Jury Member Report – Doctor of Philosophy thesis.

Name of Candidate: ZahedAllahyari

PhD Program: Materials Science and Engineering

Title of Thesis: Coevolutionary Search for Materials with Optimal Properties in the Space of Binary Systems

Supervisor: Prof.ArtemOganov

Date of Thesis Defense:6 April 2020

Name of the Reviewer:

Dr. Pierre Villars

I confirm the absence of any conflict of interest I have absolutely no conflict of interest. (Alternatively, Reviewer can formulate a possible conflict)	**Signature:** **Date: 4-3-2020**

The purpose of this report is to obtain an independent review from the members of PhD defense Jury before the thesis defense. The members of PhD defense Jury are asked to submit signed copy of the reportat least 30 days prior the thesis defense. The Reviewers are asked to bring a copy of the completed report to the thesis defense and to discuss the contents of each report with each other before the thesis defense.

If the reviewers have any queries about the thesis which they wish to raise in advance, please contact the Chair of the Jury.

Reviewer's Report

Reviewers report should contain the following items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.
- The relevance of the topic of dissertation work to its actual content
- The relevance of the methods used in the dissertation
- The scientific significance of the results obtained and their compliance with the international level and current state of the art
- The relevance of the obtained results to applications (if applicable)
- The quality of publications

Reviewers comments to below given items:

- Brief evaluation of the thesis quality and overall structure of the dissertation.

The overall structure of the thesis is well structured and the work is clearly explained. I consider the thesis as very good, and in context of its originality it is outstanding.

- The relevance of the topic of dissertation work to its actual content

The content of the thesis focuses clearly toward the target of this research work, and he found a practical solution to this target.

- The relevance of the methods used in the dissertation

The newly described 'Co-evolutionary algorithm combining the concept of evolutionary methodology USPEX (crystal structure prediction) with the multi-objective optimization method and the chemical area Mendelevian' applied to different target physical properties in parallel with minimal enthalpy above the convex hull are new and unique.

- The scientific significance of the results obtained and their compliance with the international level and current state of the art

This research work will influence international research in this research area, as it is showing a new way of materials discovery. In combination with experimental data from the world literature, experimental and simulation work will enhance each other's drastically. With time the 'trial-error approach' will become history in materials science.

- The relevance of the obtained results to applications (if applicable)

As this work centers on physical properties such as hardness, enthalpy of formation, etc. it has great practical impact. All practical applications focus on one or more optimized physical properties; this methodology can, in principle, be applied to any such practical problems. An important next step will be to extend it from binaries to ternaries (multinaries).

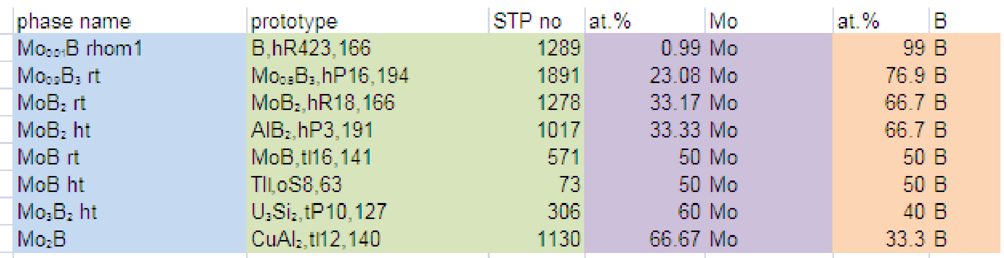
- The quality of publications

The quality of the thesis is outstanding.

The summary of issues to be addressed before/during the thesis defense:

1) Why did you select PAULING's electronegativity (clearly by Linus Pauling semi-empirically derived its reactivity behavior to other chemical elements), and not e.g. from Martynov-Batsanov's electronegativity, which is derived from its ionization energies (which is much more atomistic (fundamental))?
2) Why did you derive yourself new atomic radii set, and did not use e.g. Zunger's pseudo-potential radii set (also independent from ionic, covalent, metallic bonding, ...)? Did you use for your own derived radii as 'hypothetical' structure for all elements either cP1 (Po,cP1,221), or cI2 (W,cI2,229), or cF4 (Cu,cF4,225)? In case you used not the same prototype for all chemical elements, which modification did you choose, as most chemical elements have several modifications (depending on T, p, etc.)?
3) In your coevolutionary methodology for the search for hard and super-hard materials you restraint yourself to maximum 12 atoms per unit cell. In the PAULING FILE (also Pearson Crystal Data) there exits the following numbers of prototypes with 12 or less atoms per unit cell: 1739 P, 166 I, 17 F, 75 R, 232 S (capital letter= Bravais type) results in 2'129 different prototypes compared with about 40'000 experimentally found prototypes (using STIDTY, SCOMPA for standardization of the crystallographic data) → about 5%. Is it possible that you will miss a significant number of hard + super-hard materials by this restrain? How many different binary low energy prototypes do you have in your 500'000 simulated structure containing database?
4) In chapter 6 you give for 64 different structures (represented by a two-dimensional projection together with the space group + formula of its compound, e.g. figure 26 (1) Cmcm-VB; For this case in the literature often used prototype classification is given as "TlI,oS8,63" (classification used in ICSD and PCD (Pearson's crystal data); not given in COD (as this is a compilation of openly available cif files)). Why don't you use this classification?
5) In your different shown MN(A) versus MN(B) maps (using the 5 different scales: AN, PN, MNp, MNm, USE) we see that depending on which physical property you focus none of the 5 different scales is a 'real' winner (e.g. USE is outstanding for Hv, PN is outstanding for atomization energy). This is nicely shown on the 4 examples you gave: Hardness Hv, magnetization, enthalpy of formation, and atomization potential. I believe here is still a big potential to improve the Mendelevian space (using now R + EN (PAULING), most likely by adding a third elemental property, or combination of them. How do you comment my observation?
6) The convex hull plots can either and/or be based on stable experimentally found phases (e.g. existing published crystallographic data + phase diagrams) or derived sole by simulations (containing either experimentally missed and/or already experimentally found phases). I observed quite some difference between your given 'convex hull diagrams' focusing on the experimentally determined crystallographic data + experimentally determined phase diagrams (see below and mpds.io (Materials Platform for Data Science)):

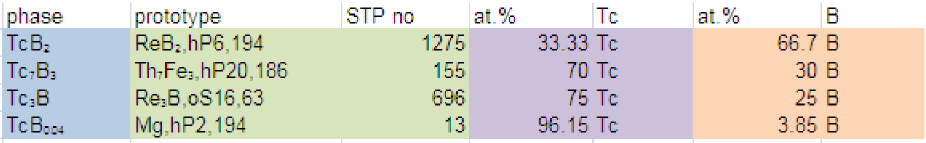
Mo-B



phase name	prototype	STP no	at.%	Mo	at.%	B
$Mo_{0.01}B$ rhom1	B,hR423,166	1289	0.99	Mo	99	B
$Mo_{0.9}B_3$ rt	$Mo_{0.8}B_3$,hP16,194	1891	23.08	Mo	76.9	B
MoB_2 rt	MoB_2,hR18,166	1278	33.17	Mo	66.7	B
MoB_2 ht	AlB_2,hP3,191	1017	33.33	Mo	66.7	B
MoB rt	MoB,tI16,141	571	50	Mo	50	B
MoB ht	TlI,oS8,63	73	50	Mo	50	B
Mo_3B_2 ht	U_3Si_2,tP10,127	306	60	Mo	40	B
Mo_2B	$CuAl_2$,tI12,140	1130	66.67	Mo	33.3	B

Here 1 phase overlaps. Your work shows MoB2, MoB3 (4 modifications), MoB4, MoB5, MoB8, Mo2B3 (2 modifications). 5(7) phases are experimentally known: Mo2B, Mo2B2, MoB (2 modifications), MoB2 (2 modifications), , Mo0.9B3 rt; all 5(7) phases are shown in its phase diagrams (determined by different research groups).

Tc-B

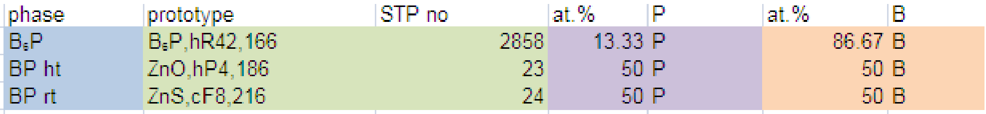


phase	prototype	STP no	at.%	Tc	at.%	B
TcB_2	ReB_2,hP6,194	1275	33.33	Tc	66.7	B
Tc_7B_3	Th_7Fe_3,hP20,186	155	70	Tc	30	B
Tc_3B	Re_3B,oS16,63	696	75	Tc	25	B
$TcB_{0.04}$	Mg,hP2,194	13	96.15	Tc	3.85	B

Here no phase overlaps. Your work shows TcB, TcB3 (2 modifications), TcB4 (3 modifications), TcB7, TcB8, Tc3B5. 3 phases are experimentally known: Tc3B, Tc7B2, TcB2; these 3 phases are shown in its phase diagrams (determined by 1 research group).

