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# Assessing the computational needs for DFT calculations on atomic-scale properties of lead alloys

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# Outline

- Motivation
- Computational details
- Discussions
- Conclusions

# Motivation

- Lead alloys used in lead-acid batteries contain 2-5 elements. Alongside Pb, they are also formed by a mixture of alloying elements in different amounts.
- Accurate computational description of the lead-bulk containing all impurities in the desired amounts is impossible.
- We thus investigate the interaction between each atom of impurity and the lead-bulk in terms of energies, forces, densities of states ...
  - even these simplified calculations are time- and resources-consuming
- We monitor the computational needs in order to calibrate the resources (time, number of processors, algorithms).

# Computational details

The computational code is SIESTA

- Use LCAO bases sets of DZP type and a LDA/CA (Ceperley-Adler) density functional; For the 5f orbitals of lead we used a single zeta orbital with a radial extent of 3 Bohr
- Use numeric atomic orbitals of Gaussian shape;
- Adapted for study of large systems.

We used two rules to optimize the material quality.

- The first one is to refer to the alloy stability which is maximized when the density of states at the Fermi level has a minimum;
- The second one is to follow the formation of alloys in which the forces acting on the impurity and the voltage induced in the elementary cell to be relatively homogeneous (i.e. comparable or equal to various types of impurities present in the alloy).

# The relevant properties as resulted from the ab-initio calculations include

- the electronic population of the impurity atom  $Q_I$ ,
- the electronic population on Pb atoms placed in the first coordination sphere of the impurity  $Q_0$ ,
- the maximum force exerted on the atom impurity by the lead matrix  $F_{max}$ ,
- the mechanical stress induced by the impurity in the lead super-cell  $S$
- the energy balance resulted by substituting one lead atom with an impurity one

$$\Delta E = E_{Pb-I} + \epsilon_{Pb} - (E_{Pb} + \epsilon_I)$$

Where

$E_{Pb-I}$  total energy for the impurity-containing super-cell

$\epsilon_{Pb}$  Pb energy of an isolated Pb atom in vacuum

$E_{Pb}$  energy of the lead super-cell (without impurities)

$\epsilon_I$  energy of the impurity atom isolated in vacuum.

# Lead bulk is generated as fcc, as follows:

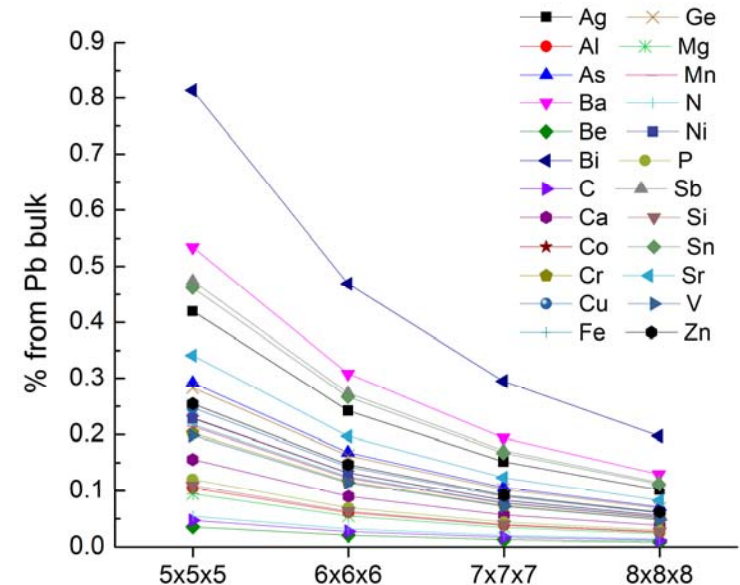
- Different dimensions (ie 5x5x5, 6x6x6, 7x7x7, 8x8x8) corresponding to different concentrations of impurities into lead alloy
- As alloying elements we considered the elements from group II (up to Ba), group VI (up to Sn), group VII (up to Bi), transition metals (V to Zn), Al and Ag.

