



5th workshop
on ab initio phonon
calculations

Cracow, December 3–6, 2019

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phonon calculations**

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Mrs Joanna Głąb
Institute of Nuclear Physics
Polish Academy of Sciences
ul. Radzikowskiego 152
31-342 Cracow, Poland
phone: +48 12 662 8093
e-mail: workshop@wolf.ifj.edu.pl

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After 15 years since the first meeting in Kraków, the 5th Workshop on *ab initio* phonon calculations is organized in the Institute of Nuclear Physics on December 3–6, 2019. From the beginning, the workshop was focused on the first-principles studies with a special emphasis on lattice-dynamical properties of materials. During the previous workshops, the lectures and posters presented recent developments in the computational techniques and softwares as well as applications of these methods to current scientific problems.

Phonons represent collective lattice vibrations in periodic atomic systems. To large extent these vibrations determine thermal properties of materials and play an important role in the phenomenon of superconductivity. Many relevant quantities like heat capacity, thermal expansion, mean-square displacements, dielectric functions, electric and heat conductivity depend on phonon spectra. Dynamical properties of materials are often modified by the presence of defects, doped atoms, grain boundaries, and show specific features in nanostructures (interfaces, thin films, nanowires).

Recent achievements in experimental and sample preparation techniques enable to study new classes of materials ranging from complex heterostructures to very small nano-objects (monoatomic layers or nanoparticles). This challenges the computational methods and stimulates further progress in theoretical physics. On the other hand, the information obtained from calculations is very supportive for experiments such as the inelastic neutron and X-ray scattering, nuclear inelastic scattering, infrared and Raman measurements. The aim of this workshop is to provide the fundamentals of phonon calculations based on the *ab initio* methods and present the applications of such methods to numerous physical problems. The lectures on the computational programs are presented by the experts who create and develop computer packages (VASP, WIEN2K, PHONON, ALAMODE, TDEP). The workshop is a good opportunity for the experts from different areas of condensed matter physics to meet and discuss, and often it becomes a starting point of new studies and new collaborations.

The workshop in 2019 will present the recent theoretical and experimental achievements in a broad range of research fields such as:

- progress in computational methods
- anharmonic properties
- phonons in nanomaterials
- phase transitions and stability of materials
- phonons in magnetic and strongly correlated systems
- superconductivity
- phonons in defected crystals
- thermal conductivity
- functional materials

Programme

Tuesday, December 3, 2019

09:00 – 09:45	Registration	
09:45 – 10:00	Opening	
10:00 – 10:35	Ion Errea	13
	<i>Anharmonic properties of solids within the stochastic self-consistent harmonic approximation</i>	
10:35 – 11:10	Terumasa Tadano	15
	<i>Development and application of ALAMODE software</i>	
11:10 – 12:00	Coffee break	
12:00 – 12:35	Krzysztof Parlinski	17
	<i>Phonon anharmonicity from <i>ab initio</i> calculations</i>	
12:35 – 13:00	Michael Leitner	19
	<i>Anharmonic phonons at elevated temperatures in Al: experiment and <i>ab initio</i> predictions</i>	
13:00 – 14:25	Lunch	
14:25 – 15:00	Olle Hellman	21
	<i>Phonons at finite temperature</i>	
15:00 – 15:25	Paweł T. Jochym	23
	<i>Phase space probability distribution in force constants estimation</i>	
15:25 – 15:50	Fredrik Eriksson	25
	<i>Application and comparison of regression methods for force constant extraction using HIPHIVE</i>	
15:50 – 16:30	Coffee break	
16:30 – 16:55	Michael Hu	27
	<i>Lattice anharmonicity revealed by nuclear resonant inelastic <i>x</i>-ray scattering</i>	
16:55 – 17:20	David Reith	29
	<i>Studying phonon lifetimes and heat conductivity of wurtzite aluminum nitride</i>	
17:20 – 18:30	Discussion panel	

Wednesday, December 4, 2019

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	<i>Magnetically induced negative thermal expansion in some frustrated J1-J2 quantum chains</i>	
09:35 – 10:10	Mohamed Zbiri	33
	<i>Dynamics of transition metal cyanides with anomalous thermal expansion behavior</i>	
10:10 – 10:35	Urszula D. Wdowik	35
	<i>Dynamics of the phase-change material GeTe across the structural phase transition</i>	
10:35 – 11:30	Coffee break	
11:30 – 11:55	Bartłomiej Wiendlocha	37
	<i>Influence of the spin-orbit coupling on the electron-phonon interaction in superconductors: several case studies.</i>	

11:55 – 12:20	Andrzej M. Oleś	39
	<i>Low-temperature phase of the $\text{Cd}_2\text{Re}_2\text{O}_7$ superconductor: ab initio phonon calculations and Raman scattering</i>	
12:20 – 12:45	Izabela Biało	41
	<i>Anomalous phonon dispersion in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ studied by inelastic x-ray scattering</i>	
12:45 – 13:10	Andrzej P. Kądziaława	43
	<i>Electron-lattice coupling and the superconductivity in hydrogen-rich systems</i>	
13:10 – 14:30	Lunch	
14:30 – 19:00	Visiting Kraków	
19:00 – 21:00	Conference dinner	
	<i>Restaurant Wesele, Market Square 10</i>	

Thursday, December 5, 2019

09:00 – 09:35	Dominik Legut	45
	<i>Finite temperatures and the alloy analogy model</i>	
09:35 – 10:10	Björn Wehinger	47
	<i>Hybridized spin-lattice correlations in quantum magnets</i>	
10:10 – 10:35	Stanisław Dubiel	49
	<i>Effect of magnetism on lattice dynamics as seen by Mössbauer spectroscopy</i>	
10:35 – 11:30	Coffee break	
11:30 – 12:05	Peter Blaha	51
	<i>The all-electron APW code WIEN2k: Applications to phonon related properties</i>	
12:05 – 12:30	Aloïs Castellano	53
	<i>Thermodynamic properties of UMo alloys from first principles</i>	
12:30 – 12:55	Lorenz Bergen	55
	<i>Low frequency phonons in rare earths langasites</i>	
12:55 – 14:15	Lunch	
14:15 – 15:00	Poster session	
15:00 – 15:35	Svetoslav Stankov	57
	<i>Phonon confinement and spin-phonon coupling in tensile-strained thin EuO films</i>	
15:35 – 16:00	Paweł Kempisty	59
	<i>First-principles phonon calculations as a method of improving the atomistic thermodynamics of III-nitrides surfaces</i>	
16:00 – 16:45	Coffee break	
16:45 – 17:10	Evgenii Roginskii	61
	<i>Raman spectra of short-period $(\text{GaN})_n(\text{AlN})_m$ superlattices: ab initio study</i>	
17:10 – 17:35	Jochen Kalt	63
	<i>Lattice dynamics and polarization-dependent phonon damping in α-phase FeSi_2 nanostructures</i>	

17:35 – 18:30 Discussion panel

Friday, December 6, 2019

09:00 – 09:35	Iyad Al-Qasir	65
	<i>Vibrational properties of irradiated nuclear graphite: Inelastic neutron scattering measurements and first-principles calculations</i>	
09:35 – 10:00	Shihao Zhang	67
	<i>AELAS: Automatic ELAStic property derivations via high-throughput first-principles computation</i>	
10:00 – 10:25	Sergiu Arapan	69
	<i>The role of lattice dynamics in phase stability of Fe-Sn binary systems</i>	
10:25 – 11:15	Coffee break	
11:15 – 11:40	Kamil Tokár	71
	<i>Thermodynamic stability and electronic response to phonon mode in silver difluoride polymorphs</i>	
11:40 – 12:05	Sylvia Gutowska	73
	<i>Electron-phonon driven superconductivity of LiBi</i>	
12:05 – 12:30	Przemysław Piekarczyk	75
	<i>Ab initio studies on lattice dynamics and Verwey transition in magnetite</i>	
12:30 – 13:00	Closing	
13:00 – 14:30	Lunch	

Presentations

Anharmonic properties of solids within the stochastic self-consistent harmonic approximation

Ion Errea

University of the Basque Country

Describing atomic vibrations from first-principles accurately is of paramount importance to understand the thermodynamic and transport properties of solids. Phonon dispersions are routinely calculated within the harmonic approximation, and transport properties can be studied by estimating the electron-phonon and phonon-phonon interactions within perturbation theory. Nevertheless, whenever the amplitude of the atomic displacements largely exceeds the range in which the harmonic potential is valid, the harmonic approximation completely fails without allowing a perturbative expansion.

The stochastic self-consistent harmonic approximation (SSCHA) that we have developed [1–4] offers an efficient method to calculate vibrational properties of solids even when the harmonic approximation completely collapses. The method is variational and takes into account quantum and thermal effects rigorously. With our recent developments on the SSCHA method [3], we show how phonon frequencies should be defined from the second derivative of the free energy, which allows calculating the transition temperature of structural second-order phase transitions. Moreover, the new developments [3] allow calculating third-order anharmonic force-constants, which determine thermal properties, beyond the perturbative limit. Also we are now capable of calculating the stress tensor including quantum/anharmonic effects and perform structural relaxations in this quantum/anharmonic energy landscape, in contrast to the classical calculations just focused on the classical Born-Oppenheimer energy surface.

In this lecture we will present the method and several applications of it in superconducting hydrides, charge-density-wave systems, and thermoelectric materials.

References:

- [1] I. Errea, M. Calandra and F. Mauri, *Phys. Rev. Lett.* **111**, 177002 (2013).
- [2] I. Errea, M. Calandra and F. Mauri, *Phys. Rev. B* **89**, 064302 (2014).
- [3] R. Bianco, I. Errea, L. Paulatto, M. Calandra and F. Mauri, *Phys. Rev. B* **96**, 014111 (2017).
- [4] L. Monacelli, I. Errea, M. Calandra and F. Mauri, *Phys. Rev. B* **98**, 024106 (2018).

Development and application of ALAMODE software

Terumasa Tadano

National Institute for Materials Science, Tsukuba, Japan

Ab initio phonon calculation plays an essential role in the modern computational materials science study, which aims to predict and elucidate thermodynamic and transport properties of materials at finite temperature. The harmonic approximation in phonon calculation is very useful and has been successful for many materials. However, it naturally fails to describe anharmonic properties and often breaks down in many energy- and light-harvesting materials. Therefore, developing a more accurate and versatile phonon calculation method that can handle strong anharmonicity is vital.

To overcome the limitation of the conventional phonon calculation method, we have been developing the ALAMODE [1], an opensource software for anharmonicity and thermal transport. In this talk, I will present several features of ALAMODE, including the self-consistent phonon calculation [2] and the efficient estimation of force constants [3,4], as well as its applications to thermoelectric materials [5] and ceramics [6].

References:

- [1] <https://github.com/ttadano/alamode>
- [2] T. Tadano and S. Tsuneyuki, Phys. Rev. B **92**, 054301 (2015); J. Phys. Soc. Jpn. **87**, 041015 (2018).
- [3] F. Zhou, W. Nielson, Y. Xia and V. Ozoliņš, Phys. Rev. Lett. **113**, 185501 (2014).
- [4] <https://alm.readthedocs.io/en/develop/>
- [5] T. Tadano, Y. Gohda and S. Tsuneyuki, Phys. Rev. Lett. **114**, 095501 (2015); T. Tadano and S. Tsuneyuki, Phys. Rev. Lett. **120**, 105901 (2018).
- [6] Y. Oba, T. Tadano, R. Akashi and S. Tsuneyuki, Phys. Rev. Materials **3**, 033601 (2019).

Phonon anharmonicity from *ab initio* calculations

Krzysztof Parlinski^{a,b}

^a*Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland*

^b*Computing for Materials, Cracow, Poland*

Applying principles similar to those used in creation the harmonic PHONON software, a novel nonperturbative approach of the anharmonic lattice dynamics of crystals is proposed. The method treats a crystal as an ensemble of supercells, each with atoms displaced from equilibrium positions, such that the created POSCAR mimics the atomic configuration arising from all allowed excited phonons with amplitudes determined by the requested temperature. Next, using VASP and PhononA softwares the computed phonon dispersion curves are averages over created atom configurations to show the anharmonic phonon peaks and their finite widths and shifts. The method also allows to treat directly the soft modes. The thermal conductivity can be estimated after adopting the Green-Kubo formalism to the present non-perturbative method. Anharmonic results for fcc-Pb, bcc-W, cubic-Si, fcc-MgO, mineral-MgSiO₃, AlN, MgB₂ and soft mode in NiTi will be shown. The calculated anharmonic behaviour of MgB₂ superconductor is well reproduced with the proposed method, including the giant width of E_{2g} phonon branch in agreement to its x-ray measurements.

For other crystals, when available, the results are compared to measured data.