→ In your thesis you stress that there exists no experimental data, but there exists minimal 3 structure determinations, as well as one full phase diagram.

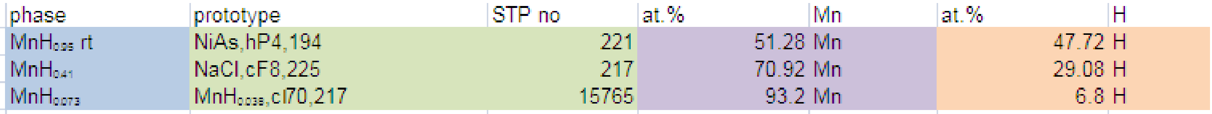
P-B



phase	prototype	STP no	at.%	P	at.%	B
B_6P	B_6P,hR42,166	2858	13.33	P	86.67	B
BP ht	ZnO,hP4,186	23	50	P	50	B
BP rt	ZnS,cF8,216	24	50	P	50	B

Here 2 phases overlap. Your work shows BP and B6P. 2 phases are experimentally known: BP (2 modifications) and B6P; no phase diagram has been published.

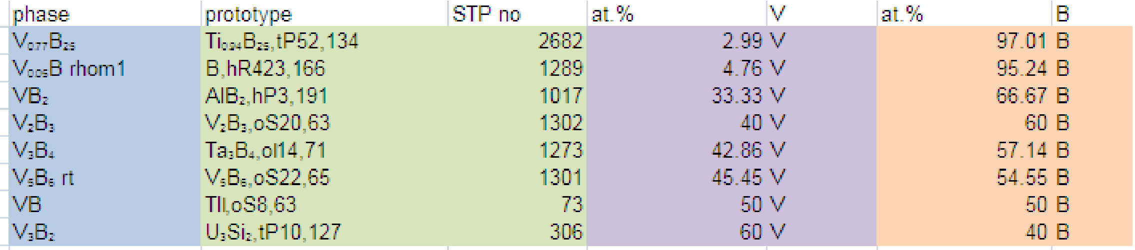
Mn-H



phase	prototype	STP no	at.%	Mn	at.%	H
$MnH_{0.95}$ rt	NiAs,hP4,194	221	51.28	Mn	47.72	H
$MnH_{0.41}$	NaCl,cF8,225	217	70.92	Mn	29.08	H
$MnH_{0.073}$	$MnH_{0.038}$,cI70,217	15765	93.2	Mn	6.8	H

Here 1 phase overlaps. Your work shows MnH (3 modifications), Mn3H2 (2 modifications), Mn4H3, Mn6H5. 3 phases are experimentally known: MnH0.95, MnH0.41, MnH0.073; only partial phase diagram has been published confirming the existence of MnH0.95 rt.