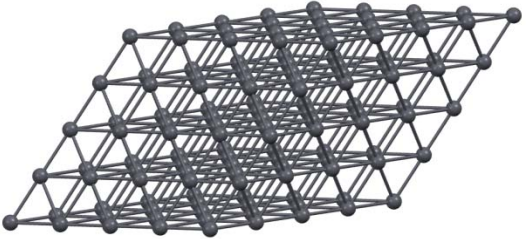
hydrogen 1 H 1.0079																	helium 2 He 4.0026						
lithium 3 Li 6.941	beryllium 4 Be 9.0122																	boron 5 B 10.811	carbon 6 C 12.011	nitrogen 7 N 14.007	oxygen 8 O 15.999	fluorine 9 F 18.998	neon 10 Ne 20.180
sodium 11 Na 22.990	magnesium 12 Mg 24.305																	aluminum 13 Al 26.982	silicon 14 Si 28.086	phosphorus 15 P 30.974	sulfur 16 S 32.065	chlorine 17 Cl 35.453	argon 18 Ar 39.948
potassium 19 K 39.098	calcium 20 Ca 40.078	scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	mandelbinder 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	seleonium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80						
rubidium 37 Rb 85.468	strontium 38 Sr 87.62	yttrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc 98	ruthenium 44 Ru 101.07	rhodium 45 Rh 101.07	paladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29						
cesium 55 Cs 132.91	barium 56 Ba 137.33	* 57-70	lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]					
francium 87 Fr [223]	radium 88 Ra [226]	* * 89-102	lawrencium 103 Lr [262]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [265]	meitnerium 109 Mt [268]	unnilium 110 Uun [271]	ununium 111 Uuu [272]	unbinium 112 Uub [277]	ununseptium 113 Uus [289]	ununoctium 114 Uuo [289]	ununoctium 115 Uuq [289]								

\* Lanthanide series

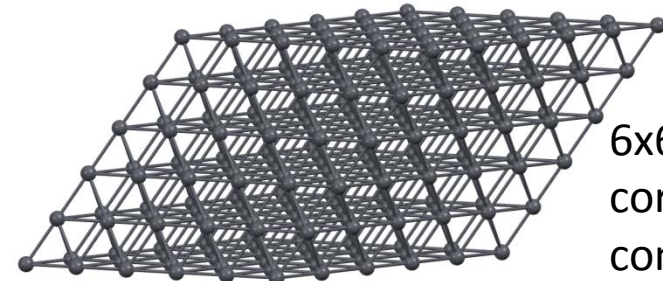
lanthanum 57 La 138.91	cerium 58 Ce 140.12	praseodymium 59 Pr 140.91	neodymium 60 Nd 144.24	promethium 61 Pm [145]	samarium 62 Sm 150.36	europium 63 Eu 151.96	gadolinium 64 Gd 157.25	terbium 65 Tb 158.93	dysprosium 66 Dy 162.50	holmium 67 Ho 164.93	erbium 68 Er 167.26	thulium 69 Tm 168.93	ytterbium 70 Yb 173.04
actinium 89 Ac [227]	thorium 90 Th 232.04	protactinium 91 Pa 231.04	uranium 92 U 238.03	neptunium 93 Np [237]	plutonium 94 Pu [244]	americium 95 Am [243]	curium 96 Cm [247]	berkelium 97 Bk [247]	californium 98 Cf [251]	einsteinium 99 Es [252]	fermium 100 Fm [257]	mendelevium 101 Md [258]	nobelium 102 No [259]

\*\* Actinide series

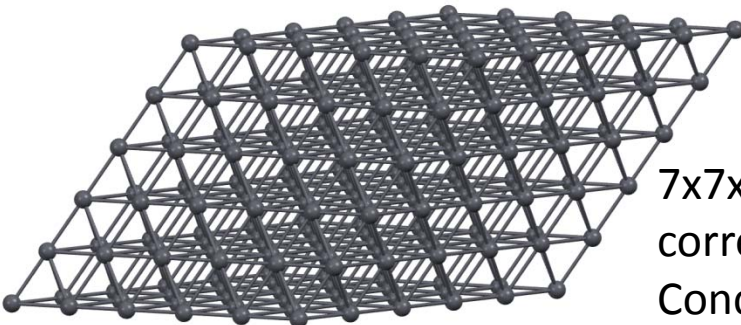




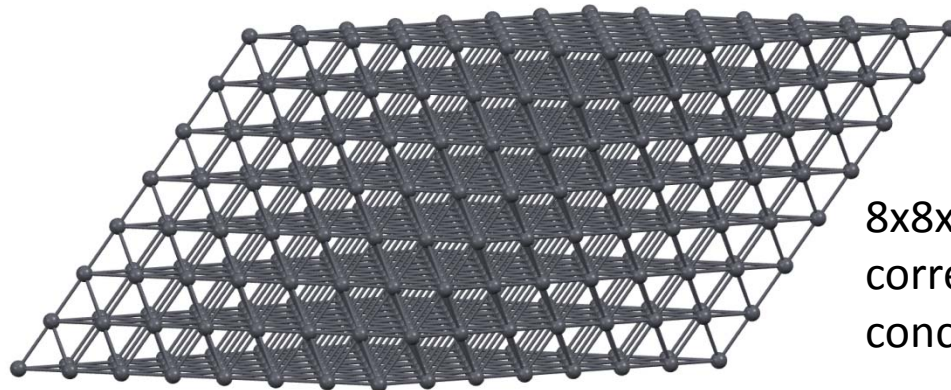
5x5x5  
corresponds to a  
concentration of 0.8 %



