Density functional calculations for small iron clusters with substitutional phosphorus

T. Nakazawa, T. Igarashi, T. Tsuru,
Y. Kaji and S. Jitsukawa
Japan Atomic Energy Agency

nakazawa.tetsuya@jaea.go.jp
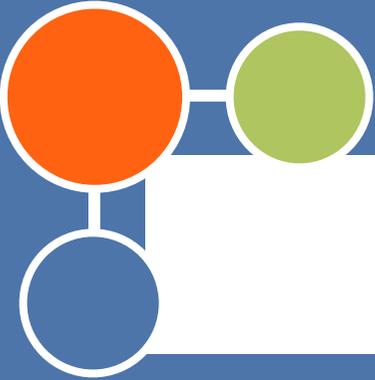
Abstract

The embrittlement is known to be caused by phosphorus (P) segregation at grain boundaries (BGs) in iron (Fe) alloy. Effects of P substitutions on binding energies and electronic structures of octahedral Fe cluster are investigated using density functional calculations in order to understand nature of bonding between P and Fe atoms at GBs. The binding energies increase in Fe_3P_3 and Fe-rich clusters while they decrease in P-rich clusters. The changes of binding energies are closely connected to the charge transfer from Fe to P atoms. The charge transfer leads to both stronger and weaker bonds in mixed Fe-P clusters. The weaker bonds due to less charge occur embrittlement. The calculations indicate that the binding energies and chemical bondings are affected by atomic configurations of P atoms in Fe-P clusters.

Background and Objective

- **Background**
  - The embrittlement in Fe alloy under thermal or irradiation environment is the serious issue for structural materials in fusion and fission reactors.
  - The embrittlement is closely connected to the segregation of impurities at GB.
  - The impurity segregation at the GBs is promoted by irradiation.
  - P atom is one of the impurities in Fe alloy, and is considered to be one of the embrittling elements.
  - The P segregation is believed to weaken cohesion at Fe GBs.
- **Objective**
  - Understanding on effects of P atoms segregated at Fe GBs.
    - We perform ab initio calculations on the changes of binding energies and structural and electronic properties of Fe_6 cluster induced by P substitutions.
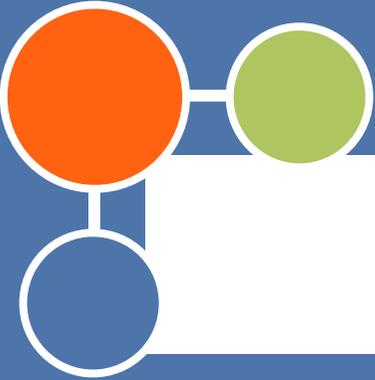
Summary

Our DFT calculations predict effects of P substitutions for equilibrium geometry, binding energy and electron properties of Fe_6 clusters. Based on the calculations the effects of chemical bonding on GB embrittlement is considered. The changes of binding energies in Fe-P clusters are found to be closely connected to the charge transfer from Fe to P atoms. As shown by calculations of Fe_3P_3 and Fe-rich clusters, a small number of P atoms stabilize the Fe GBs as well as lead to the strengthening of Fe-P bonds and the weakening of Fe-Fe bonds. The weaker bondings due to less charge occur embrittlement while the stronger bondings due to more charge stabilize GBs. In contrast to this, a large number of P atoms, which is adjacent to each other, induce unstable GBs due to weaker Fe-P and P-P bondings, and the weaker bondings occur embrittlement.

