phase diagram model of RMn₂H_x is proposed. It is shown that all the RMn₂H_x hydrides in magnetic ordering state are ferrimagnetic and their total magnetization strongly depends on hydrogen concentration. A modified model describing the changes of unit-cell volume as a function of the hydrogen concentration is proposed. The AB₅ compounds (the most famous representative is LaNi₅) also easily absorb hydrogen. In comparison to AB₂ the AB₅ absorb and desorb hydrogen at “ambient” temperature and pressure. It is strongly important when we have biohydrogen from bioreactors available. It turns out that small admixtures of selected elements can significantly change the thermodynamic parameters of the host LaNi₅ compound, which is important for the design of hydrogen storage facilities. The last results of *pcT* (pressure-concentration-temperature) investigations for LaNi₅X will be presented as well.

Acknowledgements

The presented results were partly funded by the project BIOSTRATEG2/297310/13/NCBR/2016.

Multifunctional Materials II / invited talk

Spin-crossover phenomena of a Jahn-Teller active Mn(III) complex [Mn(taa)]Prof. NAKANO, Motohiro¹¹ *Osaka University***Corresponding Author(s):** moto@chem.sci.osaka-u.ac.jp

The octahedral manganese(III) complex, [Mn^{III}(taa)] (H₃taa = tris(1-(2-azolyl)-2-azabuten-4-yl)amine), has long been known as a rare example of (3d)⁴ spin-crossover system, having a steep spin-crossover phase transition at $T_c = 48$ K between a high-spin ⁵E_g and a low-spin ³T_{2g} states [1, 2]. Since the high-spin state is obviously subject to the Jahn-Teller effect, the electronic states are coupled with lower-symmetry deformation modes lifting ⁵E_g orbital degeneracy in addition to a symmetrical breathing mode responsible for the spin crossover. This simultaneous involvement of two molecular bistabilities may afford a variety of condensed states (phases) due to competitive or cooperative interactions [3]. The phase diagram and the phase transition behavior were thoroughly explored via several probes, including dielectric measurements [4], magnetization under pulsed high field [5], HF-EPR [6], and magnetic susceptibility measurements using high-pressure clamp cell [7]. All the results were successfully interpreted in a unified fashion based on a four-state Ising-Potts model with mean-field approximation.

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Multifunctional Materials II / invited talk

Functionalization of cyanido-bridged clusters by ligand decoration and metal ion embedment**Author(s):** Dr. PODGAJNY, Robert¹; Dr. CHORAZY, Szymon¹**Co-author(s):** Prof. STANEK, Jan. Józef²; Dr. RAMS, Michał²; Dr. MAJCHER, Anna²; Mr. KOBYLARCZYK, Jędrzej¹; Prof. OHKOSHI, Shin-ichi³; Prof. SIEKLUCKA, Barbara¹¹ Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Kraków, Poland² Institute of Physics, Jagiellonian University, Łojasiewicza 11, 30-348 Kraków, Poland³ Department of Chemistry, School of Science, The University of Tokyo**Corresponding Author(s):** robert.podgajny@uj.edu.pl

Cyanido-bridged clusters serve as convenient coordination platforms for switchable materials, to mention single-molecular magnets (SMMs) or spin-crossover (SCO) systems and charge-transfer induced spin transitions (CTIST) systems combined with light induced excited spin state trapping (LIESST). Their functional potential can be strengthened by decoration of external complexes using chiral or luminescent features as well as by chemical or physical tuning [1].

In this contribution we present two structural strategies towards tunable functionality in cyanide-bridged clusters $M_9^{\text{II}}[M^{\text{V}}(\text{CN})_8]_6L_x$ (M = divalent metal ion; $M' = \text{W, Re}$; L = blocking or bridging organic ligands). Firstly, various metal ions combinations lead to diversity of spin carriers distribution and related function schemes along the bimetallic or even trimetallic cluster skeletons. Secondly, a variety of ligand sets can be coordinated at the surface of selected cluster. As a result, we obtain different magnetic behavior: from diamagnetic or weakly paramagnetic species towards high spin cluster, SMM clusters as well as dynamic networks hosting electron transfer (ET) and/or spin-structure SCO phase transition [2]. As the added value, we take opportunity to discuss also: (i) the intriguing composition-structure correlations due to the site preference along the coordination skeleton and (ii) possible routes towards structure-properties extension via anchoring of additional functional units due to coordination preference of bimodal ligands.

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Multifunctional Materials II / contributed talk

Ln(III) Complexes as Single-Ion Magnets that light can disturb**Author(s):** Prof. RAMOS SILVA, Manuela¹**Co-author(s):** Ms. SUSANO, Maria¹ ; Mr. RYBUSINSKI, Jaroslaw³ ; Prof. MARTÍN-RAMOS, Pablo⁴ ; Ms. GARDIAS, Anita³ ; Prof. SZCZYTKO, Jacek³ ; Prof. MARTÍN-GIL, Jesús⁵ ; Dr. LAHOZ, Fernando⁶ ; Dr. LAVÍN, Victor⁶ ; Prof. EUSÉBIO, Ermelinda¹ ; Dr. PEREIRA, Laura⁷ ; Dr. INOCENCIO, Martin⁶¹ *University of Coimbra*³ *University of Warsaw*⁴ *University of Zaragoza*⁵ *University of Valladolid*⁶ *University of La Laguna*⁷ *Instituto Superior Técnico***Corresponding Author(s):** manuela@uc.pt

Mononuclear lanthanide complexes, that behave as Single-Ion Magnets (SIMs) have only been studied in the last 15 years (the interest was triggered by the work of Ishikawa on terbium phthalocyaninate in 2003). In these complexes, in which the Ln(III) ion is surrounded by organic ligands in a low symmetry environment, the crystal-field splitting of the J ground state of the lanthanide ion gives several ground-multiplet sublevels where the lowest twofold degenerate sublevel may have a large $|J_z|$ value. If quantum tunnelling is inhibited, it is believed that the transition among the twofold degenerate crystal-field ground-states, $|J, J_z = \pm J\rangle$, corresponding to “spin up” and “spin down” can be made through the second-lowest sublevels, but because the energy gap is so large (up to several hundreds of reciprocal centimetres), the transition has to be very slow. Therefore, long magnetic relaxation times and magnetization hysteresis loops can be observed. Also, these compounds are luminescent with characteristic narrow-line emissions, mostly in the visible and near infrared (NIR) range, when the excitation is mediated through the ligands using UV-to-visible light. Electro-luminescence can also be observed. We herein report the results of the study of a large family of Ln(III) compounds, mainly with Er(III), using a variety of techniques like single crystal, powder X-ray diffraction, FTIR and NMR spectroscopy, DSC and thermomicroscopy. Results of the luminescent properties measurements, like absorption, emission, excitation and decay times, including confirmation of the ligand-to-lanthanide energy transfer will be presented. The temperature dependence of the magnetic susceptibility in the range 4-300K, confirming the single-lanthanide-ion behaviour, will be discussed. Magnetisation curves measured with illumination will be presented and compared to those obtained in the dark.