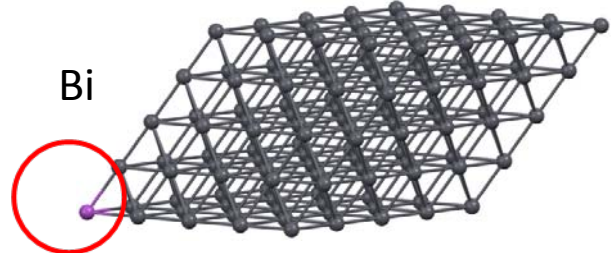
6x6x6  
corresponds to a  
concentration of 0.46 %



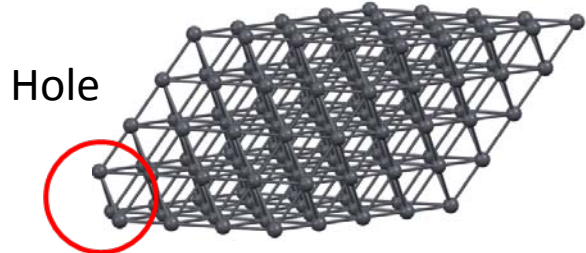
7x7x7  
corresponds to a  
Concentration of 0.29 %



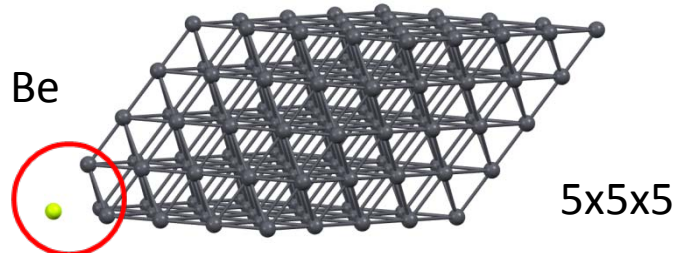
8x8x8  
corresponds to a  
concentration of 0.19 %



Bi



Hole



Be

5x5x5

# Scientific results look like

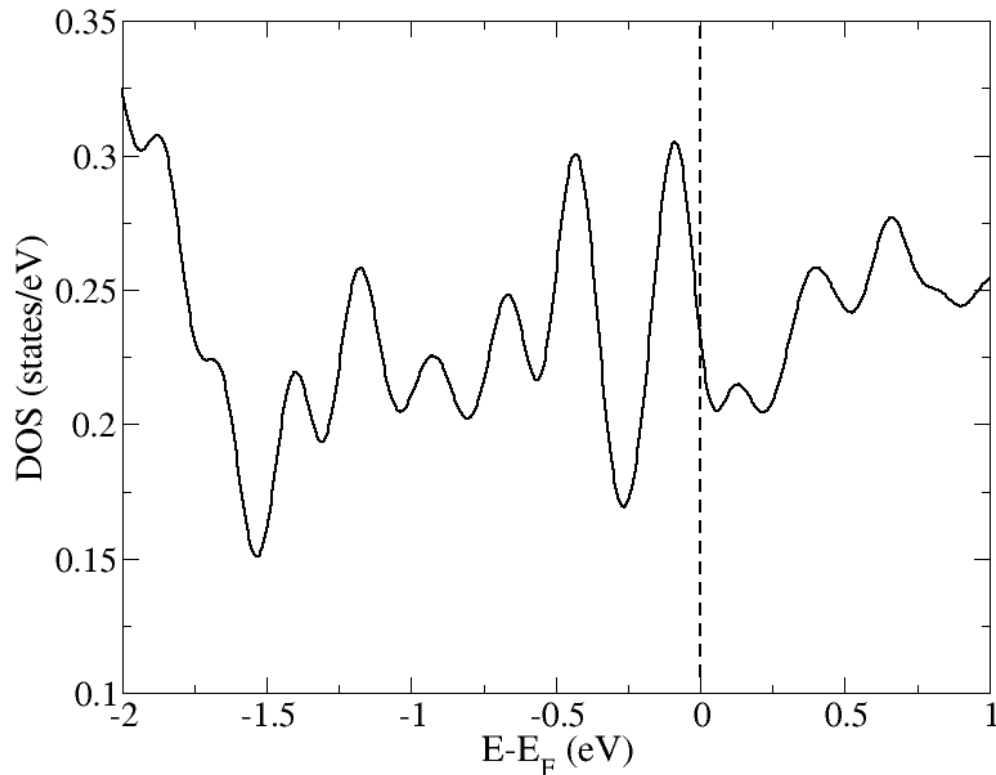
**TABLE 1.** Calculated values for concentration of impurities into the bulk lead of 0.46 % and 0.8 % . We denoted by Pb\* the model in which a structural defect was simulated by removing a Pb atom from the ideal matrix.