The complete formulations of the harmonic and anharmonic theories is only shortly presented. The details can be found in the recent paper of the author, Phys. Rev. B **98**, 054305 (2018). The method is highly parallel and computationally very fast, since using VASP, in general it requires only single run of ionic loop for each atomic configuration POSCAR. Typically, a comprehensive anharmonic study of a material takes less than a (few) day(s).

Anharmonic phonons at elevated temperatures in Al: experiment and *ab initio* predictions

Michael Leitner

Technical University of Munich, Germany

The importance of anharmonicity for describing fundamental materials properties, starting from finite heat conductivity due to phonon-phonon scattering, can hardly be overemphasized. For crystalline matter, the pertinent information is captured to a large part by considering q -dependent phonon lifetimes, leading to a broadening in energy of the phonon dispersions. The prevalent way of computing these broadenings theoretically is by employing perturbation theory, being of comparable effort as the computation of the dispersions in the harmonic approximation. Conversely, the experimental determination of phonon linewidths is much more involved, and only a small number of data sets covering large parts of reciprocal space at elevated temperatures, where anharmonic effects will be most pronounced, have been reported. Thus, theoretical computations today go largely unvalidated.

Here I will consider the case of elemental Al at temperatures up to the melting point. I will present experimental data obtained by inelastic neutron scattering with consideration to the necessary steps in data analysis for being able to extract the inherent linewidths. Further, I will present calculations of q -dependent line broadenings on the basis of density-functional theory, both in the standard approach of perturbation theory as well as via *ab initio* molecular dynamics, and discuss their discrepancies. Finally, I will analyse the short-range atomic interactions and show how numerically efficient phenomenological potentials can be constructed that allow to compute anharmonic properties beyond the limitations of perturbation theory at very small computational effort.

Phonons at finite temperature

Olle Hellman

Department of Physics, Chemistry and Biology, Linköping University, Sweden

We present recent developments using the temperature dependent effective potential technique (TDEP) to model strongly non-harmonic materials. The method employs model Hamiltonians that explicitly depend on temperature. I will present applications pertaining to thermal conductivity, inelastic neutron spectra and phase stabilities. In addition, we investigate non-linear electron-phonon coupling and its influence on phonon spectra, and recent additions to that deal with nuclear quantum effects and efficient stochastic sampling.

Phase space probability distribution in force constants estimation

Paweł T. Jochym and Jan Łażewski

Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland

Recently developed methods [1–3] of computational investigation of anharmonic and temperature-dependent aspects of lattice dynamics are based on building of some form of model potential. Parameters of such a model are derived from the forces acting on atoms and requires replication of the conditions of thermal equilibrium – to obtain proper sampling of the phase space region occupied by the system. This requirement is very challenging when performing quantum mechanical calculations. Typically, it involves large number of atoms and long simulation times needed to approximate thermodynamical limit conditions. It is usually achieved by running a long molecular-dynamics calculation on the system, to thermalize all degrees of freedom, and selecting well-separated (independent) configurations from the obtained trajectory. While this approach provides good sampling of the phase space of the system, it is computationally very expensive and exceptionally wasteful. To obtain independent samples the selected times in the trajectory must be separated by multiple time steps – often tenths or hundreds. Thus, we are throwing away a large amount of computational time, often above 80%, to obtain good sampling of the probability distribution of the system. Furthermore, in the case of lattice-dynamical calculations, we are utilizing only the positions from the trajectory - since the velocity information is not used in the process. Together, this makes the described procedure limited to fairly small systems. In this work we present an alternative scheme for creating a representation of the probability distribution in the configuration space, which aims to faithfully reproduce densities generated by the molecular dynamics, while being more effective in terms of computational time. This approach uses well-known techniques of probability distribution modelling, and apply knowledge of the behaviour of the system in thermodynamic equilibrium to obtain low sample rejection rate in the procedure. The proposed method, coupled with the effective-potential modelling provides a promising path to tackle problems of anharmonic and temperature-dependent lattice dynamics even in systems with large and complicated unit cells.

This work was partially supported by National Science Centre (NCN, Poland) under grant UMO-2014/13/B/ST3/04393.

References:

- [1] O. Hellman, I. A. Abrikosov and S. I. Simak, *Phys. Rev. B* **84**, 180301(R) (2011).
- [2] I. Errea, M. Calandra and F. Mauri, *Phys. Rev. Lett.* **111**, 177002 (2013).
- [3] T. Tadano, Y. Gohda and S. Tsuneyuki, *J. Phys. Condens. Matter* **26**, 225402 (2014).

Application and comparison of regression methods for force constant extraction using HIPHIVE

Fredrik Eriksson

Department of Physics, Chalmers University of Technology, Gothenburg, Sweden

The extraction of harmonic and anharmonic force constants from *ab-initio* calculations is often the bottleneck when calculating thermal properties. The commonly used direct approach is robust but suffers from poor scaling with respect to system symmetry, size, and force constant expansion order. During the last decade regularized regression based approaches have proved viable for efficient and accurate extraction of anharmonic force constants. Even though computational effort is saved at the *ab-initio* level the regression itself can still be a formidable task. To this point no consensus exists about what regularization method to use nor have different regression methods been comprehensively compared. In order to use regression methods in *e.g.*, high throughput computations, robust methods for sampling and fitting must be developed. Thus a flexible framework which can easily interface to other codes is needed in order to study and benchmark different methods. Here, we present the HIPHIVE package, which is entirely written in Python for easy accessibility and interfaces well with libraries such as scikit-learn, which provides a rich set of methods for linear regression and validation. The core goal of HIPHIVE is to focus on the extraction of force constants while leaving the analysis (*e.g.*, phonon dispersions or thermal conductivity) to other more specialized packages. We show that ordinary least-squares, especially in connection with feature elimination, often yields the best performance in terms of convergence with respect to training set size and sparsity of the solution. The automatic relevance determination regression (ARDR) method also shows promising performance. Regression based on the least absolute shrinkage and selection operator (LASSO) on the other hand, while useful in some cases, tends to yield a larger number of features, with a noise level that has a detrimental effect on the prediction of *e.g.*, the thermal conductivity. Finally, we also consider methods for the prediction of the temperature dependence of vibrational spectra from high-order FC expansions via molecular dynamics simulations as well as self-consistent phonons.

Lattice anharmonicity revealed by nuclear resonant inelastic x-ray scattering

Michael Hu

Argonne National Laboratory, Lemont, USA

Nuclear Resonant Inelastic X-ray Scattering (NRIXS) is a spectroscopy method to study atomic vibrations and dynamics, currently done with synchrotron radiation at a few high energy third generation facilities. It finds a wide range of applications in condensed matter physics, materials science, chemistry, biophysics, geosciences, and high-pressure researches. Many atomic dynamics and lattice thermodynamics information can be derived from NRIXS measurements. Phonon Density of States (DOS) characterizes lattice dynamics of a material and can be derived under the *quasi*-harmonic approximation. Combined with modelling and simulations, results from NRIXS can provide unique and clarifying insights into many fields of research.

The interpretation of NRIXS measurements has been done mostly in the context of *quasi*-harmonic approximation. Phonon density of states and dynamic properties like mean kinetic energy and mean force constant can be derived.

Going beyond the harmonic lattice model, we show that the anharmonic terms in the lattice potential can be measured. This opens up the NRIXS method to study anharmonicities in materials.

Given any *ab initio* model or specific model of lattice potentials, one can calculate the moments of a would-be measured NRIXS spectrum. Comparing them with NRIXS measurement results will help to restrict and adjust the models and calculations.

We will present a study of lattice anharmonicity in the sigma phase of Fe-Cr alloy, particularly the anomalous effect of magnetic structure on lattice dynamics.

Studying phonon lifetimes and heat conductivity of wurtzite aluminum nitride

David Reith^a, Krzysztof Parlinski^{b,c} and Walter Wolf^a

^a*Materials Design, Montrouge, France*

^b*Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland*

^c*Computing for Materials, Cracow, Poland*

Phonon lifetimes and heat conductivity of wurtzite aluminum nitride has been studied by two different computational methodologies. The first method uses a molecular dynamics equilibrium Green-Kubo formalism to compute the thermal conductivity. It requires large simulation cells and long simulation times, practically accessible using classical forcefield methods. The method can be extended to calculate wavevector and frequency resolved thermal conductivities and phonon lifetimes by projecting the heat flux onto the vibrational modes. The second approach used in the present study is to calculate these anharmonic processes by explicitly evaluating the anharmonic force constants. This is done using the PhononA package (Parlinski, *Ab initio* determination of anharmonic phonon peaks, 2018) and is based on forces extracted from supercell calculations.

Magnetically induced negative thermal expansion in some frustrated J1-J2 quantum chains

Reinhard K. Kremer

Max Planck Institute for Solid State Research, Stuttgart, Germany

The search for unconventional states in quantum matter is at the forefront of current research in solid state physics. In this respect, frustrated quantum magnets are topical candidates since they are widely known to be able to realize atypical ground states. In this class of systems frustrated J1–J2 quantum spin chains have attracted special attention since they have been demonstrated to realize *e.g.* helimagnetic order giving rise to spin-current induced type-II multiferroicity or they are currently discussed as candidates for spin-nematic phases. We have investigated the lattice properties of such system, like *e.g.* CuBr₂, CuCrO₄, LiCuVO₄ and observed magnetically induced negative thermal expansion, partially extending far into the short range correlated antiferromagnetically regime.

Dynamics of transition metal cyanides with anomalous thermal expansion behavior

Mohamed Zbiri

Institut Laue-Langevin, Grenoble, France

Transition metal (TM) cyanides are an exceptional class of framework materials exhibiting remarkable physico-chemical aspects in terms of: (i) photoluminescence, (ii) dimensionality, i.e. these systems can be of a 1-D, 2-D or 3-D nature, and (iii) disorder, they can be subject to different types of disorder; like a site disorder on the TM site and/or a disorder of the C \equiv N bond, as well as stacking disorder in the 2-D (layers) case or a slipping disorder in the 1-D (chains) case.

The main interest in these materials goes beyond the above mentioned properties to cover intriguing phenomena like negative linear compressibility and negative thermal expansion (NTE). In some typical cases of TM cyanides, NTE can be colossal and extending over a wide temperature range, making it quite interesting and attractive both on the fundamental level as well as on the practical side for relevant applications.

Thermal properties are intimately linked to phonons in crystalline materials. Therefore studying phonon dynamics helps to gain deeper insights into the dynamical mechanisms of TM cyanides exhibiting anomalous thermal properties. Inelastic neutron spectroscopy (INS) is an appropriate technique to study lattice dynamics of crystalline materials on the microscopic level, offering the perfect tool to cover dynamics on the targeted length and time scales.

The presentation will focus on highlighting the relationship between lattice dynamics and the observed anomalous thermal behaviour in some selected one- two- and three-dimensional TM cyanide structures, to explore the microscopic mechanisms at the origin of their intriguing thermal expansion properties, by using a combined approach of INS, underpinned by *ab-initio* phonon calculations. For the sake of complementarity, results using other techniques (PDF, NMR, *etc.*) will also be indicated as to highlight the synergistic aspect of structure and dynamics in these fascinating materials.

Dynamics of the phase-change material GeTe across the structural phase transition

Urszula D. Wdowik^a, T. Chatterji^b and S. Rols^b

^a*Institute of Technology, Pedagogical University, Cracow, Poland*

^b*Institut Laue-Langevin, Grenoble, France*

Despite successful application of the phase-change materials from the ternary Ge–Sb–Te system in a variety of optical data storage devices (CDs, DVDs and blue-ray disks) as well as in non-volatile random access memories (non-volatile RAM) [1–2], a comprehensive understanding of the mechanism underlying the phase transitions in the GST compounds is still lacking. A typical example is the temperature induced structural phase transition in GeTe, which is the parent compound of the GST phase-change materials. In particular, the nature of phase transition (displacive or order-disorder) and the driving force of the rhombohedral-to-cubic phase transformation at $T_c \approx 600$ K along with accompanying effects (volume contraction and disappearance/persistence of the Peierls distorted Ge–Te bonds above T_c) still remain a source of controversy in spite of numerous experimental and theoretical studies carried out over last 30 years [3–10]. This presentation addresses results of the inelastic neutron scattering (INS) experiments on powder GeTe samples and *ab initio* molecular dynamics (AIMD) simulations which have been undertaken to revisit lattice dynamics of GeTe as a function of temperature and examine behaviour of the local versus average structure of this compound across the structural phase transition. Generally, results of our experimental and theoretical research support observations provided by the so-called local probes (EXAFS and PDF analysis of the high-energy x-ray scattering).

