Electronic Structure & Electron Spectroscopies

V. V. Nemoshkalenko Memorial Conference and Workshop

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Preface

Recent progress in the resolving power of the experimental techniques which probe the electronic structure of solids, in particular, angle resolved photoemission spectroscopy (ARPES), has demonstrated that our understanding of the electronic band structure is generally correct and that the calculation techniques developed up to date can predict the band structure very well. It has been shown for a variety of compounds including the transition metal dichalcogenides, superconducting cuprates, iron based superconductors, and topological insulators. On the other hand, the experience with these materials shows that in order to understand their physical properties and underlying mechanisms, the electronic band structure should be defined with an extreme accuracy. This requires a combination of the state-of-the-art experiment and calculations. The scope of this meeting is to bring together the experts in the photoemission experiment and band structure calculations working on the same compounds in order to make a progress in those studies from merging the theory and experiment.

The topics cover but not limited to the superconducting cuprates, iron based superconductors, transition metal dichalcogenides, and topological insulators.

We want to devote the first ES&ES to the 80th anniversary of Vladimir Nemoshkalenko (1933-2002) who was ambitious with the idea of merging the electron spectroscopy experiment with the electronic band structure calculations and had founded both these directions of the research in the Institute of Metal Physics. The first day of the event is planned for the Memorial Conference that is followed by the ES&ES Workshop.

Program Committee

Invited Speakers

Marco Bianchi (Denmark)
Daniil Evtushinsky (Germany)
Charles Fadley (USA)
Mark Golden (Netherlands)
Genadi Grechnev (Ukraine)
Akio Kimura (Japan)
Oleg Khyzhun (Ukraine)
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Mikhail Sadovskii (Russia)
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Igor Mazin .... *Naval Research Laboratory, Washington, USA*
Mikhail Sadovskii .... *Institute for Metal Physics, Ekaterinburg, Russia*
Tonica Valla .... *Brookhaven National Laboratory, Upton, USA*

Location

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PROGRAM

May 21, Tuesday

8:45	Workshop opening
9:00-10:30	**Session 1: Iron based superconductors I** *Chair: A. Kordyuk*
9:00	**Mikhail Sadovskii** Electronic structure of iron based superconductors: pnictides versus chalcogenides and similar new systems
9:30	**Igor Mazin** Novel FeSe-based superconductors: where we are and what is to be expected
10:00	**Gennadiy Grechnev** Electronic structure and magnetic properties of LaFeAsO- and FeSe-based superconductors
10:30	Coffee break
11:00-12:30	**Session 2: Extreme ARPES I** *Chair: M. Golden*
11:00	**Charles Fadley** Hard X-ray photoemission with angular resolution and standing-wave excitation
11:30	**Dawei Shen** Probing electronic structure in novel engineered quantum states of matter — in-situ ARPES studies of epitaxial 4d and 5d-electron oxides thin films
12:00	**Volodymyr Zabolotnyy** Ultra-low temperature ARPES on strontium ruthenates
12:30	Lunch
14:00-15:30	**Session 3: Iron based superconductors II** *Chair: M. Sadovskii*
14:00	**Karina Lamonova** Electronic structure and peculiarities of the single-ion magnetic anisotropy of rare-earth ions in the iron oxypnictides RFeAsO (R = Ce, Pr, Nd, Sm, Gd)
14:30	**Maxim Korshunov** Spin-orbit coupling in Fe-based superconductors
15:00	**Yuriy Pogorelov** Impurity effects in ferropnictide superconductors: localization *vs* banding
15:30	Coffee break
16:00-17:30	**Session 4: Good evening mix** *Chair: I. Mazin*
16:00	**Yuri Kucherenko** The dual nature of 4f electrons in rare-earth intermetallics: ARPES view
16:30	**Roman Kuzian** Mechanism of temperature dependence of RIXS spectra in charge transfer insulators
17:00	**Alexander Gabovich** Stationary Josephson effect as a tool to reveal charge-density-wave gapping in cuprates
17:30	Supper

18:30-20:00   Poster session

P01   **Igor Nekrasov**
LDA'+DMFT scheme: A way to treat the double counting problem

P02   **Anastasiya Lyogenkaya**
Electronic structure and magnetic properties of $FeGe_2$

P03   **Janek Maletz**
Unusual band renormalization in the simplest iron based superconductor

P04   **Eugene Kushnirenko**
ARPES spectrum asymmetry as a hallmark of low energy renormalization in superconducting cuprates

P05   **Michael Prokopovych**
Observation of birth of "ageing" effect in Bi2Se3 photoemission spectra

P05   **Bohdan Ilkiv**
Electronic structure of hollow graphitic nanoparticles

P07   **Oleg Khyzhun**
X-ray spectroscopy study of the electronic structure peculiarities of silicon nitride nanofibers

P08   **Oleg Khyzhun**
Electronic structure of $ZrTiO_4$, $HfTiO_4$, $FeTiO_3$ and $MgTiO_3$ titanates: Theoretical calculations and x-ray spectroscopy studies

P09   **Andrei Baranovskiy**
Electronic structure and exchange interaction in GdB_4 compound

P10   **Oleg Feya**
First principles calculations of atomic structure and physical properties of calcium apatites

P11   **Lev Bekenov**
X-ray magnetic dichroism in the (Zn,Co)O diluted magnetic semiconductors from *ab initio* calculations

P12   **Inna Plyushchay**
First-principles calculations of dislocation-oxygen impurity magnetic interaction in silicon

P13   **Nataly Kurgan**
Isomorphic substitutions in the tetrahedral position of apatites and their influence on physicochemical properties

P14   **Svetlana Smolyak**
Electronic structure peculiarities of disordered diphosphates of Mn and Co

P15   **Volodymyr Vishniak**
Monatomic thickness Ag nanostructures on Si (111) surface

P16   **Taras Radchenko**
Influence of correlation of impurities on conductivity in graphene

P17   **Mykola Fedorchenko**
Gd and O depositions on Si(113)

P18   **Sebastian Döring**
Resonant tunneling in novel type Josephson heterostructures superconductor-doped semiconductor-superconductor

May 22, Wednesday

9:00-10:30	**Session 5: ARPES of topological insulators**	*Chair: E. Krasovskii*
9:00	**Mark Golden** ARPES investigations of bulk-insulating topological insulators	
9:30	**Tonica Valla** Probing the Dirac electrons in condensed matter: Graphene and topological insulators	
10:00	**Matti Lindroos** Dichromatic signal excited by circular polarized light surface state	
10:30	Coffee break	
11:00-12:30	**Session 6: Surface/spin sensitive ARPES**	*Chair: K. Rossnagel*
11:00	**Marco Bianchi** Tailoring the electronic texture of a topological insulator via its surface orientation	
11:30	**Akio Kimura** Probing spin textures of topological insulators by spin- and angle-resolved photoemission	
12:00	**Eugene Krasovskii** Spin structure of non-magnetic surfaces by angle resolved photoemission	
12:30	Lunch	
14:00-15:30	**Session 7: Extreme ARPES II**	*Chair: C. Fadley*
14:00	**Enrique Ortega** Tailoring surface and thin film electronic states with curved surfaces	
14:30	**Vladimir Strocov** *k*-resolved electronic structure by soft-X-ray ARPES: From three-dimensional systems to buried hetero-structures	
15:00	**Sergey Nikolaev** The electronic structure within the norm-conserving cluster perturbation theory	
15:30	Coffee break	
16:00-17:30	**Session 8: Electronic structure of novel compounds I**	*Chair: M. Lindroos*
16:00	**Sergey Ovchinnikov** Temperature and magnetic field dependent LDA+GTB band structure of $LaCoO_3$	
16:30	**Alexander Yaresko** Unusual magnetic properties of layered $MCrS_2$ compounds	
17:00	**Igor Nekrasov** LDA'+DMFT scheme: A way to treat the double counting problem	
17:30	Supper	
18:30-20:00	**Round table**	
18:30	**Alexander Kordyuk** Complex electronic structure of iron-based superconductors as a key to high temperature superconductivity	

May 23, Thursday

9:00-10:30	**Session 9: ARPES on layered compounds**	*Chair: V. Strocov*

9:00	**Kai Rossnagel**
	ARPES on layered compounds: From millielectron volts to femtoseconds
9:30	**Claude Monney**
	Charge density wave phase in $TiSe_2$: ARPES and excitonic insulator phase model
10:00	**Daniil Evtushinsky**
	ARPES on iron-based superconductors: leading role of $3d_{xz,yz}$ orbitals
10:30	Coffee break

11:00-12:30	**Session 10: Electronic structure of novel compounds II**
	Chair: S. Ovchinnikov

11:00	**Oleg Khyzhun**
	Electronic structure of the orthorhombic and tetragonal phases of Tl_3PbBr_5
11:30	**Sergey Sichkar**
	Phonon spectra and electron-phonon interaction in HfB_2
12:00	**Closing remarks**
12:30	Lunch and Excursion
18:30	Conference dinner

Electronic structure of iron based superconductors: pnictides versus chalcogenides and similar new systems

M.V. Sadovskii

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We present a brief review of the present day situation with studies of electronic structure of new iron pnictide and chalcogenide high-temperature superconductors. Recent discovery of superconductivity with $T_c > 30$ in $A_x Fe_{2-y} Se2$ (A=K,Cs,...) and possible observation superconductivity in single-layer FeSe up to 50 K represents the major new steps in the development of new concepts in the physics of Fe based high-temperature superconductors.

We compare LDA and ARPES data on the band structure and Fermi surfaces of novel $A_x Fe_{2-y} Se_2$ and single-layer FeSe system and those of the previously studied isostructural 122 - superconductors like $BaFe_2 As_2$ series. Electronic structure of new superconductors is rather different from that of FeAs - systems. In particular, no nesting properties of electron and hole - like Fermi surfaces is observed, casting doubts on some of the most popular theoretical schemes of Cooper pairing and magnetic ordering for these systems.

We discuss our recent results on correlated electronic structure of $K_{1-x} Fe_{2-y} Se_2$ (at different dopings) in the normal phase using the novel LDA'+DMFT computational approach. We show that this iron chalcogenide is more correlated in a sense of bandwidth renormalization (close enough to the Fermi level). Our results for spectral densities are in general agreement with recent ARPES data on this system. In general LDA'+DMFT results are in better agreement with experimental spectral function maps, as compared to the results of conventional LDA+DMFT.

We also present our results on electronic structure for several new systems like $BaFe_2 Se_3$ (Ba123), $SrPt_2 As_2$ and $APt_3 P$ (A=Cs, Sr, La).

Undoped Ba123 is antiferromagnetic with Neel temperature = 250K and rather complicated magnetic structure. Neutron diffraction experiments indicated the possibility of two possible spin structures (antiferromagnetically ordered "plaquettes" or "zigzags"), indistinguishable by neutron scattering. Using LSDA calculated exchange parameters we estimated Neel temperatures for both spin structures within the molecular field approximation and showed that "plaquettes" spin configuration is more favorable "zigzags".

Despite chemical and structural similarity of $SrPt_2 As_2$ ($T_c = 5.2K$) to 122 FeAs-based high-temperature superconductors, its electronic structure is very much different. Fermi surface of $SrPt_2 As_2$ is essentially three dimensional, with complicated sheets corresponding to multiple bands. Somehow similar situation is realized in $APt_3 P$ (A=Cs, Sr, La) system, which also demonstrates three-dimensional multiple band structure, with pretty complicated Fermi surface.

Finally, we address the general problem - which (if any) electronic structure is most favorable for high-temperature superconductivity?

Novel FeSe-based superconductors: where we are and what is to be expected?

