RECENT PROGRESS IN AB INITIO PHONON CALCULATIONS

BOOK OF ABSTRACTS

CRACOW, MAY 9, 2023

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Organizer:

Institute of Nuclear Physics

Polish Academy of Sciences, Cracow

Organizing committee:

- Przemysław Piekarz
- Paweł T. Jochym
- Jan Łażewski
- Svitlana Pastukh
- Małgorzata Sternik

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Presentations

Phonons, anharmonicity, and electron correlations in actinides

Dominik Legut[1], Lukáš Kývala[1], Andrzej Kadzielawa[1], Volodymyr Buturlim[2], Ladislav Havela[2], Urszula D. Wdowik[1,3] and Przemysław Piekarz[4]

[1]*IT4Innovations, VSB-Technical University of Ostrava, 17.listopadu 2172/15, 708 00 Ostrava, Czech Republic*
[2] *Faculty of Physics and Mathematics, Charles University, Prague Czech Republic*
[3] *Institute of Technology, Pedagogical University, Cracow, Poland*
[4] *Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland*

There are number of 1:1 properties that could be directly compared between quantum mechanical calculations (using density functional theory) based on lattice dynamics and the experimental measurements. One of the examples is lattice heat capacity, thermal expansion, and thermal conductivity. The latter two are the key parameters of the potential nuclear fuels, the former one can shed much light on the magnetic systems of actinide hydrides. Actinides and especially their carbides as prospective nuclear fuel materials for the generation IV react ors were investigated using the density functional theory. We demonstrate that their electronic, magnetic, elastic, and thermal properties can be at present well described if the spin-orbit interaction and partial delocalization 5f electrons is properly included in the computational approaches. One can well reproduce not only basic electronic structure but also elastic constants, phonon dispersions, and their density of states, provided by XPS, UPS, BIS, and inelastic neutron scattering data [1-4]. Often, the localization of the 5f electrons could be captured using a moderate value of the on-site Coulomb interaction parameter. The case s tudies include a realistic description of the ground-state properties of elemental metals as Th, U and their monocarbides ThC and UC. In this study, published in Ref. 2 and 4, the realistic description of the electronic structure and lattice dynamics (phonons) explains why there is much higher thermal expansion in pure actinides (as Th) comparing with respective actinide monocarbides. The modeling also gives an insight up to which temperature the heat transport depends on lattice vibrations and where the electron transport starts to dominate. We analyzed the force constants of defected systems in order to reveal the effect of the oxygen impurity and vacancy at carbon site on the thermal expansion, summarized in Ref. 4. Additionally investigated thermodynamic properties, such as for instance heat capacity, were compared to the experimental data in the large temperature scan showing very excellent agreement up to 2000K and explained some additional features of phonon DOS not presented before. In the second part, we present the calculations of the stability, mechanical, and magnetic properties of the uranium hydrides including 3 different cubic compounds, α- and β-UH3 and UH2, all undergoing ferromagnetic ordering. Our first-principles calculations revealed a

complex (non-collinear) magnetic order in β-UH3. Unlike the other uranium hydrides, α-UH3 and UH2, β-UH3 with two different U sites exhibits a site-dependent size and direction of U magnetic moments. While the U moments at the 2a sites are locked in the body diagonal direction, the mo ments at the 6c sites are inclined by approx. 15 degrees. The difference stems from 5f orbital moments. Comparison of results for all 3 species reveals that the U-U spacing is not the primary parameter to control the magnetism in uranium hydrides. Further insight is provided by evaluating individual exchange interactions between different neighbours, yielding the transi tion temperatures in a reasonable agreement with the experiment [5-7] as well as the lattice dynamics of all uranium-based hydrides [8].

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Phase stability of PdO_2: The role of temperature and electron correlations

Diana Fabušová[1], Kamil Tokár[1,2], **Mariana Derzsi**[1], Przemysław Piekarz[3], and Paweł T. Jochym[3]

[1]*Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava, J. Bottu 25, 917 24, Trnava, Slovakia.*
[2]*Institute of Physics, Slovak Academy of Sciences, Dúbravská cesta 9, 845 11 Bratislava, Slovakia.*
[3]*Institute of Nuclear Physics, Polish Academy of Sciences, Radzikowskiego 152, 31342 Kraków, Poland.*