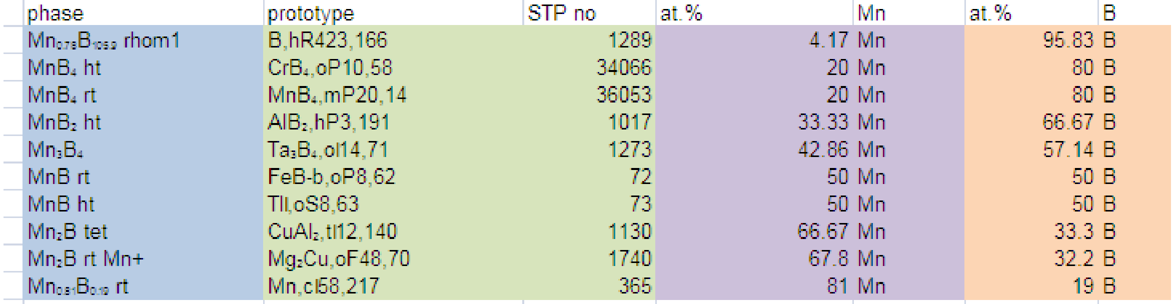
V-B



phase	prototype	STP no	at.%	V	at.%	B
$V_{0.77}B_{25}$	$Ti_{0.34}B_{25}$,tP52,134	2682	2.99	V	97.01	B
$V_{0.05}B$ rhom1	B,hR423,166	1289	4.76	V	95.24	B
VB_2	AlB_2,hP3,191	1017	33.33	V	66.67	B
V_2B_3	V_2B_3,oS20,63	1302	40	V	60	B
V_3B_4	Ta_3B_4,oI14,71	1273	42.86	V	57.14	B
V_5B_6 rt	V_5B_6,oS22,65	1301	45.45	V	54.55	B
VB	TlI,oS8,63	73	50	V	50	B
V_3B_2	U_3Si_2,tP10,127	306	60	V	40	B

Here 3 phases overlap. Your work shows VB, VB2, V3B4 (2 modifications) , VB5, VB7, VB12; 7 phases are experimentally known: V3B2, VB, V5B6 rt, V3B4, V2B3, VB2, V0.77B25; All phases, except V0.77B25, are shown in its phase diagrams (determined by several research groups).

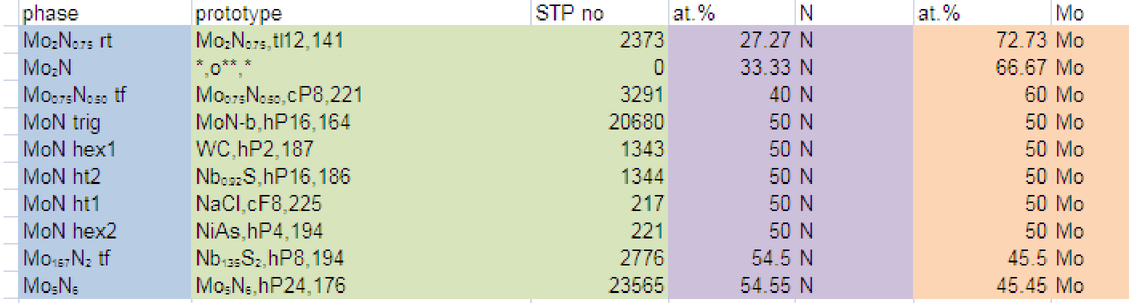
Mn-B



phase	prototype	STP no	at.%	Mn	at.%	B
$Mn_{0.78}B_{10.52}$ rhom1	B,hR423,166	1289	4.17	Mn	95.83	B
MnB_4 ht	CrB_4,oP10,58	34066	20	Mn	80	B
MnB_4 rt	MnB_4,mP20,14	36053	20	Mn	80	B
MnB_2 ht	AlB_2,hP3,191	1017	33.33	Mn	66.67	B
Mn_3B_4	Ta_3B_4,oI14,71	1273	42.86	Mn	57.14	B
MnB rt	FeB-b,oP8,62	72	50	Mn	50	B
MnB ht	TlI,oS8,63	73	50	Mn	50	B
Mn_2B tet	$CuAl_2$,tI12,140	1130	66.67	Mn	33.3	B
Mn_2B rt Mn+	Mg_2Cu,oF48,70	1740	67.8	Mn	32.2	B
$Mn_{0.81}B_{0.19}$ rt	Mn,cI58,217	365	81	Mn	19	B

Here 1 phase overlaps. Your work shows MnB3, MnB4 (3 modifications), MnB5, BMn13; 6(8) phases are experimentally known: Mn2B rt, Mn2B tet, MnB (2 modifications), Mn3B4, MnB2 ht, MnB4 (2 modifications); All phases, except MnB4 (rt or ht?), are shown in its phase diagrams (determined by several research groups).