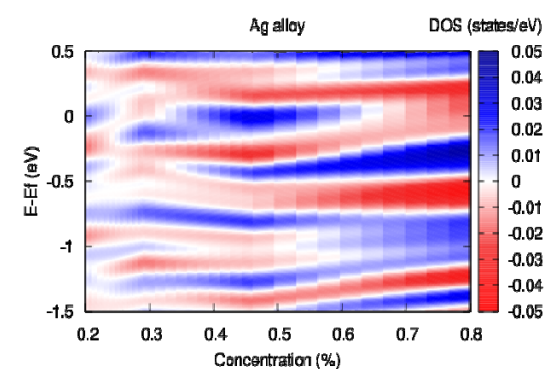
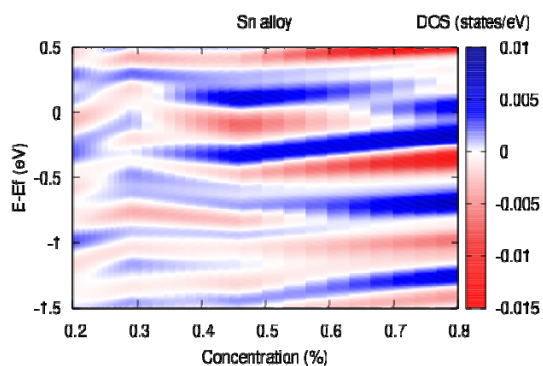
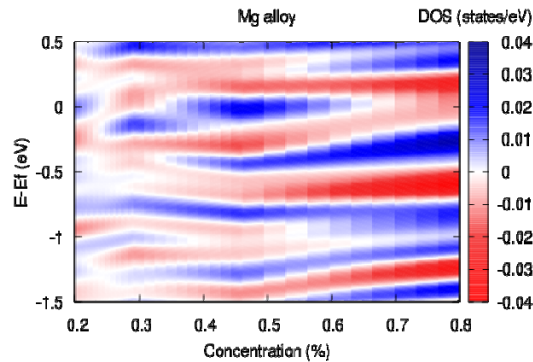
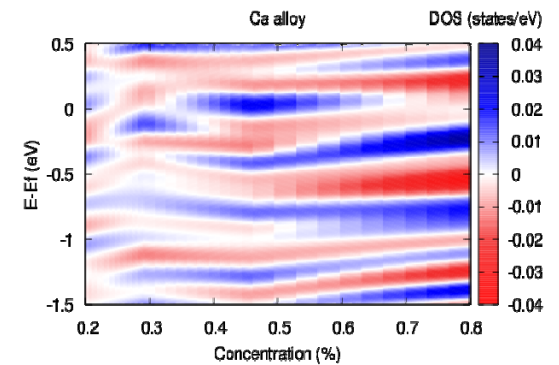
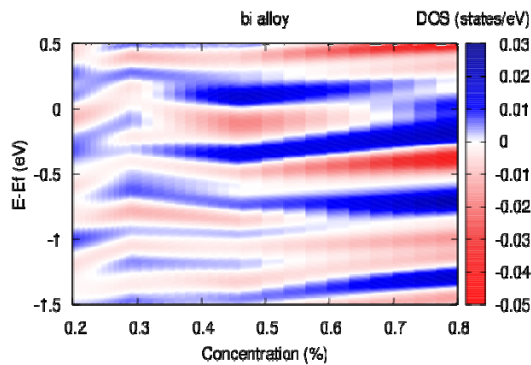
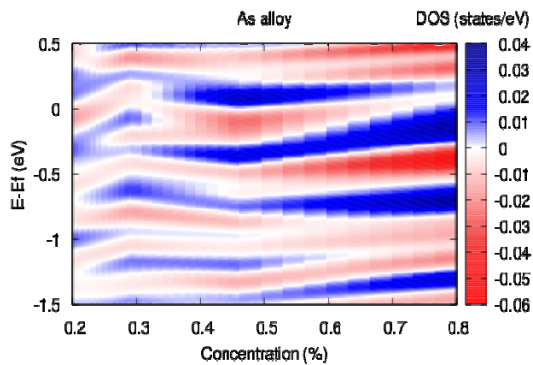
Atom	$Q_1$ [e]	$Q_1$ [e]	$Q_0$ [e]	$Q_0$ [e]	$F_{max}$ [ eV/Å]	$F_{max}$ [ eV/Å]	$S$ [eV/Å <sup>3</sup> ]	$S$ [eV/Å <sup>3</sup> ]	$\Delta E$ [eV]	$\Delta E$ [eV]
	0.46 %	0.80 %	0.46 %	0.80 %	0.46 %	0.80 %	0.46 %	0.80 %	0.46 %	0.80 %
Be	0.002	0.001	-0.024	-0.013	0.259	0.252	0.001	0.001	3.822	4.025
Mg	-0.007	-0.008	0.047	0.056	0.166	0.151	0.000	0.001	3.347	3.503
Ca	-0.012	-0.011	0.036	0.041	0.048	0.043	0.003	0.002	0.268	1.518
Sr	-0.013	-0.012	0.022	0.026	0.212	0.209	0.008	0.008	-3.308	-0.464
Ba	0.011	-0.009	-0.040	-0.035	0.478	0.480	0.011	0.010	-1.424	0.795
V	0.008	0.006	-0.163	-0.153	0.278	0.238	0.004	0.004	-2.393	-0.971
Cr	-0.014	-0.014	0.120	0.125	0.234	0.204	0.004	0.004	-0.624	0.736
Mn	-0.012	-0.013	0.110	0.118	0.162	0.145	0.003	0.004	-0.203	1.079
Fe	-0.011	-0.012	0.097	0.113	0.263	0.242	0.004	0.004	-1.244	0.084
