

## Jury Member Report – Doctor of Philosophy thesis.


**Name of Candidate:** Iosif Leibin

**PhD Program:** Materials Science and Engineering

**Title of Thesis:** Spectra and mobility of open-shell atoms in rare gas crystals: effects of interaction anisotropy

**Supervisor:** Professor Alexei Buchachenko  
Assistant Professor Dmitry Aksenov

**Name of the Reviewer:** Larin Alexander V.

I confirm the absence of any conflict of interest		<b>Date: 24-08-2024</b>
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This work is a logical prolongation of the studies realized in the group of Prof. Buchachenko A.A. where the calculation of atom-molecule potentials with higher accuracies was joined with theoretical development of technics for the computations of atomic species isolated in rare gas (RG) matrix. Some PhD studies devoted to isolated atoms in matrixes have been already done in the group as well as the one presented by I. Leibin at the Lomonosov-23 conference where I heard some part of the results for the first time.

The Thesis contains Introduction, Literature Review, Methodology and Techniques, Conclusions, and References. The Review is devoted to analysis of experimental data, theoretical approaches, and current problems starting from identification of the stable sites for an atom in different electronic configurations to calculation of its diffusion/migration inside the matrixes and electron spectroscopy. Such wide range of complex aspects is indeed characteristic feature of the works in this domain of interpretation of the spectra of atoms isolated in matrices. Together with this, the long list of atomic species in the Thesis is indeed impressive. The main fraction of the results was obtained using the bulk model of rare gas (RG = Ar, Kr, Xe) matrix developed by the group and non-relativistic (NR) diatomic-in-molecules (DIM) method constructed and modified on the basis of old DIM version. The technics developed by I. Leibin was applied to a series of neutral atomic species (H, B, C, N, O, F, Ba, Sm) while some of them are poorly described in the literature (C, N, F, Sm). He, Ne, and Na were studied in less extent to describe trapping sites and migration. Different atomic electronic states of B, C, O, F, Na, Ba, Sm have been taken into account while constructing the NR DIM potentials. The case of higher level vectorial spin-orbit coupling was studied for O@RG system and showed comparable accuracy relative to the results of NR DIM. Wide variety of trapping sites for interstitial (IS) ones, single substituted (SS) and multi-vacancies were obtained and classified for many of the atoms noted above. The calculated sites for atoms are used to calculate diffusion trajectories applying simple transition state theory (STST) including the calculation of zero-point energies in the most of cases. Migration O mechanism was studied regarding direct exchange by the positions with nearest RG atoms as well as *via* more frequent

vacancies and less frequent interstitials in the RG crystals. For atoms of the first and second rows of the Periodic Table migration was limited by the analyses of the IS-IS, SS-IS, and SS-SS trajectories. Two-step and ring exchange mechanisms were considered in parallel for some of the atoms (H, He, ...) in all three RG matrices. Obtained data allowed to the author to conclude that SS-trapped atoms nearly immobile in the most of the relevant experiments.

A novelty of the work is related to the explanation of interesting effect of quicker O diffusion than that of H due to anisotropy of ( $^3\text{P}$ )O potential at the NR DIM level (when isotropic solution fails). Despite frequent overestimation of activation barrier for migration of interstitials O and vacancies in RG matrices (within 30%) with NR DIM approach the latter opens new possibilities which are not available for B, C, and O atoms within isotropic approximation for interaction potentials.

Important qualitative answers were obtained relative to Ba@RG system where special attention was paid to emission electronic spectra due to important perspective of Ba@Xe application in nuclear physics. Successful interpretation of the Ba spectra in Ar and Kr allowed to surely assign the transitions to the theoretical sites (for nearly all violet, green, red, and blue sites). The calculated bands in Xe matrix require uniform blue shift earlier noted in literature and more elaborated approach. The main effect of this part is related to the finding of stable sites for Ba in ideal lattices of all three inert gases instead of idea of favored Ba location at grain boundary as proposed earlier.

Some questions can be formulated to the author relative to the methods of the study and their testing. Spin-orbit coupling was evaluated as minor effect for O@RG (Fig. 48, Table 13) while this estimate is of higher interest for heavier Ba or Sm atoms. For the last atoms with the larger polarizabilities the test of three-body dispersive terms is more instructive (as a criterion for DIM scheme) because Axilrod-Teller-Muto terms are proportional to atomic polarizabilities. The case of relative importance of the three-atom terms for lattice dynamics of heavier RG was done by Barker et al. [IBM Journal of Research and Development, 20, 222, 1976. doi:10.1147/rd.203.0222].

For vacancies and self-interstitials author realized the evaluations of formation enthalpy, the heights of the barrier for migration and apparent activation energy. The apparent self-diffusion activation energy was underestimated by around 30% for both vacancies and self-interstitials (or less depending on the RG atom for vacancies). No other computational results were given for these RG properties which have more general character (and should occur more frequently in any computations of RG solids) than atomic properties of isolated atomic species. Is it possible to compare activation energy with other calculations and why the agreement is rather poor (Tables 17, 18)?

VTST and CVTST methods of the calculation of rate constant are mentioned but it seems that all the results of the Thesis were considered with STST. If the VTST and CVTST are commented to facilitate the comparison with literature then it could be clearly shown.

Minor remarks could be noted relative to the presentation of the results.

In some cases a citation could be more precise. The author mentioned part 2.6.4 before Table 14 at page 110 as a source of the data commenting two sets of parameters for RG-RG potentials. However, in this part of Review no exact data on the parameters is given because of numerous potentials described there. It is reasonable to give a direct ref. to modified Aziz's data or else.

Similarly, the "gas-phase" term used in Tables 17, 18 sounds ambiguously and could be replaced by a footnote as I proposed for the Table 14 above.

The basic assumptions of DIM method are given in Part 2.6.1 but with clear assignment neither to DIM, nor to exact publication where they come from (possibly, from Ellison [129]). It creates some inconvenience because different authors used the "DIM" name for different approaches adopted for particular objects. The features of current NR DIM version (including the ones from the basic DIM involved) can be given somewhere together using some additional comments.

Misprints are not too numerous but are presented even in Conclusions. Some examples are at:  
Page 55, lines 15, 16 from the bottom.  
Page 86, line 6 from the top.  
Page 125, line 8 from the bottom.  
Page 141, line 3 from the top. Diffusion coefficient  $D$  is not used herein.  
Page 151, lines 9, 11 from the bottom.  
Page 152, line 10 from the top.  
Page 152, lines 9, 12 from the bottom.  
The ref. [33] is wrongly given in Figures 40-42 instead of ref. [15].

Finally, each step of the modelling presented above is accompanied by a comparison with experiment, if any, and detailed discussion. Full description of the Figures and Tables supplied is given. In general, thorough and complex results of the Thesis are nicely illustrated. Minor inaccuracies and remaining questions do not hinder the understanding of new and important results presented in the work and published in valuable journals such as Journal of Chemical Physics, Physical Chemistry Chemical Physics, and Molecular Physics. All conclusions are well formulated and supported by the presented data. I believe that Iosif Leibin deserves the PhD degree on the basis of presented Thesis.

#### Provisional Recommendation

*I recommend that the candidate should defend the thesis by means of a formal thesis defense*

*I recommend that the candidate should defend the thesis by means of a formal thesis defense only after appropriate changes would be introduced in candidate's thesis according to the recommendations of the present report*

*The thesis is not acceptable and I recommend that the candidate be exempt from the formal thesis defense*