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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 $Q_1$,
- the electronic population on *P*b 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

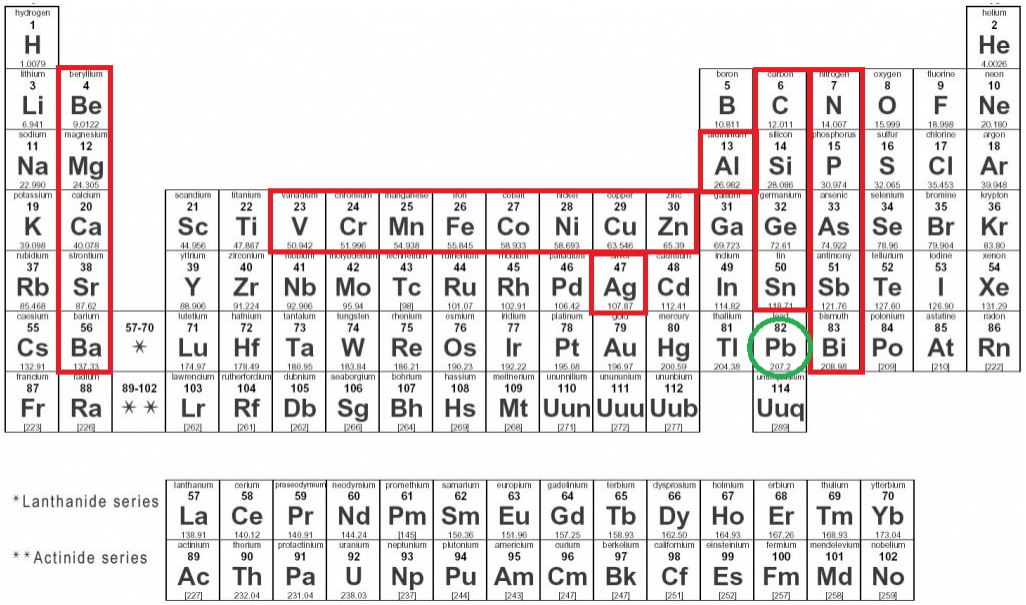
$\epsilon_{Pb}$ Pb energy of an isolated Pb atom in vacuum

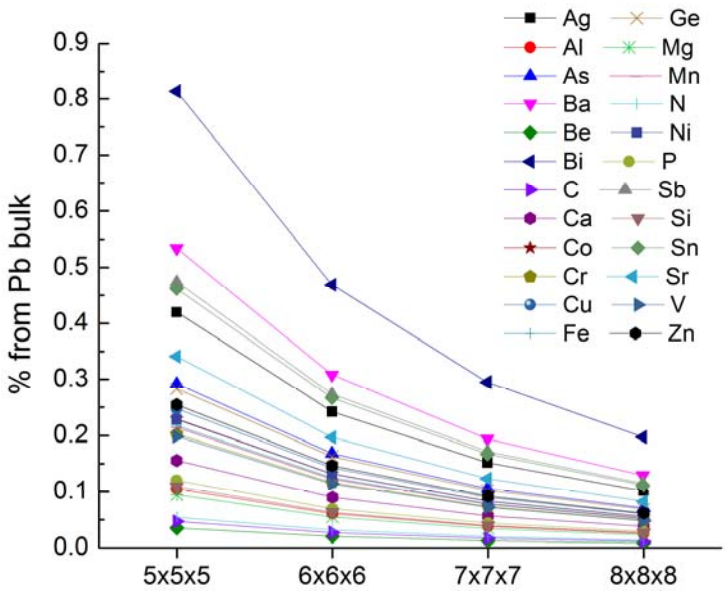
$E_{Pb}$ energy of the lead super-cell (without impurities)

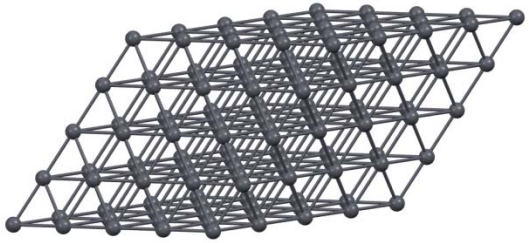
$\epsilon_I$ energy of the impurity atom isolated in vacuum.