Igor Mazin

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I will present a personal prospective on the two latest families of the Fe-based superconductors, $K_xFe_ySe_2$, and FeSe monolayers. I will argue that the simplified crystallography that is usually assumed when analyzing electronic structure and superconductivity is probably insufficient. In particularly, I will discuss the role of the interface in both cases and will present a case of intrinsic S4 symmetry breaking. Interpretation of recent orbital-selective ARPES measurements is an important, if not crucial, part of the problem, and will be discussed in the talk, as well as the role of the so-called "Se etching", necessary for superconductivity in FeSe monolayers.

Electronic structure and magnetic properties of LaFeAsO- and FeSe-based superconductors

G. E. Grechnev

B.Verkin Institute for Low Temperature Physics of National Academy of Sciences of Ukraine, Kharkov 61103

Ab initio calculations of the volume dependent band structure and the exchange enhanced paramagnetic susceptibility were performed for LaFeAsO and FeSe-based systems within the local spin density approximation. It is found that these systems are close to magnetic instability with dominating enhanced spin paramagnetism, and the van Hove singularities are revealed in the electronic spectra. The calculated values of the density of states at the Fermi level and paramagnetic susceptibility exhibit a strong dependence on the structural parameters, such as unit cell volume V and especially the height Z of pnictogen/chalcogen species from the Fe plane. The puzzling experimentally observed pressure effects on susceptibility and superconductivity in LaFeAsO and FeSe-based systems are explained in terms of the pressure dependence of structural parameters V and Z.

Hard X-ray Photoemission with Angular Resolution and Standing-Wave Excitation

Charles S. Fadley

Department of Physics, University of California Davis, Davis, CA 95616 USA
Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720

Several aspects of hard x-ray photoemission that make use of angular resolution and/or standing-wave excitation are discussed. These include hard x-ray angle-resolved photoemission (HARPES) from valence levels, which has the capability of determining bulk electronic structure in a momentum-resolved way; hard x-ray photoelectron diffraction (HXPD), which shows promise for studying element-specific bulk atomic structure, including dopant site occupations; and standing wave studies of the composition and chemical states of buried layers and interfaces. Beyond this, standing wave photoemission can be used to derive element-specific densities of states. Some recent examples relevant to all of these aspects are discussed.

Probing Electronic Structure in Novel Engineered Quantum States of Matter
-- *in-situ* ARPES studies of epitaxial novel oxides thin films

Mingying Li[1], Daniel E. Shai[2], <u>Dawei Shen</u>[1,2,3], Rui Peng[4], Darrell G. Schlom[3], Kyle M. Shen[2] and Donglai Feng[4]

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Speaker's current email address: dwshen@mail.sim.ac.cn

In this talk, I will mainly introduce how to utilize *in-situ* angle-resolved photoemission spectroscopy (ARPES) to study novel electron systems fabricated/engineered by oxide molecular beam epitaxy (OMBE) technique. Particularly, I will report the first high-resolution ARPES studies on the epitaxial pseudocubic-structured $SrRuO_3$ thin films. The long-standing quasi-particle excitations in $SrRuO_3$ are revealed, which show strong coupling with some low energy bosonic modes. Our measurements demonstrate that it is the strong electron-boson coupling but not the Coulomb interaction proposed previously that is primarily responsible for the large effective masses observed in this material. Moreover, I will present the systematic study of the dead-layer behavior in $La_{0.67}Sr_{0.33}MnO_3$ thin films. The evolution of electric and magnetic properties as a function of thickness shows a remarkable resemblance to the phase diagram as a function of doping for bulk materials, providing compelling evidences of the hole-depletion in near interface layers that causes dead-layer. Detailed electronic and surface structure studies indicate that the hole-depletion is due to the intrinsic oxygen vacancy formation.

Ultra-low temperature ARPES on strontium ruthenates

V. B. Zabolotnyy,[*1] D. V. Evtushinsky,[1] A. A. Kordyuk,[2] T. K. Kim,[3] E. Carleschi,[4] B.P. Doyle,[4] R. Fittipaldi,[5] M. Cuoco,[5] A.Vecchione,[5] and S. V. Borisenko[1]

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Strontium ruthenates are well known for their unconventional *p*-type superconductivity, metamagnetism, proximity to a quantum critical point along with the notable effects of spin–orbit coupling. In particular, understanding the superconductivity in single-layered Sr_2RuO_4 requires a detailed knowledge of its electronic structure. As the early photoemission and scanning tunnelling microscopy experiments were confronted with a problem of surface reconstruction, surface ageing was proposed as a solution to access the bulk states. We demonstrate that, in the case of Sr_2RuO_4, circularly polarized light can be used to distinguish between signals from the bulk and surface layers, thus opening a possibility to investigate many-body interactions both in bulk and surface bands [1, 2]. The

Fig. 1. Experimental Fermi surface of Sr_2RuO_4, demonstrating splitting of the surface β band. (For details see ref. [1])

proposed procedure enabled us to detect an unexpected splitting of the surface β band and a notable difference in the renormalization of the bulk and surface α band. We argue that Rashba effect at the surface might be responsible for the splitting of the surface β band, while enhanced electron-phonon coupling at the surface may explain stronger renormalization of the surface α band.

Further, combining our experimental data with tight-binding (TB) approach, we produce a maximally precise description of low energy band structure of Sr_2RuO_4 [3]. The resulting model can be used to obtain band velocity and orbital character for any arbitrary momentum point. In particular, the density of states, and hence Sommerfeld coefficient $\gamma \sim 40 mJ/molRuK_2$, is in perfect agreement with direct bulk sensitive measurements. The developed model is meant to be used as more realistic input for various calculations aimed at understanding of unconventional superconductivity in Sr_2RuO_4.

[1] Zabolotnyy V. B. *et al.* New J. Phys. 14 063039 (2012)
[2] Zabolotnyy V. B. *et al.* Phys. Rev. B 76, 024502 (2007)
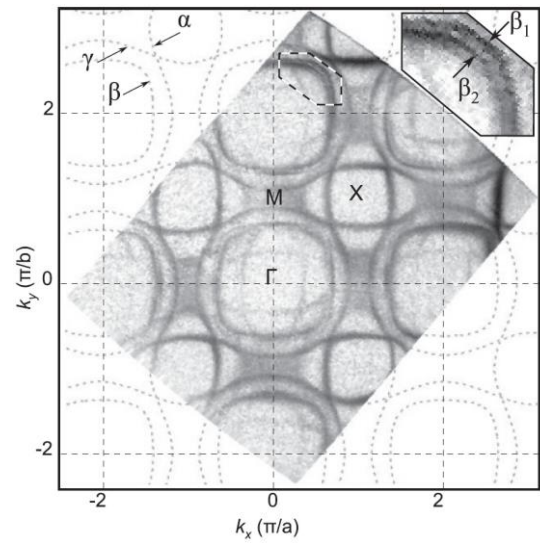[3] Zabolotnyy V. B. *et al.* ArXiv:1212.3994 (2012)

# Electronic structure and peculiarities of the single-ion magnetic anisotropy of rare-earth ions in the iron oxypnictides RFeAsO (R = Ce, Pr, Nd, Sm, Gd)

O. V. Gornostaeva, K. V. Lamonova, S. M. Orel, Yu. G. Pashkevich

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At present, the problem of the interaction between a rare-earth metal and magnetic subsystems in the iron-based high-temperature superconductors $RFeAsO_{1-x}F_x$ (R − rare-earth elements) has not been solved and requires further investigations. In particular, the substitution of La ions with Ce, Pr, Nd, and other ions leads to twice as much increase of the superconducting transition temperature. This observation is usually associated with a purely geometrical factor, namely, with the difference in the radii of the rare-earth ions and significant modification of the distance between iron ions and surrounding ligand ions. However, one can suppose that this effect can be connected with a strongly anisotropic interaction between rare-earth and iron subsystems since the rare-earth magnetic subsystem is usually highly anisotropic, and constants of the anisotropic exchange between iron and rare-earth subsystems are large enough [1]. Therefore, one can expect that fluctuations of the iron magnetic moments are allowed in a certain direction and suppressed in others. In this report we study anisotropic magnetic properties of R^{3+} ions in the RFeAsO matrix.

Energy levels of the R^{3+} ions, *g*-factor values, temperature dependences of magnetic susceptibility components and *fourth*-order anisotropy constants have been calculated using the modified crystal field theory (MCFT) [2]. The iron-subsystem effect on magnetic properties of R^{3+} ions was theoretically studied for both crystallographic phases observed experimentally. On the base of our calculations some conclusions about the nature of the magnetic anisotropy of R^{3+} ions have been made (see figure): (a) in tetragonal and orthorhombic phases the "easy" direction of the cerium-ion magnetic moment is the [110] axis; (b) the "easy" direction of the Nd^{3+} magnetic moment in NdFeAsO changes after the structural transition, namely, in the tetragonal phase it prefers the [010] axis, whereas in the orthorhombic phase it is the [110] direction; the magnetic moment of Sm^{3+} ion preserves the [001] direction in both phases.
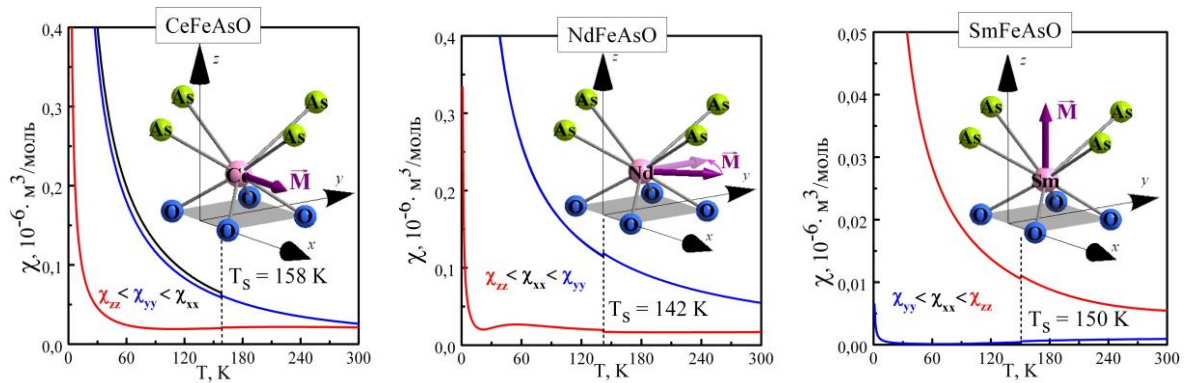
[1] H. Maeter *et al*, *Phys Rew B*, **80**, 094524 (2009).
[2] K. V. Lamonova *et al*, *J. Phys. Chem. A*. **115**, 13596 (2011).

Spin-orbit coupling in Fe-based superconductors

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Determination of the gap symmetry is an important step towards uncovering the mechanism of superconductivity in Fe-based materials. One of the key experiments in support of the $s\pm$ spin-fluctuation-mediated gap was the observation of the spin-resonance peak in many pnictides and chalcogenides. Recently, in inelastic polarized neutron scattering measurements, it was found that the peaks in the transverse and longitudinal components of the spin susceptibility exhibit rather different behavior. I will present arguments that this disparity arises from the spin-orbit coupling. It also leads to a relative shift of the two component's resonance frequency with lower one exhibiting larger enhancement.

Impurity effects in ferropnictide superconductors: localization *vs* banding

Yuriy Pogorelov

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We consider the restructuring of the quasiparticle spectrum in superconducting ferropnictides with impurities. In contrast to the well known insensitivity of common BCS superconductor to impurities by the Anderson theorem, it is shown here that multiorbital electronic structure and extended s-wave type of superconducting order can permit formation of specific narrow in-gap impurity band of conducting states. The observable effects of this spectral feature in electromagnetic (London penetration length), thermodynamical (specific heat, transition temperature), and transport (heat and optical conductivity) properties are discussed. They are compared with available experimental data.