References:

- [1] M. Wuttig and N. Yamada, *Nat. Mater.* **6**, 824 (2007).
- [2] S. Raoux, F. Xiong, M. Wuttig and E. Pop, *MRS Bull.* **39**, 703 (2014).
- [3] E. F. Steigmeier and G. Harbeke, *Solid State Commun.* **8**, 1275 (1970).
- [4] T. Chattopadhyay, J. X. Boucherele and H. von Schnering, *J. Phys. C* **20**, 1431 (1987).
- [5] P. Fons, A. V. Kolobov, M. Krbal, J. Tominaga, K. S. Andrikopoulos, S. N. Yannopoulos, G. A. Voyiatzis and T. Uruga, *Phys. Rev. B* **82**, 155209 (2010).
- [6] T. Matsunaga, P. Fons, V. Kolobov, J. Tominaga and N. Yamada, *Appl. Phys. Lett.* **99**, 231907 (2011).
- [7] U. D. Wdowik, K. Parlinski, S. Rols and T. Chatterji, *Phys. Rev. B* **89**, 224306 (2014).
- [8] T. Chatterji, C. Kumar and U. D. Wdowik, *Phys. Rev. B* **91**, 054110 (2015).
- [9] D. Yang, T. Chatterji, J. A. Schiener and M. A. Carpenter, *Phys. Rev. B* **93**, 144109 (2016).
- [10] D. Dangić, A. R. Murphy, E. D. Murray, S. Fahy and I. Savić, *Phys. Rev. B* **97**, 224106 (2018).

Influence of the spin-orbit coupling on the electron-phonon interaction in superconductors: several case studies.

Sylwia Gutowska, Gabriel Kuderowicz and Bartłomiej Wiendlocha

AGH University of Science and Technology, Cracow, Poland

Recent widespread interest in topological materials intensified studies on various compounds containing heavy elements, like Pb or Bi. This is of course related to the strong spin-orbit coupling (SOC), which should be present in such materials, and should strongly influence their physical properties. Because some of these materials exhibit superconductivity, a natural question arises what is the spin-orbit coupling effect of the electron-phonon interaction and superconductivity of such materials, containing heavy elements?

Thanks to the ongoing development of computational techniques, calculations of the electron-phonon interaction function, taking into account the spin-orbit coupling, became available recently. In this work we present several case studies, where the spin-orbit interaction effects on the electronic structure, phonons, and the electron-phonon coupling (EPC) is investigated using density-functional calculations. As the prime example we will discuss the role of spin-orbit interaction in determining the electronic and phononic properties of the type-I superconductor CaBi_2 [1]. In this case SOC, mainly via the modifications of the Fermi surface topology, reduces the strength of EPC almost twice. As the next two cases we will present Pb-Bi alloy, with extremely strong electron-phonon coupling, and noncentrosymmetric ThCoC_2 , where SOC splits the Fermi surface but surprisingly has a little impact on the electron-phonon interaction.

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References:

- [1] S. Gołąb and B. Wiendlocha, *Electron-phonon superconductivity in CaBi_2 and the role of spin-orbit interaction*, Phys. Rev. B **99**, 104520 (2019).

Low-temperature phase of the $\text{Cd}_2\text{Re}_2\text{O}_7$ superconductor: *ab initio* phonon calculations and Raman scattering

Andrzej M. Oleś^a, Konrad J. Kapcia^b, Maureen Reedyk^c, Mojtaba Hajialamdari^c, Andrzej Ptok^b, Przemysław Piekarczyk^b, Fereidoon S. Razavi^c and Reinhard K. Kremer^d

^a*Marian Smoluchowski Institute of Physics, Jagiellonian University, Cracow, Poland*

^b*Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland*

^c*Department of Physics, Brock University, St. Catharines, Canada*

^d*Max Planck Institute for Solid State Research, Stuttgart, Germany*

Using an *ab initio* approach, we report a phonon soft mode in the tetragonal structure described by the space group $I4_122$ of the 1 K 5d superconductor $\text{Cd}_2\text{Re}_2\text{O}_7$. It induces an orthorhombic distortion to a crystal structure described by the space group $F222$ which hosts the superconducting state. This new phase has a lower total energy than the other known crystal structures of $\text{Cd}_2\text{Re}_2\text{O}_7$. Comprehensive temperature dependent Raman scattering experiments on isotope enriched samples, $^{116}\text{Cd}_2\text{Re}_2^{18}\text{O}_7$, not only confirm the already known structural phase transitions but also allow us to identify a new characteristic temperature regime around ≈ 80 K, below which the Raman spectra undergo remarkable changes with the development of several sharp modes and mode splitting. Together with the results of the *ab initio* phonon calculations we take these observations as strong evidence for another phase transition to a novel low-temperature crystal structure of $\text{Cd}_2\text{Re}_2\text{O}_7$.

Anomalous phonon dispersion in $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ studied by inelastic x-ray scattering

Izabela Biało^{a,b}, B. Yu^c, W. Tabis^{a,b}, M. Greven^c, A. Bosak^d, A. Kozłowski^a and N. Barisic^b

^aAGH University of Science and Technology, Cracow, Poland

^bInstitute of Solid State Physics, Vienna Technical University, Austria

^cSchool of Physics and Astronomy, University of Minnesota, Minneapolis, USA

^dEuropean Synchrotron Radiation Facility, Grenoble, France

Understanding the charge-ordering tendencies exhibited by the cuprates might give valuable insight into the origin of superconductivity in these complex oxides. The charge correlations may appear to manifest themselves as an anomalous dispersion (softening) of the longitudinal Cu–O bond-stretching phonon mode both in the hole-doped [1,2] and electron-doped cuprates [3]. In electron-doped $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$, the Charge Density Wave (CDW) order was found at the two-dimensional wave vector $(H,K) \approx (0.2,0)$, approximately the same wave vector at which an anomalous optical phonon dispersion was observed [3]. I will present our temperature and doping depended inelastic x-ray scattering (IXS) studies of the optical phonon anomaly. I will discuss it in the context of the CDW order in this compound. Our IXS studies will be furthermore compared with the DFT calculations performed for the parent compound Nd_2CuO_4 .

References:

- [1] D. Reznik *et al.*, Nature **440**, 1170 (2006).
- [2] D. Reznik, Physica C **481**, 75 (2012).
- [3] M. d’Astuto *et al.*, Phys. Rev. Lett. **88**, 167002 (2002).

Electron-lattice coupling and the superconductivity in hydrogen-rich systems

Andrzej P. Kądziaława^{a,b}, Andrzej Biborski^c and Józef Spalek^a

^a*Marian Smoluchowski Institute of Physics, Jagiellonian University, Cracow, Poland*

^b*VŠB – Technical University of Ostrava, Czech Republic*

^c*AGH University of Science and Technology, Cracow, Poland*

Recent development in the high-pressure physics provides us with a new class of the superconducting materials, namely with the hydrogen-rich materials, such as silane (SiH₄, transition temperature $T_c=17$ K at pressure $p=96$ GPa), hydrogen sulphide (H_{2/3}S, $T_c=203$ K @ 150 GPa) or hydrogen lanthanide (H_{1-x}La, $T_c=274$ – 286 K @ 210 GPa).

We investigate the versatility of the molecular-to-atomic transitions in one-, two-, and quasi-three-dimensional hydrogen systems, using our own original approach – the Exact Diagonalization Ab-Initio (EDABI) method. Starting from the extended Hubbard model, we examine an electron-correlation-driven conductivity connected with the creation of high-symmetry hydrogen molecular and atomic planes, as well as a series of both structural and electronic-in-nature quantum phase transitions.

We discuss the suppression of molecular nature in a reversed Peierls-like transition under high pressure, as well as the proper van-der-Waals-like effective interaction derived from the first principles of quantum mechanics.

Using effective electron-phonon Hamiltonian we estimate both the zero-point motion of the lattice ions, as well as the electron-lattice coupling. Next, by using the McMillan formula we estimate the superconducting transition temperature versus the effective pressure (external and/or chemical).

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Finite temperatures and the alloy analogy model

Dominik Legut^a, David Wagenknecht^b, Karel Carva^b and Ilja Turek^c

^aVŠB – Technical University of Ostrava, Czech Republic

^bCharles University, Prague, Czech Republic

^cInstitute of Physics of Materials, Czech Academy of Sciences, Brno, Czech Republic

Theoretical description of nonzero temperatures, including effects of spin fluctuations, has been problematic for a long time. In recent years, the alloy analogy model (AAM) became popular for a treatment of finite-temperature effects from the first principles [1]. Phonons, described as uncorrelated displacements of atoms, can be combined with spin fluctuations (magnons) and chemical disorder. The realistic inclusion of spin fluctuations is crucial especially for spintronic properties such as the spin polarization of the electrical current. The AAM within the tight-binding linear-muffin-tin orbital method and the coherent potential approximation (CPA) successfully describes electrical transport at nonzero temperatures even in multisublattice half-Heusler alloys [2]. In the previous studies (i) the Debye theory was employed for a conversion between displacements and temperature, (ii) the total magnetization as a function of temperature was obtained from experiments, and (iii) a change of a volume with temperature was neglected. These simplification will be addressed in details. A route to overcome it by proper *ab initio* approaches is envisaged. Obtained corrections are a few percents (compared to the previous techniques) for some materials. However, this more precise approach is essential for systems where the Debye theory fails. Moreover, the description of finite temperatures is finally obtained completely from the first principles. It is done by synergizing precise supercell methods with the numerically efficient CPA. We will present the usage of novel techniques for pure transition metals, both nonmagnetic and magnetic, but it can be easily generalized for more complex systems, such as previously studied random and ordered [2] alloys.

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References:

- [1] D. Wagenknecht *et al.*, IEEE Trans. on Mag. **53** 11, 1700205 (2017).
- [2] D. Wagenknecht *et al.*, J. Magn. Magn. Mater **474**, 517–521 (2019).

Hybridized spin-lattice correlations in quantum magnets

Björn Wehinger

Ca' Foscari University of Venice, Italy

The coupling of spin waves to phonons allows to probe the collective spin dynamics in quantum materials via phonon spectroscopy. This allows for novel experiments and the control of magnetic interactions via lattice degrees of freedom. In this presentation, I will show, that the strong magnon-phonon coupling in the triangular lattice Heisenberg antiferromagnets LiCrO_2 and PdCrO_2 enables the measurement of magnetic correlations throughout the Brillouin zone via inelastic x-ray scattering. Our studies reveal intrinsic details of the magnetoelastic excitation spectrum. We find single particle excitations with momentum dependent lifetime and continuum scattering at low temperature [1]. In a high-pressure experiment at cryogenic temperatures we furthermore show that tuning the lattice allows for efficient control of magnetic interactions. With help of *ab initio* phonon calculations combined with linear spin wave theory we are able to quantify the spin lattice coupling and address the coupling to the two-magnon continuum. I furthermore introduce a novel methodology that allows for high-precision measurements of the full elasticity tensor from thermal diffuse scattering [2].

References:

- [1] S. Tóth, B. Wehinger, K. Rolfs, T. Birol, U. Stuhr, H. Takatsu, K. Kimura, T. Kimura, H. M. Rønnow and Ch. Rüegg, *Electromagnon dispersion probed by inelastic X-ray scattering in LiCrO_2* , Nat. Commun. **7**, 13547 (2016).
- [2] B. Wehinger, A. Mirone, M. Krisch and A. Bosak, *Full Elasticity Tensor from Thermal Diffuse Scattering*, Phys. Rev. Lett. **118**, 035502 (2017).

Effect of magnetism on lattice dynamics as seen by Mössbauer spectroscopy

Stanisław Dubiel

AGH University of Science and Technology, Cracow, Poland

An effect of magnetism on lattice dynamics is considered as negligible. Such belief is based on calculations according to which the spin susceptibility of metal is not affected by the electron-phonon interaction (EPI) ([1] and references therein). Indeed, the effect of the EPI was estimated as $E_D/E_F=10^{-2}$ ([1] and references therein) where E_F is the Fermi energy, and E_D is the Debye energy. However, Kim showed [1] that the influence of the EPI on spin susceptibility can be significantly, i.e. by a factor of 100, enhanced by exchange interactions between electrons. In other words, the effect of the EPI on magnetic properties of metallic systems, and vice versa, is much more significant than generally believed. The Mössbauer spectroscopy (MS) is a well-suited method for studying the lattice dynamics via two spectral parameters viz. (1) center shift, CS, and (2) recoil-free factor, f . The former gives information on an average squared velocity of vibrations, $\langle v^2 \rangle$, while the latter is related to average squared amplitude of vibrations, $\langle x^2 \rangle$. Presented and discussed will be relevant results obtained with the MS for sigma-phase Fe–Cr and Fe–V alloys [2,3], C14 Laves phase NbFe₂ [4], spin-density waves Cr doped with ⁵⁷Fe [5], and last but not least, the effect of magnetism on sound velocity in the σ -FeCr alloy studied with the nuclear inelastic scattering of synchrotron radiation [6].

References:

- [1] D. J. Kim, Phys. Rep. **171**, 129 (1988).
- [2] S. M. Dubiel *et al.*, EPL **101**, 16008 (2013).
- [3] S. M. Dubiel and J. Żukrowski, J. Magn. Magn. Mater., **441**, 557 (2017).
- [4] J. Żukrowski and S. M. Dubiel, J. Appl. Phys. **123**, 223902 (2018).
- [5] S. M. Dubiel *et al.*, J. Phys.: Condens. Matter **22**, 435403 (2010).
- [6] S. M. Dubiel and A. I. Chumakov, EPL **117**, 56001 (2017).