mariana.derzsi@stuba.sk

Palladium oxide PdO_2 has been long considered to crystallize in tetragonal rutile structure [1], which is common to majority of transition metal dioxides. Also, being a 4*d* element, palladium is assumed to take on low-spin configuration in PdO_2. Using Density Functional Theory, we have examined the phase stability of tetragonal PdO_2 while evaluating impact of temperature, electron correlations and spin orbit coupling [2]. Here we show that the low-spin tetragonal PdO_2 is dynamically unstable at all realistic temperatures in respect to Raman active B_{1g} mode, which relaxes structural strains, promotes opening of the electronic band gap and distorts the structure to the orthorhombic $CaCl_2$ type, which represents the true ground state structure. On the other hand, dynamical stability of the tetragonal structure is obtained at realistic temperatures when gaining a certain critical non-zero value of magnetization. The maximum dynamical stability is reached for the high-spin configuration for which the B_{1g} mode gains the highest real frequency. Overall, we found that PdO_2 can be dynamically stabilized in various spin states. The low-spin state is realized in orthorhombic $CaCl_2$ structure type, which represents a semiconducting diamagnetic phase. The intermediate- and high-spin metallic states can be accommodated by the tetragonal rutile structure. The results obtained for PdO_2 are confronted with rutile type RuO_2 and IrO_2, where new spin states have been recently discovered [3,4] as well as with $LaCoO_3$, that hosts variety of spin states reached via temperature or high magnetic fields [5].

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Acknowledgment: We acknowledge the ERDF, Research and Innovation Operational Program for project (ITMS2014 +: 313011 W085), the Slovak Research and Development Agency (grant No. APVV-18-0168), and Scientific Grant Agency of the Slovak Republic (VG 1/0223/19). The computations were carried out using the Aurel supercomputing infrastructure in CC of Slovak Academy of Sciences acquired within the projects ITMS 26230120002 and ITMS 26210120002 supported by the ERDF, and PRACE FENIX Project fnxp070004 at TGCC high performance computing infrastructure, France.

Electronic structure, phonons and superconducting gap of Pb-Bi alloy

Sylwia Gutowska[1] and Bartłomiej Wiendlocha[1]

[1]*Faculty of Physics and Applied Computer Science, AGH University of Krakow, Aleja Mickiewicza 30, Krakow*

gutowska@agh.edu.pl

The Pb-Bi family of superconducting alloys are widely used as superconducting junctions due to their high critical field and relatively high critical temperature. They have been intensively studied experimentally for many years and another applications have been found, for example they are considered as potential nuclear coolers in generation IV nuclear reactors. However, their electronic and phonon structure has not been studied, while there are at least three reasons why it can be interesting. Firstly, this series of alloys undergoes a structural transition from the f cc structure of Pb to the nearly hcp structure. We show that this transition is due to electronic preference. Secondly, we focus on the Pb0:64Bi0:36 alloy, which forms in *hcp* structure and is the strongest-coupled classical superconductor with a critical temperature Tc = 8:6 K and extremely large electron-phonon coupling constant l > 2:0. We compare its properties to elemental Pb, which has lower Tc = 7:2 K and l = 1:5. By using density functional perturbation theory the electron-phonon interactions are studied and we explain why Pb-Bi alloy is such a strongly coupled superconductor. We show how it is related to the structural transition by looking not only at phonon dispersion relation but also at force constant values. Lastly, we discuss the nature of the superconducting gap of the Pb-Bi alloy. While most studies show that Pb is two-gap superconductor (and a few show that it is not), we ask whether the same holds for the Pb-Bi alloy since the measured temperature dependence of the magnetic critical field suggests that it is not a single-gap superconductor. To address this, we calculate the k-dependent superconducting gaps using anisotropic Eliashberg equations and density functional theory for superconductors. Based on our findings, we conclude that Pb-Bi is not a two-gap superconductor like Pb but has a strongly anisotropic three-band-gap, and we explain the reason for this difference.

Acknowledgments This work was supported by the National Science Centre (Poland), project number 2017/26/E/ST3/00119, EU Project POWR.03.02.00-00-I004/16 and PLGrid infrastructure.

Ab-initio study of chiral phonons

S. Basak[1], P. Piekarz[1], A. Ptok[1]

[1]*Institute of Nuclear Physics, Polish Academy of Sciences, W. E. Radzikowskiego 152, PL-31342,Krakow,Poland.*

surajit.basak@ifj.edu.pl.

Geometry of the compounds often allow the atoms to circulate around their equilibrium position in a circular or an elliptical trajectory. The phonons emerging from these kind of vibrations inherit the properties of its parent system and have a non zero value of angular momentum associated with them. We study the presence of chiral phonons in a system with orthorhombic symmetry (YalSi) [1], and also in systems with cubic Laves phases with chemical symbol ABi_2(A = K, Rb, Cs). However, due to the presence of inversion symmetry, the total angular momentum is zero in all the mentioned system. We then artificially break the inversion symmetry by doping and propose and propose a new system with a non zero value of total Pseudo Angular Momentum (PAM) [2]. We study the dynamical stability of the final systems $KRbBi_4$, $RbCsBi_4$ and expect them to be used as platforms for studying phonon Hall effect.