Multifunctional Materials II / contributed talk

Static and dynamic magnetic properties of the ferromagnetic quasi 1D Ising system $[\text{Co}(\text{NCS})_2\text{pyridine}]_n$ **Author(s):** Dr. TOMKOWICZ, Zbigniew¹**Co-author(s):** Dr. RAMS, Michal¹ ; Prof. KATAEV, Vladislav² ; Dr. KRUPSKAYA, Yulia² ; Dr. BÖHME, Michael³ ; Prof. PLASS, Winfried³ ; Prof. NÄTHER, Christian⁴¹ *Jagiellonian University, Institute of Physics*² *Institute for Solid State Physics, IFW Dresden, Helmholtzstrasse 20, D-01069 Dresden, Germany*³ *Institut für Anorganische und Analytische Chemie, Friedrich-Schiller Universität Jena, Humboldtstr. 8, 07743 Jena, Germany*⁴ *Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth-Straße 2, 24118 Kiel, Germany***Corresponding Author(s):** z.tomkowicz@uj.edu.pl

$[\text{Co}(\text{NCS})_2\text{py}_2]_n$ (py – pyridine) is composed of irregular ferromagnetic chains of Co(II) ions linked by the double NCS bridges. The coordination polyhedron of the Co(II) ion is a distorted octahedron built from equatorial two N and two S and two apical N atoms of the pyridine ligands. There are two inequivalent Co(II) ions which are magnetically coupled along chains in the $J_1J_1J_2$ sequence and the pyridine rings show an orientation disorder. Specific heat and magnetic study showed that $[\text{Co}(\text{NCS})_2\text{py}_2]_n$ undergoes a phase transition to the ferromagnetic state at the Curie point of 3.7 K. Magnetic interactions have been determined on the base of the Ising model. By means of AC magnetic susceptibility measurements the magnetic relaxations were investigated. Using High Field-High Frequency ESR (HF-ESR) method the magnetic excitations were observed and explained in the frame of the Ising model in full accordance with magnetic studies. Energy barriers for magnetization reversal obtained from magnetic and HF-ESR measurements are compared and discussed.

Acknowledgments

This project was supported by the Deutsche Forschungsgemeinschaft (Project No. Na 720/5-1) and the State of Schleswig-Holstein. We thank Prof. Dr. Wolfgang Bensch for the access to his experimental facilities. ZT thanks the National Science Centre Poland for financial support granted under decision DEC-2013/11/B/ST3/03799. We thank the URZ of the FSU Jena for providing additional computational resources.

Multifunctional Materials II / contributed talk

Study of water sorption into magnetic coordination networks**Author(s):** Dr. NOWICKA, Beata¹**Co-author(s):** Dr. MAKOWSKI, Waclaw ¹ ; Mr. RECZYŃSKI, Mateusz ¹ ; Prof. SIEKLUCKA, Barbara ¹¹ *Jagiellonian University***Corresponding Author(s):** beata.nowicka@uj.edu.pl

The possibility of inducing structural and magnetic changes by sorption of guest molecules is one of the important aspects of molecular magnetic materials that make them different from classical magnets based on metal alloys or oxides. This so called solvatomagnetic effect may find potential application in the design of molecular switches or sensors. It also provides valuable insight into the relation between magnetic superexchange and subtle structural features, like bonding geometry and supramolecular interactions. Within the scope of our research, focused on magnetic CN-bridged bimetallic assemblies, we have developed an efficient synthetic strategy leading to structurally flexible networks and obtained a series of solvatomagnetic compounds of different dimensionality and topology. These include several microporous networks, which can accommodate water or methanol into their open framework, and change their structure and magnetic properties depending on the type and quantity of guest molecules [1,2]. We have also obtained non-porous chain structures which undergo partial dehydration, usually in a reversible process. In these coordination polymers rearrangement of hydrogen bonds causes magnetic changes [3], and in some cases a very rare and interesting additional effect of metal-to-metal charge transfer occurs [4].

The study of different solvates poses a considerable challenge. It is particularly difficult for compounds with pronounced structural flexibility, where several pseudo-polymorphic forms may exist with the same guest molecules under slightly different conditions [2]. In order to study structure and magnetic properties it is crucial to establish the temperature and partial pressure ranges in which each form is stable. The widely used volumetric methods dedicated to sorption studies are not particularly suited for this purpose. Therefore, we have developed an original method in which the sample is exposed to constant flow of carrier gas with solvent vapours. Under variable temperature conditions the de-solvation and re-solvation processes can be observed as changes in the partial pressure of the vapours which pass through the sample. By using this method we have detected a multi-step dehydration for two microporous networks.

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Poster Session / 1

Investigation of the spatial anisotropy of exchange coupling in quasi-two-dimensional quantum magnets $\text{Cu}(en)\text{Cl}_2$ and $\text{Cu}(tn)\text{Cl}_2$

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In the last decades, two-dimensional (2d) quantum antiferromagnetic systems have received a significant amount of theoretical and experimental interest [1]. The manifestation of a low-dimensionality in real compounds can be seen at temperatures disturbing interlayer interactions and it predetermines 1d, 2d magnetic systems for observation of interesting physical effects due to quantum fluctuations which do not play significant role in most of 3d magnets. Compounds with high crystal symmetry and strong spatial anisotropy approximating nearly ideal 2d antiferromagnets are characterized by the easy-plane spin anisotropy which at sufficiently low temperatures induces a topological Berezinskii-Kosterlitz-Thouless (BKT) phase transition.

One of the low-dimensional magnetic systems is an organo-metallic compound $\text{Cu}(tn)\text{Cl}_2$ ($tn = \text{C}_3\text{H}_{10}\text{N}_2$). Previous thermodynamic studies revealed high measure of spatial anisotropy of exchange coupling manifesting at helium temperatures while no phase transition to long range order was observed down to 50 mK. Application of magnetic field induced a response characteristic for the BKT transition [2].

