CMS II-8: surface and molecule

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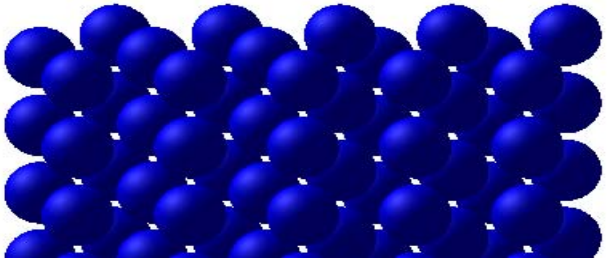
Slab model for surface calculation

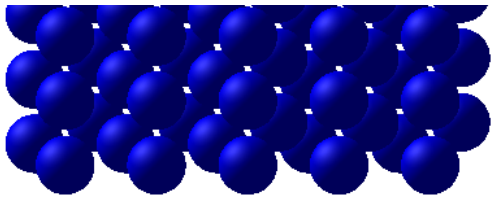
vacuum

surface

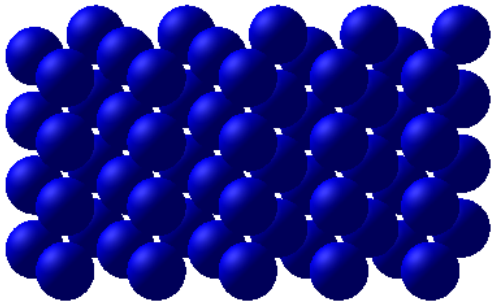


No dispersion
along z direction

Real system

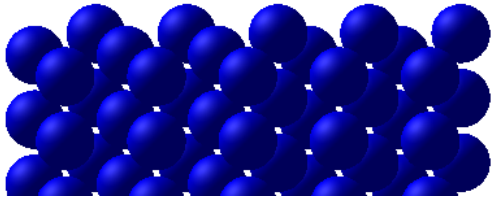


vacuum 10A

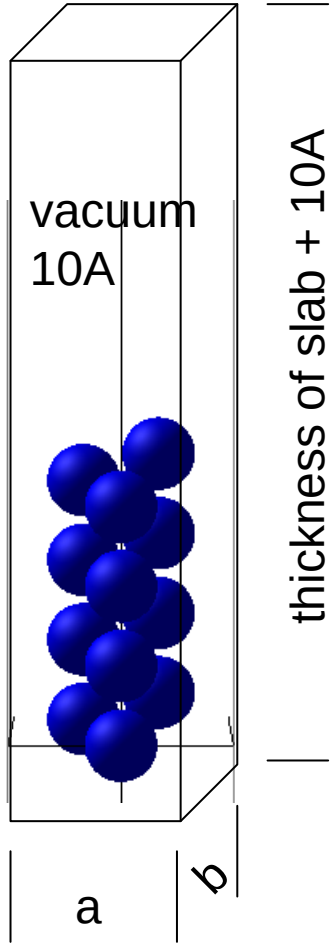


slab of
several
layers

vacuum 10A



Slab model

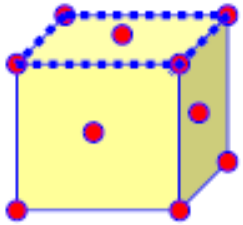


Unit cell for cal.

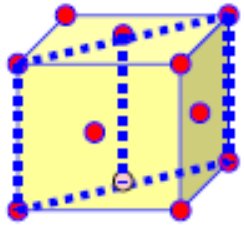
- Repeated slab model

D_v: Vacuum thickness (10 A°)

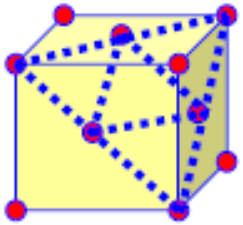
N: Slab thickness (5 ~ 13 layers)
(for usual cases)



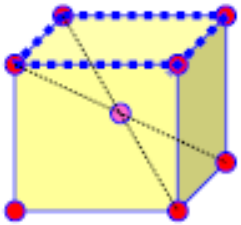
FCC(001)



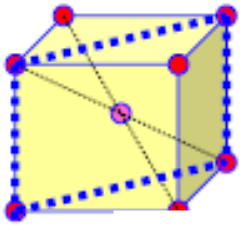
FCC(110)



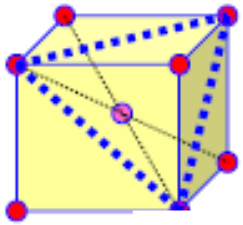
FCC(111)