Co	-0.004	-0.005	0.017	0.031	0.280	0.253	0.004	0.004	-1.610	-0.251
Ni	0.007	0.003	-0.112	-0.063	0.361	0.294	0.004	0.005	-1.707	-0.379
Cu	-0.007	-0.008	0.078	0.087	0.300	0.275	0.004	0.004	-1.488	-0.066
Zn	-0.004	-0.005	0.055	0.065	0.213	0.204	0.004	0.004	0.460	1.820
C	0.019	0.019	-0.203	-0.197	0.400	0.379	0.001	0.002	1.386	1.401
Si	0.009	0.008	-0.087	-0.084	0.332	0.313	0.001	0.001	-0.625	-0.641
Ge	0.009	0.009	-0.100	-0.098	0.303	0.285	0.001	0.001	-0.598	-0.629
Sn	0.008	0.008	-0.085	-0.083	0.101	0.083	0.000	0.000	-0.322	-0.354
Pb	0.000	0.000	-0.000	-0.000	0.000	0.000	0.000	0.000	0.014	-0.002
N	0.030	0.029	-0.309	-0.298	0.386	0.356	0.001	0.002	1.353	1.447
P	0.021	0.020	-0.190	-0.176	0.344	0.322	0.001	0.002	-0.368	-0.415
As	0.017	0.016	-0.151	-0.137	0.308	0.285	0.001	0.001	-0.502	-0.596
Sb	0.012	0.011	-0.099	-0.089	0.180	0.158	0.000	0.001	-0.729	-0.822
Bi	0.010	0.009	-0.077	-0.068	0.075	0.051	0.000	0.000	-0.675	-0.784
Ag	-0.007	-0.008	0.064	0.072	0.221	0.193	0.004	0.004	-1.717	-0.342
Al	0.006	0.006	-0.081	-0.080	0.228	0.220	0.003	0.004	-2.617	-1.351
Pb*	-0.000	-0.001	-0.002	-0.002	0.129	0.097	0.001	0.001	6.500	6.813