The all-electron APW code WIEN2k: Applications to phonon related properties

Peter Blaha

Institute of Materials Chemistry, Vienna University of Technology, Austria

I will give a review on augmented plane wave (APW) methods for the calculation of the electronic structure in solids starting with the original concept developed by J. Slater [1] long time ago up to the APW+lo method introduced by Sjöstedt *et al.* [2]. This latter method combines the superior convergence behaviour of the original APW method with the convenience of LAPW [3]. I will then give an overview of the implementation of APW+lo into the WIEN2k code [4] and summarize the available features and discuss in particular the possibilities connected with calculations of phonons. Selected results will be discussed in more detail. This will include phase transitions in RbCaF₃ [5] and PbTiO₃ [6] as well as a finite temperature (phonon) related explanation of a double peak occurring in the B-K XANES spectra of h-BN [7].

References:

- [1] J. Slater, Phys. Rev. **51**, 151 (1937).
- [2] E. Sjöstedt, L. Nordström and D. Singh, Solid State Commun. **114**, 15 (2000).
- [3] G. K. H. Madsen, P. Blaha, K. Schwarz, E. Sjöstedt and L. Nordström, Phys. Rev. B **64**, 195134 (2001).
- [4] <http://www.wien2k.at>
- [5] S. Ehsan, A. Tröster, F. Tran and P. Blaha, Phys Rev. Mat. **2**, 093610 (2018).
- [6] A. Tröster, S. Ehsan, K. Belbase, P. Blaha, J. Kreisel and W. Schranz, Phys. Rev. B **95**, 064111 (2017).
- [7] F. Karsai, M. Humer, E. Flage-Larsen, P. Blaha and G. Kresse, Phys. Rev. B **98**, 235205 (2018).

Thermodynamic properties of UMo alloys from first principles

Aloïs Castellano, Johann Bouchet, François Bottin and Boris Dorado

CEA – The French Alternative Energies and Atomic Energy Commission, ArpaJon, France

UMo alloys appear to be the most promising nuclear fuels for the conversion of highly enriched fuels that are currently used in research reactor cores, such as U_3Si_2 , UAl alloys, or U_3O_8 . These alloys have been selected because of their high uranium density, as well as their cubic crystal structure that guarantee isotropic swelling under irradiation. It is therefore crucial that we get some basic understanding of their thermal properties via the determination of phonon spectra and density of states. However, while a lot of work has been dedicated to the electronic structure of UMo with respect to the Mo content, there is little data related to the phonon dispersion curves.

In this work, we run *ab initio* molecular dynamics and we use TDEP method [1–3] and its SIFC extension [4] in order to calculate the phonon spectra of UMo alloys over the whole range of Mo concentrations. We compare the results with those of pure bcc uranium and molybdenum, as well with experimental results [5] in order to get a consistent and comprehensive picture of UMo thermodynamic properties. We show how the interplay between the addition of Mo and the temperature stabilizes the uranium bcc structure and we calculate a number of thermal properties derived from the phonon density of states, such as Gibbs free energies, phonon and electron thermal conductivities, Gruneisen parameters, expansion coefficients, *etc.*

References:

- [1] O. Hellman *et al.*, Phys. Rev. B **87**, 104111 (2013).
- [2] J. Bouchet *et al.*, Phys. Rev. B **95**, 054113 (2017).
- [3] B. Dorado *et al.*, Phys. Rev. B **95**, 104303 (2017).
- [4] N. Shulumba *et al.*, Phys. Rev. Lett. **117**, 205502 (2016).
- [5] D. Chaney, R. Springell, G. H. Lander, private communication.

Low frequency phonons in rare earths langasites

Lorenz Bergen^a, Evan Constable^a, Lukas Weymann^a, Andrei Pimenov^a, A. Kuzmenko^b and A. Mukhin^b

^a*Vienna University of Technology, Austria*

^b*Prokhorov General Physics Institute, Russian Academy of Sciences, Moscow, Russia*

Magnetic frustration is found in magnetic material when the individual spin moments cannot simultaneously minimize their magnetic interactions with their neighbored moments. As such, magnetically frustrated systems often support a highly degenerate ground state exhibiting a number of exotic physical phenomena such as spin ice [1] and spin liquid [2] states. Probing the spin and lattice dynamics in these systems provides an avenue to better understand the nature of these exotic states. Rare-earth langasites are characterized by geometric magnetic frustration, exhibiting magneto-electric effects, high piezoelectric properties, and are seen as a possible candidate for a spin-liquid ground state [3]. Phonon and crystal electric field spectra provide important information to unravel the interplay between the structural and magnetic properties of the langasite family. The langasite structure crystallizes in the P321 space group with a general formula $A_3BC_3D_2O_{14}$, where magnetic rare-earth elements are situated at the A site of the structure. Our study presents spectra of several rare-earth langasites $RE_3Ga_5SiO_{14}$ ($RE = La, Nd, Ho$) using Fourier-transform infrared (FTIR) reflection spectroscopy. Experiments have been performed with polarized radiation along the principal crystallographic axes and under different sample temperatures. Phonon excitations at unusually low frequencies are observed that brings the crystal structure of langasites close to a lattice instability. The results in the rare-earth langasite $Nd_3Ga_5SiO_{14}$ (NGS) and in a holmium-substituted langasite $Ho_{0.03}La_{2.97}Ga_5SiO_{14}$ (Ho-LGS) are compared with pure $La_3Ga_5SiO_{14}$ (LGS) langasite compound that does not show magnetic frustration. Spectra with polarization parallel to the b^* -axis of the crystal show a number of phonons between 100 and 400 cm^{-1} with a weak temperature dependence indicating a stable crystalline structure. This behavior was found in all three investigated samples. Although they have the same crystalline structure, differences in the obtained dielectric function can be observed especially at low frequencies. Phonon spectra in c -direction are dominated by a large excitation at unusually low frequencies (less than 50 cm^{-1}). In contrast to the other phonons modes, strong temperature effects are observed for the low frequency mode. For NGS the lowest phonon softens from 50 cm^{-1} at room temperature to 20 cm^{-1} at 10K that can be correlated with high static dielectric permittivity. This effect can be seen on the other crystals as well, but the effects are weaker. All phonons above a frequency of 100 cm^{-1} behave like those of the b^* -axis, no substantial shift of the frequency can be detected. Because of the observed phonon softening, an instability in the structure of the langasites along the c -direction can be expected. The intriguing prospect of how this abnormal phonon may affect the magnetic dynamics in the frustrated compounds is explored.

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References:

- [1] M. J. Harris, S. T. Bramwell, D. F. McMorrow, T. Zeiske and K. W. Godfrey, *Geometrical frustration in the ferromagnetic pyrochlore $\text{Ho}_2\text{Ti}_2\text{O}_7$* , Phys. Rev. Lett. **79**, 2554 (1997).
- [2] L. Savary and L. Balents, *Quantum spin liquids: A review*, Rep. Prog. Phys. **80**, 016502 (2017).
- [3] K. Marty *et al.*, Phys. Rev. B. **81**, 054416 (2010).

Phonon confinement and spin-phonon coupling in tensile-strained thin EuO films

Ramu Pradip^a, Przemysław Piekarczyk^b, Daniel G. Merkel^c, Jochen Kalt^a, Olga Waller^a, Alexandr I. Chumakov^d, Rudolf Ruffer^d, Andrzej M. Oleś^e, Krzysztof Parlinski^b, Tilo G. Baumbach^a and Svetoslav Stankov^a

^a*Laboratory for Applications of Synchrotron Radiation and Institute for Photon Science and Synchrotron Radiation, Karlsruhe Institute of Technology, Germany*

^b*Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland*

^c*Institute for Particle and Nuclear Physics, Hungarian Academy of Sciences, Budapest, Hungary*

^d*European Synchrotron Radiation Facility, Grenoble, France*

^e*Marian Smoluchowski Institute of Physics, Jagiellonian University, Cracow, Poland*

Europium monoxide (EuO) is the first rare-earth semiconducting oxide known for its giant magneto-optic Kerr [1] and Faraday [2] effects, metal-to-insulator transition and anomalous Hall effect [4]. Presently, it is one of the favored candidates for applications as a spin filter in future spintronic devices due to the large exchange splitting of its conduction band [5]. Employing inelastic X-ray scattering, nuclear inelastic scattering and first-principles theory we determined the lattice dynamics of this material and discovered a giant and anisotropic spin-phonon coupling [6]. This discovery imposed an intriguing question about the manifestation of this phenomenon in thin and ultrathin films related to the proposed applications. Using *in situ* nuclear inelastic scattering on ¹⁵¹Eu we investigated the phonon density of states of EuO films with thickness between 8 nm and of 1 atomic layer. The experimental results unveiled drastic lattice dynamics modifications in the ultrathin EuO films that can be comprehensively understood by the help of first-principles theory [7].

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References:

- [1] J. H. Greiner and G. J. Fan, Appl. Phys. Lett. **9**, 27 (1966).
- [2] K. Y. Ahn, J. Appl. Phys. **41**, 1260 (1970).
- [3] Y. Shapira, S. Foner and R. Aggarwal, Phys. Rev. B **8**, 2316 (1973).
- [4] P. G. Steeneken *et al.*, Phys. Rev. Lett. **88**, 047201 (2002).
- [5] R. Pradip *et al.*, Phys. Rev. Lett. **116**, 185501 (2016).
- [6] R. Pradip *et al.*, Nanoscale **11**, 10968 (2019).

First-principles phonon calculations as a method of improving the atomistic thermodynamics of III-nitrides surfaces

Paweł Kempisty^{a,b} and Yoshihiro Kangawa^{b,c}

^a*Institute of High Pressure Physics, Polish Academy of Sciences, Warsaw, Poland*

^b*Kyushu University, Fukuoka, Japan*

^c*Nagoya University, Nagoya, Japan*

In this paper, we would like to show how phonon calculations can be used to improve the thermodynamic description of III-nitride surfaces in the context of growth by epitaxial methods. Theoretical atomistic analysis of the system representing the crystal surface in contact with the gas phase are often performed. In particular, density functional theory (DFT) calculations are leading method in this field. Unfortunately, this method describes the system at the temperature of absolute zero. In the standard approach of atomistic thermodynamics, the free energy of the vapour phase at a given temperature is considered, whereas the surface is described by the total energy determined on the basis of DFT calculations at 0 K. Phonon calculations can be successfully used to improve the accuracy of this theoretical model. Recently, we presented such an analysis that more accurately describes the hot GaN surface under growth conditions [1]. We included a contribution derived from thermal vibrations determined on the basis of phonon calculations for slabs representing the surface. In this way, several temperature-dependent properties of surface, such as vibrational energy and vibrational entropy can be determined. The thermal dependence of surface free energy was included in predicting the evolution of surface reconstruction under growth conditions, and thus the phase diagrams of the GaN(0001) surface were improved. The example of hydrogen adsorption on the GaN(0001) surface has shown that adding of accurate entropy contributions (vibrational and configurational) can significantly change the predicted equilibrium hydrogen pressure above the surface [2].

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References:

- [1] P. Kempisty, Y. Kangawa, *Phys. Rev. B* **100**, 085304 (2019).
- [2] P. Kempisty, P. Strak, K. Sakowski, Y. Kangawa and S. Krukowski, *Phys. Chem. Chem. Phys.* **19**, 29676 (2017).

Raman spectra of short-period (GaN)_n(AlN)_m superlattices: *ab initio* study

Evgenii Roginskii^a, Yury Kitaev^a, Valery Davydov^a, Valentin Jmerik^a, Wsevolod Lundin^a and Mikhail Smirnov^b

^a*Ioffe Institute, St. Petersburg, Russia*

^b*Saint-Petersburg State University, St. Petersburg, Russia*

The lattice dynamics and structural properties of short-period (AlN)_m(GaN)_n ($m+n=4,8$ or 12 monolayers) superlattices (SLs) grown by MOVPE and PA MBE on the (0001) Al₂O₃ substrate are studied both theoretically and experimentally. The genesis of the SL phonon modes from the modes of bulk AlN and GaN crystals is established by applying a comprehensive group-theoretical analysis. The lattice dynamics is studied by *ab initio* calculations within the framework of the density functional theory. The dynamical matrix for a set of SLs is calculated within density functional perturbation theory (DFPT) and phonon eigenvalues and eigenvectors at the Γ -point of the Brillouin zone (BZ) are obtained. The eigenvectors analysis is performed to establish the irreducible representation of each vibrational mode. The number and symmetry of vibrational modes in the calculated phonon spectra are in complete agreement with the results of the group-theoretical analysis. The Raman tensor components are calculated within DFPT and the theoretical Raman spectra are simulated and compared with experimental ones. The results of the *ab initio* calculations are in a good agreement with the experimental Raman data. The microscopic nature of the SLs vibrational modes is established by complex analysis of the results obtained both theoretically and experimentally. It is revealed that the phonon spectrum of GaN/AlN SLs is composed by mainly two types of phonon modes (localized and delocalized). It is found that the $E(\text{TO})$ modes are localized in the constituent SL layers and can be used to obtain information about the individual characteristics of each layer forming the SL. It is shown that the localized nature of the mode of this symmetry is preserved even in the SL with the thinnest constituent layers, i.e. for $m+n=4$. In turn, the $A_1(\text{TO})$ mode has a delocalized nature. This allows one to use the parameters of this mode to estimate the averaged characteristics of the SL as a whole. The correlation dependencies between the SL structure and the frequencies of the confined and delocalized polar phonons are obtained. The results of the study form the basis for the quantitative estimation of both strain in individual layers forming the SL and the Al(Ga) content averaged over the SL period. They also open new possibilities for the analysis other important parameters of short-period GaN/AlN SLs.