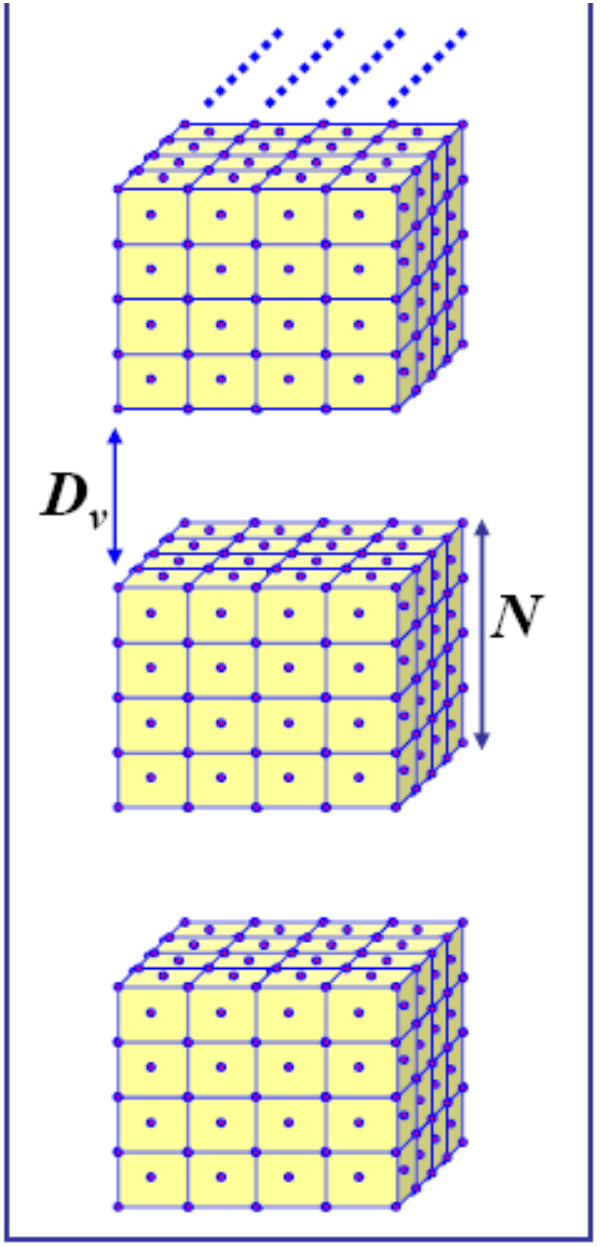
BCC(001)



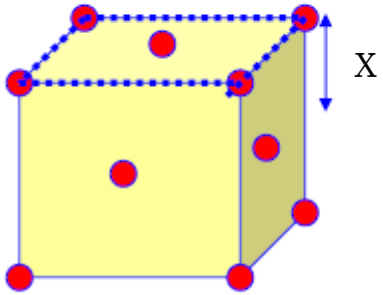
BCC (110)



BCC (111)



FCC (001) surface



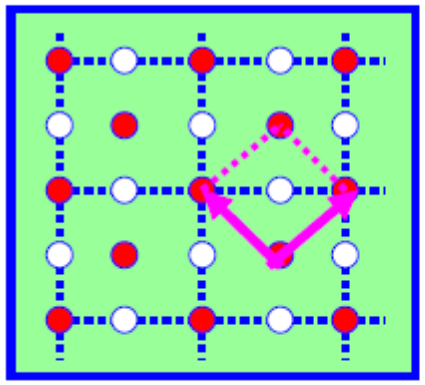
$$x = \frac{1}{2}a$$

$$\vec{a}_1 = a\left(\frac{\sqrt{2}}{2} \quad 0 \quad 0\right)$$

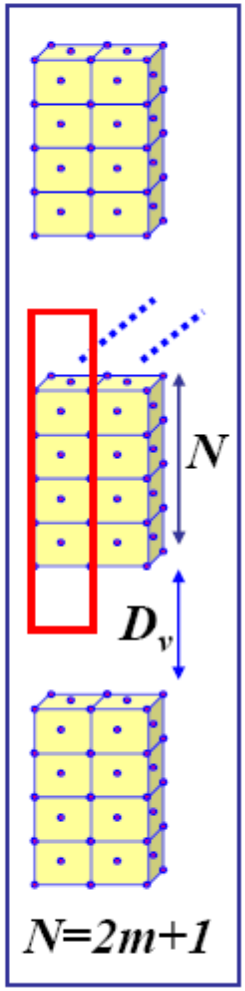
$$\vec{a}_2 = a\left(0 \quad \frac{\sqrt{2}}{2} \quad 0\right)$$