The present study is focused at the modification of exchange interactions in the studied crystal structure by replacement of the organic ligand tn by $en = \text{C}_2\text{H}_8\text{N}_2$ with smaller volume. Correspondingly, the enhancement of the interlayer coupling was expected accompanied with the observation of a magnetic phase transition at temperatures higher than 50 mK.

While the replacement of tn by en did not introduce significant changes of the local octahedral environment of Cu(II) ion, the symmetry of crystal structure was lowered from orthorhombic to monoclinic. This change affected magnetic properties of $\text{Cu}(en)\text{Cl}_2$. Our comparative study of powder susceptibilities and isothermal magnetization surprisingly revealed a significant decrease of exchange coupling, projecting in Curie temperatures $\Theta = -4.17$ K and -0.75 K for $\text{Cu}(tn)\text{Cl}_2$ and $\text{Cu}(en)\text{Cl}_2$, respectively. As expected, g -factors determined by a local Cu(II) surrounding, were found very similar, $g = 2.01 \pm 0.05$ for $\text{Cu}(en)\text{Cl}_2$ and 2.07 ± 0.05 for $\text{Cu}(tn)\text{Cl}_2$. Concerning magnetization studied at 2 K, in magnetic field 5 T, $0.45 \mu_B$ and $0.81 \mu_B$ was observed for $\text{Cu}(tn)\text{Cl}_2$ and $\text{Cu}(en)\text{Cl}_2$, respectively, again indicating weaker magnetic correlations in $\text{Cu}(en)\text{Cl}_2$. In future, the study of magnetic properties in both magnetic systems will be investigated on the monocrystalline samples.

Acknowledgments

This work has been supported by VEGA grant 1/0269/17 and APVV-14-0073.

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Poster Session / 2

Studies of slow magnetic relaxations in monocrystalline of $[\text{Mn}^{\text{III}}\text{F}_4\text{TPP}][\text{TCNE}]^*$ methanol**Author(s):** Mr. CZERNIA, Dominik¹**Co-author(s):** Mr. KONIECZNY, Piotr² ; Dr. PINKOWICZ, Dawid³ ; Prof. TOMKOWICZ, Zbigniew⁴¹ *AGH University of Science and Technology; Institute of Nuclear Physics PAN.*² *Institute of Nuclear Physics PAN*³ *Jagiellonian University, Faculty of Chemistry*⁴ *Jagiellonian University, Institute of Physics***Corresponding Author(s):** dominik.czerania@gmail.com

The $[\text{Mn}^{\text{III}}\text{F}_4\text{TPP}][\text{TCNE}]^*$ compound dissolved in methanol is a quasi 1D single chain magnet (SCM). Two families of chains in the crystal structure lie at an angle of 66 degrees relative to each other. The chains are made of alternately placed donors $\text{Mn}^{\text{III}}\text{F}_4\text{TPP}^+$ and acceptors TCNE^- . Due to strong antiferromagnetic interchain interactions $J = 100 \pm 8\text{K}$ between manganese ion with $S = 2$, $g = 2.0$ and ligand TCNE with $S = \frac{1}{2}$, $g = 2.0$ the compound is classified as ferrimagnet with ordering temperature $T_c = 10\text{K}$. Magnetic properties of monocrystalline compound was fully characterized in static and alternating magnetic field in two specific orientations of sample: $a \parallel H$ and $a \perp H$. The studied material exhibits two relaxations processes, fast and slow, which are well described by the generalized Debye model with the wide relaxation times distributions. Relaxation times were determined in two approaches: by Cole - Cole plots obtained from AC field measurements and from relaxation in DC field. Both of relaxation processes are thermally activated according to the Arrhenius equation with the different energy barrier for each process.

Poster Session / 3

Magnonic excitations in low dimensional inhomogeneous nanostructures

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There is a continuous interest in a size reduction of the magnetic data storage devices. The most promising route to the miniaturization is offered by modern spintronics, also based on molecular magnetic materials, that allows one to control the architecture of individual spin arrangements to an unprecedented precision. In the poster we will present elementary excitations in selected linear and branched chains of spins consisting of segments differing in strength of magnetic coupling. Different kinds of anisotropy will be also considered. The method of calculations originates from the dynamical matrix technique [1]. The surface and interface response function (Green function) theory [2] will be used to treat the junctions of different segments. The surface and/or interface excitations (magnons) correspond to poles of the appropriate Green functions. For some parameters the excitations appear on the background of the bands of bulk waves, whereas in other cases they transform into finite-lived interface resonances. We also calculate reflection and transmission coefficients for the magnons at the junctions.

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Poster Session / 4

Low temperature electronic state of β'' -type organic conductors

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To elucidate mechanisms of unconventional superconductivity has been one of the most important subjects in material science. The mechanisms of unconventional superconductivity occurred in high- T_c cuprates, heavy fermion, organics, and so on, are not clarified at present. In this study, we investigated into low temperature electronic state of β'' -type organic superconductors from a viewpoint of charge fluctuation because some β'' -type compounds which have strong electronic correlation show charge ordered state by inter-site Coulomb repulsion. Some recent studies imply that the degree of freedom of charge is important for the emergence of the superconductivity in these salts. However, the detailed mechanism is still open question. The arrangement of the donors in the β'' -type salts provides semimetallic nature due to the weak tetramerization of the BEDT-TTF molecules along b -axis. Thus, the compounds have very Fermi pockets which have comparatively light effective mass.

In this work, we measured electric transport, magnetic susceptibility and heat capacity of some β'' -type salts. We found that the compounds which have weaker chemical pressure show higher critical temperature to superconducting state and large negative magnetoresistance. From the results of Shubnikov-de Haas quantum oscillation, we noticed that the effective mass m^* and the number of carrier of semi-metallic Fermi surface show the chemical pressure dependence. This dependence indicates that the chemical pressure has control of the electronic correlation. Beside that, magnetic field dependence of electronic heat capacity coefficient shows quite unusual dependence implying competition between superconductivity and charge ordered state.

Poster Session / 5

Peculiar low-energy phonon excitations in organic crystal with strong charge fluctuations

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The influence of charge fluctuation on physical properties is one of the hot topics in the field of organic conductors. In particular, in the study of superconductors in the vicinity of charge-ordered insulating phase, various discussions about the relationship between the formation mechanism of superconductivity and charge fluctuation have been made from the viewpoint of both theoretical and experimental. From the heat capacity measurement of single crystal of θ -(BEDT-TTF)₂CsZn(SCN)₄ (abbreviated as θ -CsZn), we have found the boson peak-like anomalies in heat capacity at low temperature in some compounds with strong charge fluctuations. Although details of this bosonic peak have been not clear, it has been considered as the low energy excitation caused by charge fluctuation and strong phonon-electron coupling. Therefore, in this research, in order to clarify the relationship between electronic state and phonon state, we performed the thermal conductivity measurement, which is an efficient method to observe the state of phonon directly, for several organic conductors with strong charge fluctuations.