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Lattice dynamics and polarization-dependent phonon damping in α -phase FeSi₂ nanostructures

Jochen Kalt^a, Małgorzata Sternik^b, Bärbel Krause^a, Ilya Sergueev^c, Mirko Mikolasek^d, Dimitrios Bessas^d, Olga Sikora^b, Tonya Vitova^a, Jörg Göttlicher^a, Ralph Steininger^a, Paweł T. Jochym^b, Andrzej Ptak^b, Olaf Leupold^c, Hans-Christian Wille^c, Aleksandr I. Chumakov^d, Przemysław Piekarczyk^b, Krzysztof Parlinski^b, Tilo Baumbach^a and Svetoslav Stankov^a

^aKarlsruhe Institute of Technology, Germany

^bInstitute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland

^cDESY – German Electron Synchrotron, Hamburg, Germany

^dEuropean Synchrotron Radiation Facility, Grenoble, France

Nanostructures of transition metal silicides have a wide range of possible applications and constitute fundamental building blocks of current micro- and nanoelectronics [1–3]. Among these compounds, FeSi₂ is particularly interesting since it is the only representative that exists in both metallic and semiconducting bulk-phase [4]. The high-temperature metallic α -phase can be stabilized at room temperature by growth of metastable, surface-stabilized nanostructures on Si surfaces. While the electronic and magnetic properties of this material are studied extensively and reveal noteworthy results [5,6], only particular thermodynamic properties have been investigated and the lattice dynamics remains unknown until now. In this work [7], we present an experimental and theoretical study of the lattice dynamics of surface-stabilized α -phase FeSi₂ nanostructures epitaxially grown on the Si(111) surface, with average heights and widths ranging from 1.5 to 20 nm and 18 to 72 nm, respectively. The crystallographic orientation, surface morphology and local crystal structure of the nanostructures were investigated by reflection high-energy electron diffraction, atomic force microscopy and X-ray absorption spectroscopy. The Fe-partial phonon density of states (PDOS), obtained by nuclear inelastic scattering, exhibits a pronounced damping and broadening of the spectral features with decreasing average island height. First-principles calculations of the polarization-projected Si- and Fe-partial phonon dispersions and PDOS enable the disentanglement of the contribution of the *xy*- and *z*-polarized phonons to the experimental PDOS. Modelling of the experimental data with the *ab initio* results unveils an enhanced damping of the *z*-polarized phonons, while the *xy*-polarized phonons remain mostly unaffected. This phenomenon is attributed to the fact that the low-energy *z*-polarized phonons exhibit a stronger coupling to the low-energy surface/interface vibrational modes. The thermodynamic and elastic properties obtained from the experimental data show a pronounced size-dependent behaviour.

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References:

[1] S. P. Murarka, *Intermetallics* **3**, 173 (1995).

- [2] L. J. Chen, JOM **57**, 24 (2005).
- [3] A. T. Burkov, Phys. Status Solidi (a) **215**, 654 (2018).
- [4] S. Liang *et al.*, J. Cryst. Growth **295**, 166 (2006).
- [5] J. K. Tripathi *et al.*, Nanotechnology **23**, 495603 (2012).
- [6] G. Cao *et al.*, Phys. Rev. Lett. **114**, 147202 (2015).
- [7] J. Kalt *et al.*, submitted (2019).

Vibrational properties of irradiated nuclear graphite: Inelastic neutron scattering measurements and first-principles calculations

Iyad Al-Qasir^a, Anne Campbell^b, Gabriele Sala^b, Lin Jiao^b, Yongqiang Cheng^b, Douglas Abernathy^b and Matthew Stone^b

^a*Department of Mechanical and Nuclear Engineering, University of Sharjah, UAE*

^b*Oak Ridge National Laboratory, Tennessee, USA*

Research studies into the subject of radiation damage effects in graphite began in the early 1940's as a part of the development of nuclear weapons and nuclear power research. Extensive measurements were performed to study changes to the thermal and mechanical properties of irradiated graphite. Many of these properties such as the thermal expansion coefficient, heat capacity, thermal conductivity, bulk modulus and elastic constants have some level of dependency on the vibrational spectrum. In this work, a series of measurements of the phonon densities of states of different samples of irradiated nuclear graphite were performed at room temperature using the state-of-art Wide Angular-Range Chopper Spectrometer (ARCS) at the neutron spallation source in Oak Ridge National Laboratory. The samples were exposed to different levels of neutron damage (up to ≈ 30 dpa) and irradiation temperatures (300–750°C) [1]. The main differences in the phonon dispersion relations and phonon densities of states for samples with different irradiation conditions (damage and/or temperature) are identified. In addition, first-principles phonon density of states calculations of ideal and defected (di- and tetra-vacancy as well as single and di-interstitial) graphite are performed and compared with measured ones.

The irradiation of the specimens was performed at the Oak Ridge National Laboratory (ORNL) and sponsored by Tokai Carbon Co., Ltd. (NFE-09-02345) with the U.S. Department of Energy. A portion of this research at ORNL's High Flux Isotope Reactor and the Spallation Neutron Source was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, US Department of Energy. Oak Ridge National Laboratory is managed by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 for the U.S. Department of Energy. Travel and time of I. I. Al-Qasir was supported by the University of Sharjah, UAE. This material is based upon work that was conducted by I. I. Al-Qasir while a Visiting Research Fellow at the Shull Wollan Center – the University of Tennessee and Oak Ridge National Laboratory's Joint Institute for Neutron Sciences. First-principles calculations were performed at the high-performance computing facility (SAQR) at the University of Sharjah.

References:

- [1] A. A. Campbell, Y. Katoh, M. A. Snead and K. Takizawa, *Property changes of G347A graphite due to neutron irradiation*, Carbon **109**, 860–873 (2016).

AELAS: Automatic ELAStic property derivations via high-throughput first-principles computation

Shihao Zhang, Dominik Legut and Ruifeng Zhang

VŠB – Technical University of Ostrava, Czech Republic

The elastic properties are fundamental and important for crystalline materials as they relate mechanical properties to thermodynamic ones, e.g., to the phonon dispersion and structural phase transformation. However, a complete set of experimentally determined elastic properties is only available for a small number of known materials. Therefore, an automatic scheme for the derivations of elastic properties that is adapted to high-throughput computation is much demanding. Here, we present the AELAS code, an automated program to calculate second-order elastic constants, moduli, anisotropy and phase stability criteria for both two-dimensional as well as three-dimensional crystal materials with any symmetry. The implementation of the code has been critically validated by a lot of evaluations and tests on a broad class of materials including two-dimensional and three-dimensional materials, providing its efficiency and capability for high-throughput screening of specific materials with targeted mechanical properties. As examples we demonstrate the AELAS capabilities for the three-dimensional structures, e.g., diamond and BN allotropes, and for the two-dimensional structures, e.g., the MXenes family.

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References:

S. H. Zhang, R. F. Zhang, *AELAS: Automatic ELAStic property derivations via high-throughput first-principles computation*, *Comput. Phys. Commun.* **220**, 403–416 (2017).

The role of lattice dynamics in phase stability of Fe-Sn binary systems

Sergiu Arapan and Dominik Legut

VŠB – Technical University of Ostrava, Czech Republic

For many technological applications, it is important to predict the physical properties at finite temperature. For example, magnetic materials suitable for permanent magnet applications must show large saturation magnetization and high magneto-crystalline anisotropy at elevated temperatures. Thus, predictions made by using DFT calculations at $T=0$ K should be validated for finite temperatures. An interesting example is the Fe-Sn binary system with some phases, like Fe_3Sn , which is a ferromagnet, experimentally stabilized at temperatures above 750°C [1]. At finite temperatures one of the main contributions to the free energy is due to the atomic vibrations and it can be estimated, in many cases, within the quasi-harmonic approximation. In the case of Fe-Sn binary systems, however, the account of lattice dynamics is necessary for an accurate description of phase diagram even at $T=0$ K. At low temperatures, there exist three experimentally observed structures: Fe_3Sn_2 , FeSn , and FeSn_2 . The DFT calculations at $T=0$ K predict that enthalpy of formation of all these phases is positive. In this work, we show that these experimentally observed phases are energetically stabilized by phonons. We also calculate the finite temperature phase diagram at elevated temperatures.

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References:

- [1] C. Echevarria-Bonet *et al.*, *Structural and magnetic properties of hexagonal Fe_3Sn prepared by non-equilibrium techniques*, *Journal of Alloys and Compounds* **769**, 843 (2018).

Thermodynamic stability and electronic response to phonon mode in silver difluoride polymorphs

Kamil Tokár^{a,b}, Mariana Derzsi^{a,c} and Wojciech Grochala^c

^aTrnava Slovak University of Technology in Bratislava, Trnava, Slovakia

^bInstitute of Physics, Slovak Academy of Sciences, Bratislava, Slovakia

^cCenter of New Technologies, University of Warsaw, Poland

Two polymorphic forms have been reported for solid AgF_2 at ambient pressure: a layered $\text{Ag}^{\text{II}}\text{F}_2$ (α) and a charge density wave $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{F}_4$ one (β). The α phase is better known of the two. It has recently received attention due to numerous structural and electronic similarities with oxocuprate precursors of high-temperature superconductors [1]. The key common feature of AgF_2 and undoped oxocuprates is the presence of antiferromagnetic sheets of $\text{A}^{\text{II}}\text{B}_2$ stoichiometry (AgF_2 resp. CuO_2). Correspondingly, structural, electronic and magnetic properties of α form at ambient and high pressures have been thoroughly examined in number of experimental and theoretical studies [1–4]. β form has been observed before only once as a red-brown amorphous product of reaction of AgBF_4 with KAgF_4 in anhydrous HF [5]. It is known to undergo rapid exothermic conversion to the α form when temperature is raised from -80°C to ca. 0°C : $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{F}_4 \rightarrow 2\text{Ag}^{\text{II}}\text{F}_2$ [5] and its has been confirmed in an early theoretical study, which assumed that β form adopts that of KAgF_4 type structure. In the present work, we have thoroughly scrutinized the relative thermodynamic stability and lattice dynamics of the two phases, $\text{Ag}^{\text{II}}\text{F}_2$ and $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{F}_4$, in a comparative theoretical and experimental study employing Raman spectroscopy and Density Functional Theory (DFT). We provide theoretical evidence for dynamical stability of both polymorphs, calculate thermodynamic potentials, perform normal mode analysis and discuss relative thermodynamic stability of the two phases.

The individual $\text{Ag}^{\text{II}}\text{F}_2$ α -phase layers are isoelectronic with $[\text{CuO}_2]$ sheets in oxocuprates [1]. Both systems are AFM semiconductors with charge-transfer band gap. In $\text{Ag}^{\text{II}}\text{F}_2$ (α) we have identified Ag–F bond stretching modes of B_{2g} symmetry with unusually strong response to on-site Coulombic correlation. The response of electronic structure to the B_{2g} mode is characterized by modulation of intervalence charge transfer (ICT), which is accompanied by bandgap closure and subsequent reopening as the system progresses from antiferromagnetic $\text{Ag}^{\text{II}}\text{Ag}^{\text{II}}\text{F}_4$ to diamagnetic mixed-valence $\text{Ag}^{\text{I}}\text{Ag}^{\text{III}}\text{F}_4$ state. AgF_2 in this respect is analogous to oxocuprates family.

References:

- [1] J. Gawraczyński *et al.*, Proc. Natl. Acad. Sci. USA **116**, 1495 (2019).
- [2] J. Gawraczyński *et al.*, Inorg. Chem. **56**, 14651 (2017).
- [3] D. Kurzydłowski *et al.*, Chem. Commun. **54**, 10252 (2018).
- [4] T. Jaroń and W. Grochala, Phys Stat Sol (RRL) **2**, 71 (2008).
- [5] B. Žemva *et al.*, Inorg. Chem. **38**, 4570 (1999).