The dual nature of 4*f* electrons in rare-earth intermetallics: ARPES view

Yuri Kucherenko

G.V. Kurdjumov Institute of Metal Physics of NAS of Ukraine

Rare-earth intermetallic compounds have taken a central place in condensed matter physics over the past three decades. Different types of magnetic order, unconventional superconductivity, magnetic heavy-fermion behavior and break-down of the Fermi-liquid properties are prominent examples of the astonishing low-temperature physics of these systems. Investigation of these phenomena is an intriguing task since a profound understanding of the underlying mechanisms might enable to control these effects and to create new materials with tailored properties. Most of these properties are related to a delicate interplay between the partially filled 4*f*-shell and conduction electrons.

Our last experiments provide an important insight into the fine electronic structure near the Fermi level (E_F) and the Fermi surface (FS) of YbRh$_2$Si$_2$. This compound has been in the focus of recent research for its unusual magnetic and Kondo properties and its close proximity to a quantum critical point. Here, we made the observation of crystal-electric field (CEF) splittings of a 4*f* state by means of *k*-resolved photoemission. This allowed us to disclose that interaction with extended valence bands can force the localized CEF-split 4*f* states to become dispersive and thus induce formation of hybridization gaps and E_F crossings in specific parts of the *k*-space. This can change the ground-state symmetry as well as the occupancy, number, energy separation, energy order and degeneration of the CEF-split magnetic 4*f* states *k*-dependently, i.e. very different from the widely believed scenario based on non-interacting atomic-like 4*f* orbitals.

Finally, we got direct access to the FS of this system and: (i) detected its strong *f*-character, (ii) disentangled its topology and features reflecting *f-d* coupling at the surface and bulk of the material, (iii) explored evolution of the iso-energy surfaces closely below the Fermi energy that indeed change dramatically at the meV range. These results create a solid platform to further attack on the outstanding low-temperature properties of rare-earth intermetallics including the Kondo phenomenon, heavy-fermion behavior and quantum-criticality.
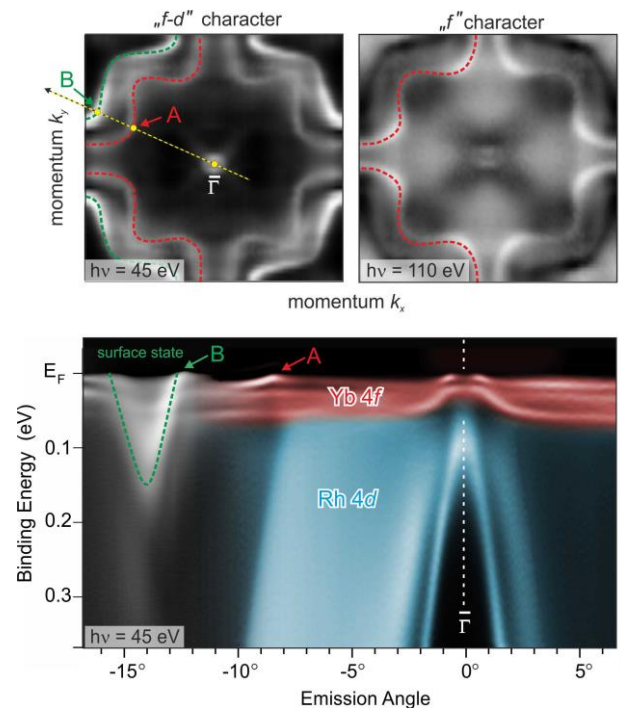
[1] M. Höppner, et al., Nature Communications (2013) *in press*.
[2] S. Danzenbächer, et al., Phys. Rev. Lett. **107**, 267601 (2011).
[3] D. V. Vyalikh, et al., Phys. Rev. Lett. **105** 237601 (2010).

Mechanism of temperature dependence of RIXS spectra in charge transfer insulators

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We consider a simple model, which reflect basic properties of charge transfer insulator oxides: antiferromagnetic ground state and charge transfer excitations of Zhang-Rice singlet type. The model allows to obtain analytically various response functions [optical conductivity, X-ray absorption spectrum (XAS) and oxygen K-edge resonant inelastic X-ray scattering spectrum (RIXS)]. Mechanism of temperature dependence of these functions is elucidated. Recent experimental and numerical studies [1, 2] of edge-shared cuprates are discussed.

[1] C. Monney, V. Bisogni, K.-J. Zhou, R. Kraus, V. N. Strocov, G. Behr, J. Malek, R. Kuzian, S.-L. Drechsler, S. Johnston, et al., Phys. Rev. Lett. **110**, 087403 (2013).

[2] R. Kuzian, S. Nishimoto, S.-L. Drechsler, J. M_alek, S. Johnston, J. van den Brink, M. Schmitt, H. Rosner, M. Matsuda, K. Oka, et al., Phys. Rev. Lett. **109**, 117207 (2012).

Stationary Josephson effect as a tool to reveal charge-density-wave gapping in cuprates

A. M. Gabovich, A. I. Voitenko

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The theory of the stationary Josephson tunnel current I_c is proposed for junctions involving *d*-wave superconductors partially gapped by biaxial or unidirectional charge density waves (CDWs). Specific calculations were carried out for symmetric and non-symmetric junctions. Allowances were made for the directionality of tunneling. The dependences of I_c on the angle γ between the chosen crystal direction and the normal to the junction plane were found to be significantly influenced by CDWs.

It was shown in particular that the d-wave driven periodicity of $I_c(\gamma)$ in the CDW-free case is transformed into double-period beatings depending on the parameters of the system. The results of calculations testify that the orientation-dependent patterns $I_c(\gamma)$ measured for CDW superconductors allow the CDW configuration (unidirectional versus checkerboard) and the symmetry of superconducting order parameter to be determined. The predicted effects can be used to indirectly reveal CDWs in underdoped cuprates where pseudogaps are observed, which we consider as a consequence of the CDW appearance.

[1] A. M. Gabovich, M. S. Li, H. Szymczak, A. I. Voitenko, *Phys. Rev. B* **87**, 104503 (2013).

ARPES investigations of bulk-insulating topological insulators*

Mark S. Golden

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In this talk I will communicate the latest results from our programme aiming at generating single-crystalline, truly bulk-insulating 3D topological insulators and their investigation using angle-resolved photoemission spectroscopy and related techniques. Both topologically interesting and trivial surface states will be discussed (the latter both spin degenerate and spin polarized), with a focus on the time-, temperature- and adsorbate-dependent changes we track in the observed energetics of the different features in the electronic structure of these systems.

Probing the Dirac electrons in condensed matter: Graphene and topological insulators

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Recent discoveries of graphene and topological insulators have shown that charge carriers in these materials form two-dimensional gas of massless quasiparticles whose dynamics can be described by the relativistic Dirac's equation. Due to the nearly linear electronic bands and special topological constraints, these systems show a wide range of exotic phenomena, some of which could be utilized for quantum computing and low-power electronic devices. Here, we will present angle-resolved photoemission studies of these materials.

Dichromatic signal excited by circular polized light surface state

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We have investigated the dichromatic signal in high *Tc* superconductors, graphene and in Au(111). The angle-resolved photoemission intensity calculations are based on the one-step model and multiple-scattering theory. In case of HTSC's and graphene non-relativistic approach was used, but in case of Au fully relativistic formalism is applied.

The Dirac-like electronic structure of graphene originates from the equivalence of the two basis atoms in the honeycomb lattice. We show that the characteristic parameters of the initial state wave function (sublattice symmetry and isospin) can be determined using angle-resolved photoemission spectroscopy (ARPES) with circularly polarized synchrotron radiation. At a photon energy of $hv = 52$ eV, transition matrix element effects can be neglected allowing us to determine sublattice symmetry and isospin with high accuracy using a simple theoretical model.

The behavior of the dichromatic signal of the Au(111) surface state at Fermi energy is complicated and we have found 13 different patterns of dichromatic signal with photon energies in the range of 7 . . . 100 eV.

The origin of the photon energy dependence in dicromatic signal is discussed.

Tailoring the electronic texture of a topological insulator via its surface orientation

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Topological insulators are characterised by an insulating bulk band structure, but topological considerations require their surfaces to support gap-less, metallic states. Meanwhile, many examples of such materials have been predicted and found experimentally, but experimental effort has concentrated on the closed-packed (111) surface of these materials. Thus, the theoretical picture of an insulating bulk embedded in a metallic surface from all sides of a crystal still needs to be confirmed.

Here we present angle-resolved photoemission spectroscopy results from the (110) surface of the topological insulator $Bi_{1-x}Sb_x$ ($x \approx 0.15$). As expected, this surface also supports metallic states but the change in surface orientation drastically modifies the band topology, leading to three Dirac cones instead of one. This illustrates the possibility to tailor the basic topological properties of the surface via its crystallographic direction. Here it introduces a valley degree of freedom not previously achieved for topological insulator systems.

Probing spin textures of topological insulators by spin- and angle-resolved photoemission

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Three-dimensional topological insulators (3D TIs) with a gapless topological surface state (TSS) in a bulk energy gap induced by a strong spin-orbit coupling have attracted much attention as key materials to revolutionize current electronic devices. A spin helical texture of a TSS, where the electron spin is locked to its momentum, is a manifestation of a 3D TI.

A number of well-known thermoelectric and phase-change materials have so far been predicted to be 3D TIs. In order to experimentally confirm their topological natures, spin- and angle- resolved photoemission spectroscopy (SARPES) is one of the most powerful tools and it has actually been playing major roles in finding some real 3D TIs [1]. Among the established 3D TIs, Bi_2Se_3 has been most extensively studied because of its relatively large energy gap and the simplest TSS. However, the topological nature is apparently obscured near and below the Dirac point, which is disadvantageous for spintoronic applications.

SARPES experiments were performed at the ESPRESSO end station attached to the APPLE-II type variable polarization undulator beam line (BL-9B) at Hiroshima Synchrotron Radiation Center (HSRC) [2]. The VLEED-type spin detector utilized in the ESPRESSO machine achieves a 100 times higher efficiency compared to that of conventional Mott-type spin detectors [2]. Photoelectron spin polarizations are measured by switching the direction of in-plane target magnetizations, thereby simultaneously eliminating the instrumental asymmetry, which is a great advantage for a quantitative spin analysis of nonmagnetic systems such as 3D TIs. Our machine can resolve both out-of-plane and in-plane spin polarization components with high angular/momentum and energy resolutions

In this talk, some of the ternary 3D TIs such as $GeBi_2Te_4$ [3], Bi_2Te_2Se, and Bi_2Se_2Te [4] are shown to possess TSSs with marked spin polarizations. It has been revealed for $GeBi_2Te_4$ that a disorder in the crystal has a minor effect on the surface-state spin polarization, which is ~70% near the Dirac point in the bulk energy gap region (~180 meV). Highly spin-polarized features are also found for Bi_2Te_2Se and Bi_2Se_2Te, which are persistent across the Dirac point. The availability of both upper and lower TSSs promises to extend the variety of spintoronic application, for instance, to dual gate TI devices and topological p-n junctions.

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Spin structure of non-magnetic surfaces by angle resolved photoemission

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Theory of angle and spin-resolved photoelectron spectroscopy of systems with strong spin-orbit interaction will be presented, in particular, photoemission from spin-split and spin-polarized states will be discussed.

Starting with a complex-band-structure view on the Rashba splitting of surface states, a qualitative analysis of the Rashba effect for surface as well as for bulk continuum states will be given within a one-dimensional model [1]. Special attention will be paid to the spin polarization of the photocurrent from bulk continuum states, which has been recently experimentally observed on Bi(111) [2] and W(110) [3]. The role of photoemission final states and dichroism effects will be discussed.