# Lead bulk is generated as fcc, as follows:

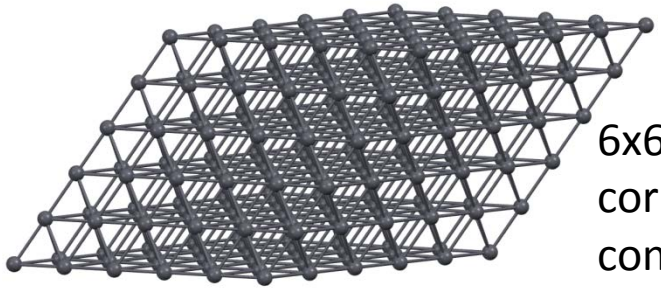
- Different dimensions (ie 5x5x5, 6x6x6, 7x7x7, 8x8x8) corresponding to different concentrations of impurities into lead alloy
- As alloying elements we considered the elements from group II (up to Ba), group VI (up to Sn), group VII (up to Bi), transition metals (V to Zn), Al and Ag.



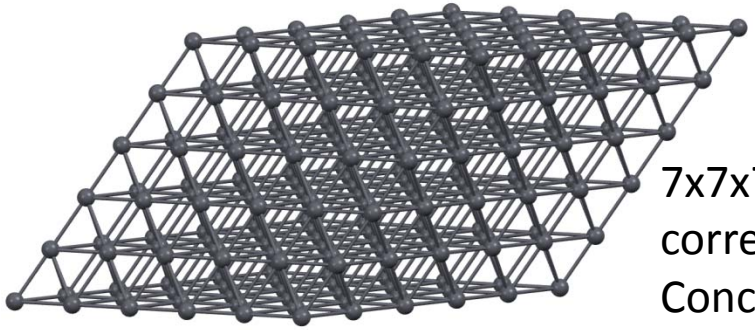





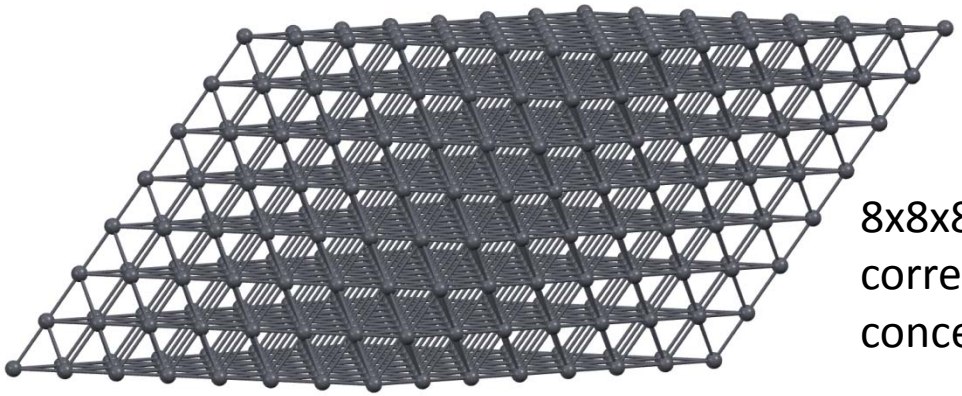
5x5x5
corresponds to a
concentration of 0.8 %



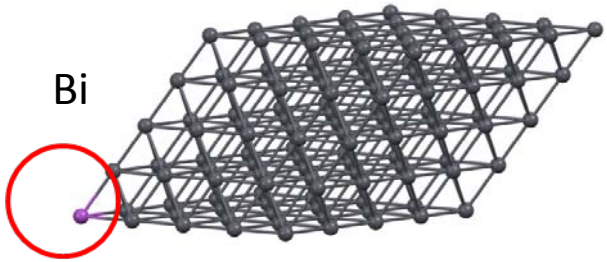
6x6x6
corresponds to a
concentration of 0.46 %



