Evaluation of PhD Thesis

entitled "Numerical Simulations on structural, mechanical and magnetic properties of some Nano systems"

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Initial Remarks

I had the pleasure of reading and evaluating the PhD thesis entitled "Numerical Simulations on structural, mechanical and magnetic properties of some Nano systems". The work has been conducted by MSc Dung Nguyen Trong at the Faculty of Physics and Astronomy of the Zielona Góra University (UZ), and supervised by dr hab. Van Cao Long, Prof. UZ.

My evaluation is based on the Resolution of the Senate of the Zielona Góra University from June 28, 2023, in relation to the actions taken throughout the process of awarding the doctoral degree for MSc Dung Nguyen Trong (the candidate).

The following assessment criteria were adopted in the *Evaluation of PhD Thesis*:

I. Presentation of the thesis

II. Scientific evaluation of the thesis

III. Formal evaluation

IV. Comments, questions, and discussion points

V. Final conclusions

The copy of the thesis by MSc. Dung Trong Nguyen sent to me was printed in the form of an A4-size book and presented as a written dissertation in English. Therefore, the *Evaluation of the Ph.D. thesis* is prepared in English. The key, and final formal statement is provided in English and Polish.

I. PRESENTATION OF THE THESIS

The reviewed thesis can be described as a theoretical study, since the author used the numerical calculation methods to simulate the nature of physical phenomena. The main part of this work consists of chapters 1-3 (pp. 15 -156), chapter 4 as conclusions and plan of further research (pp. 156 - 157), detailed lists of his and co-authors publications, and references (pp. 158 - 181). The first part of the thesis (pp. 1 -14) contains the title page, acknowledgements, table-of-contents, list of figures, and preamble. This part adds up to the prelude to the previously mentioned chapters.

The thesis seems to be quite significant because, together with the bibliography, lists of tables, and figures, it covers a total of 181 pages. However, the quality of presentation is so poor that extensive rewriting and English proofreading by native speakers are required if the author and supervisor choose to publish this thesis to a large audience, even with only the public doctorate thesis presentation.

Let me highlight a few serious flaws that regularly appear in the thesis: a) non-use of the article; b) typographic errors; c) incorrect use of vocabulary; d) incorrect use of punctuation; e) editorial errors; f) the application of new concepts, phrases, and terms without any explanation and justification; g) coherence and cohesion mistakes. I will point out the kind of grammatical error in square brackets, e.g., [a, b..] , and the questioned text in double quotation marks "..." .

1. Page 1 - [b, a, d, c] On the title page, the title "Numerical Simulations on (?) structural, mechanical(?) and magnetic properties of some Nano(?) systems" is recommended to be replaced by "Numerical simulations of the structural, mechanical, and magnetic properties of some nanosystems".

2. Abstract in English. I) [c, d, e, f] As an example, the first paragraph of the abstract is recommended to be modified as follows: "In this thesis, studying the characteristic quantities of microstructure, mechanical, and magnetic properties of some nanomaterials by numerical simulation methods is presented. Simulation methods as (are) considered as a third branch of scientific research(???). In practice, to study the characteristic quantities of materials, researchers often have to use one of two research methods, which are the experimental method and the theoretical method. With simulation methods, there are 3 types of popular simulation methods, namely molecular dynamics simulation (MD), Monte-

Carlo method simulation (MC)(,) and density function theory simulation method (DFT) belonging to Ab initio M(m)ethods. Within the scope of this thesis, we use mainly two first (delete first) of them: The (the) MD simulation method (delete) and the MC simulation method(s). In the framework of the MD simulation method(s), we study the microstructural characteristic quantities of materials because of their simplicity. Then we use the equation of Newton's second law to study the kinematic motion of each atom and then use the average statistical method to determine the characteristic quantities of dynamics such as temperature (T), pressure. (P), the total energy of the system (Etot). At dynamic equilibrium, we determine the microstructure shape, number of structural units, link angle, radial distribution function (RDF), where RDF is determined by the length of the links and the height of the radial distribution function. The MC simulation method is used to study the mechanical characteristic quantities and the magnetic characteristic quantities of materials. The reason for this is that when we need to determine these quantities, we only need to pay attention to the values in the initial equilibrium and the latter without having to go into the nature of the problem. After determining the values at the next equilibria, we use the average field method to determine the values to look for. However, in the case for (of) determining the mechanical properties, we use (Change The to the) mentioned simulation methods in combination with the uniaxial strain-stretching method".