Calculations of the spin-resolved photocurrent from Bi(111), W(110), and the Ag_2Bi surface alloy within an *ab initio* theory of photoemission will be presented based on the one-step formalism, in which the final states are treated as time-reversed LEED states. The theory employs the Bloch waves approach to electron scattering within the augmented plane waves formalism [4]. Relativistic effects are included within the two-component approximation. The spin-orbit coupling is shown to lead to a Rashba-type spin polarization of the angle-resolved photocurrent from bulk continuum states of a non-magnetic system.

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Tailoring surface and thin film electronic states with curved surfaces

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Surfaces that are vicinal to high symmetry directions have frequently demonstrated their enormous potential for surface science research and applications. Vicinal surfaces exhibit distinct chemical and physical properties due to the high density of atomic steps, but they are also useful as templates for nanostructure growth, and, more generally, to transmit uniaxial and/or chiral symmetry to epitaxial layers. Moreover, vicinal planes may respond better than high-symmetry surfaces during thin-film growth, e.g., by eliminating azimuthal domains, and hence dislocation boundaries, or by enabling defect-free layer-by-layer growth through "step-flow".

A curved substrate is an obvious alternative for a fast, thorough surface analysis, i.e., for a rational optimization of physical-chemical and growth properties that are sensitive to atomic steps. Despite the clear advantage of having a tunable surface orientation at hand, the curved crystal approach has barely been used. The reason is mainly the difficulty to fabricate a customized curved surface with high precision, but also the inconveniences that a curved sample imposes, due to its inherent complexity, to surface preparation, data taking, or data analysis. However, the recent evolution of analytical surface science techniques toward laterally-resolved, scan probes at different length scale has brought the curved surface back to the scene in Surface Science.

In the past few years we have used Ag(111), Cu(111) and Au(111) curved noble metal surfaces to thoroughly explore different surface science phenomena linked to surface steps [1,2,3]. In particular, we have characterized the fundamental changes in electronic properties that metallic surface states and quantum wells of thin films exhibit in the presence of surface steps, thereby demonstrating the possibilities that this curved surface approach offers to tune all surface properties.

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k-resolved electronic structure by soft-X-ray ARPES:
From three-dimensional systems to buried heterostructures

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A fundamental benefit of pushing the ARPES experiment into the soft-X-ray energy range is the photoelectron escape depth increasing by a factor of 3-5 compared to the conventional VUV-ARPES. This gives a boost to bulk sensitivity as well as enables access to buried heterostructures. However, until recently the spead of soft-X-ray ARPES (SX-ARPES) has been severely impeded by a loss of the valence band photoexcitation cross-section by a few orders of magnitude compared to the VUV energy range. This problem has recently been solved at Swiss Light Source with the new SX-ARPES facility at the ADRESS beamline [1] which delivers X-ray radiation with variable polarizations in a photon energy range from 300 to 1600 eV with routine energy resolving power $E/\Delta E$ up to 20000. High photon flux topping up 10^{13} photons/s/0.01%BW combined with small spot size and grazing X-ray incidence angle experimental geometry has not only overpowered the notorious cross-section problem but also enabled access to buried heterostructures despite the photoelectron attenuation in a few monolayers thick overlayers.

Applications of SX-ARPES to 3-dimensional (3D) materials are based on the fact that the increase of the photoelectron escape depth, by the Heisenberg uncertainty principle, improves intrinsic definition of surface-perpendicular electron momentum. One of our first application examples was the paradigm transition metal dichalcogenide VSe_2 [2]. The experimental 3D band structure and Fermi surface (FS) of this material taken in a photon enegy range from 885 to 945 eV (Figure) demonstrate a textbook clarity achieved by virtue of free-electron final states, their sharp definition in 3D momentum and smooth atomic-like photoemission
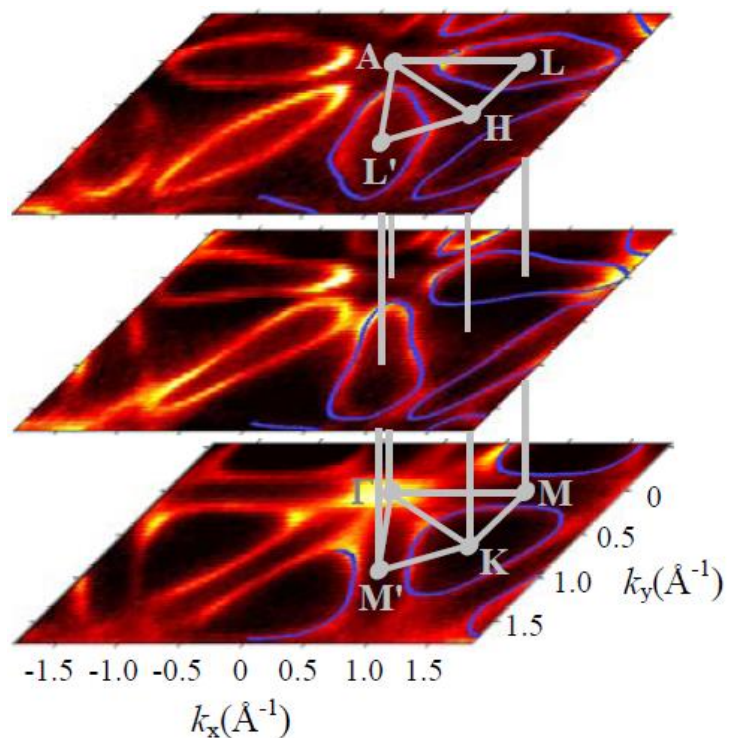
matrix elements delivered in the soft-X-ray energy range. An intriguing feature of VSe2 is that despite its layered quasi-2D structure this material develops 3D charge density waves (CDWs). Autocorrelation analysis of the experimental FS has revealed its pronounced out-of-plane nesting which acts as the precursor of these exotic CDWs [2]. Other examples of applications of SX-ARPES to 3D materials include polarization dependence and alternating FS shapes in pnictide HTSCs, demonstrating their 3D character and intra-cell

interference effects, bulk Rashba spin splittings in noncentrosymmetric topological insulator BiTeI [3], etc.

The high brilliance of the ADRESS beamline has enabled the move from bulk materials to buried heterostructures. We illustrate this by resonant SX-ARPES of 2D electron gas at buried $LaAlO_3/SrTiO_3$ interfaces, which unveils different subbands and FS sheets formed by the interface states. Increase of temperature suppresses the momentum selectivity and allows depth profiling of the 2D electron gas from variations of the SX-ARPES signal with emission angle [4]. Another example is resonant spectroscopy of Mn magnetic impurities in the paradigm magnetic semiconductor GaMnAs, which reveals the energy position of the ferromagnetic Mn impurity band and mechanism of its hybridization with the 3D host GaAs bands [5]. These results have immediate implications for the origin of ferromagnetism in GaMnAs. The whole body of our unfolding results demonstrates an immense potential of SX-ARPES to deliver a clear **k**-resolved picture of electronic structure from 3D materials to buried heterostructures and impurities.

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The electronic structure within the norm-conserving cluster perturbation theory

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Within a new norm-conserving (NC) approach to the cluster perturbation theory (CPT) for the 2d Hubbard model we study the electronic structure. We have studied the hole doping dependence of the quasiparticle (QP) band structure and the Fermi surface within NC-CPT. We have reproduced the cascade of the quantum phase transitions of the Lifshitz type with increasing doping. In the present approach both the static and dynamical correlations inside each cluster are treated exactly. That is why it allows to describe both the shape of the Fermi surface and the non-uniform spectral weight distribution along the Fermi contour. In the numeric computation of spectral density we substitute a delta-function by a Lorenzian curve with a broadening parameter. It allows to model experimental resolution of ARPES and finite QP life time that may appear due to high order perturbation contributions from the intercluster hopping. The increase of the broadening parameter transforms the small hole pocket in the underdoped region in the arc. Previously similar conclusion has been found by C-DMFT method.

Temperature and magnetic field dependent LDA+GTB band structure of LaCoO$_3$

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Quasiparticle band structure of spin singlet Mott insulator LaCoO$_3$ is calculated within the multielectron LDA+GTB approach. The low spin (LS) Co^{+3} ground term is separated by a small spin gap $E_s \sim 10$ meV from the nearest excited high spin (HS) term. At $T = 0$ the top of the valence (bottom of conductivity) band is determined by the electron removal (addition) to the LS terms of d^5 (d^7) configuration. The large insulator gap is equal to $Eg = 1.5$ eV. At finite temperature, the nonzero population of the HS d^6 configuration results in the additional HS d^6 - HS d^5 electron removal excitation forming the in-gap band below the bottom of the valence band. The width of the in-gap increases with temperature, Eg decreases up to zero at $T_{IMT} = 585$. Smooth insulator–metal transition occurs around this temperature. The magnetic susceptibility has two maxima, the first at $T \sim E_s$, and the second at T_{IMT}. Strong magnetic field also decrease E_s and at $T = 0$ the insulator–metal transition takes place at $H > 65$T. For another ReCoO$_3$ higher value of the spin gap shifts spin transition and insulator–metal transition to higher temperatures.

Unusual magnetic properties of layered MCrS$_2$ compounds

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A chromium sulfide AgCrS$_2$ has recently attracted considerable attention due to its multiferroic properties and unusual double-stripe magnetic order which appear below the Néel temperature of 50 K. AgCrS$_2$ belongs to a family of layered MCrS$_2$ (M^+ = Li, Na, K, Cu, Ag, Au) compounds in which magnetic Cr^{3+} ($3d^3$) ions form a triangular lattice. Although charge and orbital degrees of freedom in these compounds are frozen, geometrical frustrations of magnetic interactions, inherent in the triangular lattice, lead to fascinating magnetic properties: depending on the size of an M^+ ion magnetic order in Cr planes changes from non-collinear 120° (Li) antiferromagnetic, to double stripes (Ag, Au), and, finally, to ferromagnetic (K). In order to understand this strong variation of the magnetic properties we calculated band structures and total energies $E(\mathbf{q})$ as a function of a wave vector $\mathbf{q}$ for various spin spiral structures. Effective exchange coupling constants j between Cr spins are then estimated by fitting $E(\mathbf{q})$ to an appropriate classical Heisenberg model. We found that depending on the M size the nearest neighbor coupling j_1 changes from strongly antiferromagnetic in LiCrS$_2$ to ferromagnetic in KCrS$_2$, whereas the coupling j_3 between the 3rd Cr neighbors is strong and remains nearly constant in all the compounds. In AgCrS$_2$ with $j_1 << j_3$ the double stripe magnetic order is stabilized by monoclinic distortions of the crystal structure. We discuss the microscopic origin of various j and show that similar considerations help to understand the magnetic properties of other frustrated Cr compounds ACr$_2$S$_4$ with a spinel structure.

LDA'+DMFT scheme: A way to treat the double counting problem

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We discuss the recently proposed LDA'+DMFT approach providing consistent parameter free treatment of the so called double counting problem arising within the LDA+DMFT hybrid computational method for realistic strongly correlated materials. In this approach the local exchange-correlation portion of electron-electron interaction is excluded from self consistent LDA calculations for strongly correlated electronic shells, e.g. d-states of transition metal compounds. Then the corresponding double counting term in LDA+DMFT Hamiltonian is consistently set in the local Hartree (fully localized limit - FLL) form of the Hubbard model interaction term. We present the results of extensive LDA'+DMFT calculations of densities of states, spectral densities and optical conductivity for most typical representatives of two wide classes of strongly correlated systems in paramagnetic phase: charge transfer insulators (MnO, CoO and NiO) and strongly correlated metals ($SrVO_3$ and Sr_2RuO_4). It is shown that for NiO and CoO systems LDA'+DMFT qualitatively improves the conventional LDA+DMFT results with FLL type of double counting, where CoO and NiO were obtained to be metals. We also include in our calculations transition metal $4s$-states located near the Fermi level missed in previous LDA+DMFT studies of these monooxides. General agreement with optical and X-ray experiments is obtained. For strongly correlated metals LDA'+DMFT results agree well with earlier LDA+DMFT calculations and existing experiments. However, in general LDA'+DMFT results give better quantitative agreement with experimental data for band gap sizes and oxygen states positions, as compared to the conventional LDA+DMFT. Also LDA'+DMFT method applied to the hole doped KFe_2Se_2 novel superconductor gives almost quantitative description of available ARPES data.