# Model for improvement of properties

- Free electron model: stability of an alloy is ensured when density of states has a minimum at Fermi level
- DOS of lead:



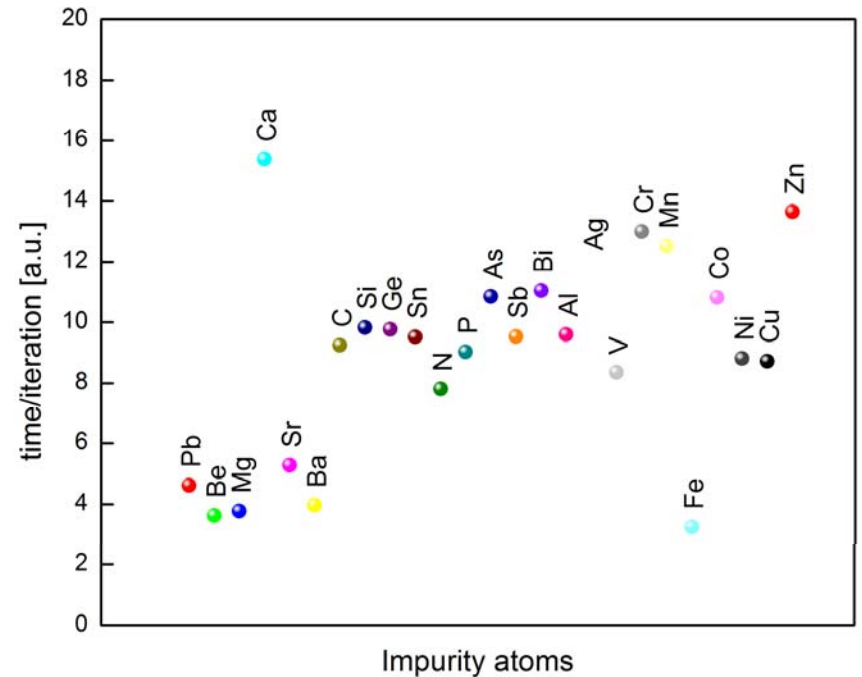
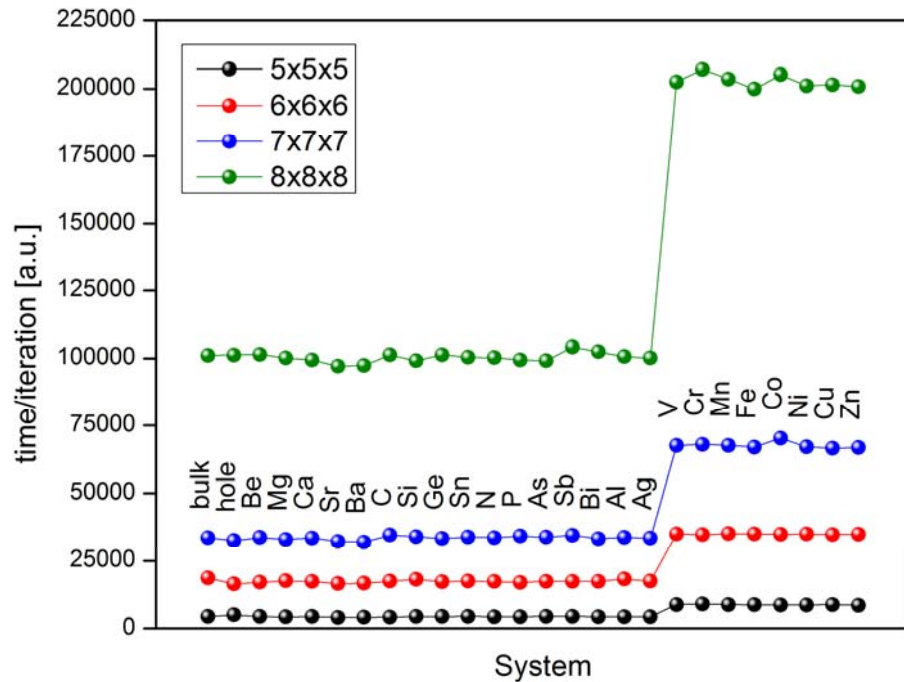


Variation of the density of states,  $DOS_{PB}(E) - DOS_{ALLOY}(E)$  on the concentration of some alloying elements.

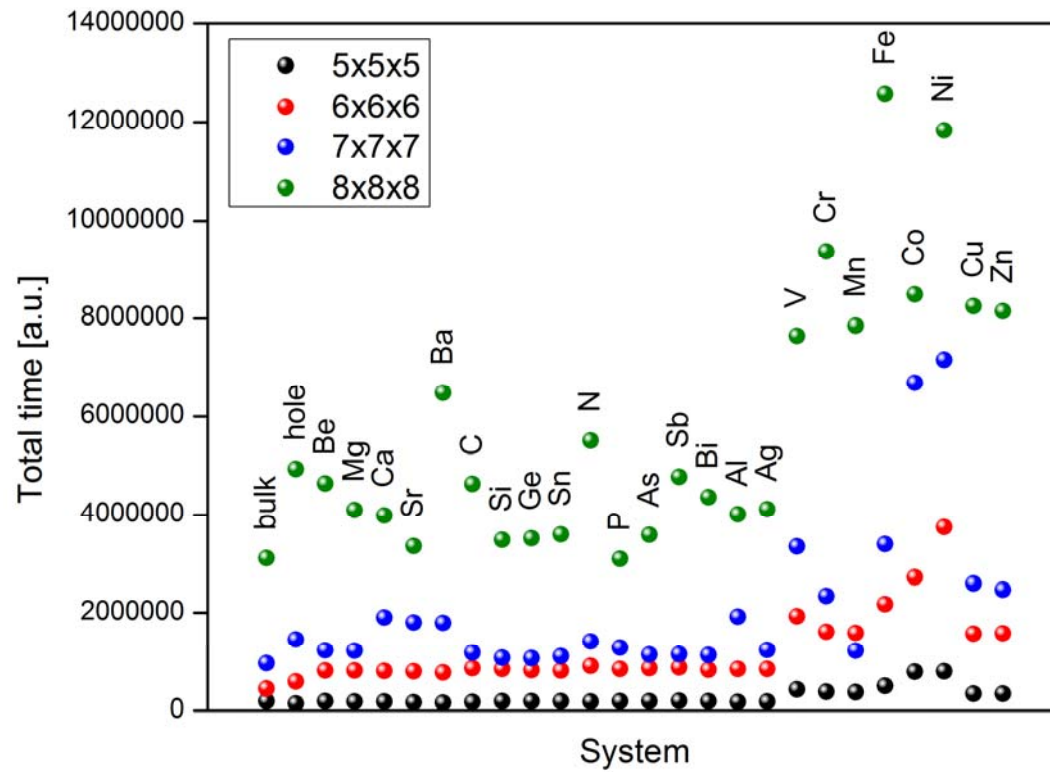
# Conclusion:

- We provide a database suited for further experimental search for new alloying elements and concentrations
- Density of states analysis allow us to propose predictions over the future tests.
- The data for the traditional alloying elements (Ca, Sn) are in full agreement with the common experience in the field

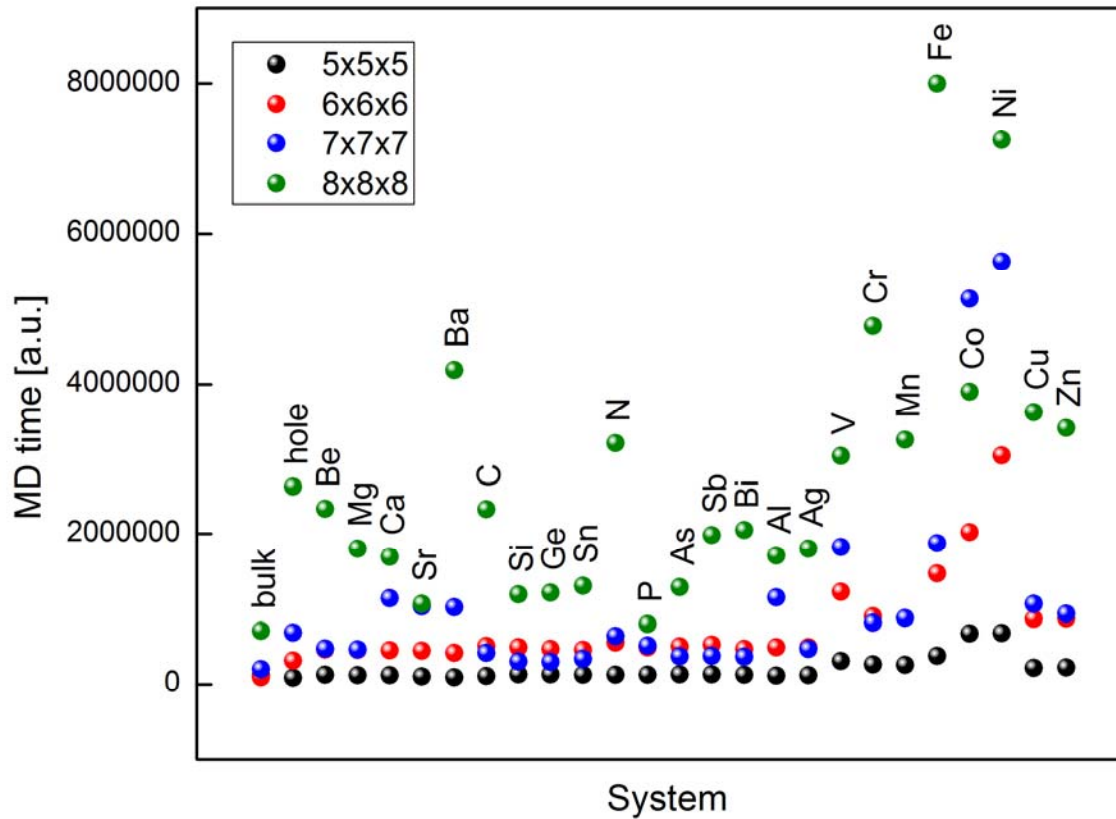
# Computational resources analysis - time per iteration



