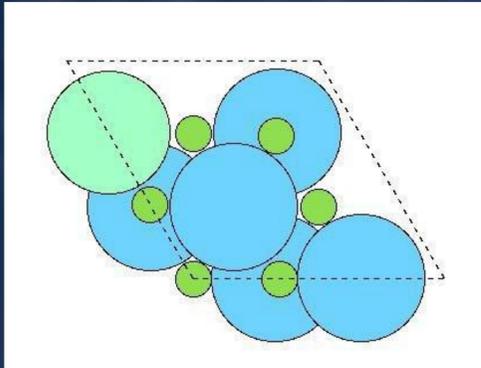




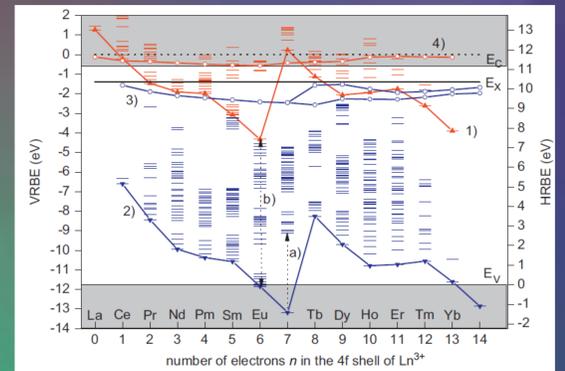
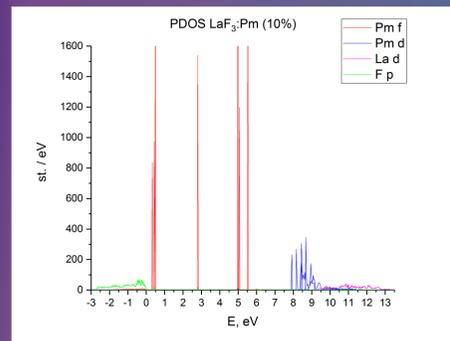
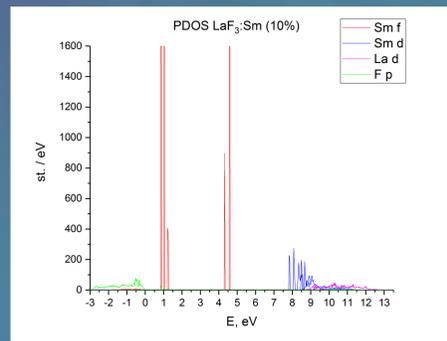
ELECTRONIC ENERGY STRUCTURE CALCULATION OF $\text{LaF}_3:\text{Pm}$ AND $\text{LaF}_3:\text{Sm}$ CRYSTALS

V. O. Karnaushenko¹, Y. M. Chornodolskyy¹, V. V. Vistovskyy¹, S. V. Syrotyuk², A. S. Voloshinovskii¹¹ Ivan Franko National University of Lviv, 8 Kyryla and Mefodiya str., 79005, Lviv, Ukraine² National University "Lviv Polytechnic", 12 S. Bandera Str., 79013, Lviv, UkraineFig. 2. $\text{LaF}_3:\text{RE}^{3+}$ latticePersson, Kristin *Materials Data on LaF_3 (SG:165)* by Materials Projects, 2014, 1(1), 011002. doi:10.17188/1272758

Heavy inorganic scintillating crystals based on fluoride compounds with rare-earth elements become more popular among researchers due to high temperature stability and high luminescence intensity [Sharma, 2017]. In particular, an important advantage of these compounds, compared to similar oxide compounds, is the low phonons energy, which makes the light yield efficiency much higher [Ha, 2017]. Big amount of experimental studies of $\text{LaF}_3:\text{Sm}$ [Macfarlane, 1986] and $\text{LaF}_3:\text{Pm}$ [Shinn, 1988] crystal's optical properties have been reported in recent years, but there is almost no theoretical information about their energy structure, what is very important for their effective use in lasers and scintillation detectors.

At present, the most complete information about the energy positions of 4f and 5d ion levels of rare earth elements in the structure of LaF_3 are collected in the work [Dorenbos, 2013] and presented in Fig. 1. These results are a logical continuation of the fundamental work [Dieke, 1968], in which it was first analyzed and presented.

In the current work the results of the theoretical calculations of the partial and total density of states of $\text{LaF}_3:\text{Sm}$ and $\text{LaF}_3:\text{Pm}$ crystals have been reported. The energy positions of 4f and 5d states of activator ions in the energy structure of the host material have been analyzed. Electronic band structures of the crystals have been calculated and the energies of the most probable optical transitions have been analyzed. Quantitative and qualitative comparison between the energy structure of $\text{LaF}_3:\text{Sm}$ and $\text{LaF}_3:\text{Pm}$ crystals has been provided.