Complex electronic structure of iron-based superconductors as a key to high temperature superconductivity

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The iron based superconductors (FeSC) promise interesting physics and applications, and, while the interplay of superconductivity and magnetism, as well as their mechanisms remain the issues of active debates and studies, one thing in FeSC puzzle is clear, namely that it is the complex multi-band electronic structure of these compounds that determines their rich and puzzling properties [1, 2]. What is important and fascinating is that this complexity seems to play a positive role in the struggle for understanding the FeSC physics and also for search of the materials with higher T_c's. This is because the multiple electronic bands and resulting complex Fermiology offer exceptionally rich playground for establishing useful empirical correlations. This is also because this electronic structure is well understood—the band structure calculations well reproduce its complexity: all the bands and their symmetry. The role of the experiment, in this case, is just to define the exact position and renormalization for each band. This piece of experimental knowledge, however, appears to be vitally important for understanding of the electronic properties of these new compounds.

Considering all the electronic band structures of FeSCs that can be derived from ARPES [3-7], it has been found that the Fermi surface of every optimally doped compound (the compounds with highest T_c) has the Van Hove singularities of the Fe $3d_{xz/yz}$ bands in the vicinity to the Fermi level. This suggests that the proximity to an electronic topological transition, known as Lifshitz transition, for one of the multiple Fermi surfaces makes the superconductivity dome at the phase diagram. Based on this empirical observation, one can predict, in particular, that the hole overdoping of KFe_2As_2 and $LiFeAs$ compounds is a possible way to increase the T_c.
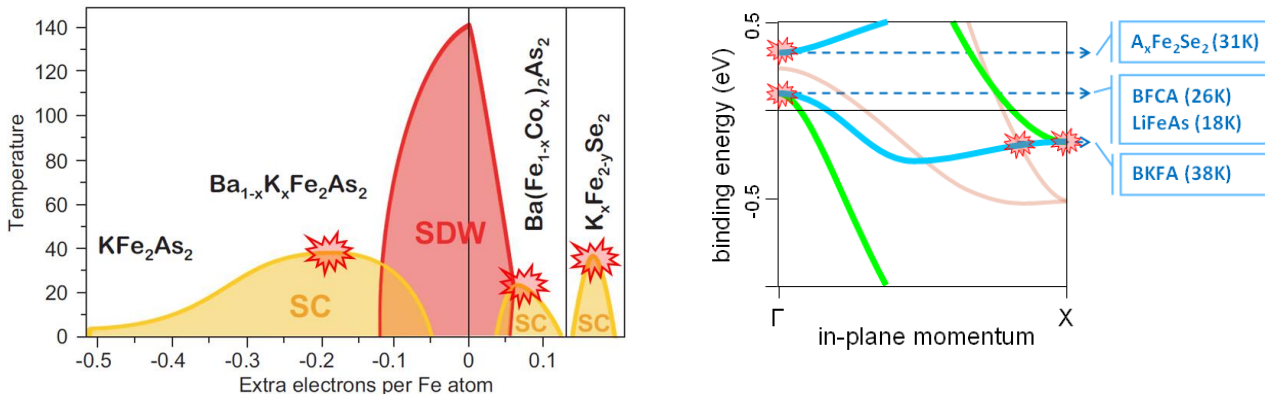

Figure 1. Phase diagram of the 122 family complemented by the 122(Se) family as a generalized band structure driven diagram for FeSCs (left) and common electronic band structure of the FeSCs (right): the compounds with highest T_c has either top or bottom of the Fe $3d_{xz/yz}$ bands crossing the Fermi level.

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ARPES on layered compounds: From millielectron volts to femtoseconds

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The latest results from our research program on the electronic structure and dynamics of layered transition-metal dichalcogenides will be presented. The specific aims here are to clarify the interrelationship of charge-density waves and superconductivity in the low-temperature superconductors $2H$-NbSe$_2$ and electron-doped $1T$-TiSe$_2$ and to disentangle the interplay of electron-phonon and electron-electron interactions in the Peierls-Mott insulator $1T$-TaS$_2$ and the possible excitonic insulator $1T$-TiSe$_2$. Two complementary experimental approaches are used: synchrotron-based static ARPES with 5-meV energy resolution at temperatures down to 1 K (at the 1^3 endstation of BESSY) and laser-based time-resolved ARPES with 30-fs time resolution employing a high-harmonic-generation source (in the Bauer lab at the University of Kiel).

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Electron-hole fluctuations driving the charge density wave phase transition in TiSe$_2$

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There is a longstanding open question about the existence of a condensate of electron-hole pairs (excitons) in a way as it is well known for pairs of electrons, Cooper-pairs, in superconductivity. TiSe$_2$ exhibits an unusual temperature-dependence of transport experiments and a specific band configuration that has been related to the possible formation of excitons. Indeed, at the temperature of 200K, the layered, quasi-two-dimensional TiSe$_2$ undergoes a phase transition towards a charge density wave (CDW) phase, which is accompanied by a periodic lattice distortion (PLD) [1].

I propose the exciton condensate phase model [2] as the electronic origin of the CDW phase of TiSe$_2$. This scenario is supported by the good agreement between measured angle-resolved photoemission spectroscopy data and photoemission intensity maps calculated by the spectral function within this model [3]. With the help of perturbation theory calculations, I will motivate that above 200K, strong electron-hole fluctuations are provoking an electronic instability towards the CDW phase [4]. Eventually, this instability drives the PLD via the electron-phonon coupling [5].

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ARPES on iron-based superconductors: leading role of $3d_{xz,yz}$ orbitals

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I will start with a short overview of the available ARPES results on iron-based superconductors. Despite of the large variety of the observed Fermi surfaces [1-6], phenomenologically one can point out several common tendencies for iron high temperature superconductors — namely, band renormalization of factor of three at the Fermi level [3, 6-8], often a two-gap behavior [2, 7-10], noticeable electronic coupling to low-energy bosonic modes. Our recent results indicate clear correlation between the superconducting gap magnitude and orbital origin of the electronic states, with the largest gap solely for iron $3d_{xz,yz}$ orbitals. Interestingly, the electron coupling to bosonic modes was found to be stronger also for $3d_{xz,yz}$ bands. Further analysis of the electronic structures of differently doped iron arsenides consistently points to the significance of $3d_{xz,yz}$ bands for superconductivity in these materials.
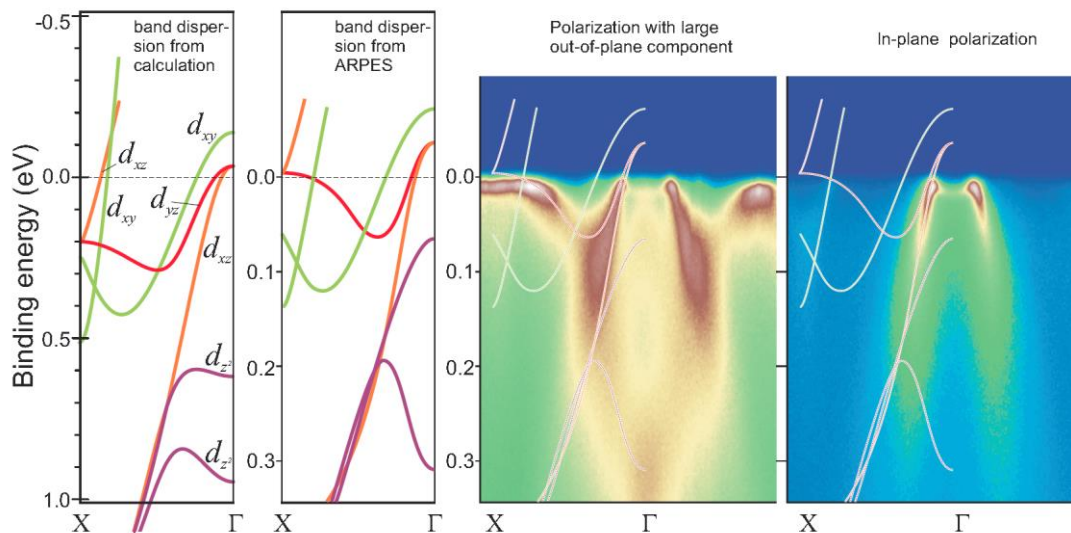
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Electronic structure of the orthorhombic and tetragonal phases of Tl$_3$PbBr$_5$

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Trithallium lead pentabromide, Tl$_3$PbBr$_5$, is recognized as a new low-phonon energy host material operating in mid-IR and far-IR regions. Two polymorphous forms, namely orthorhombic low-temperature (LT) and tetragonal high-temperature (HT), have been detected for this compound: the *LT*-Tl$_3$PbBr$_5$ phase crystallizes in the space group $P2_12_12_1$, with the lattice parameters $a = 15.397$ Å, $b = 9.061$ Å, and $c = 8.537$ Å, whilst the *HT*-Tl$_3$PbBr$_5$ phase possesses the lattice parameters $a = b = 15.486$ Å and $c = 8.903$ Å (space group $P4_1$). The non-central space groups adopted by both polymorphous forms of the Tl$_3$PbBr$_5$ compound make it a very prospective material for optoelectronics and non-linear optics devices (lasers, luminophors, narrow-band optical filters). In the present work, X-ray photoelectron core-level and valence-band spectra for pristine and Ar$^+$-ion irradiated surfaces of a Tl$_3$PbBr$_5$ single crystal grown by the Bridgman-Stockbarger method have been measured. Our X-ray photoelectron spectroscopy (XPS) results reveal high chemical stability of Tl$_3$PbBr$_5$ single crystal surface. Total and partial densities of states of constituent atoms of the orthorhombic *LT*-Tl$_3$PbBr$_5$ and tetragonal *HT*-Tl$_3$PbBr$_5$ phases have been calculated using the first-principles full potential linearized augmented plane wave (FP-LAPW) method. The FP-LAPW data reveal that contributions of the Br 4p-like states dominate in the valence band of the both phases of Tl$_3$PbBr$_5$; they contribute mainly into the top and the central portion of the valence band with also significant contributions throughout the whole valence-band region. The bottom of the valence band of the orthorhombic and tetragonal phases of Tl$_3$PbBr$_5$ is composed mainly of the Tl 6s-like states. Additionally, the unoccupied Pb 6p- and Tl 6p-like states in almost equal proportion dominate at the bottom of the conduction band of *LT*-Tl$_3$PbBr$_5$, whilst the unoccupied Pb 6p-like states are the dominant contributors at the bottom of the conduction band of the *HT*-Tl$_3$PbBr$_5$ phase. Our theoretical data reveal that the orthorhombic *LT*-Tl$_3$PbBr$_5$ and tetragonal *HT*-Tl$_3$PbBr$_5$ phases are indirect-gap materials with band gap of 3.05 and 2.26 eV, respectively. The theoretical predictions are confirmed by the XPS measurements carried out for the both phases of Tl$_3$PbBr$_5$.

Phonon spectra and electron-phonon interaction in HfB$_2$

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Ceramics based on transition metal borides such as HfB2 have a unique combination of mechanical and physical properties: high melting points (>3000 °C); high thermal and electrical conductivity; chemical inertness against molten metals; great thermal shock resistance. Thus, the diboride HfB2 is a very attractive candidates for high temperature thermomechanical structural applications up to temperatures ≈ 3000 °C. Potential applications include thermal protective structures for leading-edge parts on hypersonic re-entry space vehicles, propulsion systems, furnace elements,refractory crucibles and plasma-arc electrodes.

