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Referee's assessment of PhD thesis entitled *Ab-initio modeling of reactivity of materials against fluorine under high pressure conditions*, by Madhavi Dalsaniya, MSc, supervised by Prof. Krzysztof J. Kurzydłowski, Faculty of Materials Science and Engineering, Warsaw University of Technology, and by assistant supervisor Dr. hab. Dominik Kurzydłowski, Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University in Warsaw

Contemporary materials research reaches out for the uttermost properties in extremely unfavourable conditions. This requires an in-depth understanding of the basic principles of the structure-property relations in elements and relevant chemical compounds. Despite decades of experimental and theoretical research, we still miss the full understanding of the behaviour of chemical compounds both at the atomic and macroscopic scale. The most abundant element in the Universe, hydrogen, still lacks the characterization which would explain its form and transformations under extreme conditions present in the stars and large planets, not to mention the convenient storage of hydrogen for its use in fuel batteries. The research dedicated to other elements and compounds is even less advanced.

The PhD thesis by Ms. Madhavi Dalsaniya is devoted to the structure and reactivity of bromine against fluorine under high pressure conditions. This thesis has been prepared at the Faculty of Materials Science and Engineering, Warsaw University of Technology jointly with the Faculty of Mathematics and Natural Sciences, Cardinal Stefan Wyszyński University in Warsaw. The thesis has the form of four scientific articles bound together with about 70 pages of the PhD Candidate's commentary. The commentary includes the title page, acknowledgments, *Abstract* in English and Polish (*Streszczenie*), *Table of Contents*, and four sections: Introduction (8 pages), *Computational Methods and Formalisms* (23 pages), *Summary of Results* (8 pages) and *Conclusions and Future Work* (1 page), as well as

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References (161 positions). This is a correct and transparent arrangement of chapters in the thesis. The References give a complete up-to-date overview of the relevant literature.

The main subject of the thesis well aligns with the recently evoked cumulative experimental and theoretical efforts aimed at understanding the transformations of halogens under the ambient and extreme conditions. In the *Introduction*, the PhD candidate outlines a broader context of the motivation for undertaking this subject. Notably, the strong effects of high pressure are described in the first pages and in the first figure, which illustrates enormous scale of the transformations induced by pressure, which can change the nature of interactions and can lead to completely new properties. This approach justifies the choice of the high-pressure conditions to in-depth investigate the structure and properties of materials. Later in Introduction, subsection 1.1 *High-Pressure Science and Modern Research*, a one-page very brief history of high-pressure techniques are mentioned. Subsection 1.2 *Molecular Crystals* is focused on diatomic elements of H_2, N_2, O_2 and move on to the main subject of the thesis – halogen elements and in particular bromine. Its similar transformations to those in other halogens as well as the discrepancies between the experimental results and theoretical predictions by density functional theory (DFT) are indicated. These discrepancies and the lacking accuracy of the current computational simulations stimulated the research undertaken by the PhD candidate.

Further subsections of Introduction briefly relate the *Reactivity of Fluorine* (section 1.3), *Mechanical Properties* (1.4), *Objectives, Hypothesis and Scope of the Work* (1.5); two next subsections 1.6 and 1.7 list the Ms. Dalsaniya's papers and conference activities. The list of papers has been confined to those three included in the PhD thesis and the fourth one currently under review. According the Research Gate, Ms. Madhavi Dalsaniya published 11 articles (including one arXiv, but excluding the abovementioned submission under consideration) published between 2020 and 2025, which is a remarkable achievement for such a young scientist. Also the participation in international conferences, including three oral presentations, one of them distinguished by the Best Oral Presentation Award, show that Ms. Dalsaniya has been an active young scientist and PhD student.

Section 2 *Computational Methods and Formalisms* briefly describes the theoretical background of performed simulations, starting from the Schrödinger equation and Born-Oppenheimer approximations; wavefunction approach, Hartree and Hartree-Fock approximations, DFT theory – its development through theorems, exchange correlation functionals, local-density and generalized-gradient approaches (GGA), meta-GGA and hybrid functionals, van der Waals corrections and programs used for the simulations of solid-

state and crystal structures: LOBSTER, XtalOpt. Subsection 2.8 describes the lattice dynamics and phonon structure, subsection 2.9 is on Raman spectroscopy and the last subsection 2.10 is dedicated to stress-strain relation and mechanical properties.

Section 3 summarizes the results published as articles and a preprint (under review).

Article A, entitled ***Insights into the high-pressure behaviour of solid bromine from hybrid DFT calculations***, published in *Phys. Rev. B* 106 (2022) 115128, Ms. Dalsaniya co-authored with the supervisors. The paper reports the simulations of the crystal structures of bromine phases up to 200 GPa. The application of several D3 dispersion corrections to hybrid functionals afforded the reproduction of the bromine molecular *Cmca* phase at ambient pressure, persisting to 89 GPa, when it enters an intermediate modulated structure till 92 GPa, leading to orthorhombic space group *Immm*, which in turn at 128 GPa transformed to tetragonal phase of space-group symmetry *I*4/*mmm*; it at 188 GPa transformed to a cubic phase of space group *Fm*3*m*. The most interesting elements of the structural transformations are the metallization of bromine at 80 GPa, preceding the dissociation of molecules to the 2-dimensional and 3-dimensional metal structures.