Atomic configurations of GBs with P-enrichment induced by irradiation are complex. As shown by our calculations, the cause of P embrittlement is affected by the atomic configurations of P atoms in GB. Thus, the effects of more than one P segregation should not be neglected.
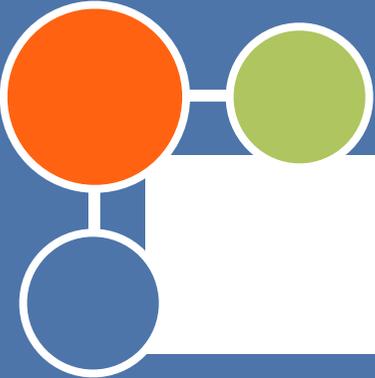
Computational details

- Theory: DFT-(U)B3LYP/LanL2DZ

- Code: Gaussian03

- Clusters: $Fe_{6-x}P_x$ ($0 \leq x \leq 6$)

- Binding energies (E_b): The binding energies per atom of clusters are calculated with respect to the Fe atom with $M = 5$ and P atom with $M = 4$. M means spin multiplicities.

- Natural population analysis: electron configuration, natural population and natural atomic orbital (NAO) bond order are calculated.

Optimized Fe-P clusters
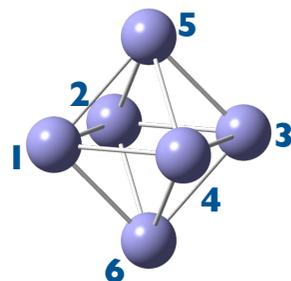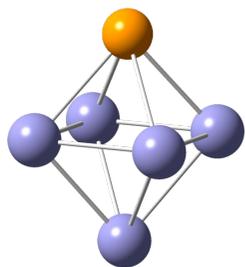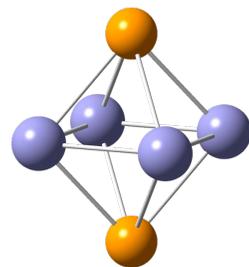
(a) Fe$_6$ (D$_{4h}$)   (b) Fe$_5$P (C$_{4v}$)   (c) Fe$_4$P$_2$ (D$_{4h}$)   (d) Fe$_4$P$_2$ (C$_{2v}$)   (e) Fe$_3$P$_3$ (C$_{3v}$)
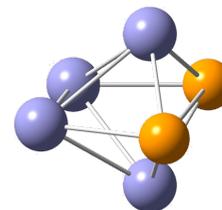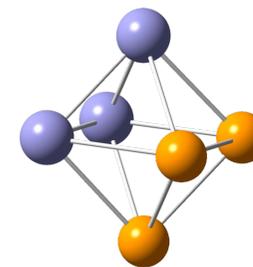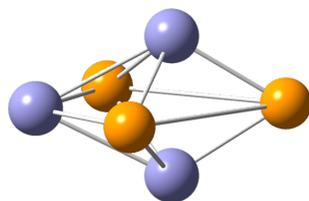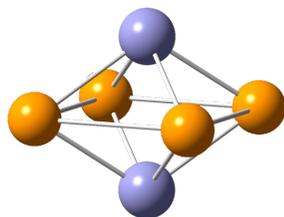
(f) Fe$_3$P$_3$ (C$_{2v}$)   (g) Fe$_2$P$_4$ (D$_{4h}$)   (h) Fe$_2$P$_4$ (C$_{2v}$)   (i) FeP$_5$ (C$_{4v}$)   (j) P$_6$ (D$_{4h}$)
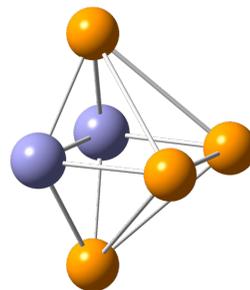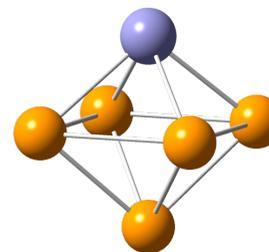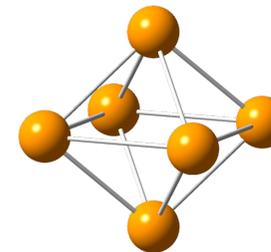
:Fe atom,   :P atom