2. II) [e, f] "Simulation methods as considered as a third branch of scientific research". Grammatically: Simulation methods are considered a third branch of scientific research. Beside the grammatical error mentioned above, I hope the author will allow me to disagree with him on the statement that "simulation methods" to be "a third branch of scientific research." I propose to use "a pillar of the scientific methods" instead.

3. Abstract in Polish I): This "abstract" has probably been translated by "Google Translator" from the English version. The result of this operation is very funny. Perhaps the author doesn't know the sense of "Abstrackcyjny". Let see "Słownik Języka Polskiego, PWN". The word "abstrakcyjny" has several meanings: 1. «oderwany od rzeczywistości» 2. «niemożliwy do zrealizowania lub zrozumienia» 3. «zgodny z zasadami abstrakcjonizmu» 4. «uzyskany przez abstrahowanie». This means that "Abstrakcyjny (in Polish)" is not "Abstract (in English)", and therefore cannot be accepted. In Polish "Abstrakt" or "Streszczenie" are used.

3. II) The word "Amor" = "roman god of love, Cupid" appears twice in the "abstrakt",

has nothing to do with the state of materials.

4. page 2. Acknowledg(e)ments - (c) The sentence "...dedication during the past three years." is better modified to "...dedication over the last three years. Besides, there are many more mistakes of type d and a.

5. pp 3 - 4. Table of Contents (e) The table of contents should contain not only descriptions of first-, second-, and third-level headings but also their respective page numbers. (c) : Initial Principlal Method Ab initio is recommended to change by the "Ab initio method". The words "Initial Principal" can (fanny) be translated on "Początkujący Dyrektor = Novice Director".

(g): The headings contain "Effect of..." or "Influence of ..." are recommended to add "on...", since this is based on the languish structure: "Influence OF something ON Something/somebody. "

(c): "2D Structural Materials" is recommended to delete "Structural".

6. pp. 6 -10 - List of Figures (b, e, g). A lack of the coherence as presented in the "Table of Contents", e.g., a lack of dotted line after the headings. Even more importantly, the author should provide page numbers for the figures listed.

7. page 11. (e, g) "Table of Contents" occurs twice!

8, page 11 It is difficult for me to understand the idea that Table 1.1 is a table but similar diagram (Metropolis algorithm) is a Figure. 1.3.

(e): Table 1.2 appears twice on pages 40 and 42.

9. pp 12 - 14. Preamble: (d, e) , e.g. "Temperature Neel", "meta material", "metals material", "materialand", "Magnetic field on....biomedical applications", "Chapter I, II, III, IV".

10. Chapter 1 (pp. 15 - 66) [b, d, e, f]:

(10. 1) I must point out that the presented PhD version contains a number of editorial mistakes that require solid correction. **All** mathematical formulae must be verified because the present state of formulae in the PhD thesis provides such material information in an unclear, unintelligible, ambiguous, or untimely manner.

(10. 2) Using punctuation marks, and printing worlds are voluntary. e.g.: "...[20, 21], and... " (page 17), "...with basic knowledge A paper..." (page 17), "...Theorem. Newton's second law." (page 34), "...surface effects), size effect..." (page 41), "...even through The influence of..." (page 56), "...[48] In addition..." (page 58), "...simple and easy We have studied..."

(page 64).