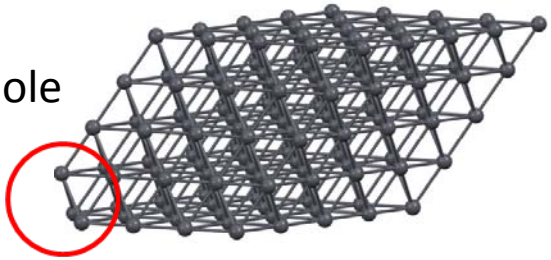
7x7x7
corresponds to a
Concentration of 0.29 %



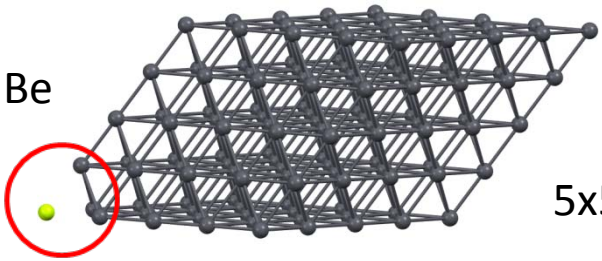
8x8x8
corresponds to a
concentration of 0.19 %



Bi



Hole



Be

5x5x5

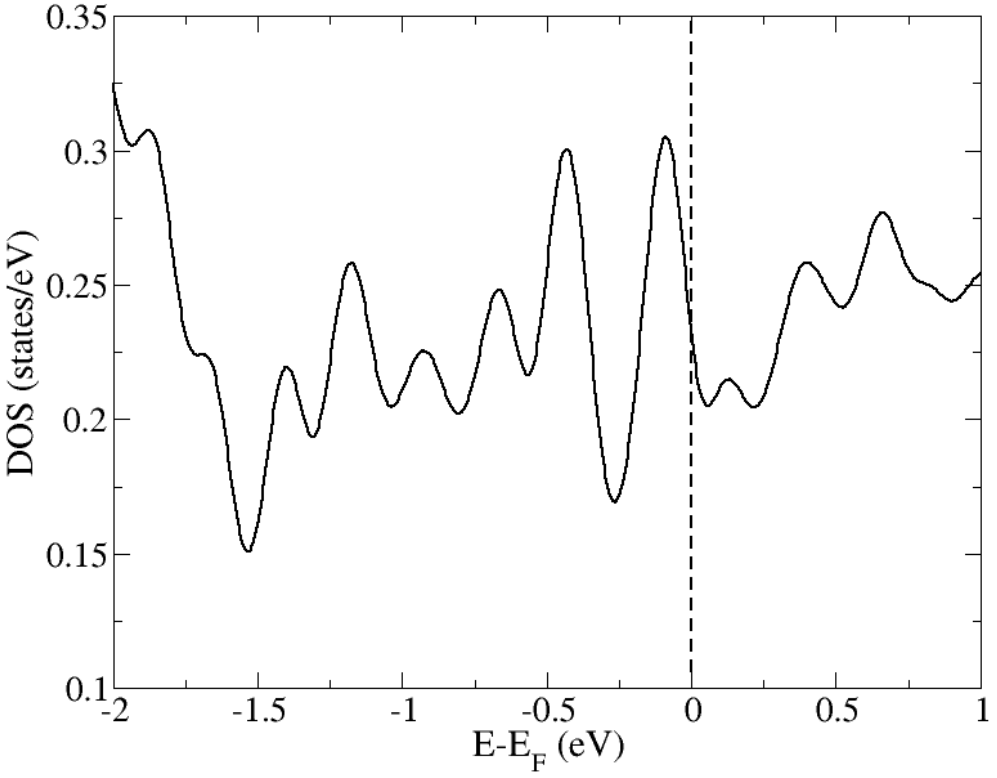
# Scientific results look like

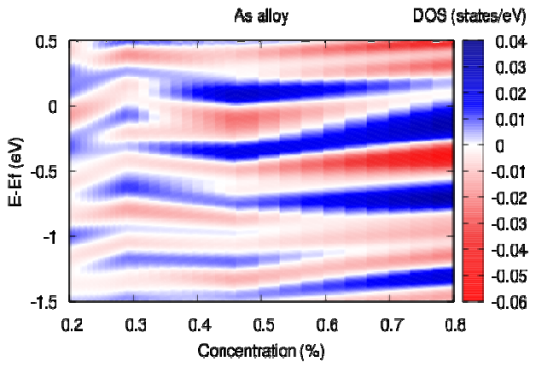
**TABLE 1.** Calculated values for concentration of impurities into the bulk lead of 0.46 % and 0.8 % . We denoted by Pb* the model in which a structural defect was simulated by removing a Pb atom from the ideal matrix.

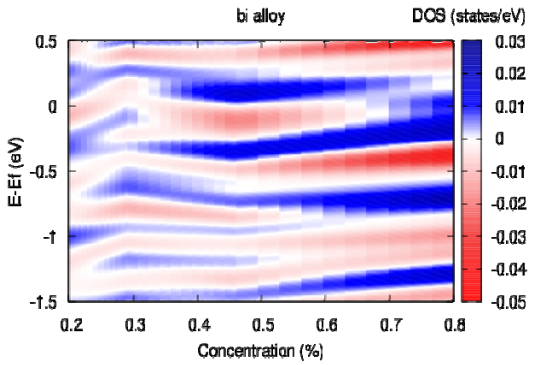