Article 2, entitled ***High-pressure stabilization of open-shell bromine fluorides***, published in *PCCP* 26 (2024) 1762 is co-authored by four researchers: M. Dalsaniya, D. Upadhyay, K.J. Kurzydłowski and D. Kurzydłowski. The article describes the simulations of bromine fluorides structures. The most interesting results are the prediction of disproportionation of BrF_3 into BrF_2 and BrF_6, as well as the pressure-induced solid-state transitions of the BrF_3, BrF_5 and BrF_6 phases. Particularly intriguing is the confirmation of BrF_5 structures in space group *Pnma* (observed below T_m=211.85 K) and space group $P2_1/c$ below 142 K; and the stability of triclinic structure of space group *P*1 above 1.8 GPa, transforming to space group *P*-1 above 8 GPa. The information in page 53, lines -2 to -1, that liquid under ambient conditions compound BrF_5 freezes at 1 atm in the phase of space group *P*1 is confusing.

Article 3, entitled ***Pressure-Dependent Thermal and Mechanical Behaviour of a Molecular Crystal of Bromine***, published in *Molecules*, 29 (2024) 4744, was written by six co-authors. They use the DFT and quasi-harmonic theory for computing the Raman spectra, thermodynamic and mechanical properties, as well as the thermal expansion of the molecular bromine in its *Cmca*-symmetric phase up to 90 GPa and 1000 K. The computed vibrational well agree with the experimental Raman spectra. The article reveal various other mechanic characteristics of the molecular bromine under high pressure.

Article 4, by Eric Edmund, Madhavi H. Dalsaniya, Ross. T. Howie, E. Greenberg, Vitali Prakapenka, Miriam Peña-Alvarez, Michael Hanfland, Philip Dalladay-Simpson,

Dominik Kurzydłowski and Andreas Hermann, entitled ***Close Packed Atomic Bromine up to 230 GPa***, was submitted to *Physical Review B* and was under review when the PhD thesis was submitted, but there is still no information about its acceptance. This article combines the theoretical computations with experimental X-ray diffraction extended in static measurements using synchrotron facilities APS in Argonne, USA and ESRF in Grenoble, France. The conclusions are that transformations in bromine mirror those in iodine, but require much higher pressure. The character of the phase transitions in bromine was discussed and significant differences were noted for the range of stability of phases and the transitions character between the lighter halogens.

Ms. Dalsaniya's contribution to Articles 1-4 is leading, according to her first position in the list of authors in Articles 1-3 and her second position in Article 4, where the first author is Dr. Eric Edward, the experimental scientist from HPSTAR, China. The latter article combines experimental with theoretical approaches, which yields a comprehensive description of the behaviour of bromine under pressure. Articles 2 and 3 contain specifications of authors' contributions, which indicate the leading contribution from Ms. Dalsaniya.

In my opinion, the most significant achievements of Ms. Dalsaniya's PhD thesis are:

1. The simulation of transformations of bromine in a wide range of pressure up to 230 GPa;
2. The correct prediction of the series of structural phase transitions in bromine as a function of pressure;
3. The correlation of the electronic and mechanical properties of bromine with its compression;
4. The simulation of the compression of bromine fluorides BrF_3 and BrF_5, and postulating the disproportionation of these compounds into BrF_2 and BrF_6;
5. Prediction of phase transitions in bromine fluorides.

I am particularly impressed by the prediction of the transitions to triclinic phases of space-group symmetry $P1$ and $P\text{-}1$ in BrF_5. The BrF_5 phase of symmetry $P1$ occurs at relatively low pressure, most likely coinciding with the freezing pressure of this compound at room temperature. The thesis has been well and clearly written, although I noted typographical mistakes in the text (indicated in my copy of the thesis). The solution of an original scientific subject has been achieved without any doubt. During the PhD defence, I should be grateful if the Candidate addressed the distinction between chemical reactions and phase transitions under high pressure: while the disproportionation of bromine fluorides BrF_n is surely a

chemical reaction, and so it is the dissociation of Br_2 molecules, but the latter reaction is spread over the broad pressure range and several different types of transformations.

In conclusion of this assessment of the PhD thesis by Ms. Madhavi H. Dalsaniya, I highly value the choice of the interesting subject of research, the clearly formulated scientific problems and their competent solution by applying the appropriate state-of-the-art computer software. The predictions of the high-pressure phases of bromine as well as chemical stability of various bromine fluorides and their phases are undoubtedly the significant achievement of this thesis. The conducted research clearly indicates that Ms. Madhavi H. Dalsaniya has successfully concluded a serious scientific project. She also participates in other projects and her publications and conference presentations are impressive. Therefore, I declare that the doctoral thesis submitted to me for assessment fully fulfils the requirements the conditions set by the Polish Act on Academic Degrees and Titles (Act of 20 July 2018 - Law on Higher Education and Science; current reference to the legal act - consolidated text: Journal of Laws of 2022, item 574, as amended), which authorizes me to submit to the Scientific Council of the Discipline of Materials Engineering of the Warsaw University of Technology my recommendation for the admission of Ms. Madhavi H. Dalsaniya, M.Sc., to further stages of proceeding the PhD procedure.

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