In the work we present following results for Na_2RuO_3. (i) The resistivity, susceptibility and heat capacity measurements which gave us no signs of any phase transitions. (ii) The X-ray absorption and emission spectroscopy, which result in determination of band gap width about 0.08 eV. (iii) The density of electronic states calculated using the Wien2k package [5] for O are in good agreement with XES and XAS spectra. The system lowest total energy corresponds to zig-zag antiferromagnetic.

The research was carried out within the state assignment of Russia (theme "Electron" No. AAAA-A18-118020190098-5 and "Spin" No. AAAA-A18-118020290104-2) and by Russian ministry of education and science via contract 14.Z50.31.0025.

References:

1. S. A. J. Kimber, I. I. Mazin, J. Shen, H. O. Jeschke, S. V. Streltsov, D. N. Argyriou, R. Valenti, D. I. Khomskii, Phys. Rev. B, 2014, Vol. 89, pp. 081408-1-081408-5.
2. K. Momma, F. Izumi, J. Appl. Crystallogr., 2011, Vol. 44, pp. 1272-1276.
3. K. M. Mogare, K. Friese, W. Klein, M. Jansen, Zeitschrift fur anorganische und allgemeine Chemie, 2004, Vol. 630, pp. 547-552.
4. J. C. Wang, J. Terzic, T. F. Qi, F. Ye, S. J. Yuan, S. Aswartham, S. V. Streltsov, D. I. Khomskii, R. K. Kaul, G. Cao, Phys. Rev. B, 2014, Vol. 90, pp. 161110-1-161110-6.
5. P. Blaha, K. Schwarz, G. Madsen, D. Kvasnicka, J. Luitz, WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties, Techn. Universitat Wien, Wien (2001).

Ab initio investigation of optical properties of $LuLiF_4$ compound under hydrostatic pressure

Anastasia V. Petrova[1*], Oleg V. Nedopekin[1], Dmitrii A. Tayurskii[1]
[1]*Laboratory for computer design of new material, Institute of Physics, Kazan Federal University, 420008, Kazan, Russia*
* Anastasia.Petrova@kpfu.ru

The present work is devoted to investigation of pressure influence on vibrational spectrum of $LuLiF_4$ ($I4_1/a$, Z=4) sheelite phase in the context of its instability at high pressures. It is well known that $LuLiF_4$ is effectively used to generate laser radiation [1], so it is important to know its operating pressure range. Also, the study of optical properties allows to obtain another confirmation of the phase transition presence at 10.7 GPa [2, 3].

The phonon frequencies calculation of a crystal structure is one of the fundamental problems considering phase stability, phase transitions, and thermodynamics of crystalline matter. The vibrational properties of the crystal determine a wide range of macroscopic properties: specific heat capacity, sound velocity, infrared and Raman absorption [4]. In addition, low-frequency modes can be associated with phase transitions, while imaginary frequencies indicate that the calculated structure is not stable.

The electronic structure optimization of $LuLiF_4$ was carried out by the first principles by the DFT method [5, 6], which is implemented in the Vienna Ab Initio Simulation Package (VASP 5.2) [7–9]. PHONON module (part of software package MedeA[1]) was used for calculation of lattice dynamics and vibrational properties of $LuLiF_4$. PHONON calculates the lattice vibrations by «direct» method [10]. The values of the force-constant matrices in the finite range of interactions and, as a consequence, the dynamic matrix and phonon dispersion curves obtained from forces which were calculated by Hellmann-Feynman theorem [10].

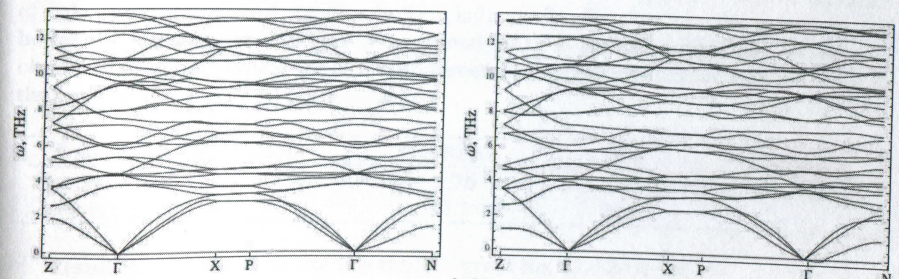

Fig. 1. Dispersion curves at pressure 0 GPa (left side) and 8 GPa (right side) for $LuLiF_4$ compound

In our study the dispersion phonon curves of $LuLiF_4$ ($I4_1/a$, $C12/c1$ symmetries) were calculated in the pressure range from 0 GPa to 20 GPa. The complex frequencies appear near the Γ point at a pressure of 8 GPa (see Fig. 1). The calculation of the phonon dispersion curves was carried out for k-points lying along the directions Z (0.5, -0.5, -0.5), Γ (0,0,0), X (-0.5,0,0), P (-0.25, -0.25 , -0.25), N (0, -0.5,0) in the Brillouin zone. The appearance of complex frequencies in the spectrum at pressures above 8 GPa points to Born instability of $LuLiF_4$ phase with $I4_1/a$ symmetry [11].