Fig. 1. 4f-electron and 5d-electron binding energies for lanthanide impurities in LaF_3 [Dorenbos, 2013]Fig. 3. $\text{LaF}_3:\text{Pm}$ partial density of statesFig. 4. $\text{LaF}_3:\text{Sm}$ partial density of states

As it can be seen from the Fig. 1, levels of Samarium and Promethium ions, occupy equivalent positions, and differ only in the splitting energy and the presence of additional levels near the conduction band bottom for Samarium. Promethium is similar to praseodymium in its laser properties [Shinn, 1988], but since all its isotopes are radioactive, and element is extremely rare, our study of this element presents rather academic interest than a practical one. Instead, Samarium, widely used in optoelectronics and lasers as well. Numerous studies about 4f Sm^{2+} levels splitting of have been reported on the basis of Judd-Ofelt (J-O) theoretical model. There is enough information in the literature about the main optical properties of divalent and trivalent samarium, hosted in the LaF_3 matrix, but theoretical information about the energy positions of 4f and 5d levels, relative to the valence band top, are absent.

The model of the LaF_3 primitive lattice cell [doi: 10.17188 / 1272758], which was used for calculations, is presented on Fig. 2, after replacement one of the La ions by the Pm^{3+} or Sm^{3+} appropriately. The spatial group of this structure is $P3c1$, and the cell parameters are as follows: $a = b = 7.247 \text{ \AA}$; $c = 7.391 \text{ \AA}$.

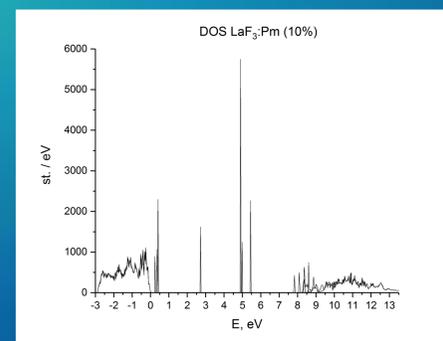
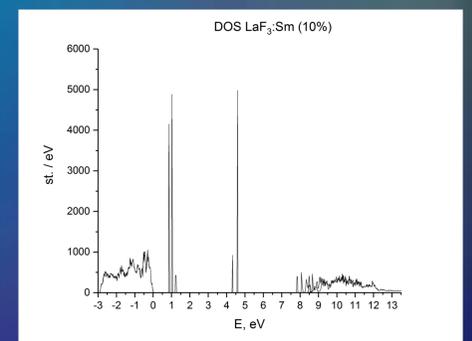
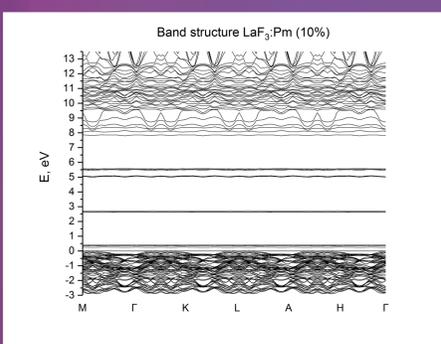
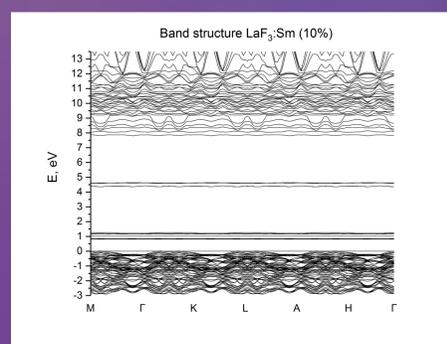
To take into account the spin-orbit interaction, which causes additional splitting of levels, spin value of $2.5\hbar$ for promethium and $3\hbar$ for samarium were taken for calculations. The occupation of energy levels were formed according to Fermi-Dirac distribution.

The calculation of the crystals electron-energy structure in this work is carried out using the projected augmented waves (PAW) method within density function theory framework. The Hubbard correction (DFT + U) is used to take into account the peculiarities of strongly localized states of lanthanides. In the general case, the exchange-correlation interaction energy, between electrons, have been determined from the PBE potential. All of the above approaches are implemented in the Abinit software, distributed with GPL open license.