To measure thermal conductivity, we developed a thermal conductivity measurement system for tiny single crystals. We attached the both end of the tiny single crystal sample to the two temperature regulated plates using thin gold wires. The temperature differences between the plates were measured by two different thermometers.

The temperature dependences of the thermal conductivity of θ -CsZn was successfully conducted. In ordinary well ordered crystals, the thermal conductivity has a peak structure due to phonon-phonon scattering (Umklapp process) around 10 K. However, this material does not have such a peak structure and monotonically increases with increasing temperature. And there is a plateau structure of thermal conductivity between 3 K and 7 K. In addition, the temperature dependence of the thermal conductivity around 1 K was followed to the T^2 dependence. These features are typical for glassy material like SiO₂ glass. We thought that the charge ordered domains that exist spatially heterogeneously act as an effect of adding disorder to the lattice and as a result the crystal structure and its phonon property was changed into glassy state. And if assuming such scenario, we can understand the boson peak in the heat capacity at low temperature as the anomalous temperature dependence of glassy materials. We analyzed these results by the soft potential model, which is used to explain the physical properties of glassy material, and we found this model agree with the temperature dependence of thermal conductivity and heat capacity of this compound. The systematic study including charge ordered compounds with the same crystal packing is presented.

Poster Session / 6

Molecular dynamics in the smectic liquid crystal 4-n-butyloxybenzylidene-4'-n'-octylaniline (BBOA) in bulk and under confinement

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The molecular dynamics of 4-n-butyloxybenzylidene-4'-n'-octylaniline (BBOA, abbreviated also as 4O.8) was studied by broadband dielectric spectroscopy (BDS) for bulk samples that were exposed to various thermal treatments. Phase transitions between different liquid crystalline phases (N, SmA, SmBhex, and SmBCr) were evidenced by the alteration in the temperature dependence of the dielectric permittivity spectra and dielectric relaxation rates. A particularly complex molecular mobility was found for the highly ordered SmBCr phase that showed clear evidence for cooperative dynamics of a glass-forming liquid as manifested by a Vogel–Fulcher–Tammann (VFT)-type temperature dependence of its structural relaxation time $\tau(T)$. At low temperatures, dependence $\tau(T)$ again changes from VFT to Arrhenius behavior, a phenomenon commonly observed for supercooled liquids confined to nanometer length scales. The isothermal crystallization kinetics of the metastable SmBCr phase was described in terms of the classic Avrami approach and by the analytical method proposed by Avramov. Finally, the effect of geometrical confinement was studied for BBOA molecules enclosed in anodic aluminum oxide membranes with unidirectional pores of mean diameters 35, 55, 80, 100 and 150 nm. We analysed the impact of pore sizes on molecular mobility and thermodynamic stability of nematic and smectic phases.

Poster Session / 7

Magnetic properties of new molecular compounds based on single cobalt (II) ion

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Low-dimensional molecular magnets that show slow relaxation of magnetization are of interest because of their possible applications.^[1] The smallest among those are Single Ion Magnets.^[2] Based on cobalt salt, pyridine and 4-vinylpyridine, two new mononuclear compounds were synthesized: $\text{CoBr}_2(\text{py})_2$ and $\text{CoBr}_2(4\text{vpy})_2$. The measurements of AC susceptibility at temperatures below 5 K confirmed the occurrence of field-induced relaxation of magnetization for both. Based on Cole-Cole model fits to AC susceptibility vs. frequency, times of relaxation and energy barriers were determined: $\text{CoBr}_2(\text{py})_2$ - $\tau_0 = 8 \cdot 10^{-10}$ s, $\Delta/k_B = 29(4)$ K, $\text{CoBr}_2(4\text{vpy})_2$ - $\tau_0 = 1.4 \cdot 10^{-11}$ s, $\Delta/k_B = 35(7)$ K. The low values of the α parameter (below 0.3 for both compounds) confirmed that the measured compounds are indeed Single Ion Magnets. Despite the low values of τ_0 and Δ/k_B , these compounds are very interesting because of one among the smallest sizes of the molecule (high density of magnetic centers per volume) and the possibilities to use other pyridine-based ligands to obtain other SIM compounds.

Acknowledgments

This research was financed by the Polish National Science Centre within the SONATA Project UMO-2015/19/D/ST5/01936.

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Poster Session / 8

Polymer dynamics and morphology in LDPE nanocomposites studied by NMR spectroscopy and relaxometry

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Low density polyethylene (LDPE) is commonly used for food packaging [1]. The addition of nano-clays often improves the mechanical, thermal and gas-barrier properties of the polymer matrix, making the composite a potentially superior industrial product. In this work, solid state NMR spectroscopy and ¹H NMR relaxometry techniques were applied to a neat LDPE and a LDPE/montmorillonite nanocomposite sample [2] in order to investigate the effect of the filler on polymer morphology and dynamics, molecular level properties which are related to the mentioned macroscopic properties. The studied LDPE sample showed a glass transition at -45°C and a melting point at 114°C. The analysis of ¹H low field NMR Free Induction Decays in the temperature range between 26 and 100°C allowed three components with different mobility to be identified: crystalline, amorphous, and rigid amorphous fractions. ¹³C direct excitation NMR spectra were also recorded at room temperature to further characterize these fractions. In addition, in order to get insight into the phase heterogeneity we measured the ¹H longitudinal relaxation times in the laboratory frame (T₁) at 300 MHz and in the rotating frame (T_{1ρ}) using ¹³C detection through Cross Polarization Magic Angle Spinning (CP MAS) at room temperature and performed spin diffusion experiments. Moreover, the chain segmental and collective dynamics was characterised by measuring ¹H T₁ at Larmor frequencies ranging from 10 kHz to 30 MHz, exploiting a Fast Field-Cycling NMR relaxometer in the 26-120°C temperature interval. The results obtained for the neat polymer and the nanocomposite were compared and discussed.

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Poster Session / 9

Magnetic anisotropy and magnetization reversal mechanisms of nanoporous Co/Pd multilayers and CoPd alloy thin films

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In present work we demonstrate that magnetic anisotropy and magnetization reversal mechanism of Co/Pd thin films is highly dependent on the substrate morphology in submicron scale. Nanoporous lattice of holes, called antidots, were fabricated by deposition of Co/Pd multilayers on anodized aluminum oxide (AAO), where the pores are located in the middle of hexagonal packed hemispherical deepenings.