Also, the infrared and Raman modes of $LuLiF_4$ compound were analyzed in pressure range from 0 to 20 GPa. The optically active modes were identified.

References:

1. A.A. Kaminskii, Laser crystals: their physics and properties. Vol.14, Springer (2013).
2. A. Grzechnik, K. Friese, V. Dmitriev [et al.], J. of Physics: Condensed Matter, 2005, Vol.17, no. 4, P.763.
3. A. V. Petrova, B. Minisini, O.V. Nedopekin, D.A. Tayurskii, Phase Transitions, 2015, Vol. 88, no.5, pp.534–539.
4. G. Ackland, M. Warren, S. Clark, Journal of Physics: Condensed Matter, 1997, Vol.9, no.37, P.7861.
5. P. Hohenberg, W. Kohn, Phys. Rev., 1964, Vol.136, pp. B864–B871.
6. W. Kohn, L. J. Sham, Phys. Rev., 1965, Vol.140, pp. A1133–A1138.
7. G. Kresse, J. Hafner, Phys. Rev. B., 1993, Vol. 47, pp. 558–561.
8. G. Kresse, J. Furthmuller , Computational Materials Science, –1996, Vol. 6, no.1., pp. 15–50.
9. G. Kresse, J. Furthmuller , Phys. Rev. B., 1996, Vol. 54, pp. 11169–11186.
10. K. Parlinski, Z. Li, Y. Kawazoe, Physical Review Letters, 1997, Vol. 78, no.21, P.4063.
11. M. Born, K. Huang, Dynamical theory of crystal lattices. Oxford University Press: London (1956).

[1] Materials Design, S.A.R.L.

XVII International Feofilov Symposium
on Spectroscopy of Crystals Doped with Rare Earth and Transition Metal Ions

Band gap design of solar cell chalcopyrite materials using hybrid-functional ab initio methods

Danil I. Radzivonchik[1]*, Lyubov N. Gramoteeva[2], Alexey V. Lukoyanov[1,2]
[1]*M.N. Miheev Institute of Metal Physics of Ural Branch of Russian Academy of Sciences, 620108, Ekaterinburg, Russia*
[2]*Ural Federal University named after the first President of Russia B.N.Yeltsin, 620002, Ekaterinburg, Russia*
*radzivonchik@mail.ru

In this work, we design a band gap of CIGS materials using PBE0 and HSE hybrid exchange-correlation functionals and compare them with the results of GGA-PBE calculations and experimental studies obtained by spectroscopic methods.

At the present time leaders in terms of conversion efficiency (beyond 20%) and stability are solar cells based on ternary chalcopyrite compounds $CuInSe_2$, $CuInS_2$, $CuGaSe_2$ and their solid solutions $CuInGa(Se,S)_2$ (CIGS). The effect of elemental variation of the composition plays a nontrivial role in the band gap formation and therefore it requires an electronic structure investigation.

It is well known that a band gap is underestimated within density functional theory (DFT) methods. In order to our theoretical results could be more faithful we sample hybrid exchange-correlation functionals in DFT calculations. In this work, we design a band gap of CIGS materials using PBE0 and HSE hybrid exchange-correlation functionals and compare them with the results of our previous GGA-PBE calculations and experimental studies obtained by spectroscopic methods [1-3]. This approach allow us to more accurately account for the impact on the electronic band energies caused by deviation in the stoichiometric [In]/[Ga] and [Se]/[S] ratios in CIGS materials. Electronic bands, total and partial density of states, band gap have been calculated using Quantum Espresso package [4]. Scalar relativistic projector augmented wave (PAW) pseudopotentials were used in calculations. Kinetic cut-off energy of 540 eV (40 Ry). Screening parameter in HSE case equal to 0.2. The example of calculation result and its details for chalcopyrite $CuInSe_2$ are presented in the bottom table. Using the HSE hybrid functional for CIGS materials generally allow us to obtain a wider gaps, which are in better agreement with the experimental data than in the cases of PBE and PBE0 functionals.

Functional	PBE	PBE0	HSE	Experiment
Band gap (eV)	0.80	1.76	1.10	1.03 – 1.05
Mixing par.	-	0.1	0.25	-

Research has been supported by the RSF grant No. 17-12-01500.

References: