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REVIEW**of the Doctoral Dissertation of Madhavi Dalsaniya, M.Sc.****"Ab-initio Modeling of Reactivity of Materials Against Fluorine
under High Pressure Conditions"**Discipline of science - **Materials Engineering**; Field of science - **Engineering and technology**

The presented for review doctoral thesis of Ms. Madhavi H. Dalsaniya entitled "Ab-initio Modeling of Reactivity of Materials Against Fluorine under High Pressure Conditions" comprises essentially four thematically coherent scientific articles published in acknowledged international journals and is augmented by a kind of treatise that contains introductory material describing the methodology employed in performed research work and a fairly comprehensive review of the original articles. The thesis presents the results of computational studies on bromide and bromine fluorides under high pressure, pointing out the sequence of phase transitions to the high pressure crystallographic structures. The obtained results constitute mostly theoretical predictions, however, the obtained results compare excellently with the available experimental data and also with the experimental data provided by the collaborating experimental groups and reported in the fourth publication of the thesis's series. This agreement corroborates the accuracy of the theoretical methodology employed in the studies.

Before I present the detailed analysis, I would like to express my appreciation of the thesis. It deals with the actual and important problems of materials science and condensed matter physics, employs the state-of-the-art theoretical methodology, and, what I consider the most important, delivers interesting and novel findings relevant for both scientific disciplines.

The doctoral thesis has been presented in the form of a booklet written in English. It consists of abstract, (also abstract in Polish), 58 pages of a **treatise**, which is thought as a kind of introduction to the material presented in the four published regular papers. These articles constitute essential part of the thesis, and are included in the thesis booklet as Appendices 1-4. They are:

- Madhavi H. Dalsaniya, Krzysztof Jan Kurzydłowski, and Dominik Kurzydłowski, "Insights into the high-pressure behavior of solid bromine from hybrid density functional theory calculations", *PHYSICAL REVIEW B*, **106**, 115128 (2022), [PRB106-2022];
- Madhavi H. Dalsaniya, Despak Upadhyay, Krzysztof Jan Kurzydłowski, and Dominik Kurzydłowski, "High-pressure stabilization of open-shell bromine fluorides", *J. Phys. Chem. Chem. Phys.* **26**, 1762 (2024), [PCCP26-2024];

- Madhavi H. Dalsaniya, Despak Upadhyay, Paras Patel, Prafulla K. Jha, Krzysztof Jan Kurzydłowski, and Dominik Kurzydłowski, "Pressure-Dependent Thermal and Mechanical Behaviour of a Molecular Crystal of Bromine", *Molecules* **29**, 4744 (2024), [MOL29-2024];
- E. Edmund, M. H. Dalsaniya, R. T. Howie, E. Greenberg, V. B. Prakapenka, M. Pena-Alvarez, M. Hanfland, P. Dallday-Simpson, D. Kurzydłowski, and A. Hermann, "Close-packed atomic bromine up to 230 GPa", *PHYSICAL REVIEW B* **112**, 134101 (2025), [PRB112-2025].

The **treatise** consists of four parts: (1) **Introduction**, (2) **Computational Methods and Formalism**, (3) **Summary of Results**, (4) **Conclusions and Future Work**, and extensive list of references containing 161 positions.

In the part (1) **Introduction**, doctoral candidate explains the role of high pressure research in modern materials science stressing the role of reliable theoretical calculations (for example employing density functional theory - DFT) for the interpretation of the experimental data, providing valuable predictions, and deepening the understanding of the physico-chemical mechanisms governing the processes (in particular phase transitions) in crystals under high pressure. Further, the molecular crystals are introduced and the possible structural transformations under high pressure conditions are pointed out. There are also mentioned the previous studies of high pressure behaviour of such molecular crystals as H₂, other diatomic molecules O₂, N₂, and halogens F₂, Cl₂, Br₂, I₂. Description of the highly incomplete research status quo in the field of B₂ molecular crystal can be considered as motivation for undertaking the studies of this system in the framework of DFT methods (the results are presented in the article PRB106-2022). The Introduction section is continued with brief summary of the fluorine's reactivity issue and further with motivation for performing work described in the article CPPC28-2024. Also the research status of mechanical properties of bromine crystals is presented shortly and the paper MOL29-2024 is pointed out as the source of solutions to the unsolved up to then problems. The highlight of this section is clear formulation of objectives, hypothesis, and scope of the work.

The part (2) of the treatise **Computational Methods and Formalism** contains the description of the methodology employed for the studies performed by the doctoral candidate. It starts with the historical approaches for computations of many-electron systems, *i.e.*, Hartree and Hartree-Fock methods, with their very crude description of the electron-electron interaction. Then the basics of the density functional theory (DFT) are presented with focus on the Kohn-Sham realisation of the DFT, where the essential issue is the choice of the as good as possible approximation for the exchange-correlation functional. Presently there are more than fifty various exchange-correlation functionals on the market, but three important classes of functionals are mentioned in the treatise, and their representatives are pointed out and selected for further calculations performed within doctoral work. Up to this point, the part (2) contains purely book material, and few citation could make the job without diminishing the quality of the doctoral work. However, the material is presented nicely in the treatise, and it could be useful for later PhD students performing the similar calculations in the framework of DFT. It could also facilitate the understanding and assessment of the thesis for people not familiar with the DFT theory. Providing such presentation of the DFT method, I would rather avoid to mention the archaic formulation of DFT in the form of Hohenberg-Kohn Theorem. Since years it has been known that not all electron densities are V-representable, and then the Hohenberg-Kohn theorem is not valid. It is much better to base the DFT on the Mel Levy's *Constrained Search Formulation of the Density Functional Theory* that avoids V-representability issue and constitutes the generalisation of the Hohenberg-Kohn formulation (see for example, M. Levy, *Proc. Natl. Acad. Sci. (USA)* **76**, 6062 (1979); M. Levy, *Phys. Rev. A* **26**, 1200 (1982); or M. Levy & J. P. Perdue

in *Density Functional Methods in Physics*, eds. Reiner M. Dreizler and Joao Da Providencia, 1985 Plenum Press, New York, p. 11)

In the part (2) of treatise, doctoral candidate gives arguments for the choice of the hybrid functional HSE06 in the performed calculations. The argument that the HSE06 provides the better values of the energy gaps (as I suppose calculated as the difference of the Kohn-Sham energy for LUMO & HOMO levels) is not so relevant as the argument that the HSE06 enhances the accuracy of formation energy predictions. As accurate as possible calculations of these energies are crucial for the reliability of studies undertaken in the thesis. Further in the part (2), there is described the semi-empirical van der Waals correction to the total energy. The doctoral candidate decides to use Grimme D3 correction and claims that for the systems investigated the vdW correction improves decisively the results. However, it cannot be taken as a general rule, and there are systems where this correction does not improve accuracy of calculations (see for example, Ching-Chien Chen *et al.*, *Comp. Materials Science* **247**, 113458 (2025) "How accurate is density functional theory at high pressures?").

The part (2) contains also description of numeric tools that are used for post-processing of the data produced by the DFT code (VASP in the case of the thesis). The most important of these is an open source tool for crystal structure predictions, XtalOPT. The LOBSTER program is used for analysis of bonding and charge analysis. The methods for calculation of phonons, Raman tensor components, and elastic constants are also presented. For calculation of phonons the very popular *PHONOPY* package has been used, what is very common procedure nowadays. This part of treatise is very important for the assessment of the results presented in the four articles. The real details of the computations are placed just here, and they are very helpful for understanding the original articles.

What in my opinion could be included in the part (2) of the treatise is description of the possible equations of state (EOS), such as, for example, Birch-Murnaghan EOS. This provides analytic expression for the total energy of a system as a function of its volume $E(V)$, or pressure $p(V) = -\frac{\partial E}{\partial V}$. Then a fit of the EOS to the numerical data $E(V)$ can directly provide the value of bulk modulus, which in the doctoral work is obtained from elastic constants. The values of bulk modulus obtained in these two manners can differ. Plotting EOS for different structures, one can obtain transition pressure between two structures as tangent to two $E(V)$ curves. Such description of high pressure effects in the crystal structure is fairly common procedure in the literature, and I have to admit that I am used to such picture.

The part (3) of the treatise **Summary of Results** contains the concise description of four articles constituting the thesis. For each article, some details of the calculations, and the most important results are pointed out.

The treatise ends with part (4) **Conclusion and Future Work**. According to the doctoral candidate, the future studies should focus on the issue of fluorine reactivity with other electronegative nonmetals such as oxygen, sulfur, and chlorine, and also nitrogen rich materials. It is very positive aspect of the thesis that its author is able to formulate reasonable plans of future activities.

In spite of the fact that treatise contains mostly information that can be found in the original articles (with exception of that part of the Section (2) where the computational details are provided), it constitutes very valuable part of the thesis. It is written in good English, is concise and comprehensive, and I have read it with interest and pleasure. This text assures me that the

PhD student understands well the theoretical methods, which are employed in her studies, and also she is able to present the achieved results clearly and provide a critical assessment of them. After reading these fifty pages, it was much easier for me to go later on through the original articles.

These four articles are in my opinion solid pieces of scientific work, presenting high quality research and novel interesting results.

The main achievements of the first article PRB106-2022 are:

- demonstration that for the studies of crystal bromine under high pressure studies of the employed hybrid functional HSE06 clearly over performs the simple GGA functional of Perdew-Burke-Erzerhof (PBE) that is very popular and commonly used in DFT calculations;
- good agreement of theoretical results with available experimental data concerning properties of bromine's molecular phase I (*Cmca* symmetry) and the value of the transition pressure to the metallic non-molecular phase II (*Immm* symmetry), which confirms the suitable choice of theoretical methodology employed;
- prediction of the existence of bromine's experimentally yet unknown crystal phases: metallic phase of *I4/mmm* symmetry at the pressure of 128 GPa and *fcc* lattice at 188 GPa.

The second article (PCCP26-2024) deals with the issue of high-pressure stabilisation of open shell bromine fluorides. Its main findings are:

- prediction that at relative moderate pressure of 15 GPa the phase BrF_3 becomes unstable and two new phases BrF_2 and BrF_5 emerge that exhibit quite different bond character in comparison to the phase BrF_3 , and finding that both new phase contain radical molecules while being non-metallic;
- explanation of the properties of compressed bromine fluorides with molecular orbital diagrams and the VSEPR model.

In the third article (MOL29-2024), the pressure-dependent thermal and mechanical properties of bromine as obtained from the DFT computations with thermal effects taken into account within the Quasi Harmonic Approximation are presented. In principle it is a continuation of the studies described in the article PRB106-2024. As the highlights of these studies, I would like to point out:

- calculation of the thermal expansion and specific heat capacities of solid bromine over temperature range from 0 to 1000 K and pressures up to 90 GPa. The atomistic first-principle calculations of thermal properties of crystalline materials are rather rare;
- calculation of the mechanical properties, i.e., elastic constants, which expands considerably the knowledge about these materials.

The fourth paper of the series (PRB112-2025) has mostly experimental character. The high pressure (up to 230GPa) X-ray diffraction experiments for bromines have been performed by experimental groups from various laboratories. These studies were augmented by the DFT calculations

- The close cooperation of theoretical and experimental groups leads to better understanding of the pressure effects in bromines
- This article confirms the ability of doctoral candidate to cooperate with experimental groups, which possibly turns relevant in the future profesional career.

In summary, the thesis presents valuable scientific achievements. The submitted for review material clearly demonstrates that doctoral candidate, Ms. Madhavi Dalsaniya, has reached scientific maturity in the field of computational materials science and demonstrates proficiency in the materials modelling employing methodology in the framework of the density functional theory.

The four articles included in the doctoral dissertation are collective works. However, in all three theoretical articles Ms. Madhavi Dalsaniya is the first author, and she is the second author in the fourth article (PRB112-2025) presenting mostly experimental data. This strongly suggests that the PhD student played a leading role in planning the research, conducting it, analyzing the results, and preparing the manuscripts for publication. The series of publications included in the doctoral dissertation is a thematically coherent, valuable scientific output.

The doctoral dissertation submitted for evaluation meets the conditions set out in Art.187 sec. 1-4 of the Act of 20 July 2018 Law on Higher Education and Science (Prawo o szkolnictwie wyższym i nauce, Dz. U. z 2018 r. item 1668, as amended). Therefore, I recommend to admit Ms. Madhavi H. Dalsaniya, M.Sc., to the further stages of the procedure for conferring a doctoral degree in the Discipline of Science - **Materials Engineering**.

Due to extraordinary high level of the assessed dissertation, I would like to apply for **distinction of the thesis**, mostly due to the broad and advanced research workshop employed for the studies. This allowed for providing novel, reliable, and interesting research findings considerably advancing the materials science and condensed matter physics. All articles constituting the thesis have been published in high esteemed international journals.

Yours faithfully



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