(10. 3) Other, more frequent, errors were noted regarding the edition. In Vietnamese: "oxit" (page 40), "và" (page 48), misapplying nouns: "Piple" (pape 20) (have to change to Pople), "Von" (page 20) (must be von), "Monte-Carlo" (pp. 21, 30, 32, 33) have to change to Monte Carlo, "Kenvin" (page 44) must be changed with "Kelvin", "Van der waals", "Van Der Waals" (Fig. 1.7, page 38) must be changed with: van der Waals, "Bozman's" (page 143) must be corrected with Boltzmann's, and using incorrect nouns: nano materail (page 39), meta material (pp. 40, 45), alloys materials, and "Gromac" (page 69).

(10.4) (pp 30-31) "1.3.3.3 Types of phase transitions...." It should be distinguished between "types of phase transitions" and "orders of phase transitions". In the Ehrenfest classification, we qualify first and second (or higher) orders transitions, but not Type 1 phase transitions, Type 2 phase transition.

11. Chapter 2. In addition to duplicated mistakes as before, a serious error appears in this chapter when the author introduces an unphysical basic concept. A few examples can be mentioned below:

(11.1) "...oxide materials are materials make up of two alloy components and they have a cubic structure..." (page 66). Please bring back one of the well-known superconducting oxides, YBa2Cu3O7 which undergoes a superconducting state below 93 K. The compound is formed by four elements, and crystallizes in an orthorhombic structure.

(11.2) (page 66) "When the structure of the material changes from metal, alloy, or oxide materials to nanomaterials, their microstructural properties are almost unchanged, but their properties have a big change, for example the shape from a cubic to a sphere". First of all, on the one hand, the "structure" (the ordered arrangement of atoms, ions, or molecules in a crystalline material) is a physical property. On the other hand, "metal, alloy, oxides, and nanomaterials" are a diverse class of materials in terms of physical properties. Therefore, one cannot make any comparison. Besides, spheres are not unit properties of nanomaterials, which can exist in different forms.

(11.3) (page 67) "Three-dimensional (3D) structural materials have the form of a cube, called metal materials if they contains 01 metal such as Cu, whereas alloy materials are materials made of 02 or more metals such as NiAu, CuAu, FeNiCo, the oxide material is made of 01 Si metal element (or 01 Fe metal component) with 01 O component for creating SiO2 and Fe2O3 oxide materials, and nanomaterials are made up of 02 metals as CuNi." It is an

inaccurate and imprecise definition. Please remember that hexagonal, tetragonal, trigonal, orthorhombic, and monoclinic structures are also observed in various metallic elements.

(11.4) (page 85) "Nanomaterials are spherical materials. Thanks to this feature, nanomaterials are used more flexibly in biomedical applications and refrigeration devices for bonding with other materials such as thin films, DNA or protein chains etc." It is a wrong statement because nanoparticles include nanotubes and nanowires with various shapes, such as helices, zigzags, belts, nanowires, etc. Small morphologies exhibit spherical, oval, cubic, prismatic, helical, or pillar shapes. Importantly, the applications of nanomaterials are mainly due to their huge surface energies.

(11.5) (page 95) "Low temperature belongs to the area with temperature (T), T $<$ 273 K. So why call this region low temperature? (This question is grammatically incorrect) By converting the temperature from 0 °C to K we have 1 °C = 273 K. According to such calculation, the temperature region $<$ 273 K corresponds to the negative temperature region or the so-called low-temperature region or the temperature zone of liquefied gases. The temperature of liquefied gas í negative such as helium 4.22 K (-268.78 °C), nitrogen 70 K (-203 °C), argon 83.8058 K (-189.1942 °C), oxygen 90K (-183 °C), carbon 194.5 K (-78.5 °C)." In my opinion, the definition given by the author is too voluntary and not scientific. As a physicist, the author should know the relationship between temperature scales, i.e., between Fahrenheit, Kelvin, and Celsius scales. So, for the convention 0 °C = 273.15 K at ambient pressure (or taking 273.16 K as the triple point of VSMOW), the author will have 1 °C = 274.15 K (or 274.16 K). Next, the author wrongly equates "the temperature region $<$ 273 K corresponds to the negative temperature region or the so-called low-temperature region or the temperature zone of liquefied gases". In physics, the concept of temperature is defined as the average kinetic energy per molecule in a substance. Namely, the term low temperature means a low value of the kinetic energy, and likewise, high temperature means a high value of the kinetic energy of considered molecules or atoms. Therefore, there is no definitive point that divides out into two temperature ranges, as the author established. Nonetheless, the term "low temperatures" is assumed contractually to those lower than the boiling temperature of the air.