The studies concern the properties of as deposited films and annealed in vacuum at 300°C. To determine the contribution of pore morphology to magnetic properties of the systems, Co/Pd MLs on flat Si substrates was also prepared. SEM imaging confirmed nanoporous morphology of the films. Perpendicular magnetic anisotropy was observed for continuous films ($K_{\text{eff}} \approx 2 - 4 \cdot 10^6$ erg/cc) and conserved for antidots before and after annealing ($K_{\text{eff}} \approx 0.5 - 1 \cdot 10^6$ erg/cc). MFM imaging of Co/Pd multilayers and CoPd alloy compared to continuous films showed more complex magnetic contrast with smaller magnetic domains. The difference in MFM images can be explained by the pinning effect of the magnetic domains on the pore borders and edges of pore cells.

Magnetic reversal mechanism of continuous Co/Pd multilayers is based on domain-wall motion and can be described by modified Kondorsky model. For nanostructured films the transition of magnetization reversal mechanism to coherent rotation mode was observed and can be approximated by Stoner-Wohlfarth model.

Acknowledgments

The support from the NCN grant 2014/13/N/ST8/00731 is acknowledged.

Poster Session / 10

Physical properties of a new magnetic liquid crystal based on Co(II) ions.

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Our aim was to obtain a new Co(II) – based material that would show both liquid crystalline properties and slow magnetic relaxations. The compound was obtained in a reaction of 4, 4' – dinonyl – 2, 2' – bipyridine (4D2B) with CoCl₂. The choice of the ligand was determined by the fact that cobalt salts with pyridine alone form Single Ion Magnets, which is proven by other research done in our group, and the likelihood of LC properties to be induced by the long chains attached to the bipyridine. Differential Scanning Calorimetry was used to check for multiple phase transitions. The DSC curves for the ligand and the compound are different, so the reaction has certainly altered the properties of the material. Polarizing microscopy and X-Ray Diffraction were also used to characterize this new compound. Magnetic measurements proved that it is a spin glass and does indeed exhibit slow magnetic relaxations with $\tau_0 = 340.41$ s and $\Delta/k_B = 0.78$ K. However different these relaxations may be from the ones shown by Single Ion Magnets, we think that our research opens a new chapter, which will connect magnetism and the science of liquid crystals. This path is very interesting; such multifunctional materials can have many applications, and will join two fields of material research. In the future, we want to use other ligands.

Acknowledgments

This research was financed by the Polish National Science Centre within the SONATA Project UMO-2015/19/D/ST5/01936.

Poster Session / 11

Mesoporous silica thin films containing propyl-copper-phosphonate units inside vertically aligned pores as a novel material with tunable nonlinear optical (NLO) properties.

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In this work we propose the compound based on porous silica matrix containing polar functional units to use as a material for desirable second and third order nonlinear optics (NLO) properties. As a matrix we postulate mesoporous silica in the form of thin films, having 2D hexagonally ordered pores with diameter about 2 nm, aligned perpendicularly to the substrate. This material plays a role of neutral (non-polar) matrix for active polar units. One of a crucial feature of our matrix is its transparency in the visible spectral range which allows the functional groups that are inside the material to be excited efficiently. As an optically active centres we propose copper propyl phosphonate units that are polar - bounding between copper and oxygen atoms at the phosphonate units have polarized covalent character. Such copper-containing functional groups are regularly distributed and anchored inside silica matrix. By modification of functional groups concentration inside the matrix we are able to tune degree of supramolecular interactions and also charge distribution in functional groups. Therefore modification of functional groups content can be used for tuning the NLO susceptibilities. Nevertheless, modification of functional groups content can result in systems reorganization, what can lead to quasi phase transition. For this reason it is a vital task to investigate this phenomenon in details, to be able to take it into account during NLO properties tuning.

Poster Session / 12

Time scale effects in perception of acoustic signals**Author(s):** Mrs. MARTINSON, Karolina¹**Co-author(s):** Mr. MAJKA, Marcin¹ ; Mrs. SENDERECKA, Magdalena² ; Prof. ZIELIŃSKI, Piotr¹ ; Mrs. GWARDA, Magdalena³ ; Mr. SOBIESZCZYK, Paweł¹ ; Mrs. KUŹMA, Dominika¹

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The uncertainty principle (Heisenberg [1] as used in quantum mechanics, or Gabor [2] in signal processing), states that it is impossible to measure the energy (frequency) and duration time simultaneously with the infinite measurement accuracy [1]. In the realm of acoustic pulses as perceived by human hearing it would mean that too short pulses cannot produce a sensation of pitch, the latter being represented by a logarithm of frequency. It is surprising that, despite physical restrictions, humans associate some effective pitch to millisecond pulses up to about 20 ms. The effective pitch has been found to increase with decreasing duration time of the pulse [3,4] and we have shown that the relation between the duration time of the pulse and the effective pitch follows a variant of the Weber-Fechner law [5]. Some differences in the timbre are also noticed by some subjects examined.

Thirty-six musicians and thirty-nine nonmusicians have been examined. The behavioural test was held in controlled conditions; every person used the same software and the same audio tools parameters. The participants marked the just noticeable difference in the pitch and the timbre. Statistical analyses of the results will be presented in the communication.

Poster Session / 13

Formation of nanopatterned metal/oxide/metal multilayered structures using anodization process

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In this studies we present a new approach to preparation of a nanopatterned metal/metal-oxide/metal (M/M-O/M) junctions using the anodization method. The junctions are composed of a 3d transition metals (i.e. Ti, Fe) and their oxides. The patterning is performed with especially designed anodization process. First an aluminum prepatterned templates are prepared, where after removing anodized aluminum oxide (AAO), a bowl-like U-shape structures remain. Next titanium or iron thin layer is deposited on anodized aluminum substrate and then metallic layer is shortly anodized to create thin layer of TiO_x or FeO_x oxide. The thickness of oxide layer can be controlled by choosing appropriate time of anodization. Furthermore, to enhance crystallization process of the oxide layer an annealing in vacuum or O₂ rich atmosphere at high temperatures is performed. Finally the formation of the M/M-O/M junction is completed with deposition of Ti or Fe metallic layer.

Acknowledgements

This work was supported with Polish National Science Center grant no. NCN-2015/19/D/ST3/01843.