| Atom | $Q_1$ [e] 0.46 % | $Q_1$ [e] 0.80 % | $Q_0$ [e] 0.46 % | $Q_0$ [e] 0.80 % | $F_{max}$ [ eV/Å] 0.46 % | $F_{max}$ [ eV/Å] 0.80 % | $S[eV/Å^3]$ 0.46 % | $S[eV/Å^3]$ 0.80 % | $\Delta E$ [eV] 0.46 % | $\Delta E$ [eV] 0.80 % |
|---|---|---|---|---|---|---|---|---|---|---|
| Be | 0.002 | 0.001 | -0.024 | -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 |

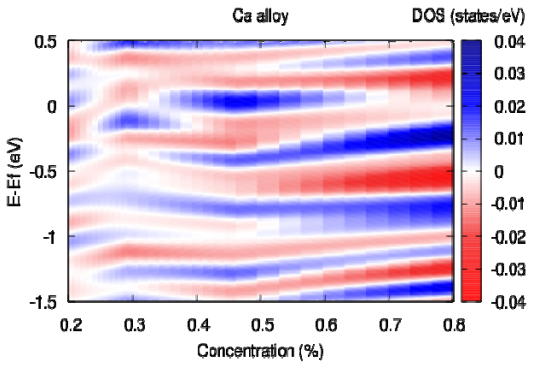
# Model for improvement of properties

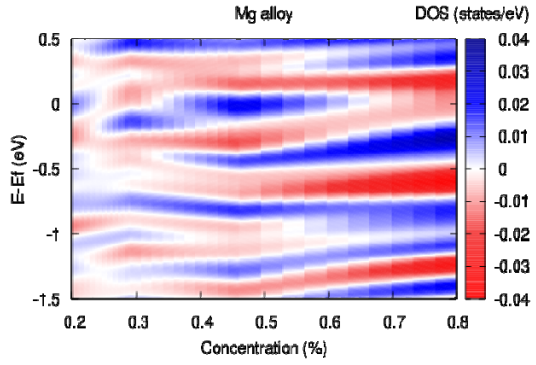
- Free electron model: stability of an alloy is ensured when density of states has a minimum at Fermi level
- DOS of lead:

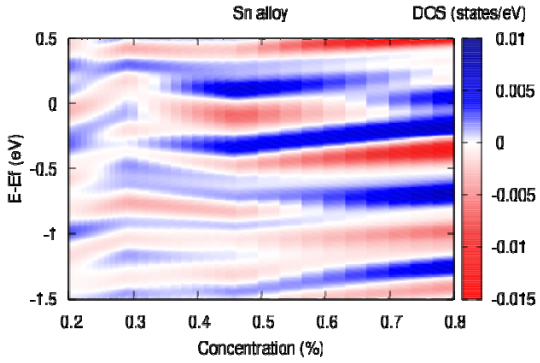


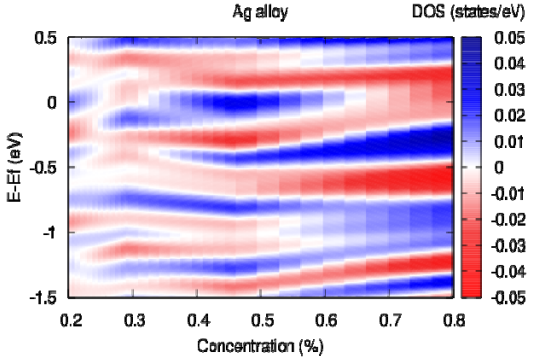


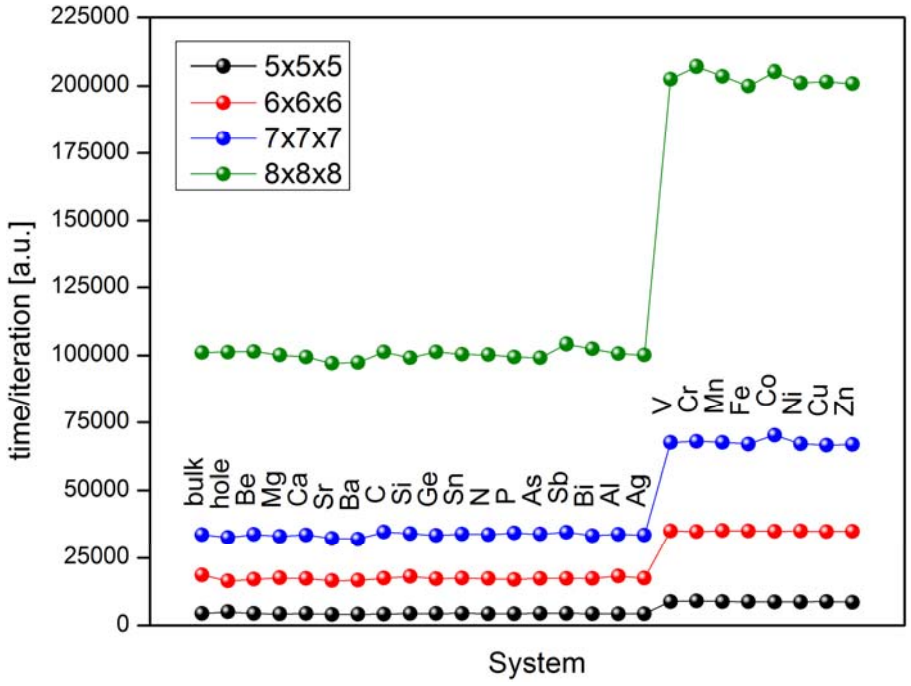



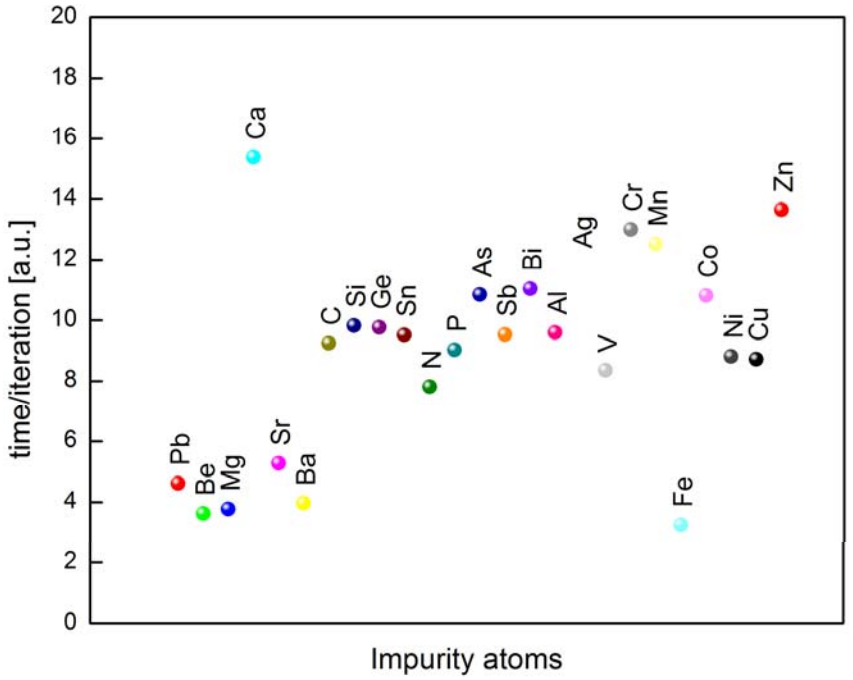

Variation of the density of states, $DOS_{PB}(E)$-$DOS_{ALLOY}(E)$ on the concentration of some alloying elements.

# Conclusion:

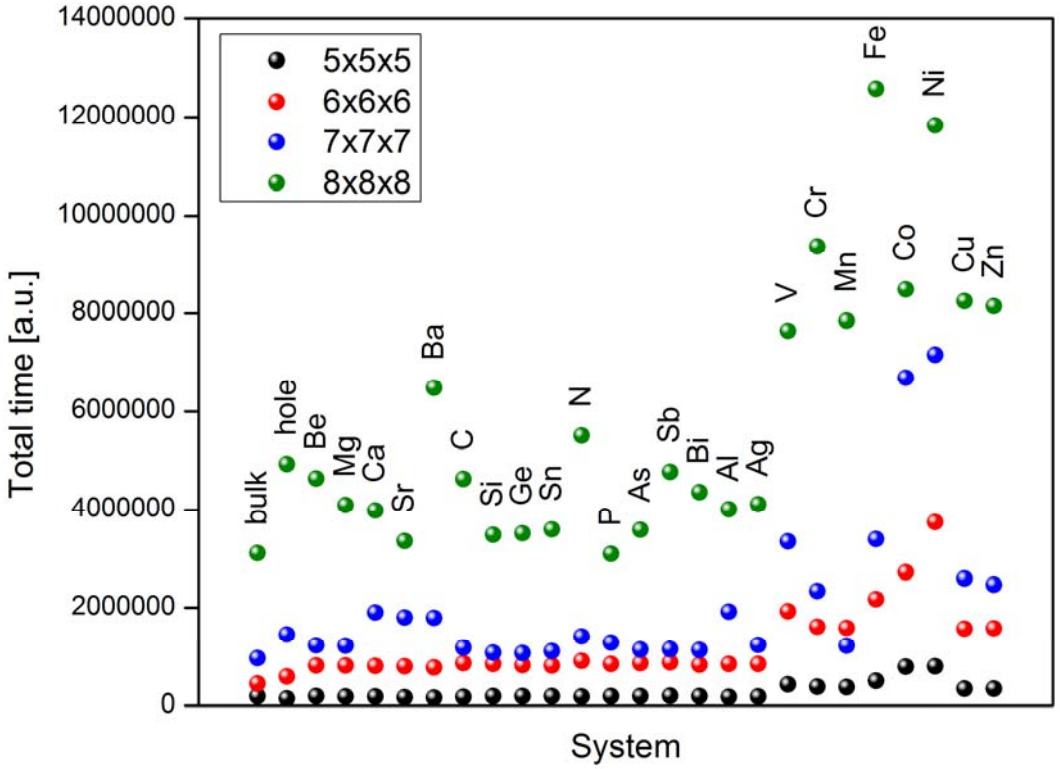
- We provide a database suited for further experimental search for new alloying elements and concentrations
- Density of states analysis allow us to propose predictions over the future tests.
- The data for the traditional alloying elements (Ca, Sn) are in full agreement with the common experience in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