Figure 1 Theoretically calculated phonon density of states (full blue line) for HfB$_2$ by Deligoz [3] and Lawson [4] (VASP), respectively.

For the calculation of the phonon spectra and electron-phonon interaction a scalar relativistic FP-LMTO method [1] was used. Figure shows theoretically calculated phonon density of state for HfB2 (full blue curve). The DOS for HfB2 can be separated into three distinct regions. Based on our analysis of relative directions of eigenvectors for each atom in unit cell, we find that the first region (with a peak in phonon DOS at 5.2 THz) is dominated by the motion of Hf atoms. This region belongs to the acoustic phonon modes. The second wide region (14-20 THz) results from the coupled motion of Hf and the two B atoms in the unit cell. The E1u, A2g, B1g phonon modes lie in this area. The phonon DOS in the third region extends from 22 THz to 26 THz. This is due to the movement of boron atoms and is expected since boron is lighter than Hf. The covalent character of the B-B bonding is also crucial for the high frequency of phonons. The in-plane E2g mode belongs to this region. The second and third regions represent optical phonon modes in crystals. The most significant feature in the phonon DOS is a gap around 6-13 THz. This gap is a consequence of the large mass difference between B(10.8 a.u.) and Hf (178.49 a.u.), which leads to decoupling of the transition metal and boron vibrations. We compare our results with theoretically calculated phonon DOS by Deligoz et al. [2] and Lawson et al. [3]. Calculations of Deligoz et al. were based on the so-called "frozen phonon" technique and built an optimized rhombohedral supercell with 36 atoms. This method is inconvenient for calculating phonon spectra for small q-points as well as for compounds with large number of atoms per unit cell. Lawson et al. used two different codes to calculated the phonon spectra. VASP, the supercell method, based un the projected augmented wave potentials. Second method, ABINIT, used Fritz Haber Institute pseudopotentials in the Troulliers-Martin form. VASP results of Lawson et al. is slightly closer to our calculation with respect to ABINIT data. There is an energy shift towards smaller energies of the all peaks of the Lawson et al. [3] calculations in comparison with the Deligoz et al. [2] data. Our results are just in between these two calculations.

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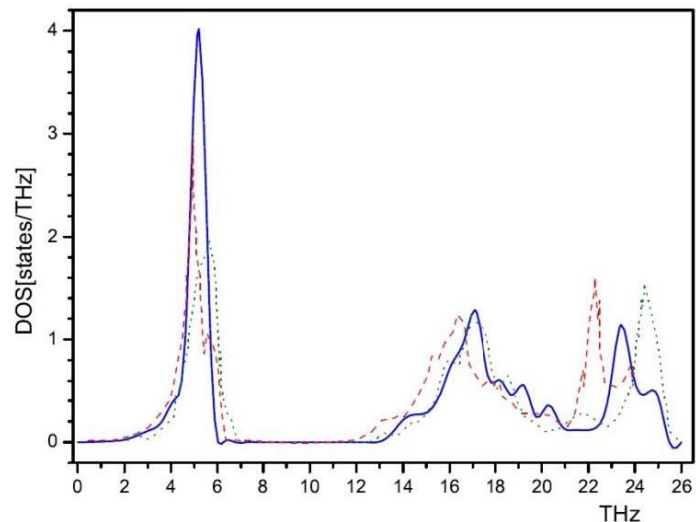[3] Lawson J W, Bauschlicher C W and Daw M S 2011 *J. American Ceramic Society* 94 3494

Electronic structure and magnetic properties of FeGe$_2$

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The transition metal compounds with germanium and tin having the tetragonal C16-type crystal structure exhibit unusual magnetic, electrical and structural properties. These properties make them the subject of continuous experimental and theoretical investigations. FeGe$_2$ is an itinerant electron antiferromagnet, which has a second-order transition from a paramagnetic phase to an incommensurate phase at 289 K with a long-wavelength modulation in the basal plane, and the other first-order transition from an incommensurate to a commensurate antiferromagnetic phase at 263 K. In our work we report results of theoretical calculations of electronic structure and magnetic properties of FeGe$_2$. Ab initio calculations of the volume dependent electronic structure and magnetic properties were performed by employing the full-potential LMTO and LAPW methods for paramagnetic and magnetic configurations of FeGe$_2$ compound. It is unambiguously established that the collinear antiferromagnetic configuration has clearly the lowest total energy so that it is the ground state of the bulk FeGe$_2$. The calculated magnetic moments of FeGe$_2$ appeared to be about 1.2 µB per formula unit and arise from the iron-derived 3d states. This is in agreement with neutron experiments, which reported the magnetic moments about 1.2—1.3 µB, and this clearly indicates the itinerant nature of antiferromagnetism in FeGe$_2$.

It is expected, that a pressure can provide drastic changes in electronic and magnetic properties. Therefore we studied a behavior of magnetic susceptibility χ under uniform and uniaxial pressures for the paramagnetic and antiferromagnetic phases. The spin and orbital Van Vleck contributions to χ and their volume dependences were calculated *ab initio* in an external magnetic field and were found in agreement with the available experimental data. It is appeared that the calculated $d\ln\chi / d\ln V$ derivative in the PM phase of FeGe$_2$ is large but somewhat lower than the corresponding derivatives in the PM compounds with highly enhanced spin susceptibility (e.g. CeCo$_2$, YCo$_2$, TiCo, Ni$_3$Al). Also, for the antiferromagnetic phase of FeGe$_2$ the substantially anisotropic and pressure dependent magnetic susceptibilities were evaluated *ab initio* , which allowed to shed light on results of recent experiments, including magnetostriction and uniaxial pressure effect on magnetic susceptibility.

Unusual band renormalization in the simplest iron based superconductor

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The electronic structure of the iron chalcogenide superconductor FeSe$_{1-x}$ was investigated by high-resolution angle-resolved photoemission spectroscopy (ARPES). The results show some significant differences between the experimental electronic structure of FeSe$_{1-x}$, DFT calculations and existing data on FeSe$_x$Te$_{1-x}$. The bands undergo a pronounced orbital dependent renormalization, different from what was observed for FeSe$_x$Te$_{1-x}$ and any other pnictides.

ARPES spectrum asymmetry as a hallmark of low energy renormalization in superconducting cuprates

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A hallmark of weak low energy renormalization of quasiparticle spectrum measured by ARPES is known as a 'kink' on experimental dispersion. It was introduced for the superconducting cuprates along the nodal direction but observed virtually for any metallic crystal with essentially different underlying reasons. Nevertheless, the kinks are often considered as evidence for common scattering mechanism in different families of compounds. For example, the observation of the kinks in traditional metals and cuprates had been considered as evidence for strong electron-phonon interaction. Later, 'similar' kinks in cuprates and ferropnictides have been used to prove the spin-fluctuation nature of renormalization in both families. Here we study a feature in ARPES spectra, the asymmetry of the momentum distribution curves (MDCs), which can help to distinguish different renormalization mechanisms. We have found that noticeable MDC asymmetry is observed for the superconducting cuprates above the kink energy but not for the ferropnictides. We show that the observed asymmetry can be associated with strong momentum dependence of the self-energy.

Observation of birth of "ageing" effect in Bi_2Se_3 photoemission spectra

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Using the comparative ARPES spectra analysis to explore the detector non-linearity [1], we have developed a procedure to strongly enhance the "ageing" effect in the spectra. The method consists in filtering of useful data on the intensity-intensity plot of two comparing images. The conceiving appearance of quantum well states [2,3] at the surface of topological insulator Bi_2Se_3 is shown as an example.

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Electronic structure of hollow graphitic nanoparticles

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Monoatomic layer of graphite possesses such unique properties like nontoxicity, high conductivity and significant mechanical strength [1-3]. These properties make graphene promising unit for formation of 3D structures. Such structures are desirable for use in energy technologies such as hydrogen storage, fuel cells, solar cells, lithium batteries, and capacitors, which have a strong requirement for superior storage devices. This causes necessity of study of the electronic structure of these materials that determine their properties. It is well-known that *p*-type electronic states in a variety of carbon modifications contribute mainly in interatomic interaction [4]. Therefore for study of the energy distribution of valence C*p*-electrons in carbon nanomaterials it is necessary to investigate their CK_α-bands. Ultra-soft X-ray emission spectroscopy allows getting full information about the energy distribution of occupied valence states lower Fermi level in carbon materials, for this reason this method is useful instrument for investigation of the electronic structure of hollow graphitic nanoparticles.

Hollow graphitic nanoparticles CK_α noticeably differ from graphite one by possessing lower intensity of the π-sub-band. Different degrees of π-overlapping of p_z-orbitals in hollow graphitic nanoparticles appear due to increasing curvature of the spherical atomic surfaces when deepening into hollow graphitic nanoparticle. As a result degree of π-overlapping of the p_z-orbitals decreases over the surface and increases inside hollow graphitic nanoparticles. It has been revealed that *sp*-hybrid bonds form between carbon and residual iron atoms when high-energy $3d+4s$-states overlap with sp^n-hybrid orbitals ($2<n<3$). This indicates that part of iron atoms can locate in hollow graphitic nanoparticles walls. Iron atoms could remain after washing in acids.

However CK_α spectrum of hollow graphitic nanoparticles is by 0,2-0,8 eV wider than that of carbon onions band due to larger contribution of the $pp\pi+pp\sigma$-states overlapping in greater amount of hollow graphitic nanoparticles walls due to larger diameter of particles.

Surfaces of hollow graphitic nanoparticles are less corrugated than surfaces of graphene nanosheets therefore difference in degrees of overlapping of πp_z-states and sp^n-hybrid orbitals due to corrugation decreases whereas overlapping of these orbitals increases in a result of increasing curvature of layers when deepening into hollow graphitic nanoparticles.

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X-ray spectroscopy study of the electronic structure peculiarities of silicon nitride nanofibers

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Last years intensive investigations on development and study of reinforced ceramic materials are carried out. Such materials can be applied effectively at high-temperature conditions in oxidizing medium. Whiskers and in last decade nanofibers of refractory compounds such as SiC, Si_3N_4 are used. Si_3N_4 whiskers are promising reinforcing materials for high-temperature ceramic matrixes aimed on increasing their strength and fracture strength

In present work process of synthesis of micro and nanofibers of Si_3N_4 by nitriding of silicon powder was investigated. Results of investigations employing scanning electron microscopy method showed that at 1500 °C and synthesis time of 1 hour some fibers appear among silicon particles. An increase of nanofibers quantity and presence of some microfibers were observed with increasing synthesis temperature to 1530 °C. Further increase of temperature and synthesis time promotes increasing quantity of formed nanofibers, and at synthesis temperature of 1550 °C the only synthesis products were Si_3N_4 nanofibers.

From X-ray photoelectron (XPS) Si $2p$ and N $1s$ core-level spectra it is obvious that values of binding energies of Si $2p$ and N $1s$ core-level electrons of Si_3N_4 nanofibers synthesized by silicon powder nitridation for 2 hours at 1530 and 1550 ^{o}C coincide within the accuracy of the present XPS measurements with those of the corresponding core-level electrons of the reference Si_3N_4 powder This fact indicates that charge states of the constituent atoms in the Si_3N_4 nanofibers under study correspond to those in the reference Si_3N_4 powder.

It was revealed that maxima of XPS O $1s$ and C $1s$ spectra are at 532.8±0.1 eV and 285.0±0.1 eV, respectively in three samples under investigation and these binding energies refer to oxygen- and carbon-bearing compounds absorbed by surfaces of sample. We did not detected any features on the XPS O $1s$ and C $1s$ core-level spectra that could be attributed to oxygen/carbon atoms being in chemical binding with the material under consideration. It was revealed that XPS valence-band spectra of the Si_3N_4 nanofibers and the reference powder are similar.