Electron-phonon driven superconductivity of LiBi

Sylwia Gutowska^a, Karolina Górnicka^b, Michał Winiarski^b, Weiwei Xie^c, Robert Cava^d, Tomasz Klimczuk^b and Bartłomiej Wiendlocha^a

^aAGH University of Science and Technology, Cracow, Poland

^bGdansk University of Technology, Gdansk, Poland

^cDepartment of Chemistry, Louisiana State University, Baton Rouge, USA

^dDepartment of Chemistry, Princeton University, Princeton, USA

LiBi is a very intriguing material, as it is built up from the heaviest and the lightest nonradioactive metals in the periodic table. Bismuth is a semimetal with interesting Dirac-like electronic states, while lithium contains only one valence electron and has nearly free-electron Fermi surface. LiBi superconducts below $T_c = 2.45$ K and its crystal structure is tetragonal and can be seen as bcc structure distorted along z -axis.

In this work, theoretical and experimental studies of LiBi are presented. The experimental part consists of magnetic susceptibility and heat capacity measurements. *Ab initio* calculations of the electronic structure, phonons and the electron-phonon interaction function were done. On this basis two important features of superconductivity are calculated, the transition temperature and electron-phonon coupling constant. The band structure of LiBi is affected by structural distortion and is an interesting interplay between dominating p -states of Bi and states of Li, while phonons reflect the huge mass difference of these two elements. Superconductivity of this material is driven by the electron-phonon coupling with moderate magnitude.

Finally, our results are confronted with properties of NaBi, superconductor with $T_c = 2.15$ K, which is isostructural and isoelectronic with LiBi and whose bandstructure was reported to show a topological character [1].

References:

[1] R. Li, *et al.*, Scientific Reports **5**, 8446 (2015).

***Ab initio* studies on lattice dynamics and Verwey transition in magnetite**

Przemysław Piekarz

Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland

Magnetite is the first discovered magnetic material. At $T=125$ K, the Verwey phase transition is observed, in which the electric conductivity decreases by two orders of magnitude [1]. At room temperature, magnetite crystallizes in an inverse spinel structure, in which tetrahedrally coordinated A-sites are occupied by Fe^{3+} ions, while octahedrally coordinated B-sites are occupied by randomly distributed Fe^{3+} and Fe^{2+} ions. At the Verwey temperature, magnetite exhibits the structural phase transition from the cubic to monoclinic phase with the charge-orbital order [2].

Using the density functional theory, we studied the lattice dynamical properties of magnetite in the cubic symmetry [3]. We found a strong electron-phonon coupling, which plays the important role in the Verwey transition. The anomalous phonon broadening resulting from this interaction was observed by the inelastic X-ray scattering studies [4]. The discrepancy between the calculated and measured phonon density of states (DOS) indicates the existence of short-range order with local deformations in the cubic phase. In contrast, the phonon DOS obtained for the monoclinic structure shows a very good agreement with the nuclear inelastic scattering [5]. The interplay between the structural and dynamical properties of magnetite was demonstrated by the recent pump-probe experiments [6], which revealed new features of the collective modes.

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References:

- [1] E. J. W. Verwey, *Nature* **144**, 327 (1939).
- [2] M. S. Senn, J. P. Wright and J. P. Attfield, *Nature* **481**, 173 (2012).
- [3] P. Piekarz, K. Parlinski and A. M. Oleś, *Phys. Rev. Lett.* **97**, 156402 (2006).
- [4] M. Hoesch, P. Piekarz, A. Bosak, M. Le Tacon, M. Krisch, A. Kozłowski, A. M. Oleś and K. Parlinski, *Phys. Rev. Lett.* **110**, 207204 (2013).
- [5] T. Kołodziej, A. Kozłowski, P. Piekarz, W. Tabiś, Z. Kąkol, M. Zając, Z. Tarnawski, J. M. Honig, A. M. Oleś and K. Parlinski, *Phys. Rev. B* **85**, 104301 (2012).
- [6] S. Borroni, E. Baldini, V. M. Katukuri, A. Mann, K. Parlinski, D. Legut, C. Arrell, F. van Mourik, J. Teyssier, A. Kozłowski, P. Piekarz, O. V. Yazyev, A. M. Oleś, J. Lorenzana and F. Carbone, *Phys. Rev. B* **96**, 104308 (2017).

Posters

Multiscale modeling of magnon-phonon dynamics

Pablo Nieves Cordones^a, David Serantes^b, Sergiu Arapan^a, Oksana Chubykalo-Fesenko^c and Dominik Legut^a

^aVŠB – Technical University of Ostrava, Czech Republic

^bUniversity of Santiago de Compostela, Spain

^cInstitute of Materials Science, Madrid, Spain

Magnon-phonon scattering processes play an essential role in many novel and exciting magnetic phenomena such as domain wall motion under thermal gradients, temperature-assisted magnetization switching, ultra-fast magnetization dynamics, *etc.* Typically, the influence of temperature on the magnetization dynamics is studied. However, there is an inverse effect when the magnetization dynamics produces temperature change, for example in the magnetocaloric effect or during the heating under an ac applied magnetic field. Promising applications like magnetic refrigeration or magnetic hyperthermia treatment for cancer are based on these processes. Recently, we have developed a self-consistent micromagnetic approach for describing both magnetization and phonon temperature dynamics [1]. The approach consists in the simultaneous solution of the quantum Landau-Lifshitz-Bloch (qLLB) micromagnetic equation [2,3] coupled to the equation for the phonon temperature dynamics. The latter equation is derived from the self-consistent quantum mechanical treatment of the spin-phonon Hamiltonian, which includes direct transformation and Raman processes, based on the general theory for a spin system interacting weakly with a thermal bath. Here, we will show the main features of this novel micromagnetic approach, possible applications and its deep connection to many body classical spin-lattice simulations [4,5] within a multiscale approach. These new concepts might constitute a step forward towards more realistic large scale modeling of many interesting phenomena where there is a relevant interplay between magnon and phonon dynamics.

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References:

- [1] P. Nieves, D. Serantes and O. Chubykalo-Fesenko, *Phys. Rev. B* **94**, 014409 (2016).
- [2] D. A. Garanin, *Physica A* **172**, 470 (1991).
- [3] P. Nieves, D. Serantes, U. Atxitia and O. Chubykalo-Fesenko, *Phys. Rev. B* **90**, 104428 (2014).
- [4] J. Tranchida *et al.*, *J. Comput. Phys.* **372**, 406–425 (2018).
- [5] Xufei Wu, Zeyu Liu and Tengfei Luo, *J. Appl. Phys.* **123**, 085109 (2018).

Lattice dynamics of W–Cr alloys by first-principles calculations

Michal Farana, Andrzej P. Kądziaława and Dominik Legut

VŠB – Technical University of Ostrava, Czech Republic

Tungsten alloys currently represent prospective candidates to replace tungsten in the first wall applications in future fusion facilities. Main purpose of the alloying of tungsten is to gain additional properties such as ability of self-passivation under accidental conditions. The self-passivating alloys are designed to minimize possible accident consequences related mainly to a LOCA (Loss of Coolant Accident) event with simultaneous air ingress into the reactor vessel [1,2]. According to the W–Cr phase diagram, the single solid BCC solution experiences tendency for phase separation within the miscibility gap to reach thermodynamic equilibrium, (1950 K for 50:50 W–Cr alloy and a melting point estimated around 2700 K [3]). We applied the Density Functional Theory (DFT) both within the Special Quasirandom Structure (SQS) and Virtual Crystal Approximation frameworks to obtain a realistic model of Tungsten–Chromium alloy, with the elastic (via deformation of the crystal) and thermodynamic (via the phonon spectra within the Quasiharmonic Approximation) properties to-be-compared with experimental data. Based on our results we promote a possible route to enhance both melting temperature as well as the miscibility gap in the Cr–W alloys.

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References:

- [1] F. Koch *et al.*, *Self passivating W-based alloys as plasma facing material for nuclear fusion*, *Physica Scripta* **128**, 100–105 (2007).
- [2] M. Vilémová *et al.*, *Microstructure and phase stability of W–Cr alloy prepared by spark plasma sintering*, *Fusion Engineering and Design* **127**, 173–178 (2018).
- [3] A. Calvo *et al.*, *Manufacturing and testing of self-passivating tungsten alloys of different composition*, *Nuclear Materials and Energy* **9**, 422–429 (2016).

Structure and electronic properties of KO_2 revealed by *ab initio* calculations

Dorota Gotfryd^{a,b}, Olga Sikora^c, Andrzej Ptok^c, Andrzej M. Oles^{b,d}, Krzysztof Wohlfeld^a and Przemysław Piekarczyk^c

^a*Institute of Theoretical Physics, University of Warsaw, Poland*

^b*Marian Smoluchowski Institute of Physics, Jagiellonian University, Cracow, Poland*

^c*Institute of Nuclear Physics, Polish Academy of Sciences, Cracow, Poland*

^d*Max Planck Institute for Solid State Research, Stuttgart, Germany*

Potassium superoxide KO_2 is a strongly correlated insulator with spin, orbital, and lattice degrees of freedom. Its high temperature phase is a tetragonal paramagnet, and the crystal symmetry is lowered in several phase transitions, eventually reaching a triclinic symmetry with antiferromagnetic ordering. Below 197 K, an intermediate monoclinic C2/c phase is reported with O_2 molecules rotated by about 20° with respect to their positions in the tetragonal phase [1,2]. Although the phase transitions were described in the 1970s, many open questions remain concerning their mechanisms and structural details.

We used density functional theory and lattice dynamics calculations to obtain a better insight into the structural and electronic properties of KO_2 . The phonon spectra in the tetragonal structure revealed several instabilities. After identifying a soft phonon leading to the C2/c symmetry, we optimized a new distorted phase resulting from this mode and analysed its structural properties. We observe that different magnetic orders and a direction of magnetic axis in the (canted) antiferromagnet do not have a significant influence on phonon dispersion relations.

We compared the electronic structure of KO_2 with antiferromagnetic spin order in the tetragonal and monoclinic phases. While relatively strong on-site Coulomb interactions on magnetic oxygen molecules ($U = 4$ eV) open a small gap (≈ 0.3 eV) in the monoclinic phase, the tetragonal phase is metallic. Including the spin-orbit coupling gives rise to an insulating gap in the tetragonal phase and widens its value up to over 1 eV in the monoclinic phase. This indicates that the interplay of Coulomb interactions, spin-orbit coupling, and pronounced lattice distortions is responsible for the formation of the insulating phase.

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References:

- [1] W. Känzig and M. Labhart, *J. Phys. (Paris)* **37**, C7–39 (1976).
- [2] M. Labhart *et al.*, *Phys. Rev. B* **20**, 53 (1979).

Superconductivity and soft-mode behavior in LiPd_2X compounds (X = Si, Ge, Sn)

Gabriel Kuderowicz^a, Karolina Górnicka^b, Tomasz Klimczuk^b, Elizabeth M. Carnicom^c, Robert J. Cava^c and Bartłomiej Wiendlocha^a

^aAGH University of Science and Technology, Cracow, Poland

^bGdansk University of Technology, Gdansk, Poland

^cDepartment of Chemistry, Princeton University, Princeton, USA

Heusler material classes are known for more than 100 years and they reveal all kinds of physical phenomena such as heavy fermion, shape-memory effect, thermoelectric effect, ferromagnetism including half-metallic ferromagnetism and superconductivity. Some of these compounds show anomalies in their phonon structure. In a recently synthesized LiPd_2X (X = Si, Ge, Sn), which crystalize in a cubic Fm-3m structure, superconductivity was found only in LiPd_2Ge with $T_c = 1.96$ K.

In this work electronic structure, phonons and electron-phonon interaction was studied in LiPd_2X basing on *ab initio* computations, using plane wave pseudopotential implemented in *Quantum Espresso* [1]. Effect of the spin-orbit interaction on the electronic structure and electron-phonon coupling was investigated. LiPd_2G exhibits the strongest electron-phonon coupling within the studied series, in agreement with the observation of superconductivity. In all the compounds a phonon soft mode is found in the Γ –K direction, and it is most pronounced in the case of the superconducting LiPd_2Ge , which suggests its correlation with the electron-phonon interaction.

References:

[1] P. Giannozzi *et al.*, J. Phys.: Condens. Matter **29**, 465901 (2017).

Thermal conductivity of Th and ThC

Lukas Kyvala and Dominik Legut

VŠB – Technical University of Ostrava, Czech Republic

Thermal conductivity is one of the most important property of nuclear fuel materials affecting many processes such as swelling, grain growth, and fission gas release and limits the transfer of the linear power [1].

However, the measurement of thermal conductivity is difficult even for simple elements like silicon. Loss of heat through convection, conduction, and radiation coexist at the same time. Measuring radioactive elements is even more difficult because of the sample self-heating. This makes the theoretical calculations perspective and valuable tool.