# Computational resources analysis - time per iteration



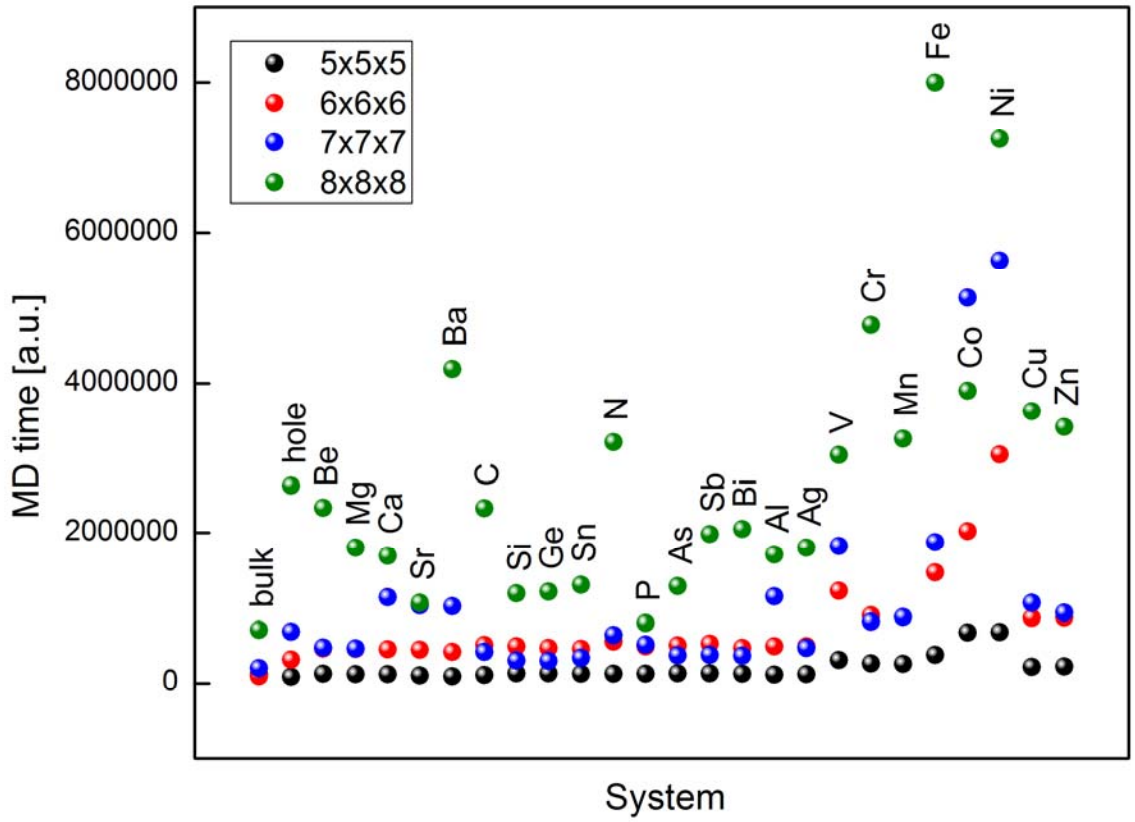



# Computational resources analysis - total time



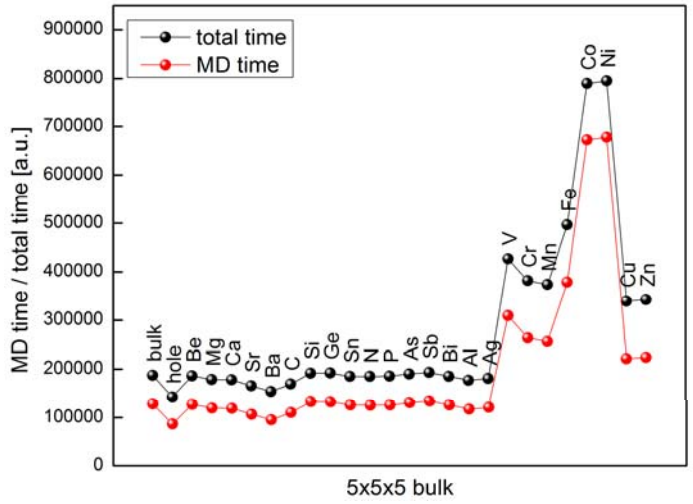
Computational resources analysis -

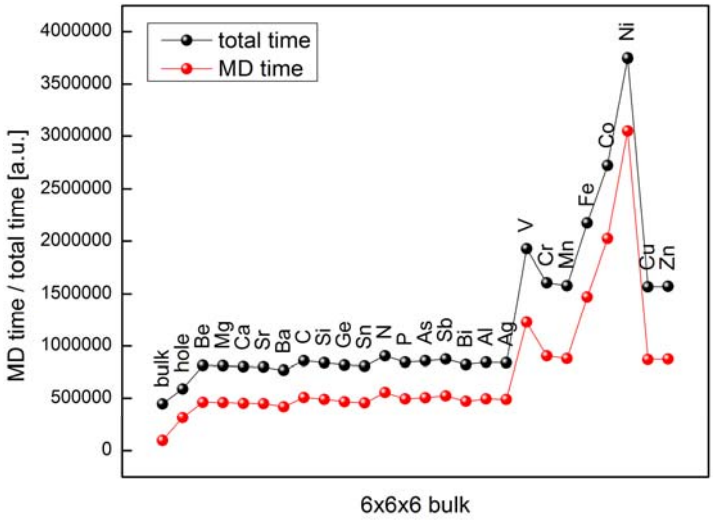
# time per MD iteration

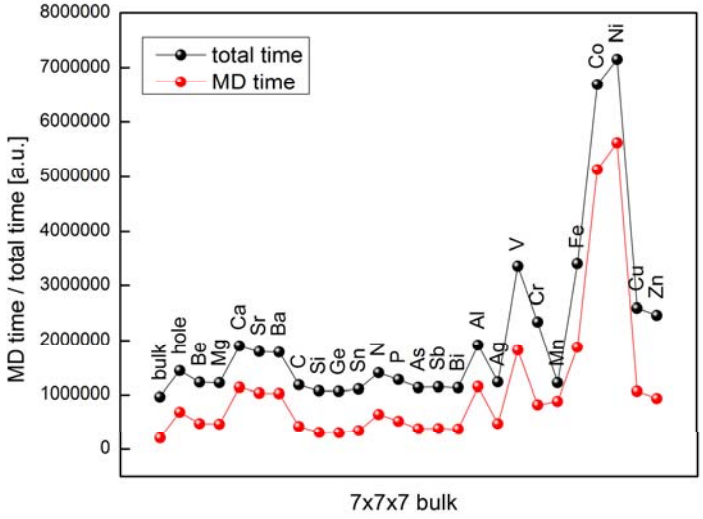