Poster Session / 14

Inducing exchange bias in Co/Au multilayers by oxygen ion implantation

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Exchange bias occurs at the interface between ferromagnetic (FM) and antiferromagnetic (AFM) materials and manifests itself by shift of the hysteresis loop in applied magnetic field axis, among other things. A method to obtain AFM CoO clusters inside the FM Co material can be oxygen ion beam implantation. The accurate selection of implantation process parameters, with special emphasis on oxygen depth profiles, allows to tailor the magnetic switching mechanism leading to the stepwise reversal process. A series of three Si(100)/Au/[Co/Au]_n multilayers was implanted using 150 keV O ions with different doses. Energy and doses were adjusted on the basis of Monte Carlo simulations, using SRIM/TRIM package. Magnetic properties such as loop shift, coercivity, and magnetization components of the implanted multilayers are reported.

Poster Session / 15

Structural research of ternary nanoparticles for energy production

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Fuel cells fueled by ethanol became a very popular and interesting alternative as an energy source. This is related to the benefits of ethanol: less toxic compared to methanol, easier stored and transported than hydrogen and available from renewable resources[1,2]. However, the usage of ethanol as fuel, creates various challenges such as the difficulty to split the C–C bond [3]. Therefore the key challenge is to design and develop the appropriate type of catalysts. So far, the best catalysts for ethanol oxidation seem to be ternary PtRh / SnO₂ nanoparticles designed by the Adzic group [1,4,5]. Additionally to improve the SnO₂ electrocatalytic activity, F or Sb can be added [6]. Each of the three constituents has its own role in the oxidation pathway. The role of Rh is to cleave the C-C bond of ethanol, while SnO₂ provides OH species to oxidize intermediates and to free Pt and Rh sites for further ethanol oxidation [7]. The motivation for the present work is a better understanding of the synergistic effect between these three components in the nanocatalysts, develop the knowledge about electrocatalytic ethanol oxidation and try to replace rhodium in the ternary catalyst PtRh / SnO₂ by rhenium. In the present study three types of nanoparticles were synthesized: tin dioxide, platinum and rhenium nanoparticles. Subsequently, the Pt and Re nanoparticles were mixed together and deposited on the synthesized SnO₂ supports. The obtained PtRe / SnO₂ catalysts were deposited on carbon black (Vulcan XC-72R). Global information about the nanoparticle size was obtained by Photon Correlation Spectroscopy (PCS). The structural and chemical analyzes of the nanocatalysts were carried out using transmission electron microscopy in the STEM mode using the HAADF detector. The structural analysis clearly showed that the all nanoparticles had a crystalline structure. The Pt and Re NPs had similar dimensions of around 3 nm and did not show a strong agglomeration compared to tin oxide NPs. This research is aimed to study surface properties of these nanocatalysts and determine their selectivity for the total oxidation of ethanol to CO₂.

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Acknowledgments

Financial support from the Polish National Science Centre (NCN), grant UMO-2014/13/B/ST5/04497 is acknowledged.

Poster Session / 16

Mechanism of magnetisation reversal in thin L1₀ FePd nanopatterned layers

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Thin magnetic films of FePd, FePt and CoPt alloys are technologically important because of their large anisotropy ($\sim 10^7$ erg/cm³) and strong coercivity (~ 1000 Oe). Many studies are performed in order to obtain thin magnetic films of ordered L1₀ FePd alloy with tuned magnetic parameters. The shape of hysteresis loops and coercivity values of magnetic systems are directly dependent on mechanisms of the magnetization reversal. Defects in continuous film created by magnetic layer deposition on ordered porous templates cause changes in magnetization reversal mechanisms. In this study we examined the influence of template morphology on coercivity, remanence and magnetization reversal mechanism of thin FePd alloy film with L1₀ structure. The alloys were obtained from Pd_{2nm}/[Fe_{4nm}Pd_{6nm}] \times 4/Fe_{4nm}/Pd_{4nm} multilayers after vacuum annealing at 600°C. In our study we investigated films deposited on Al₂O₃ nanoporous templates of two kinds: with flat (template F) or with hemispherically curved (template C) interpore areas. The films on flat Si/SiO₂ wafer were used as reference samples. The angular dependencies of $M_R/M_S(\varphi)$ reveal isotropic properties of films deposited on template C, and in-plane magnetic anisotropy for flat films on Si/SiO₂ wafer and on template F. The mechanisms of reversal magnetization inherent for the systems were investigated by determination of the angular dependence of coercivity $H_C(\varphi)$ and compared with theoretical models of Kondorsky, modified Kondorsky and Stoner-Wolfarth (Figure 2 b). Isotropic properties of curved films were also proved by $H_C(\varphi)$. Film on template F and on flat Si/SiO₂ wafer exhibit different magnetization reversal mechanisms. The differences in the magnetization reversal mechanisms can be explained by the loss of continuity of the film and formation of islands during partial dewetting after annealing. In the same conditions porous film maintains its uniformity as observed by SEM imaging.

Acknowledgments

The support from the NCN grant 2014/13/N/ST8/00731 is acknowledged.

Poster Session / 17

Cyano-bridged bimetallic chains based on cyclam complexes of Ni(III) or Mn(III) and hexacyanometallates(III)

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Four new compounds of the general formula: $\{[M_A(\text{cyclam})][M_B(\text{CN})_6] \cdot 6\text{H}_2\text{O}\}_\infty$, where $M_A = \text{Ni}^{\text{III}}, \text{Mn}^{\text{III}}$; $M_B = \text{Fe}^{\text{III}}, \text{Cr}^{\text{III}}$; were obtained in the reaction between the respective cationic building blocks: $[\text{Ni}(\text{cyclam})]^{3+}$ and $[\text{Mn}(\text{cyclam})]^{3+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane), and anionic building blocks: $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Cr}(\text{CN})_6]^{3-}$ [1,2]. All compounds are isostructural and crystallise in space group $C 2/m$. They are characterised by one-dimensional chain topology, in which the metal centres are connected by CN-bridges. At the temperature of 40 °C partial dehydration takes place which leads to the relatively stable forms containing 2-3 water molecules. Powder X-ray diffraction studies show that the process causes significant structural changes. Moreover, it is reversible for compounds based on the Ni^{3+} ions and irreversible for those based on Mn^{3+} ions. Ferromagnetic interactions are observed within the NiFe, NiCr and MnFe chains mediated by the CN-bridges, while in MnCr compound the intra-chain interactions show antiferromagnetic character. In all four compounds antiferromagnetic interactions between the chains are present. In the case of the MnCr chain it leads to long range ferrimagnetic ordering and appearance of magnetic hysteresis. The partial dehydration process causes marked changes in the magnetic properties of all compounds.