Binding energies, bond lengths, and NAO bond orders of Fe-P clusters

System	Symm.	M	E_b	R_e			NAO bond order		
				Fe-Fe	Fe-P	P-P	Fe-Fe	Fe-P	P-P
Fe_6	D_{4h}	21	1.85	2.43, 2.45			0.36		
Fe_5P	C_{4v}	16	2.00	2.42, 2.53	2.49		0.28, 0.34, 0.38	0.39, 0.40	
Fe_4P_2	D_{4h}	13	2.11	2.42	2.50		0.22	0.37, 0.40	
	C_{2v}	13	2.19	2.56, 2.74	2.38, 2.40	3.72	0.23, 0.28	0.49, 0.44	0.07
Fe_3P_3	C_{3v}	12	1.97	2.46	2.60	2.50	0.41	0.29	0.54
	C_{2v}	10	2.06	2.46, 2.67	2.34, 2.36, 2.42	3.47	0.14, 0.12	0.46, 0.48, 0.42	0.10
Fe_2P_4	D_{4h}	7	1.83		2.37	2.82		0.37, 0.38	0.37
	C_{2v}	7	1.86	2.37	2.37, 2.48	2.23, 3.07	0.25	0.48, 0.34	0.89, 0.21
FeP_5	C_{4v}	4	1.58		2.48	2.57, 2.76		0.33, 0.35	0.49, 0.35
P_6	D_{4h}	3	1.09			2.61, 2.82			0.45, 0.26

E_b: eV/atom, R_e: Å

Natural electron configurations and natural populations of Fe-P clusters (1)

System	Symm.	Atom	Natural electron configuration	Natural population
Fe_6	D_{4h}	Fe(1-4)	$[core]4s^{1.09}3d^{6.81}4p^{0.08}5s^{0.01}4d^{0.02}$	0.00
		Fe(5, 6)	$[core]4s^{1.09}3d^{6.80}4p^{0.08}5s^{0.01}4d^{0.02}$	0.01
Fe_5P	C_{4v}	Fe(1, 3)	$[core]4s^{0.86}3d^{6.82}4p^{0.06}4d^{0.015}5s^{0.01}4d^{0.01}$	0.24
		Fe(2, 4)	$[core]4s^{0.74}3d^{6.93}4p^{0.06}4d^{0.01}$	0.25
		P(5)	$[core]3s^{1.90}3p^{4.01}$	-0.91
		Fe(6)	$[core]4s^{1.18}3d^{6.76}4p^{0.10}5s^{0.02}4d^{0.01}$	-0.06
Fe_4P_2	D_{4h}	Fe(1, 3)	$[core]4s^{0.58}3d^{6.84}4p^{0.04}4d^{0.01}$	0.53
		Fe(2, 4)	$[core]4s^{0.62}3d^{6.92}4p^{0.03}4d^{0.015}5p^{0.01}$	0.41
		P(5, 6)	$[core]3s^{1.91}3p^{4.02}$	-0.94
	C_{2v}	Fe(1,2)	$[core]4s^{0.85}3d^{6.82}4p^{0.07}4d^{0.01}$	0.24
		P(3,4)	$[core]3s^{1.91}3p^{3.88}$	-0.80
		Fe(5,6)	$[core]4s^{0.60}3d^{6.78}4p^{0.05}4d^{0.02}$	0.55
Fe_3P_3	C_{3v}	Fe(1, 2, 5)	$[core]4s^{0.81}3d^{6.64}4p^{0.08}4d^{0.01}$	0.44
		P(3, 4, 6)	$[core]3s^{1.90}3p^{3.54}$	-0.44

Natural electron configurations and natural populations of Fe-P clusters (2)