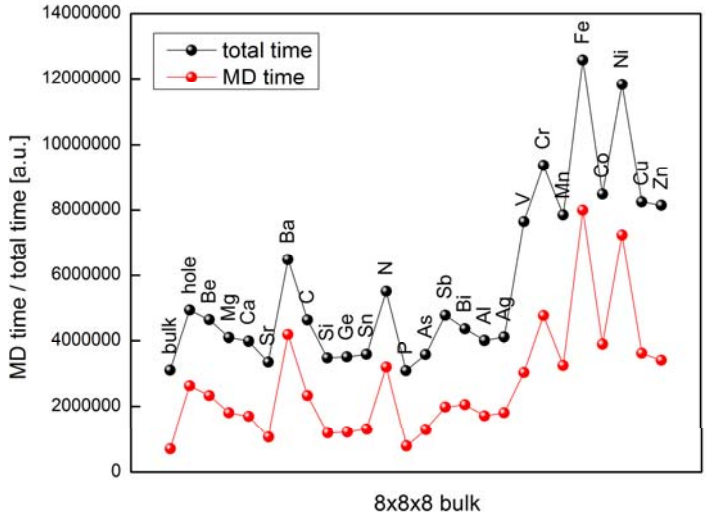
Computational resources analysis -

# MD time per total time



# Conclusion

- Strong nonlinear dependence of computing time to the super-cell 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 that the one for electronic structure