The X-ray emission Si Lα bands of reference Si_3N_4 powder and of Si_3N_4 nanofibers synthesized by silicon powder nitridation for 2 hours at 1530 ^{o}C and 1550 ^{o}C studied reveal similar elements of fine structure, i.e. their shapes are similar with the exception of insignificant differences.

Electronic structure of $ZrTiO_4$, $HfTiO_4$, $FeTiO_3$ and $MgTiO_3$ titanates: Theoretical calculations and x-ray spectroscopy studies

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The modified augmented plane wave (APW) method as incorporated in the WIEN2k code [1] and/or cluster FEFF8 program [2] have been used to calculate total and partial densities of states of the constituent atoms in $FeTiO_3$, $MgTiO_3$, $ZrTiO_4$ and $HfTiO_4$ titanates, prospective materials for their application in the field of microwave communication and dynamic random access memory (DRAM) devices and they are indispensable components used intensively in wireless-communication systems (e.g. in the mobile phones satellite communications), catalysts in some oxidation reactions, humidity sensors, optical devices, and high-k gate insulator.

To verify the theoretical results, in the present work, the X-ray emission Ti $L\alpha$, Fe $L\alpha$, Zr $L\beta_{2,15}$ and O $K\alpha$ bands representing the energy distribution of mainly the Ti 3d-, Fe 3d-, Zr 4d- and O 2p-like states, respectively, as well as the X-ray photoelectron (XPS) valence-band and core-level spectra have been measured for $FeTiO_3$, $MgTiO_3$, $ZrTiO_4$ and $HfTiO_4$ oxides.

The theoretical APW/FEFF8 data reveal that the valence band of the above oxides under consideration is dominated by contributions of the O 2p states. These states contribute throughout the whole valence-band region; however their maximum contributions occur in the upper portion of the band. The calculations render that the bottom of the conduction band of $FeTiO_3$, $MgTiO_3$, $ZrTiO_4$ and $HfTiO_4$ is dominated by contributions of the Ti 3d* states. The experimental data were found to be in good agreement with the theoretical results for all the compounds studied.

Measurements of XPS core-level binding energies for the constituent atoms of the $ZrTiO_4$ to $HfTiO_4$ titanates indicate that Ti and Zr(Hf) atoms are in the formal valence states +4. When going from $ZrTiO_4$ to $HfTiO_4$, the XPS Ti 2p and O 1s core-level binding energies do not alter within the accuracy of the present measurements.

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Electronic structure and exchange interaction in GdB$_4$ compound

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Ab initio band structure calculations have been carried out using the LDA+U theoretical method with the all-electron Full Potential Linearized Augmented-Plane Wave (FP-LAPW) code for antiferromagnetic GdB$_4$ compound. The densities of electronic states and ground state energies were calculated for various hypothetic magnetic configurations, including the realistic Shastry-Sutherland lattice. The results obtained were examined and analyzed in the framework of the Heisenberg model in order to shed light on peculiarities of exchange interaction within RB$_4$ series.

First principles calculations of atomic structure and physical properties of calcium apatites

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Electronic structure of calcium apatites $Ca_{10}(ZO_4)_6X_2$, where Z=P, As, V; X=OH, F, Cl was investigated by quantum-mechanical modelling methods in the density functional theory (DFT) in the generalized gradient approximation (GGA) and LMTO-approximation using the ABINIT package. It was shown that $Ca_{10}(PO_4)_6Cl_2$ and $Ca_{10}(PO_4)_6F_2$ organizes in space group P6$_3$/m, but not in P6$_3$. Small deviations of the total energy per unit cell indicate that the anions F-and Cl-stored relative lability position on the axes of the sixth order. Phonon density of states for all series apatite $Ca_{10}(PO_4)_6X_2$, where X = F, Cl, OH, have a distinct band character with different length of the individual sub-bands. The first band contains most vibrational states and is localized in the range of wave vectors from 0 to 370 cm^{-1}, the second band – from 380 to 500 cm^{-1}, the third band is localized in 600-800 cm^{-1}, and the fourth – 800-1150 cm^{-1}.The first, second and third bands correspond to the vibrations of the PO$_4$ tetrahedra in the apatite, the frequencies of which are in good agreement with the experimental phonon frequencies of isolated PO$_4$ tetrahedron. Also, the dielectric tensor and the elastic constants of calcium apatite are calculated.

X-ray magnetic dichroism in the (Zn,Co)O diluted magnetic semiconductors from *ab initio* calculations

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Diluted magnetic semiconductors (DMSs), obtained by doping magnetic element as impurity into the host semiconductor, can be used for spintronic devices. As a wide-band-gap II-VI semiconductor, ZnO has recently been considered as a base material for realizing transparent DMSs.

Using the fully relativistic Dirac linear muffin-tin orbital (LMTO) band structure method, we have investigated theoretically from first principles the electronic structure of $(Zn_{1-x}Co_x)O$ DMSs, the x-ray absorption spectra (XAS), x-ray magnetic circular dichroism (XMCD), and x-ray linear dichroism (XLD) spectra at the Co, Zn, and O K and Zn, Co $L_{2,3}$ edges.

Since the local density approximation fails to describe correctly strongly localized d states in ZnO we treated these states within the LSDA+U approach. The effective on-site Coulomb repulsion U was considered as an adjustable parameter. The application of LSDA+U leads to a shift of the Zn d states downward in energy and makes the bandgap larger (2.12 eV within the LSDA+U versus 0.8 eV within the LSDA in pure ZnO wurtzite). The same effect can be achieved treating the Zn d states as core states. In our calculations we tried both approaches and did not find any significant difference in the XAS and XMCD spectra. The Co d states were treated within the LSDA as well as the LSDA+U approach. We tried various U values for the description of the XAS and XMCD spectra and found that the agreement between the theoretically calculated and experimental spectra does not significantly changes in comparison with the LSDA method.

The theory reproduced the shape and energy positions of major fine structures of the Co XAS, XLD, and XMCD spectra at the K and $L_{2,3}$ edges reasonably well. We found that oxygen deficiency is responsible for some fine structures of the Co L_3 XAS and XMCD spectra and has minor influence on the shape of the O and Zn K x-ray absorption spectra.

We found that a small peak at about 528 eV at the O K edge XAS evolves with Co doping, and its intensity increases with Co concentration suggesting a strong hybridization of O $2p$ states with Co $3d$ states. This feature originates in the Co doped ZnO alloys, and it is ascribed to dipole transitions from O $1s$ to O $2p$ states that are hybridized with the unoccupied $3d$ states of Co. Thus, the intensity of this peak is a fingerprint of the Co $3d$ density of states. A continuous increase of this peak with Co doping indicates more unoccupied states at the Co $3d$ levels.

First-principles calculations of dislocation-oxygen impurity magnetic interaction in silicon

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Recently, the experimental evidences of magnetic field effect on dislocation-oxygen impurity interaction in silicon [1-2] and other so called magneto-mechanical effects were reported. Today there is no consistent theory to explain these effects. Most researchers explain the presence of the ferromagnetic manifestations of the diamagnetic materials by means of so-called the d_{0} or sp magnetism, in which no traditional magnetic ions are involved. The last has attracted considerable attention due to the possible applications in spintronics.

With first-principles calculations, the possibility of formation of magnetic ordering on the edge dislocation and oxygen impurities as well as the dislocation-oxygen impurity magnetic interaction in silicon are analyzed in presented work.

The atomic structure and electronic spectra of the edge dislocation in crystalline Si are calculated by the density functional theory (DFT) [3] in the generalized gradient approximation (GGA) [4] using the ABINIT package [5]. The atomic structure of the dislocation core is modeled by simulating annealing [6] of 180 Si atoms supercell containing dislocation dipole. Changes in the density of electronic states of the supercell with dislocation dipole as well as the possible formation of magnetic ordering on the dislocation core dangling bonds are discussed. The mechanism of the magnetism can be understood well through Stoner criterion. The spin-polarized calculation of the edge dislocation in crystalline Si confirms the possibility of magnetic ordering on the dislocation core dangling bonds with the spin polarized energy is around 0,015 eV and the uncompensated magnetic moment is 1,25 $\mu_\text{Б}$ per the supercell containing two segments of the dislocation line unit length.

The electronic spectrum of 64 Si atoms supercell with oxygen impurity in the interstitial position is calculated. The atomic positions of atoms in the supercell are modeled by simulating annealing [6]. It is shown that the impurity subband is formed in a vicinity of the Fermi level which can lead to the magnetic ordering according to the Stoner criterion. The uncompensated magnetic moment 1,75 $\mu_\text{Б}$ per the O impurity atom was obtained by the spin-polarized calculation.

Thus the formation of magnetic moments on the dangling bonds in the dislocation core and on the oxygen impurities which leads to the additional magnetic interaction of dislocation-oxygen impurity in silicon are theoretically investigated in this paper. The last has found the experimental acknowledgements [1].

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ɪsomorphic substitutions in the tetrahedral position of apatites and their influence on physicochemical properties

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Structural modification by isomorphic replacements in tetrahedral sublattice results in essential changes of physical properties of apatites. In this work influence of anharmonicity vibration in a lattice of apatites mixed structure $Ca_{10}(PO_4)_{6-x}(VO_4)_x(M)_2$, where $M = OH^-$, F^-, Cl^-, $x = 0, 1, 3, 5, 6$ on its physical and chemical characteristics is investigated.

It was established, that for chlorine-containing apatites of any level doping of topotetrahedral matrix significant decrease of tetrahedrons absorption band - from ~ 400 sm^{-1} up to ~ 90 sm^{-1} for boundary concentration is observed. Similar effects are observed for fluor- and hydroxylapatites too however theirs are less expressed. Decrease of width occurs from ~ 200 sm^{-1} up to ~ 95 sm^{-1}. High sensitivity of a chloroapatites matrix to changes of fluctuations of tetrahedral sublattice after doping should have an effect on the thermal stability, as it was revealed after thermogravimetric analysis. The fusion temperature of compound shifts as the decrease with VO_4 ions fraction increase in calcium fluor- and chloroapatites.

Thus, decrease IR absorption band half-width describing XO_4 tetrahedrons, is related to decrease of interaction between tetrahedrons of one type, and, as a consequence, to anharmonicity vibrations suppression in quasi-free tetrahedrons.

It was established, that vibration anharmonicity in the lattice of apatite may change depending on the concentration of tetrahedron that type in crystal structure. These changes are local and by means of various replacements it is possible to create necessary spatial distribution of anharmonic component in the crystal that opens the prospect of controllable change of heat conductivity, factor of temperature expansion and other parameters in the crystal which depend on the vibration anharmonicity of the lattice.

Electronic structure peculiarities of disordered diphosphates of Mn and Co

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Disordered diphosphates are of scientific interest in terms of modifying their operational properties by varying the nature of the cations and their content in the structure.

In these work the electronic structure peculiarities of disordered diphosphate - $Mn_{2-x}Co_xP_2O_7 \cdot 5H_2O$, were x=0, 0.6, 1.0, 1.9, 2.0, have been studied out by the XPS and X-ray emission spectroscopy.

The data obtained suggest that the substitution of manganese by cobalt is accompanied by both a redistribution of the electron density between the atoms of the metal sublattice, proceeding according to their electronegativity values, and the change in the chemical bond nature between the metal atoms and the surrounding oxygen.

The increase of cobalt content leads to an increase in the covalent component of the chemical bond in the overall charge balance.

Substitution of cobalt by manganese is accompanied by an essential increase in the electron density on the oxygen atoms involved in formation of the chemical bond with metal atoms, which leads to the formation of states laying in the upper part of the valence band of the investigated samples.