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Poster Session / 18

Photomagnetic $\text{Cu}^{\text{II}}\text{-}[\text{Mo}^{\text{IV}}(\text{CN})_8]^{4-}$ coordination polymers

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The exciting property exhibited by certain cyanide compounds is photomagnetism, which allows for the control of the magnetic properties with light irradiation. Although photomagnetic effects are known to generate various effects, the most common are the spin crossover (light-induced excited spin state trapping or LIESST) and charge transfer phenomena.

The motivation for our research in this area is to investigate the photomagnetic properties of heterometallic $\text{Cu}^{\text{II}}\text{-Mo}^{\text{IV}}$ coordination polymers with cyanide bridges that would display spin crossover (SCO) phenomena on the Mo^{IV} centre of $4d^2$ electronic configuration (singlet-triplet spin transition, S-T). We have chosen the family of the structurally related $\text{Cu}^{\text{II}}\text{-}[\text{Mo}^{\text{IV}}(\text{CN})_8]^{4-}$ molecular systems, which are known to exhibit complex photomagnetic properties.

In the present work, two coordination polymers $[\text{Cu}(\text{chxn})_2(\text{H}_2\text{O})_2][\{\text{Cu}(\text{chxn})_2\}_3\{\text{Mo}(\text{CN})_8\}_2]\cdot\text{H}_2\text{O}$ and $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2][\{\text{Cu}(\text{pn})_2\}\{\text{Mo}(\text{CN})_8\}]\cdot 2\text{H}_2\text{O}$ (chxn=1,2-diaminecyclohexane, pn=1,2-diaminepropane) have been investigated for optical and photomagnetic properties (irradiation with 436 nm line, in the range of the LF band of Mo^{IV} complex). The molecular structures of $[\text{Cu}(\text{chxn})_2(\text{H}_2\text{O})_2][\{\text{Cu}(\text{chxn})_2\}_3\{\text{Mo}(\text{CN})_8\}_2]\cdot\text{H}_2\text{O}$ and $[\text{Cu}(\text{pn})_2(\text{H}_2\text{O})_2][\{\text{Cu}(\text{pn})_2\}\{\text{Mo}(\text{CN})_8\}]\cdot 2\text{H}_2\text{O}$ reveal the topologies of a 2-D coordination layer built of hexagonal grids shown and 1-D chain, respectively. The negative charge of the cyanido-bridged polymeric motifs is compensated by the isolated Cu^{II} complexes. Both systems display paramagnetic properties due to the presence of Cu^{II} centers ($S=1/2$) separated by the diamagnetic $[\text{Mo}(\text{CN})_8]^{4-}$ units in the ground state. In both cases the compounds are photosensitive and the photoexcitation has been found to correlate with the singlet-triplet transition on the Mo^{IV} sites.

Poster Session / 19

Polymorphism and vibrational investigations (FT-IR and IINS) of glass-forming 2-phenylbutan-1-ol (BEP), 2-(trifluoromethyl)phenethyl alcohol (2TFMP) and 4-(trifluoromethyl)phenethyl alcohol (4TFMP)

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The complex polymorphism and vibrational dynamic of three glass-forming single-phenyl-ring alcohols (with and without fluorine atoms) have been studied by complementary methods. Glass of isotropic liquid and cold crystallization of metastable supercooled liquid state were detected. Temperature investigation of vibrational motions point at hydrogen bond as an important intermolecular coupling in these materials. Quantum chemical (DFT) calculations for isolated molecule as well as a hydrogen-bonded dimer provide a satisfactory description of experimental spectra. The particular position of the CF₃ group in a phenyl ring (ortho/para) does not influence the intermolecular interactions.

In neutron inelastic scattering, the glass of supercooled liquid (disordered) and ordered crystal phase at 5 K can be easily distinguished. Comparing low temperature spectra of ordered crystal phase with glass of isotropic liquid, one can easily notice broadening of vibrational modes caused by rotational and translational molecular disorder, frozen in glassy state. An additional significant difference below 40 cm⁻¹ provides an evidence for the excitations in glass of disordered phase being localized and anharmonic, other than collective phonon excitations propagating in the crystal with a long-range order of molecules. Low energy barrier for torsional motions of CH₃-CH₂-CH- and OH-C₂-CH- (functional groups connected to phenyl ring) are visible on neutron spectra in the lattice vibrational region.

Poster Session / 20

Total transmission of elastic waves in solid-solid interface

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When encountering a mismatch of characteristic impedance a bulk acoustic wave transforms into up to three reflected and refracted waves of different polarizations. The effect is known as mode conversion. The lack of the specularly reflected wave is called total mode conversion because then all the outgoing waves propagate at speeds different than that of the incident one, what it's known at the half-space of elastic media [1, 2]. Conversely, if the only outgoing wave reflects in the specular way one speaks of no-conversion. Existence of those both phenomenons for a particular angle of incident wave give a rise to lack of reflected wave and it is called total transmission. Discovery of materials with negative Poisson's ratio [3] enlarged the range of possible impedance mismatch and of the related phenomena. The conditions for the total mode conversion and no-conversion in reflection and for total transmission will be presented for interfaces between two elastic media. The region of existence of total transmission as well as related angles of incident waves will be presented in relation to region of existence of Stoneley waves for whole range of Poisson's ratio.

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Poster Session / 21

Optimization of anodization parameters for nanoporous Al₂O₃ templates fabrication

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Nanoporous Al₂O₃ have a wide range of applications as a sensors, biosensors or energy storage devices. These templates are attractive due to their low fabrication costs.

The Al oxides with hexagonal close packed porous structure can be prepared by two step anodizing process with features tunable by the electrolyte composition and voltage. It was already shown [1], [2] that degree of pore ordering depends on first anodization time and the initial surface roughness. This work is focused on Al foil surface pretreatment procedure and first-step anodization parameters influence on order parameter of pore structure.

A series of porous anodic aluminium oxide samples were prepared by two-step anodization of the high purity (99.999%) aluminium foil in oxalic acid at temperature ~ 17 °C. The preparation of Al foils consisted of annealing at 600 °C for 48 hours, oxide layer removal and fine chemical polishing. It was found that such a sequence allows to obtain a surface with roughness of approximately 10 nm.