System	Symm.	Atom	Natural electron configuration	Natural population
Fe_3P_3	C_{2v}	Fe(1)	$[core]4s^{0.54}3d^{6.85}4p^{0.05}4d^{0.01}$	0.55
		P(2, 4)	$[core]3s^{1.91}3p^{3.80}$	-0.72
		P(3)	$[core]3s^{1.93}3p^{3.48}$	-0.42
		Fe(5, 6)	$[core]4s^{0.52}3d^{6.76}4p^{0.05}4d^{0.02}5p^{0.01}$	0.65
Fe_2P_4	D_{4h}	P(1-4)	$[core]3s^{1.91}3p^{3.36}$	-0.27
		Fe(5, 6)	$[core]4s^{0.38}3d^{7.01}4p^{0.04}4d^{0.02}$	0.54
	C_{2v}	Fe(1, 2)	$[core]4s^{0.55}3d^{6.77}4p^{0.06}4d^{0.02}5p^{0.01}$	0.61
		P(3, 4)	$[core]3s^{1.87}3p^{3.26}4p^{0.01}$	-0.14
		P(5,6)	$[core]3s^{1.93}3p^{3.53}$	-0.47
FeP_5	C_{4v}	P(1, 3)	$[core]3s^{1.91}3p^{3.29}$	-0.21
		P(2, 4)	$[core]3s^{1.91}3p^{3.22}$	-0.14
		Fe(5)	$[core]4s^{0.41}3d^{6.88}4p^{0.05}4d^{0.01}$	0.64
		P(6)	$[core]3s^{1.87}3p^{3.07}4p^{0.01}$	0.05
P_6	D_{4h}	P(1-4)	$[core]3s^{1.93}3p^{3.09}$	-0.02

Calculations on Fe$_6$ cluster

- Our calculated bond lengths are consistent with the previous results (2.29 - 2.53 Å) and are very close to nearest neighbour distance of bulk iron (2.48 Å), while calculated binding energy is smaller than the previous results (3.77 eV/atom).

- The electron configuration calculated for Fe atom is $4s^{1.09}3d^{6.80}$ which is very close to that of the metal or large clusters ($4s^1 3d^7$).
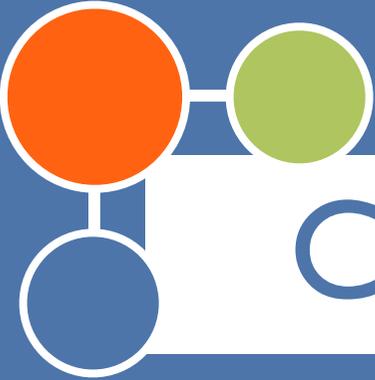
Calculations on P_6 cluster

- For P_6 (D_{4h}) cluster, our calculations find the M=3 ground state with bond length of 2.61 - 2.82 Å and binding energy of 1.09 eV/atom.

- The previous LSDA calculations based on the Car-Parrinello method on various structure of P_6 have predicted that bond length range from 2.01 to 2.40 Å. The binding energies of P_6 (C_{2v} and D_{3h}) clusters calculated using the generalized gradient approximations have predicted to be 3.06 and 3.02 eV/atom, respectively.

- The above differences between our calculations and previous calculations result from different treatment of electron in clusters rather than differences in structure and exchange-correlation energy. The spin-restricted calculations generally lead to shorter bond lengths and larger binding energies because of neglecting the spin dependence of exchange and correlation.

Effects of P substitutions (1)

- Effects on binding energy:
  - Fe_3P_3 and Fe-rich clusters have larger binding energies.
  - P-rich clusters have smaller binding energies.

- Effects on bonding strength:
  - In the Fe_3P_3 (C_{2v}) and Fe-rich clusters, the stronger Fe-P and weaker Fe-Fe bondings caused by the charge transfer due to the P substitutions.
  - In Fe_3P_3 (C_{3v}) cluster, stabilization of Fe3 and P3 units lead to the weaker Fe-P bonding.
  - In P-rich clusters, decrease in binding energies corresponds to the weaker Fe-P and P-P bondings.

Effects of P substitutions (2)

- Effects on electronic structure:
  - The P substitution causes the charge transfer from Fe to P atoms.
  - The charge transfer leads to the stronger and weaker bondings in Fe-P clusters.

The P embrittlement of Fe GB is closely connected with the change of electronic structure due to atomic configurations of P atoms in GBs.

Thank you for your stop.

If you have a interest in this work, please contact me.

Email: nakazawa.tetsuya@jaea.go.jp