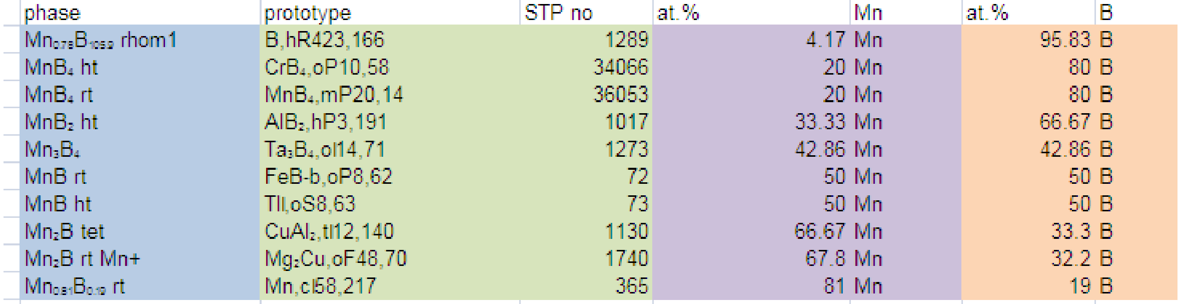
Mo-N



phase	prototype	STP no	at.%	N	at.%	Mo
$Mo_2N_{0.75}$ rt	$Mo_2N_{0.75}$,tI12,141	2373	27.27	N	72.73	Mo
Mo_2N	*,o**,*	0	33.33	N	66.67	Mo
$Mo_{0.75}N_{0.50}$ tf	$Mo_{0.75}N_{0.50}$,cP8,221	3291	40	N	60	Mo
MoN trig	MoN-b,hP16,164	20680	50	N	50	Mo
MoN hex1	WC,hP2,187	1343	50	N	50	Mo
MoN ht2	$Nb_{0.92}S$,hP16,186	1344	50	N	50	Mo
MoN ht1	NaCl,cF8,225	217	50	N	50	Mo
MoN hex2	NiAs,hP4,194	221	50	N	50	Mo
$Mo_{1.67}N_2$ tf	$Nb_{1.35}S_2$,hP8,194	2776	54.5	N	45.5	Mo
Mo_5N_6	Mo_5N_6,hP24,176	23565	54.55	N	45.45	Mo

Here 2 phases overlap. Your work shows MoN, MoN2, Mo2N, Mo3N2. 5(10) phases are experimentally known: Mo2N rt (=Mo2N0.75 rt), Mo2N ht, Mo0.75N0.50 tf, MoN (5 modifications), Mo1.67N2 tf (2 modifications). In its partial phase diagrams all phases, except Mo2N0.75 rt, are shown (determined by several research groups).

Fe-B



phase	prototype	STP no	at.%	Mn	at.%	B
$Mn_{0.78}B_{10.52}$ rhom1	B,hR423,166	1289	4.17	Mn	95.83	B
MnB_4 ht	CrB_4,oP10,58	34066	20	Mn	80	B
MnB_4 rt	MnB_4,mP20,14	36053	20	Mn	80	B
MnB_2 ht	AlB_2,hP3,191	1017	33.33	Mn	66.67	B
Mn_3B_4	Ta_3B_4,oI14,71	1273	42.86	Mn	42.86	B
MnB rt	FeB-b,oP8,62	72	50	Mn	50	B
MnB ht	TlI,oS8,63	73	50	Mn	50	B
Mn_2B tet	$CuAl_2$,tI12,140	1130	66.67	Mn	33.3	B
Mn_2B rt Mn+	Mg_2Cu,oF48,70	1740	67.8	Mn	32.2	B
$Mn_{0.81}B_{0.19}$ rt	Mn,cI58,217	365	81	Mn	19	B

Here 1 phase overlaps. Your work shows FeB3, FeB4 (3 modification), Fe2B11; 7(8) phases are experimentally known: Fe3B, Fe2B (2 modifications), FeB, FeB2, Fe2B7 ht-hp, FeB4 ht-hp, Fe0.8B25 ht-hp; In its phase diagrams only the following three phases are shown: Fe2B, FeB, FeB19 (= Fe0.66B25 ht-hp) (determined by several research groups).

7) As for the real existence of a predicted phase the enthalpy above the convex hull should be as low as possible. How does the above outlined situation influence your procedure? Do your convex hull plots (lowest values) include only phases being hard or super-hard materials?
8) You mention that in your 500’000 simulated binary database you included also ICSD entries, as well as COD entries. I recommend being very carefully to include COD entries (not ‘curated’, just open-access available cif files included). The ICSD covers in comparison to the PAULING FILE

(LPF) (mpds.io) only about 60% of the world literature. Here some LPF numbers: For 7’900 binary phases (under ambient conditions); 13’650 binary phases including ht, lt, hp, tf, stab, etc. crystallographic data available (in most cases multiple determinations by different authors). This leads to 2’217 binary systems with at least 1 phase having a binary prototype, + 780 binary systems without any phase having a binary prototype (→ non-formers, having at least one complete phase diagram determination); this means for almost 3’000 binary chemical systems experimental data have been published since 1900.
Provisional Recommendation
Yes *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*