The time of the first anodization was varied from 10 min to 15 hours, while the second anodization time was 10 minutes. Pores ordering was estimated by self-ordering parameter determined from the number of violations in hexagonal symmetry for 100 pores, and by comparison of Fast Fourier Transforms (FFT) obtained for SEM images of sample surfaces. It was found that increasing of first-step anodization time from 10 minutes to 2.5 hours significantly enhances self-ordering parameter from 0.66 to 0.87, respectively. Improvement of FFTs' symmetry confirms ordering enhancement. Further extension of anodization time do not affect the ordering. Therefore, the time of 2.5 h for first-step anodization followed by the annealing and chemical polishing of Al foil was found to be an optimum for well-ordered templates fabrication.

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Poster Session / 22

Nanoporous Al₂O₃ templates: a route towards flexible humidity sensors with linear response

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Nanoporous and nanotubular anodic oxides of valve metals (Al, Ti, W, Ta etc.) possess larger surface area with more reaction sites and more developed surface morphology than flat materials. These unique properties of the templates are used to address their technological applications in different types of sensors. For example, capacitance of porous oxides is sensitive to air humidity and allows their use as humidity sensors. Furthermore, fabrication of porous anodic oxides on flexible kapton foil provides an unique possibility to adjust the shape of the sensor and affords significant advantages over the conventional rigid sensors.

The main objective of the work is to determine optimal morphology (pore diameter and interpore distance) and thickness of flexible Al₂O₃ which provide the largest linear response. For these purpose we produced a series of rigid Al₂O₃ samples with various pore diameters ($D_P \sim 30-270$ nm), interpore distances ($D_{IN} \sim 65-420$ nm) and thicknesses ($t \sim 0.250 \mu\text{m} - 1 \mu\text{m}$) by anodization of thick Al foil. In order to investigate sensor response of the samples we measured impedance sensitivity to air humidity at four working frequencies of 100 Hz, 500 Hz, 1 kHz and 10 kHz, and the largest impedance sensitivity was found for the frequency of 1 kHz. The samples exhibited exponential electrical response with the largest impedance changes for high humidity (from 70% to 100%). The best performance was achieved for sensor with $D_P \sim 47$ nm, $D_{IN} \sim 96$ nm and $t \sim 0.5 \mu\text{m}$. In order to get the linear response of the sensor the sample was modified by boiling in water for 100 minutes. This modification resulted in linear electrical response of the sample, however, the sensor sensitivity decreased 100 times.

Then we fabricated the sample with the same structural parameters as mentioned above on flexible kapton foil. The sample on flexible substrate showed a linear response with larger impedance sensitivity than for the sample prepared on aluminium foil. The results have shown the potential of future application of flexible porous Al₂O₃ coatings as humidity sensors.

Poster Session / 23

Ionic conductors based on metal-closo-borates

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Solid state compounds with ionic conductivity larger than 1 mS/cm at room temperature can compete with liquid electrolytes when applied in rechargeable batteries. Recently new sulfide materials with this property were discovered, extending family of ionic conductors based on oxides.

Very high conductivity of sodium reported in Na₂B₁₂H₁₂ competes with the best solid state conductors known for this metal. Further developments brought borane based Na superionic conductors that are by orders of magnitude better than those based on β -alumina.

We will present theoretical study, based on DFT calculations, explaining the conductivity mechanism in closo-borates, as well as pointing out the differences in conductivity of lithium and sodium.

Poster Session / 24

Phase diagram and molecular dynamics in the antiferroelectric liquid crystal (2S)-octano-2-yl-4'-(2-fluoro-4-{[5-(1,1,2,2,3,3,3 heptafluoropropoxy) pentylo]oxy}benzoyloxy)-[1,1'-biphenyl]-4-carboxylate

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The phase diagram and molecular dynamics of (2S)-octano-2-yl-4'-(2-fluoro-4-{[5-(1,1,2,2,3,3,3 heptafluoropropoxy) pentylo]oxy}benzoyloxy)-[1,1'-biphenyl]-4-carboxylate (2F5) were studied for samples which were exposed to various thermal treatment. 2F5 is composed of the chiral molecules and shows rich polymorphism of liquid-crystalline and solid phases. Studies by means of Differential Scanning Calorimetry (DSC) and polarizing microscopy (POM) revealed the following phase sequence: ferroelectric smectic C- (SmC*), antiferroelectric smectic C (SmC_A*), smectic A (SmA*) and the glassy phase of SmC* (GSmC_A*). Additionally, on slowly heating (< 2 K/min) a „cold crystallization” was observed. The molecular dynamics of 2F5 in various mesophases and on approaching of the glass transition temperature was studied by broadband dielectric spectroscopy (BDS). The glass transition temperature (T_g) determined from BDS studies and DSC measurements coincides with the value estimated based on observation of cracks in polarizing microscopy textures. The bias field was applied to identify the mechanism of complex dynamics (molecular and collective).

Acknowledgements

Łukasz Kolek acknowledges the National Science Centre (Grant SONATA11: UMO-2016/21/D/ST3/01299) for financial support.

Poster Session / 25

How does the molecular structure of the bent–core molecules affects the occurrence of twist–bend nematic phase?: a mean–field study

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A newly observed – heliconical (twist–bend) nematic phase (N_{TB}) of nanoscale pitch [1] has recently caught much of attention. Initially, the theoretical concept of this phase has been presented by R. B. Meyer [2] in 1973, where he assumed that the director of the molecules precesses on a cone forming an oblique helicoidal structure. Subsequently in 2001 Dozov [3], in 2002 Memmer [4] and in 2004 Lorman et al. [5], suggested that the formation of the N_{TB} can be facilitated by the shape of bent–core molecules.

Here we present theoretical investigations on relation between biaxiality and bend angle on stability of twist–bend nematic phase. We use a generalized Maier–Saupe type of model for N_{TB} [6], with intrinsic molecular biaxiality on both of the arms of the molecule, quantified by a 3×3 second–rank traceless symmetric tensor \mathbf{Q} . Values of bend angle ranging from 130° to 170° were investigated. The detailed results show the influence of the molecular biaxiality parameter [7] on the relative stability of the N_{TB} , nematic, isotropic phase and the related phase transitions. For the bend angles equal or larger than 140° we observe all five possible phases: uniaxial and biaxial twist–bend nematics, together with uniaxial and biaxial nematics and isotropic phase.

Acknowledgments

This work was supported by Grant No. DEC–2013/11/B/ST3/04247 of the National Science Centre in Poland and in part by PL–Grid Infrastructure. W. T. acknowledges support from Marian Smoluchowski Scholarship (KNOW/58/SS/WT/2016) granted by Marian Smoluchowski Cracow Scientific Consortium “Matter–Energy–Future” within the KNOW funding.

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