(11.6) (page 99) "...we choose the temperature T = 70 K to study, the cause of this selection because is that this is the temperature concentration of liquefied petroleum gas N2 ....". That is untrue. First, there is no concept " temperature concentration". Secondly, N2

gas is relatively inert and is not flammable. Normally, pure liquid nitrogen is achieved by distilling it from liquid air.

(11.7) (page 105) "...the link Fe-Fe, link Fe-O, and link O-O, average coordination numbers and link angles are shown in Figure 2.17, Table 2.5, and Table 2.6." Table 2.5 gives microstructural information on Cu1-xNix. Table 2.6 does not exist.

12 (Chapter 3) In a typical doctoral thesis, the author should present data on several chapters based on investigation, along with analysis and interpretation of the data. Unfortunately, I have seen only a presentation of data (taken from a published paper) without deep knowledge, thorough analysis and convincing interpretation from the physical point of view. In addition the author introduced several questioned concepts. There are a few of them:

(12.1)"the Curie temperature (T_{Ntot})", "Neel phase transition temperature (T_N) ", "synthesized Neel transition temperature T_{Ntot}", "phase Neel's magnetism transition temperature (T_N)". "T_{NzE}", "T_{Nz}": My question is: *what is the meaning of different symbols* $T_{N...}$?

(12.2)"M", "M_{zE}", "$M_{zEdward}$, "M_{tot}", "M_z": *Is the orbital angular momentum L taken into account for Mtot*?

(12.3) "total entropy S_{tot}", "synthetic etropy (page 145) and "synthesis entropy" S_{tot}": *Are "total entropy", "synthetic etropy" and "synthesis" entropy the same thing? Does "Stot" involve strain, lattice, and magnetic entropies*?

(12.4) From a fundamental point of view, the laws of classical thermodynamics suggest that the entropy of any real matter at a temperature larger than 0 K always has a value larger than 0. So, please explain *the physics underlying negative values of entropy presented in the thesis.*

(12.5) In physics, physical quantities (presented in italic) should be given by their values and their units or mathematical constants, and labels (are roman). In this chapter, magnetic moment and entropy are given without units. Please addendum. In addition, the author is still dubious in concepts of some physical quantities. "KPa" (page 125), magnetic field strength (Oe, A/m) but not in (T) (page 148) because T is the unit for magnetic induction.

(12.6) (page 151) "The intersection point of these two curves intersects at one point called the Neel phase transition temperature (T_N) of the material". This definition does not convince me in any way. Usually, the T_N value is related to the cohesive and exchange energies. In academic literature, there exist numerous theories for itinerant, localized, mixed

magnetism systems and also the models taken into account dimensions, various magnetic interactions and magnetic couplings. I strongly recommend that the author spend the necessary time on magnetism's fundamentals before presenting nonphysical interpretations.

(12.7) (page 143). "The cause of the appearance of the Neel transition temperature is due to the change in the state of Spin, in which, the state of Spin is the state in which the Spin rotates around itself." In fact, the magnetism originates from the spin and orbital magnetic moments of electron, but magnetic orderings (including ferromagnetic, ferrimagnetic and antiferromagnetic...arrangements) depend on the exchange interactions, spin-orbit couplings..itc... So the reason due to spin rotation alone is not sufficient for magnetic ordering. Please remember that in a paramagnetic state, each electron does rotate its spin, but there is no magnetic ordering.