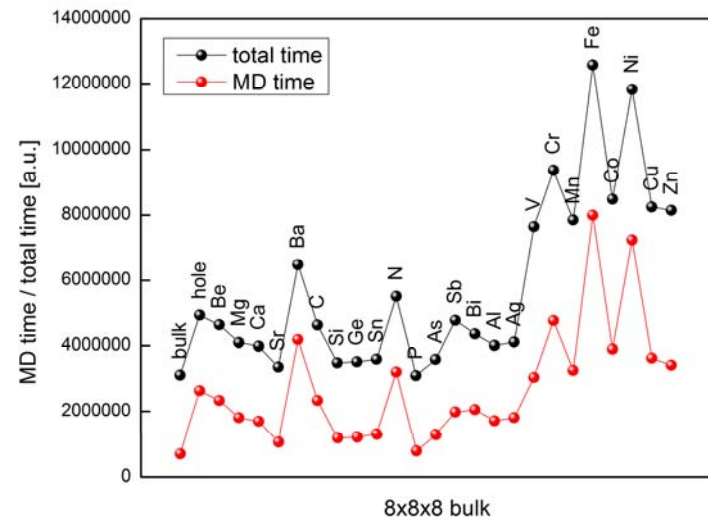
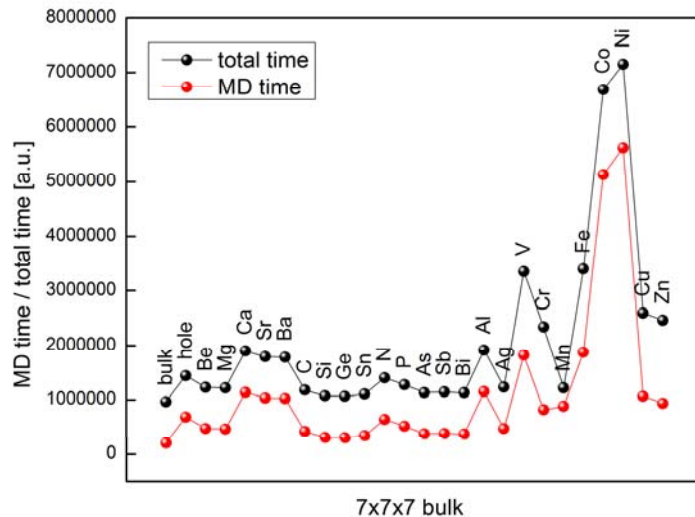
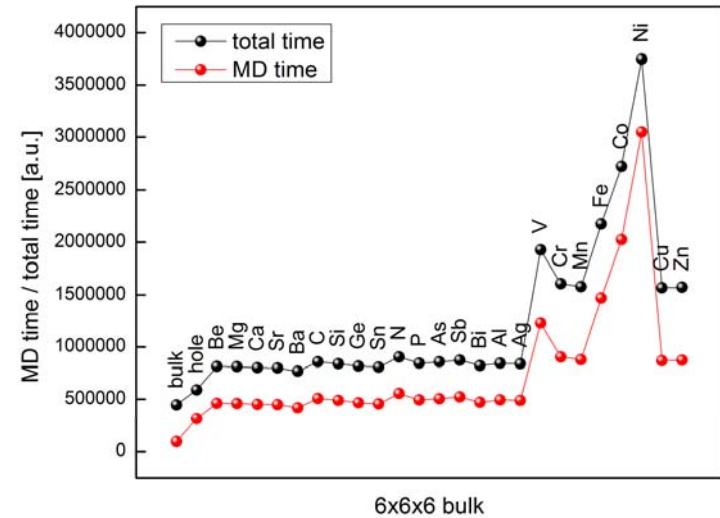
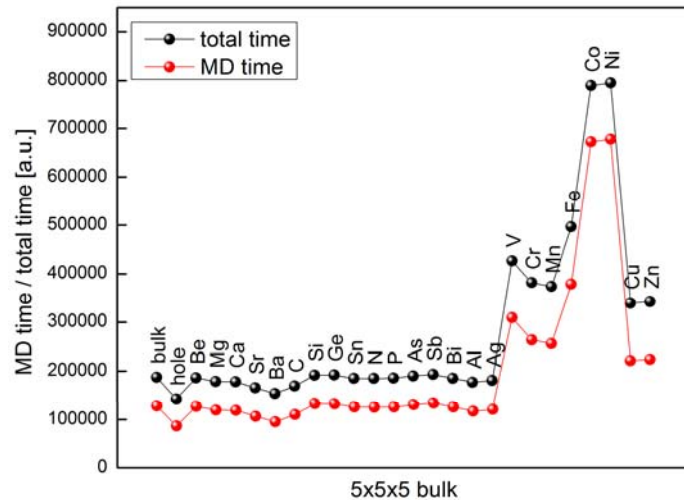
# Computational resources analysis - total time



# Computational resources analysis - time per MD iteration



# Computational resources analysis - MD time per total time



# Conclusion

- Strong nonlinear dependence of computing time to the supercell size – electronic structure part
- Spin polarization is the most important feature in terms of time consuming
- Remarkably, there is practically no dependence of computing time on the chemical element used in the alloy
- The scaling of calculation for dynamical properties is much better than the one for electronic structure