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High efficiency sampling of probability distributions

Paweł T. Jochym[1], Jan Łażewski[1]

[1]*Institute of Nuclear Physics, Polish Academy of Sciences, W. E. Radzikowskiego 152, PL-31342,Krakow,Poland.*

Sampling of probability distributions is an important problem in multiple fields of research from physics to social sciences. For example, in physics it is used in modelling and design of the high energy physics experiments, and in building configuration databases for the interaction model construction in lattice dynamics. Multiple algorithms for this process have been developed. The major ones are the family of Markov-Chain Monte-Carlo methods, with prominent member of Metropolis-Hastings algorithm. In lattice dynamics calculations, the molecular dynamics is often used in sampling of the thermodynamics ensemble in equilibrium. The Metropolis-Hastings-type algorithm is used at the core of the HECSS scheme [SciPost Phys. 10, 129 (2021)] proposed recently. In our presentation we introduce a new variant of the Monte-Carlo sampling of the energy probability density, which greatly increases effectiveness of the sampling process by using a well-tuned prior and new method of sample weight derivation. The proposed scheme is implemented and used in the upcoming release of the new version of the HECSS sampler.

Dynamical properties of isolated silver difluoride 1D structure understrain

K. Tokár[1], M. Derzsi[1]

[1]*Advanced Technologies Research Institute, Faculty of Materials Science and Technology in Trnava, Slovak University of Technology in Bratislava, Trnava, Slovakia*

kamil.tokar@stuba.sk

Common polymorph of silver difuoride (AgF2) at ambient pressure has layered antiferromagnetic structure. In the solid phase exhibits numerous structural and electronic similarities with oxocuprate precursors of high-temperature superconductors [1]. X-ray diffraction (XRD) study of phase transitions at high pressure and Density Functional Theory modeling (DFT) [2] showed that at an elevated pressure of 15 GPa, AgF2 solid could transform to an unprecedented orthorhombic high-pressure polymorph (HP2) featuring an array of tubular subunits, which are built of corner sharing (AgF4) squares. This features the first 1D-type of a metal fluoride nanowire, which is the only one showing rigid square planar rather than common hexagonal or octahedral moieties. The observed tubular structured high-pressure polymorph opens a possibility to design a new 1D type of silver difluoride-based nanostructures. The fact that the individual AgF2 nanowire units behave as neutral suggests that they could be in principle isolated from the crystal. In this work we focused on pure first-principles investigation of the mechanical stability, elasticity, response of electronic band structure and lattice dynamics to applied uniaxial strain in isolated 1D-AgF2 subunit structure, which is derived from HP2 bulk phase. The mechanical properties, range of stability, phonon system, magnetic configuration and band gaps in new nanowire were predicted and analyzed by use of DFT+U and hybrid (HSE06) exchange-correlation functionals and quasiharmonic direct method [3].

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Acknowledgment: We acknowledge the ERDF, Research and Innovation Operational Programme, for project No. ITMS2014+: 313011W085; the Slovak Research and

Development Agency, grant No. APVV-18-0168 and Scientific Grant Agency of the Slovak Republic, grant No. VG 1/0223/19; PRACE providing access to Irene TGCC within Fenix infrastructure partially funded from Horizon 2020 research and innovation programme through the ICEI project under the grant agreement No. 800858.

Mechanism of the structural phase transition in the Mott insulator Cu2P2O7

Svitlana Pastukh[1], Paweł T. Jochym[1], Oleksandr Pastukh[1], Jan Łażewski[1], Dominik Legut[2], and Przemysław Piekarz[1]

[1]*Institute of Nuclear Physics, Polish Academy of Sciences, PL-31342 Kraków, Poland*
[2]*IT4Innovations, VSB-Technical University of Ostrava, 708 00 Ostrava, Czech Republic*

svitlana.pastukh@ifj.edu.pl

The β phase of copper pyrophosphate has garnered significant interest due to its intriguing electronic and lattice properties. In order to gain a deeper understanding of this phase, ab initio calculations using density functional theory were employed. This study aimed to investigate the intricate interplay between the electronic structure and lattice characteristics of β-Cu2P2O7, shedding light on its dynamic behavior and the underlying mechanisms governing its structural phase transition.

The initial focus of the investigation was on the lattice parameters, aiming to establish their agreement with experimental data. To achieve this, the calculations took into consideration the inclusion of Coulomb interactions and van der Waals corrections. Notably, the results exhibited satisfactory correspondence, bolstering the validity of the employed methodology.