The Hubbard corrections usage allows to take into account strong correlations of RE levels, with limited computational resources. Similar experiments, using the hybrid exchange-correlation potential PBE0 with different mixing parameters α (from 0.05 to 0.95), allows to obtain good positions of 4f RE^{3+} levels or correct splitting of 5d RE^{3+} levels and a adequate band gap, but not both qualities simultaneously, using a cutting energy of 30 Ha, and a k-grid $8 \times 8 \times 8$.

The calculations in this work were based on the Hubbard potential reported in work [Topsakal, 2014], but with some modifications. In this way, it was found that changes in correlation potential of 5d La states interaction results in a significant change of the band gap and strongly affects the 4f splitting of RE^{3+} levels. Instead, changing this parameter for 4f RE^{3+} levels affects on the position of these levels relative to the top of the valence band.

The obtained partial and total densities of states for $\text{LaF}_3:\text{Pm}$ are presented in Fig. 3 and Fig. 5 appropriately. As it can be seen from the graphs, the width of the 2p F states is 2,7 eV, the width of the 5d La levels is 3.2 eV. The 5d Pm levels undergo a strong splitting with a total width of 1,6 eV and a centroid position at 8.6 eV. Peaks of the 4f Pm levels are characterized by strong intensity and relatively small width, what is typical for them. The position of these peaks is determined by the energy of 0,4 eV, 2,9 eV, 5 eV and 5,5 eV, what corresponds to the results of the experimental data analysis presented on Fig. 1. The main difference with the experimental predictions is the level of splitting, which is smaller for obtained results and may be caused by too low correlation energy.

Fig. 5. $\text{LaF}_3:\text{Pm}$ total density of statesFig. 6. $\text{LaF}_3:\text{Sm}$ total density of statesFig. 7. $\text{LaF}_3:\text{Pm}$ electron energy band structureFig. 8. $\text{LaF}_3:\text{Sm}$ electron energy band structure

Similar results, for $\text{LaF}_3:\text{Sm}$, are shown on Fig. 4 and Fig. 6. Comparing these results with the data for $\text{LaF}_3:\text{Pm}$, we can see almost identical values of the width of 2p F and 5d La levels. Although 5d Sm levels are characterized by a similar width and position of the centroid, but have less expressed splitting, with some smearing of peaks after energy of 8,5 eV.

The 4f Sm levels have the same properties as in the case of Pm and have the following energy positions: 0,9 eV, 1 eV, 1,2 eV, 4,4 eV and 4,6 eV. It is important to note that despite the insufficient splitting of these levels, their positions correlate with the positions showed on Fig. 1, except for the absence of the third group of 4f levels what is located just below the 5d levels of Sm. Aforementioned disadvantage of the obtained results, as well as the relative small smearing of 5d levels, is associated with a small Hubbard correction value for 5d La levels and will be refined in future researches.

The band energy structures for the investigated crystals are shown on Fig. 7 and Fig. 8. The results are obtained along the line of highly symmetry points M-G-K-L-A-H-G. The valence band bottom of the crystals, in both cases, is formed by 2p F levels, and the top of conduction band - by 5d La levels. Activators levels are situated in the forbidden zone and are characterized by low dispersion with respect to the wave vector k . From the calculated band diagrams, also can be seen a stronger tightening of the 5d La levels in the region of 5d activator's levels, in the case of Sm. The calculated band gap is 9,6 eV in the case of $\text{LaF}_3:\text{Pm}$, and 9,4 eV in case of $\text{LaF}_3:\text{Sm}$. The fact of smaller $\text{LaF}_3:\text{Sm}$ band gap confirms the above-mentioned inaccuracy of Hubbard correction for samarium levels once again.

Conclusions:

- Experiments, with different methods to electron energy structure calculations for strongly correlated materials, have been performed and effectiveness of DFT+U approach in comparison with hybrid exchange-correlation PBE0 usage, in case of limited computational resources has been shown
- Investigated that changes in Hubbard correction for 5d levels affects splitting 4f and 5d levels, as well as energy band gap width
- Represented results are in good agreement with experiment based predictions of Sm and Pm levels positions, except absence of 4f Sm levels at the top of forbidden zone
- Analyzed, that the valence band top of $\text{LaF}_3:\text{Sm}$ and $\text{LaF}_3:\text{Pm}$ is formed by 2p F levels and conduction band bottom - by 5d La levels.
- Demonstrated that 5d $\text{Sm}^{3+} / \text{Pm}^{3+}$ are splitted and situated just before the conduction band bottom
- Shown that 4f $\text{Sm}^{3+} / \text{Pm}^{3+}$ levels are placed in the forbidden band and are characterized by small width, high intensity and similar energy levels positions for both crystals