Here, we demonstrate to determine the conductivity of thorium metal and thorium monocarbide as well as their electronic and phononic (lattice vibrations) contributions as a function of temperature based on quantum-mechanical calculations.

We discuss why the total thermal conductivity of thorium is more than twice as large as thorium monocarbide. Attention to the optical phonon modes accounting only for approximately 6% of the phonon thermal conductivity of ThC. This result differs significantly from NpO₂ case when the optical branches contribution is about 27% [2].

Despite it, ThC has the higher phonon thermal conductivity than NpO₂, as the heat transfer is provided by much larger extent by the acoustic phonons [3].

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References:

- [1] T. R. G. Kutty, J. Banerjee and A. Kumar, in *Thoria-based Nuclear Fuels* (Springer London, 2013) pp. 11–70.
- [2] P. Maldonado, L. Paolasini, P. M. Oppeneer, T. R. Forrest, A. Prodi, N. Magnani, A. Bosak, G. H. Lander and R. Caciuffo, *Physical Review B* **93**, 144301 (2016).
- [3] L. Kývala and D. Legut, *Lattice dynamics and thermal properties of thorium metal and thorium monocarbide*, *Phys Rev. B* (under review 2019).

Electron-phonon scattering mechanism on the transport properties of ZrS₂ from first principles

Hitoshi Mori, Masayuki Ochi and Kazuhiko Kuroki

Osaka University, Japan

Multi-valley structure is one of the favourable band structures for enhancing thermoelectric efficiency, which is realized in several good thermoelectric materials such as PbTe and Bi₂Te₃. N-type TiS₂ also has electronic structure with multi-valley character, and its power factor is relatively high: $\approx 40 \mu\text{W}/\text{cmK}^2$ at room temperature [1]. In previous experimental studies, the electrical resistivity of TiS₂ has been found to exhibit strong temperature dependence of $\sim T^2$. One of the previous studies indicated that inter-valley scattering among conduction band valleys may be related to the peculiar temperature dependence of the electrical resistivity [2]. Since understanding the inter-valley scattering effect on the transport properties may provide a clue toward designing materials with higher thermoelectric efficiency, in the present study, we perform electronic and phonon band calculations based on DFT, and calculate the electronic transport properties by considering the electron-phonon scattering effect using the EPW code [3–6]. As a target material in this study, we consider not TiS₂, but instead its analogous compound ZrS₂. We will discuss the role of the inter-valley scattering played in the electronic transport properties of ZrS₂.

References:

- [1] H. Imai, Y. Shimakawa and Y. Kubo, Phys. Rev. B **64**, 241104(R) (2001).
- [2] P. C. Klipstein *et al.*, J. Phys. C: Solid State Phys. **14**, 4067 (1981).
- [3] F. Giustino, M. L. Cohen and S. G. Louie, Phys. Rev. B **76**, 165108 (2007).
- [4] S. Ponce *et al.*, Comput. Phys. Commun. **209**, 116 (2016).
- [5] S. Ponce, E. R. Margine and F. Giustino, Phys. Rev. B **97**, 121201 (2018).
- [6] A. A. Mostofi *et al.*, Comput. Phys. Commun. **185**, 2309 (2014).

Raman spectrum and elastic properties of rare-earth oxyorthosilicates R_2SiO_5 : *ab initio* calculation

Dmitrii Nazipov and Anatolii Nikiforov

Ural Federal University, Ekaterinburg, Russia

Oxyorthosilicate single crystals R_2SiO_5 , where R – rare earth ion, are actively studied at the present time as a good optical matrices and advanced laser materials. Doped with rare-earth ions the crystals are used as gamma rays detectors [1] and in positron emission tomography [2]. Investigation of optical spectra of crystals with monoclinic syngony R_2SiO_5 (R – rare-earth ion) is complicated from an experimental point of view due to low symmetry of these crystals. The authors of Ref. [3] have done a detailed experimental study of the Raman spectra of the oxyorthosilicates Lu_2SiO_5 , Gd_2SiO_5 in the wide range of temperatures 300–2300 K and provided a full identification of the spectra for the first time. In this work *ab initio* calculation of crystal structure, Raman spectra and elastic properties for range of rare-earth oxyorthosilicates R_2SiO_5 (R – La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb) has been performed within the framework of density functional theory (DFT) using hybrid DFT/HF functionals. Calculations made in program package CRYSTAL14 using molecular orbitals approximation (MO LCAO) with gauss-type basis sets and pseudopotentials. This model shows good results when calculating the crystal structure and the vibrational spectra of dielectric materials and semiconductors. The results for lutetium oxyorthosilicate are compared with recent experimental data [3]. Calculated parameters of the crystal structure are in good agreement with experiment, as well as the width of the forbidden gap 6.4 eV (6 eV). For the first time the complete set of fundamental vibrations, their frequencies, types and intensities in the Raman spectrum for various polarizations are calculated. The analysis of the phonon spectrum by the isotopic substitution method is carried out and determined the ions involved in vibrations.

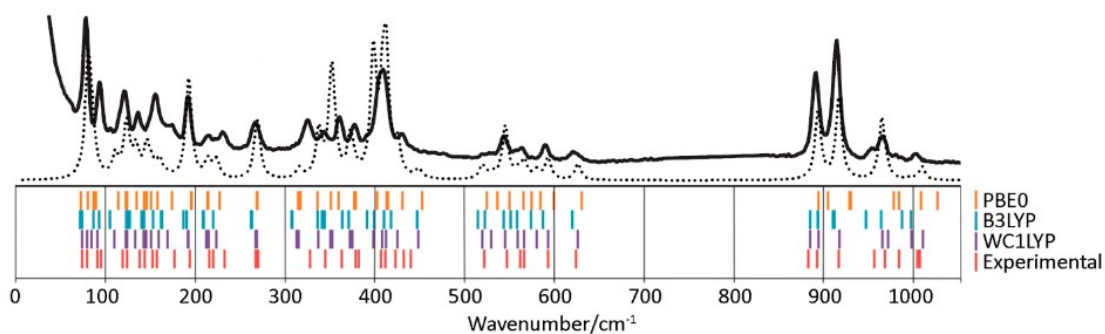


Figure 1: Comparison between the experimental [3] and calculated (dotted line) Raman spectrum of Lu_2SiO_5 . Results for different hybrid functionals are presented.

Among all 48 modes ($24A_g + 24B_g$) active in the Raman spectrum, $24A_g$ and $18B_g$ modes were experimentally identified. Figure 1 shows the experimental frequencies of fundamental vibrations calculated in this paper for various functionals. With general agreement with experiment, there are differences in some regions of frequencies. Crystals of R_2SiO_5 with rare-earth ion in range from La to Tb have a A-type crystal structure, Dy-Lu oxyorthosilicates have a B-type crystal structure. Crystal structure parameters have been calculated for full range of rare-earth ions. The result are in good agreement with existing experimental data. In spite of different types of structure and different ions in R sublattice, Si-O bond

lengths remains unchanged for all range of oxyorthosilicates. Based on crystal structure calculations, elastic moduli for all range of R_2SiO_5 also predicted. Spatial dependences of Bulk modulus, Young modulus and Poisson's ratio have been described. Calculated values of elastic moduli allowed us to obtain mean sound velocities, then the Debye temperature and thus estimate the minimum thermal conductivity. Lu_2SiO_5 is being studied as a material with good characteristics for use as a thermal barrier coating. It is important to predict the thermal conductivity coefficient for not investigated oxyorthosilicates in range La-Yb to find new candidates for further experimental studies. Calculated in this work values of lattice thermal conductivities for range R_2SiO_5 (R – La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu) presented in Figure 2.

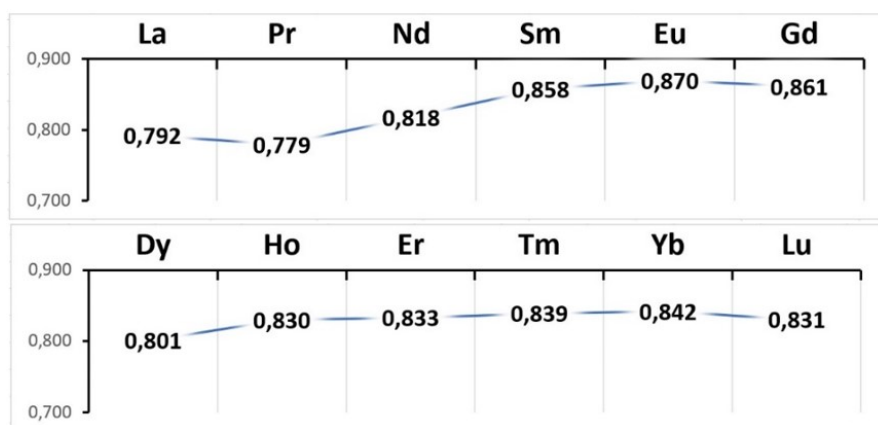


Figure 2: Theoretically predicted lattice thermal conductivities of R_2SiO_5 A-type structure (upper) and B-type structure (lower).

Thus, the results of this work can motivate to perform experimental studies and help to search for compounds based on silicates, with good characteristics for use as thermal barrier coating materials.

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References:

- [1] C. L. Melcher and J. S. Schweitzer, IEEE Trans. Nucl. Sci. **39**, 502–505 (1992).
- [2] C. W. E. van Eijk, Phys. Med. Biol. **47**, R85–R106 (2002).
- [3] Y. K. Voronko, A. A. Sobol, V. E. Shukshin, A. I. Zagumennyi, Y. D. Zavartsev, S. A. Koutovoi, Opt. Mat. **33**, 1331–1337 (2011).
- [4] URL: <http://www.crystal.unito.it/>

Phase stability of Uranium and Thorium sesquicarbide

Jakub Oprštný and Dominik Legut

VŠB – Technical University of Ostrava, Czech Republic

The electronic, structural, mechanical, and magnetic properties of U and Th based sesquicarbides (U_2C_3 and Th_2C_3) are investigated by means of the first-principles calculations. The electronic structure models utilizing various exchange-correlation terms, the spin-orbit coupling or Hubbard U methodology were calculated with respect to number of known quantities. The static (enthalpy of formation) as well as dynamical stability of the systems was determined. Ferromagnetic and two antiferromagnetic arrangements are compared to determine the preferable spin orientation for the Uranium based system.

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The lattice dynamics and Raman spectra of mixed $\text{TeO}_2/\text{TeO}_3$: *ab initio* study

Evgenii Roginskii^a, Mikhail Smirnov^b and Vladimir Kuznetsov^b

^a*Ioffe Institute, St. Petersburg, Russia*

^b*Saint-Petersburg State University, St. Petersburg, Russia*

Raman spectra of the series of tellurium oxides, namely TeO_2 , Te_4O_9 , Te_2O_5 , and TeO_3 have been theoretically studied. The calculations were performed by using local density approximation (LDA) to the density functional theory (DFT) including Hubbard correction for density functional (LDA+*U*) in order to correctly treat *d*-electrons strong correlation effect. The Raman tensor components have been determined as a linear susceptibility derivative calculated by finite difference method. The approach was based on calculation of linear susceptibility for structural configuration distorted along phonon eigenvectors. The finite difference method for Raman tensor calculation was validated by comparison with the technique based on perturbation theory as implemented in ABINIT software package. The results of Raman spectra simulation within LDA+*U* approximation were found in a good agreement with experimental data, and unambiguous assignment for all prominent Raman lines was established. This result gives an insight into relations between structural peculiarities and observed spectral features for the crystals promising as non-linear optical materials. The results of calculations confirm that the computer modelling based on the quantum-mechanical DFT calculations are able to describe crystal structures and phonon spectra of the mixed TeO_2 – TeO_3 oxides in good agreement with available experimental data. The guiding issue of the spectrum interpretation was structural peculiarity of the studied structures: all of them are built of the corner-sharing polyhedra – the TeO_6 octahedra and the TeO_4 disphenoids. Spectroscopic studies showed that the spectral bands are generally distributed within three frequency intervals: 550–800 cm^{-1} , 300–550 cm^{-1} and 0–300 cm^{-1} . The modes falling in different intervals correspond to particular vibrations localized within the Te–O–Te bridges. The high-frequency modes belonging to the first interval are most convenient for analysis of the structure-spectrum relations. Thus, it is stated that the Raman bands at 550–600 cm^{-1} indicate presence of the corner-sharing disphenoids, the Raman bands above 800 cm^{-1} indicate presence of the octahedra and the Raman bands at around 700 cm^{-1} indicate presence of the disphenoid-octahedron bridges. Another common feature of the crystals under study is presence of an intense Raman peak around 60–70 cm^{-1} . It is established that the peak is related to the rigid unit modes which consist in concordant rotations of the polyhedra (disphenoids and octahedra) without their internal deformations. Existence of such modes is an inherent feature of the framework lattices which are built of the corner-sharing polyhedra.