Moving on to the electronic properties, the Mott insulating energy band gap (Eg) was determined to be 2.94 eV using the GGA+U method. This significant energy gap arises from the intricate interplay of electron correlations within the copper ions. These findings provide valuable insights into the nature of the electronic behavior exhibited by the β phase.

In addition to electronic properties, the dynamical properties of the β-Cu2P2O7 crystal were thoroughly analyzed through the investigation of phonon dispersion relations and the projected density of states (PDOS). A noteworthy discovery was the identification of a soft mode at the A point, suggesting the presence of dynamical instability within the β phase at low temperatures. This soft mode plays a pivotal role in the structural phase transition of copper pyrophosphate from the high-temperature β phase to the low-temperature α phase [1].

Further analysis revealed that the soft mode induces primarily vibrations of the O1 atoms, leading to static displacements along the b direction within the α phase as the temperature decreases. Consequently, this structural deformation results in a reduction in crystal symmetry, ultimately causing the lattice parameter c of the crystallographic unit cell to double in the α phase. These observations align with previous studies that have associated negative thermal expansion (NTE) with vibrations of the O1 atoms along the direction perpendicular to the P–O–P bridge.

Interestingly, the analysis also indicates that the lowest optical Ag mode, responsible for the NTE phenomenon, corresponds to the soft mode identified in the β phase. This finding establishes a direct link between the soft mode and the NTE behavior, highlighting the importance of understanding the dynamic properties in the context of structural phase transitions and NTE in pyrophosphate materials.

Overall, the findings presented in this study contribute to the growing body of knowledge surrounding the β phase of copper pyrophosphate and provide a foundation for further investigations into structural phase transitions and NTE phenomena in materials of pyrophosphate composition.

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Strong electron-phonon coupling and superconducting gap in Heusler-type superconductor $ScAu_2Al$

G. Kuderowicz[1], B.Wiendlocha[1]

[1]*Faculty of Physics and Applied Computer Science, AGH University of Kraków, Aleja Mickiewicza 30, 30-059 Kraków, Poland*

Heusler compounds is large family of intermetallics with over a thousand systems. They remain a very active field of research because of plethora of physical properties which can be easily tuned by chemical substitution and pressure. To our knowledge, superconductivity was reported in approximately 30 Heusler compounds to date. These materials are low temperature superconductors, with transition temperature T_c below 5.5 K, and the pairing is the electron-phonon interaction. Recently characterized $ScAu_2Al$ was reported to have T_c=5.1 K [1] which is one of the highest among Heusler compounds. To better understand superconductivity in $ScAu_2Al$ we performed ab initio calculations. We examined the electronic-structure, phonons and electron-phonon coupling using Quantum Espresso [2,3] and we calculated the superconducting gap with Superconducting Toolkit [4]. In the electronic structure a van Hove singularity appears 10 meV below the Fermi level. The electron-phonon coupling constant λ=1.25 is the highest among Heusler compounds and it classifies $ScAu_2Al$ in a strong coupling regime. Obtained T_c=5.4 K is in a good agreement with the experiment. The spin-orbit coupling significantly changes the electronic structure and phonons. With removed degeneracy the flat electronic bands move away form the Fermi level and acoustic phonon modes are strongly softened. The calculated superconducting gap exhibits slight anisotropy.

Acknowledgements
This work was supported by the National Science Centre (Poland), Project No. 2017/26/E/ST3/00119 and in part by the PL-Grid infrastructure.

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Ab initio determination of thermal conductivity in crystals

Krzysztof Parlinski[1, 2]

[1]*Institute of Nuclear Physics, Polish Academy of Sciences, PL-31342 Kraków, Poland*
[2]*Computing for Materials, Kraków,*

Krzysztof.Parlinski@ifj.edu.pl

The calculations of thermal conductivity requires to know anharmonic properties of the crystal. For this purpose a non-perturbative anharmonic theory is applied, which do not make use of the potential energy expansion over atomic displacements, but instead, runs ab initio calculations of Hellmann-Feynman forces for atomic patterns of atoms with specific displacements to rebuild the anharmonic phonon frequencies and group velocities [see K.Parlinski, Phys. Rev. B 98, 054305 (2018)]. The Green-Kubo equation for the thermal conductivity needs to know the above quantities and the phonon relaxation times, which are related to the 4th-order phonon correlation function expressed in terms of phonon anihilation and creation Bose operators. In currect formulation of anharmonic theory the relaxation times can be derived as analitical expression. The Green-Kubo formulae was succesfully applied to find thermal conductivity of Si and conductivities, related to the phonon and elastic waves, respectivily, were computed.