(12.8) (page 149) "If the material has a Neel transition temperature, the size of the material must be small." This is the completely wrong statement.

(12.9) (page 149) "The cause of the change in the Neel TN phase transition temperature value is that when the external magnetic field strength B increases, the Spins rotate in the forward direction of the magnetic field and rotate very strongly with the external magnetic field, leading to the increase of Neel transition temperature." This is the wrong interpretation. Please take into account exchange interactions, magnetic correlations,

(12.10) (page 156) Why page 156 numbering is double quote?

13 (List of published articles, Articles not used in the thesis, References). My opinion is that the edition of this part is very sloppy.

(13.1) There is a lack of several references, e.g. nr. 158, 159, and 173.

(13.2) The citation format for all references (names, surnames of authors, and journal names) must be given in a uniform manner.

(12.3) Given DOI information is not required in a PhD thesis, but I think that it is better to give DOI information in the Bibliography.

II. SCIENTIFIC VALUE OF THE THESIS: ORIGINALITY, METHODS OF RESEARCH, BACKGROUND, AND SCIENTIFIC QUALITY

A. Originality

To explore the concept of originality in the PhD thesis, I will take into account the following points: objectives, background based on a review of published literature, techniques of research, discussion, and conclusion. The presentation of objectives and goals is a very important part of a PhD thesis. The author must identify, formulate, and articulate his own individual contributions to knowledge. In truth, the author avows that "The aim of the thesis: study the microstructural, mechanical and magnetic properties of some nanosystems by simulation method, namely: -Studying the microstructural characteristics, phase transition and crystallization of meta material Cu, alloys material NiAu, CuAu, FeNiCo, nanoparticle material CuNi and oxide materials SiO2, Fe2O3. -Study on the mechanical properties of epoxy thin films and magnetic properties of Fe2O3 thin films." In my opinion, the author must first consider the question: *What is the physics problem the author would like to solve?* **This question is just the aim of the thesis, and next step: how to do it? will be the subjective of the PhD study. Answers to these questions will be the result of the PhD candidate's realization.** At present, my opinion is that the author has only a plan to follow but not the aim or subjective aspects for the thesis.

Further, in order to look for "originality" in the PhD research, I had to search new ideas from the author, so I spent some time reading the literature cited in the thesis and comparing it to the results obtained by the author and his co-workers. Finally, I found that the results presented in the thesis have no breakthrough level and are not new enough to state "ORIGINALITY". Likewise, as the author admitted several times that their results are consistent with previously published data.

B. Methods of research

The author presented PhD thesis based on 11 own publications, in which only one work [nr 10] applies Monte Carlo simulations (MCS), three works utilize DFT [nr 5, 7, 9], and seven ones [6, 8, 11, 12, 14, 15, and 17] use Molecular dynamics (MD). However, the author

describes in quite detail MCS (pp. 20 - 32) and MD (pp. 32 - 62) only, but the description of DFT was practically neglected. Critical remarks, in addition to the lack of proportionality in the description of calculation methods mentioned above, include several pieces of lacking information *(i) What is the hardware and software access control? (ii) What is the reliability of calculated data compared to those from other software codes? (iii) How did the author choose the time step size, number of time steps, and maximum iteration? (iv) How energy, inter-atomic potentials and exchange interactions for magnetic atoms have been considered? (v) How the aggregation effects of Cu, iron oxide, etc. on their properties were studied?*

C. Background

A review of relevant, published literature relating to the originality of the author is an important point in the PhD thesis. Because the author has an opportunity to demonstrate his knowledge of how and in what manner, his studies yield a meaningful contribution to the common sciences. Moreover, the readers, by comparing the literature and presented results, can reach a conclusion on the originality of the thesis. Unfortunately, the candidate missed this opportunity. Numerous references have not been taken into account, or some references have been cited incorrectly.