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Phase transition of Hg_2F_2 crystal induced by soft-mode condensation under high pressure

Evgenii Roginskii and Yuri Markov

Ioffe Institute, St. Petersburg, Russia

Using the X-Ray diffraction (XRD) data of the Hg_2F_2 powder the Rietveld Refinement method with Hg_2Cl_2 structure parameters as initial ones is applied in order to estimate lattice parameters and atomic positions. The significant reduce of the lattice parameter perpendicular to C_4 axis with respect to Hg_2Cl_2 one is found. In XRD measured at both room and low (7 K) temperature significant difference is not revealed. Therefore, in a contrast to Hg_2Cl_2 the low temperature phase transition (PT) is not observed. The set of *ab initio* calculations is performed in order to estimate the most stable phase at ambient conditions. The calculations of electronic structure and dynamical properties is performed using local density approximation to the Density Functional Theory (DFT). Among three suggested phases (monoclinic $P2_1/m$ suggested in Ref. [1], orthorhombic $Cmcm$ and tetragonal $I4/mmm$) the tetragonal phase is found as the most stable one. The dispersion of phonon branches of Hg_2F_2 is calculated, and the unstable modes with imaginary frequencies are not obtained. Therefore, the tetragonal phase is the stable one with respect to phonon states. Moreover the determinant of the stiffness tensor is positive, thus the phase is stable with respect to elastic properties also. The tetragonal phase reveals the stability in a long range of hydrostatic and monoaxial applied pressure. The baric dependence of phonon spectra is studied within LDA approximation. The soft modes which leads to ferroelastic phase transition (PT) is found at high pressure. In case of hydrostatic pressure the phonon with irreducible representation X_3^+ which is bound with libration vibration of the linear molecule softening at the boundary M-point of Brillouin zone (BZ) with pressure increasing and "freeze" at $P_c=9.3$ GPa. The mode induces PT with unit cell doubling. The group theory predicts three isomorphic subgroups of the supergroup $I4/mmm$, namely face centered orthorhombic $Cmce$, orthorhombic $P4_2/nm$ and orthorhombic $Pccn$. By applying the atomic displacements along eigenvector of the soft mode the final $Cmce$ symmetry of the structure was discovered. In opposite in case of monoaxial applied pressure along C_4 axis the soft mode irreducible representation is X_3^- the mode is acoustical TO-branch at the boundary X-point of BZ. The phase transition induced by "freezing" of X_3^- phonon accompanied with doubling unitcell and lowering the symmetry to $Cmcm$.

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References:

- [1] S. Emura, J. Phys.: Condens. Matter, **2**, 7877 (1990).

Electrochemical behaviours in Li/Na ion battery systems from KKR–CPA calculations

Michał Rybski, Janusz Tobola and Janina Molenda

AGH University of Science and Technology, Cracow, Poland

Among energy storage systems, lithium-ion battery materials are still considered as the most promising and efficient due to their high functional parameters (*i.e.* energy and power density, long life cycle, lightness and safety). To some extent, electrochemical properties can be interpreted and predicted using quantum electrodynamics methods, essentially based on the DFT methods [1–3]. This fundamental insight into the ion battery processes seems to be crucial to solve both performance and security issues.

In this work we present first principles calculations of $A_x\text{MO}_2$ ($A=\text{Li, Na}$; $M=3d$ elements) battery cathode materials, paying special attention to the influence of oxygen vacancy and relative occupancy of Li/Na sites on their electronic structure features. Electronic structure calculations of selected materials have been performed using the Korringa-Kohn-Rostoker method combined with the coherent potential approximation (KKR–CPA) [4–6] to treat chemical disorder. Electronic density of states (DOS) especially in the vicinity of the Fermi energy (E_F), has been analysed with variation of Li/Na content and alloy compositions. It resulted in specific evolution of total-, site-decomposed and l-decomposed DOS leading to semiconducting-like, half-metallic-like or metallic-like properties, strongly depending on composition.

Besides, it appears that relative variation of E_F in a studied system, as calculated from the KKR-CPA method, can be related to the characteristics of observed electromotive force as already applied to different cathode materials [7–9]. Here, some correlations between computed E_F with Li/Na content as well as the features of experimental discharge curves are presented. Furthermore, spin-polarised KKR–CPA computations of $\text{Li}_x\text{Ni}_{0.65}\text{Co}_{0.25}\text{Mn}_{0.1}\text{O}_2$ and $\text{Li}_x\text{Ni}_{0.55}\text{Co}_{0.35}\text{Mn}_{0.1}\text{O}_2$ [7] have showed that magnetic moments might appear for critical Li concentration.

References:

- [1] A. Urban, D-H. Seo and G. Ceder, *npj Computational Materials* **2**, 16002 (2016).
- [2] T. Zhang, D. Li, Z. Tao and J. Chen, *Prog. Nat. Sci. : Mater. Int.* **23**, 256 (2013).
- [3] K. Suzuki *et al.*, *PRL* **114**, 087401 (2015).
- [4] S. Kaprzyk and A. Bansil, *Phys. Rev. B* **42**, 7358 (1990).
- [5] A. Bansil, S. Kaprzyk, P. E. Mijnen and J. Tobola, *Phys. Rev. B* **60**, 13396 (1999).
- [6] T. Stopa, S. Kaprzyk and J. Tobola, *J. Phys.: Condens. Matter* **16**, 4921 (2004).
- [7] M. Rybski, J. Tobola, S. Kaprzyk and J. Molenda, *Solid State Ionics* **321**, 23 (2018).
- [8] J. Molenda, D. Baster, M. Molenda, K. Swierczek and J. Tobola, *Phys. Chem. Chem. Phys.* **16**, 14845 (2014).
- [9] J. Molenda, A. Plewa, A. Kulka, L. Kondracki, K. Walczak, A. Milewska, M. Rybski; L. Lu and J. Tobola – submitted to *Journal of Power Sources*

Thermodynamic properties of 2H-MoSe₂ from *quasi*-harmonic approximation

Oleksandr Vasiliev^{a,b}

^a*Frantsevich Institute for Problems in Materials Science NAS of Ukraine, Kyiv, Ukraine*

^b*Igor Sikorsky Kyiv Polytechnic Institute, Ukraine*

The last decade has seen a tremendous increase in the scientific interest to layered transition metal dichalcogenides due to their excellent electronic and optical properties [1]. Hexagonal molybdenum disulfide attracted the most attention so far, but recently, other dichalcogenides started to get their share and are currently regarded as more promising in some specialized applications. Particularly, 2H-MoSe₂ is expected to have better performance in catalytic, optoelectronic, and energy storage systems [2]. Molybdenum diselenide does not occur naturally and must be produced by synthetic routes, most probably using the CVD synthesis. Thermodynamics is among the key factors that determine the ability to control this process to get the product in a desired state. It is even more important in bulk synthesis routes (CVD or PVD) to produce the material in nanoform or nanoheterostructures based on it. The objective of this work was to obtain the values of thermodynamic properties of hexagonal layered molybdenum diselenide devoid of the influence of real samples specifics by *ab initio* calculation within the *quasi*-harmonic approximation. Temperature dependences of constant-volume thermodynamic properties in this work were calculated using the finite displacement method and supercells as realized in the phonopy software [3]. The supercell size of 2×2×1 unit cells was chosen for the calculation. Atomic displacements in the unit cell were set to 0.02 Bohr. For the *quasi*-harmonic calculations, electronic total energies at zero temperature and pressure and vibrational free energies were calculated at 11 unit cell volumes (0.95 to 1.05 of the relaxed cell) and fitted to the Vinet equation of state (EOS). Isobaric thermodynamic properties were then obtained using the phonopy-qha script. *Ab initio* calculations of total energies and forces in displaced supercells were done using the Density Functional Theory (DFT) with Quantum Espresso (QE) package [4]. Local Density Approximation was used for exchange-correlation potential. The plane wave basis set kinetic energy cut-off was set to 60 Ry. The Brillouin zone integrations were done using the Monkhorst-Pack (MP) scheme 8×8×2 points mesh displaced by half a step in a and b directions. The calculated low-temperature heat capacity is in excellent agreement with experimental data up to about 180 K, and negative deviations at temperatures up to 300 K are within the typical errors of calorimetric measurements or close to them. This enables the calculation and statistical assessment of the standard values of such thermodynamic properties as enthalpy, entropy, and Gibbs free energy. With the temperature increase, the negative deviation of the calculated data increases and the quasi-harmonic approximation is incapable to close the gap and provide reliable values of high-temperature thermodynamic properties, which are of particular interest for the directions indicated in the objective of this work. Other methods of calculation, capable of a complete account of temperature effects are needed to obtain reliable values of thermodynamic properties at elevated temperatures (300–1000 K), e.g. Temperature Dependent Effective Potential or Self-Consistent Phonons approaches.

References:

- [1] M. Samadi *et al.*, *Nanoscale Horizons* **3**, 90–204 (2018).
- [2] A. Eftekhari, *Appl. Mater. Today* **8**, 1–17 (2017).
- [3] A. Togo, L. Chaput and I. Tanaka, *Phys. Rev. B* **91**, 094306 (2015).
- [4] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **29**, 465901 (2017).

Comparison of density functional theory methods in layered MS₂ compounds under compression

J. Ibáñez^a, Tomasz Woźniak^b, F. Dybala^b, R. Oliva^b, S. Hernández^c and R. Kudrawiec^b

^a*Institute of Earth Sciences Jaume Almera, Barcelona, Spain*

^b*Wroclaw University of Science and Technology, Poland*

^c*University of Barcelona, Spain*

We report high-pressure Raman-scattering measurements on the transition-metal dichalcogenide (TMDC) compound HfS₂. The aim of this work is twofold: (i) to investigate the high-pressure behaviour of the zone-center optical phonon modes of HfS₂ and experimentally determine the linear pressure coefficients and mode Grüneisen parameters of this material; (ii) to test the validity of different density functional theory (DFT) approaches in order to predict the lattice-dynamical properties of HfS₂ under pressure. For this purpose, the experimental results are compared with the results of DFT calculations performed with different functionals, with and without van der Waals (vdW) interaction corrections. We find that DFT calculations within the generalized gradient approximation (GGA) properly describe the high pressure lattice dynamics of HfS₂ when vdW interactions are taken into account. In contrast, we show that DFT within the local density approximation (LDA), which is widely used to predict structural and vibrational properties at ambient conditions in 2D compounds, fails to reproduce the behaviour of HfS₂ under compression. Similar conclusions are reached in the case of MoS₂. This suggests that large errors may be introduced if the compressibility and Grüneisen parameters of bulk TMDCs are calculated with LDA. Therefore, the validity of different approaches to calculate the structural and vibrational properties of bulk and few-layered vdW materials under compression should be carefully assessed. [1]

References:

- [1] J. Ibáñez, T. Woźniak, F. Dybala, R. Oliva, S. Hernández and R. Kudrawiec, *Sci. Rep.* **8**, 12757 (2018).

Tuesday December 3		Wednesday December 4		Thursday December 5		Friday December 6	
09:00-09:45	<i>registration</i>	09:00-09:35	Kremer 31	09:00-09:35	Legut 45	09:00-09:35	Al-Qasir 58
09:45-10:00	<i>opening</i>	09:35-10:10	Zbiri 33	09:35-10:10	Wehinger 47	09:35-10:00	Zhang 59
10:00-10:35	Errea 13	10:10-10:35	Wdowik 35	10:10-10:35	Dubiel 49	10:00-10:25	Arapan 69
10:35-11:10	Tadano 15	10:35-11:30	<i>coffee</i>	10:35-11:30	<i>coffee</i>	10:25-11:15	<i>coffee</i>
11:10-12:00	<i>coffee</i>	11:30-11:55	Wiendlocha 37	11:30-12:05	Blaha 51	11:15-11:40	Tokár 71
12:00-12:35	Parlinski 17	11:55-12:20	Oleś 39	12:05-12:30	Castellano 53	11:40-12:05	Gutowska 73
12:35-13:00	Leitner 19	12:20-12:45	Biało 41	12:30-12:55	Bergen 55	12:05-12:30	Piekarz 75
13:00-14:25	<i>lunch</i>	12:45-13:10	Kądziaława 43	12:55-14:15	<i>lunch</i>	12:30-13:00	<i>closing</i>
14:25-15:00	Hellman 21	13:10-14:30	<i>lunch</i>	14:15-15:00	POSTERS 79-103	13:00-14:30	<i>lunch</i>
15:00-15:25	Jochym 23	14:30-19:00	<i>visiting Kraków</i>	15:00-15:35	Stankov 57		
15:25-15:50	Eriksson 25			15:35-16:00	Kempisty 59		
15:50-16:30	<i>coffee</i>			16:00-16:45	<i>coffee</i>		
16:30-16:55	Hu 27	19:00-21:00	<i>conference dinner</i>	16:45-17:10	Roginskii 61		
16:55-17:20	Reith 29			17:10-17:35	Kalt 63		
17:20-18:30	discussion			17:35-18:30	discussion		