Monatomic thickness Ag nanostructures on Si (111) surface

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Scanning tunneling microscopy study the processes of formation of monatomic silver nanostructures on the Si (111) was carried out under UHV conditions.

Before deposition of silver topography images of the surface of Si(111) 7x7 reconstruction were obtained in order to proof cleanness of substrate. After that on the surface Si(111) was deposited silver by thermal evaporation. The STM topography image shown on Figure 1a. testifies the formation of monatomic thickness silver layers with an average step height of 0.23 nm. In the STM image observed up to four single layers.

After annealing of the sample at 300 ^{0}C the STM images shows up to three single layers of the nanostructure (Fig.1b).

At temperature of 400 ^{0}C during second annealing the silver was evaporated from the surface and reconstruction of Si(111) 7x7 was found.
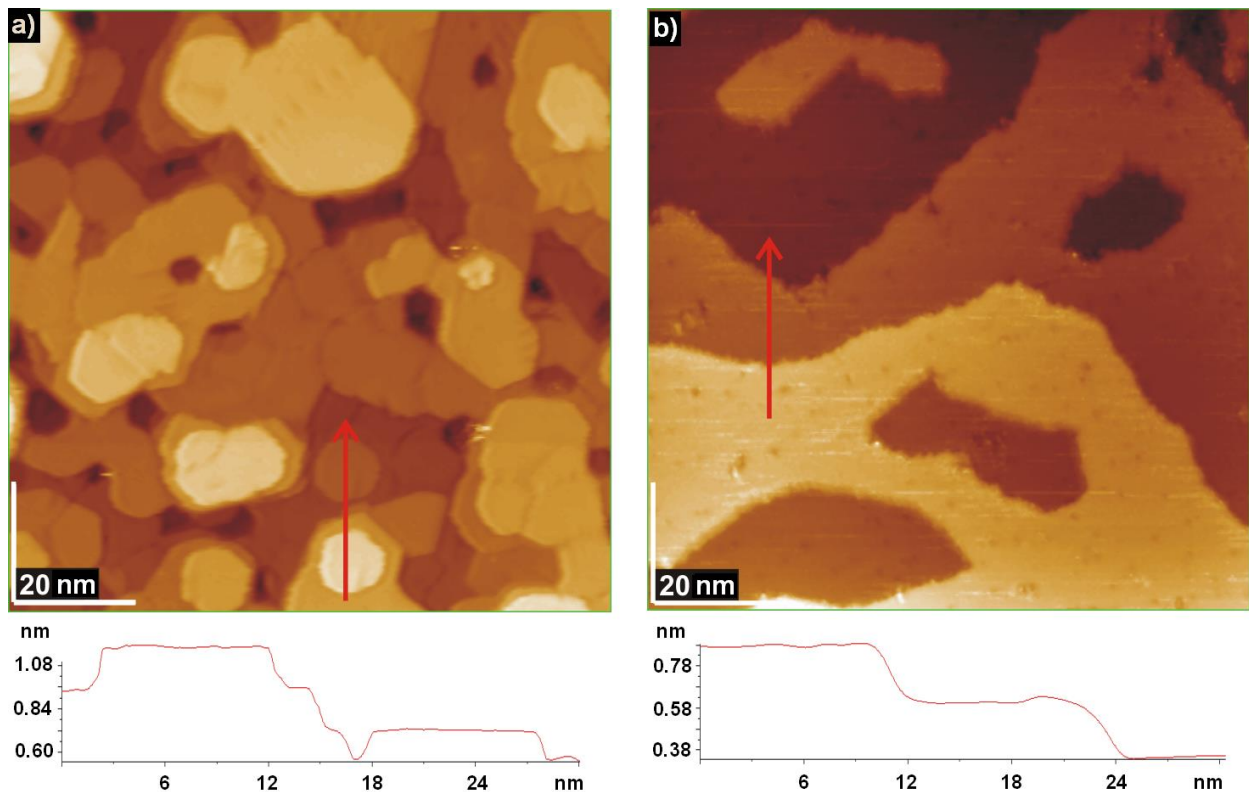

Figure 1. Silver on the surface of a single crystal silicon Si(111).

Ag on the surface of the Si can form a monatomic layered structure. With increasing temperature, occurs the evolution of the surface nanostructure. The amount of layers decreases. When the sample is heated to a temperature of 400 ^{0}C takes place desorption of silver atoms, and recover the structure of the Si (111) 7x7.

Influence of correlation of impurities on conductivity in graphene

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We present numerical studies of the effect of spatial correlation of impurities on the conductivity of graphene sheets. To calculate electronic and transport properties of graphene we use the real-space time-dependent Kubo–Greenwood formalism within the tight-binding approach, where the diffusion coefficient and conductivity are obtained from the temporal spreading of electron wave packets over the graphene sheets.

The conductance is calculated as a function of the electron density, $\sigma = \sigma(n_e)$, for the cases of random and correlated impurities. To describe both charged impurities on the substrate and neutral adatoms on the graphene sheets, we use the long- and short-range scattering potentials respectively.

The short-range potential is considered in the limiting cases of strong and weak scattering, where the on-site energies respectively $V >> |u|$ and $V \leq |u|$, with u being the hopping energy in the tight-binding Hamiltonian. For the case of the strong scattering ($V >> |u|$) we find that the graphene conductivity is not affected by the spatial correlation of impurities. On the contrary, for the case of the weak impurities ($V \leq |u|$), we demonstrate that the spatial correlation leads to increase the conductivity as the correlation length is increased. Such an effect is similar to that one occurring in conventional solid solutions (alloys). We compare our numerical findings with the corresponding predictions based on the Boltzmann transport equation within the Born approximation and discuss the validity of the latter.

Finally, we study the effect of correlation for the case of the long-range scatterer modeled by the commonly used Gaussian-shaped potential. As for short-range impurities, the long-range Gaussian potential does not lead to any enhancement of the conductivity in comparison to the uncorrelated case.

Gd and O depositions on Si(113)

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The co-adsorption of gadolinium and oxygen on high-index Si(113)–3x2 plane has been investigated.

The aim of the present work was to study experimentally the co-adsorption of gadolinium and oxygen on high-index Si(113) surfaces and to determine the correlation between electronic and adsorption properties of such interfaces.

The experiments were done in the homemade ultra-high vacuum chamber with a base pressure $\approx 2 \times 10^{-10}$ Torr. Gd was evaporated by resistive heating of a tantalum filament. Atomic oxygen generation was performed by hot tungsten filament. Auger electron spectroscopy, low-energy electron diffraction, ultra-violet photoelectron spectroscopy (UPS) were used for analyzing the adsorption systems.

The Si(LVV), Gd(NON) and Gd(NVV) Auger line shapes were investigated with increasing of Θ_{Gd}. They indicate on forming a well-defined silicide-type interfacial reaction product.

UPS measurements have shown that the work function of Si(113) surface monotonously decreases with increasing of Θ_{Gd}. At $\Theta_{Gd} \approx 6ML$ the work function decreases to $\approx 1.2eV$ and becomes stabilized.

The exposure of Gd films in atomic oxygen atmosphere was accompanied by the reduction of electronic state density near the Fermy level, oxidation of Gd atoms and some work function rising by the change of band bending near the surface.

The preliminary model that provides the explanation of correlation between structure and the work function of Si(113):Gd:O system is discussed.

Resonant tunneling in novel type Josephson heterostructures superconductor- doped semiconductor- superconductor

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MoRe-Si(doped by tungsten)-MoRe junctions have been fabricated by using thin films deposition techniques. Current-voltage characteristics (I-V curves) of the fabricated Josephson junctions have been measured at various temperature and magnetic field values. For the pure silicon barriers and silicon barriers doped by tungsten fabricated with small W concentration ($\sim$ 3-4at.%) we observed the existence of an over-barrier direct tunneling effect and a direct tunneling effect through an impurity level within the barrier. At relatively high concentrations ($\sim$ 6-9at. %) of tungsten in the silicon barriers an existence of a resonant tunneling effect is observed (if percolation limit is overcome) through localized levels of scattering centers (W atoms). Simultaneously, at some conditions in these junctions a superconducting Josephson current appears on the base of the resonant tunneling (see Fig. 1). Usually, the differential resistance values of the quasiparticle I-V curves of these junctions are high enough (10-100 times) in comparison to the differential resistance values of the quasiparticle I-V curves for the Josephson tunnel junctions with well-known direct tunneling and having the same values of their Josephson critical currents. So, it means the fabricated junctions have large enough values (up to 10-30) of the $I_C R_N$ product (Josephson critical current I_C multiplied by R_N – resistance of the junction in normal state). The reason of this phenomenon is unclear at the moment.

It is important and interesting that the high voltage asymptotes of the quasiparticle I-V curves of the fabricated junctions do not cross the origin of coordinates, it means they are not described by Ohm low in the high voltage region, and it means that the sufficient excess quasiparticle currents flow through these junctions (the asymptotes of the quasiparticle I-V are parallel to the Ohm low curves for the junctions in the normal state).

Basing on the predictions of the well-known Blonder-Tinkham-Klapwijk (BTK) theory model [1] from our point of view this is a real evidence of the existence of two S/N interfaces with very small barriers ($Z \sim$ 1-1,5) on both sides of the fabricated junctions with resonant tunneling. The same interpretation of the excess quasiparticle currents appearance in our junctions can also be done on the base of multiple Andreev reflections in Josephson junctions. Let us take into account that the theory models should describe the current flow through a number of the scattering centers (i.e. through the tungsten atoms), every of these events could have small enough probabilities and these probability distributions depends on the kind of transparency distribution function in silicon doped by tungsten.
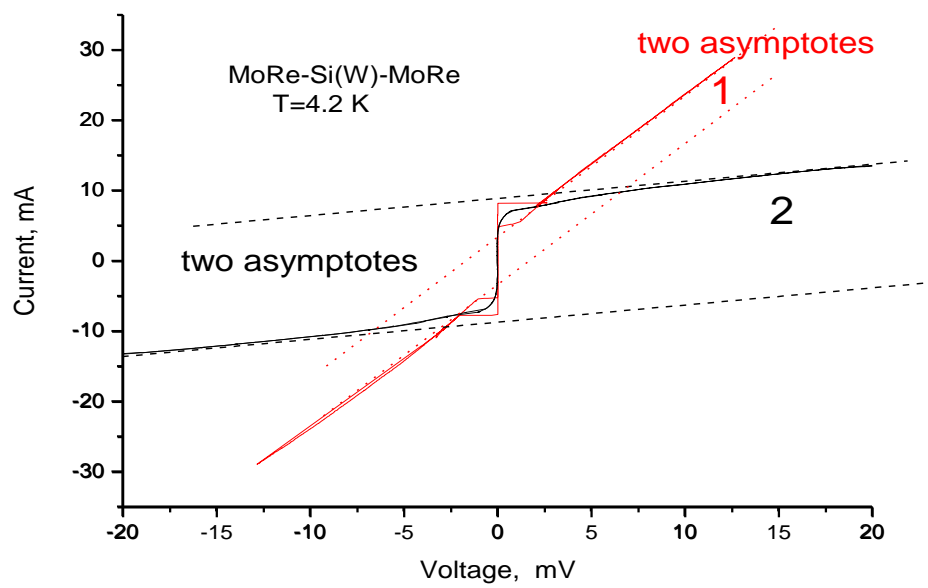
Fig.1. I-V characteristics of MoRe-Si(doped by W)-MoRe junctions with $n_W \sim$ 6-9at.%: 1 – with hysteresis, 2 –without hysteresis and their asymptotes.

[1] G. Blonder, M. Tinkham. and T. Klapwijk, Phys. Rev. B, 25, 4515-4532 (1982).