I have really been disappointed with presentation of the candidate. I feel that the candidate has a gap in his basic scientific background. In the section "Presentation of the thesis" I have a list of a couple of the shortcomings. In a consequence, I strongly recommend the candidate improve his knowledge of magnetism and thermodynamics.

By the way, the Ehrenfest classification has proven to be useful for the classification of the first observed phase transitions such as the magnetic transitions, and the solid/liquid/gas ones. However, this classification is not powerful enough to account for more complicated transitions such as the superconducting, spin-glass, or topological phase transitions which show more subtle features (non-trivial behaviour of correlation length, phase stiffness, robust ground state degeneracy...), hence as the Physics PhD candidate the author is required to discuss new classification methods, in more deeper than that shown in page 31.

D. Scientific quality

It should be noted that as many as 25 papers based on the candidate's and co-workers research have been published during the candidate's 3-year PhD realization. This merely outlines that his scientific activity is sufficient to show that the doctoral candidate is ready for defence and evaluation by the appropriate scientific committee. Overall, the dissertation of Msc. Dung Nguyen Trong represents an important scientific contribution to the understanding of the physical properties of materials. However, after submitting statements from each co-worker about their contribution and allowing the use of the materials for the Ph.D. defence.

III. FORMAL EVALUATION

According to § 5 act 2. from January 19, 2018 "Ordinance MINISTER OF SCIENCE AND HIGHER EDUCATION "on the detailed procedure and conditions for conducting activities in the doctoral procedure," I must look for statements of the co-authors of the works forming the consent to the use of publication data for the purposes of conducting the doctoral dissertation and specifying the individual contribution of each of them to the creation of the publication. At the present, I must state that the absence of demanding statements means that the formal issue does not meet the criteria pursuant to the above-mentioned art for a dissertation defence.

IV. COMMENTS, QUESTIONS, AND DISCUSSION POINTS

In a corrected version of the PhD thesis, the author is asked to consider the issues raised above. Moreover, I propose to include: (i) Abstract, (ii) Streszczenie , (iii) The contents, (iv) A list of abbreviations, (v) A list of symbols, (vi) A list of figures, and (vii) A list of tables. Except for (iv) - A list of abbreviations, the other parts iii - vii must include page numbering.

However, the weakest point in the thesis is vague physics underlying method of determining Ne'el temperature for Fe_2O_3 films, therefore, the results presented in the dissertation do raise significant substantive concerns. In a consequence, there are two compelling questions that the author is asked to address: (i) *please present scientific justification of the method,*

(ii) what is the reliability of the data compared to the results of other methods e.g. mean field approximation, the random phase approximation, DFT calculations?

Further, in order to confirm the reliability of negative entropy values, the author is asked to *give literature examples and propose experimental methods to measure them.*

V. FINAL CONCLUSIONS

The doctoral dissertation submitted for evaluation based on the scientific activities of the candidate involves numerous contributions to the development of materials science. Therefore, the thesis may be worthy of defence. However, the written version of the PhD thesis has major shortcomings that should be corrected before it can be defended.

I am appealing to the Doctoral Committee appointed by the Senate of the Senate of the Zielona Góra University to allow MSc. Dung Nguyen Trong to correct his doctoral thesis and be admitted to the next stages of the doctoral process after submitting a corrected version of the thesis.

Rozprawa doktorska przedstawiona do oceny na podstawie działalności naukowej kandydata wnosi duży wkład w rozwój inżynierii materiałowej. Dlatego rozprawa ta może zasługiwać na obronę. Jednak, że pisemna wersja pracy doktorskiej ma istotne braki, które należy poprawić zanim będzie można ją obronić.

Zwracam się do Komisji Doktorskiej powołanej przez Senat Uniwersytetu Zielonogórskiego o umożliwienie mgr Dung Nguyen Trong poprawienia pracy doktorskiej i dopuszczenie do kolejnych etapów przewodu doktorskiego po dostarczaniu poprawionej wersji pracy.