$$\vec{a}_3 = a(0 \quad 0 \quad C)$$

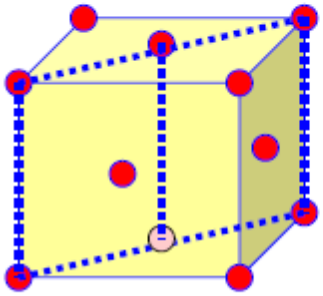
?	?	mx
....	....	....
0.0	0.0	$2x$
0.5	0.5	x
0.0	0.0	0
0.5	0.5	$-x$
0.0	0.0	$-2x$
....	....	....
?	?	$-mx$



C=slab thickness
+10A

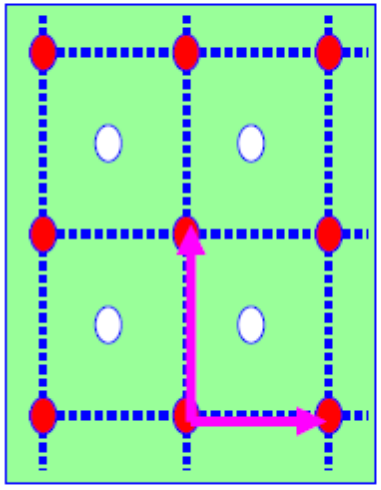


FCC (110) surface



$x = \frac{\sqrt{2}}{4}a$

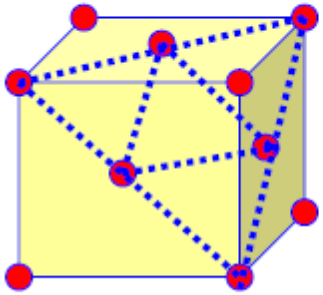
$$\vec{a}_1 = a(\frac{\sqrt{2}}{2} \quad 0 \quad 0)$$
$$\vec{a}_2 = a(0 \quad 1 \quad 0)$$
$$\vec{a}_3 = a(0 \quad 0 \quad C)$$



C=slab thickness
+10A

?	?	mx
....	....	....
0.0	0.0	$2x$
0.5	0.5	x
0.0	0.0	0
0.5	0.5	$-x$
0.0	0.0	$-2x$
....	....	....
?	?	$-mx$

FCC (111) surface (HEX)

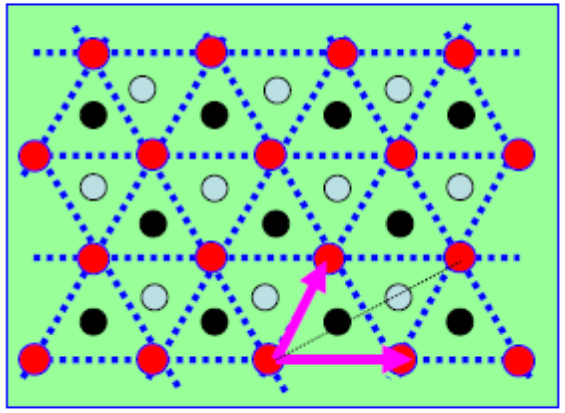


$x = \frac{\sqrt{3}}{3} a$

$$\vec{a}_1 = \frac{\sqrt{2}}{2} a(1 \quad 0 \quad 0)$$

$$\vec{a}_2 = \frac{\sqrt{2}}{2} a(\frac{1}{2} \quad \frac{\sqrt{3}}{2} \quad 0)$$

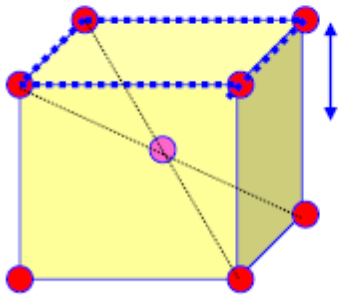
$$\vec{a}_3 = a(0 \quad 0 \quad C)$$



C=slab thickness
+10A

?	?	mx
....	....	....
2/3	2/3	$2x$
1/3	1/3	x
0.0	0.0	0
−1/3	−1/3	$-x$
−2/3	−2/3	$-2x$
....	....	....
?	?	$-mx$

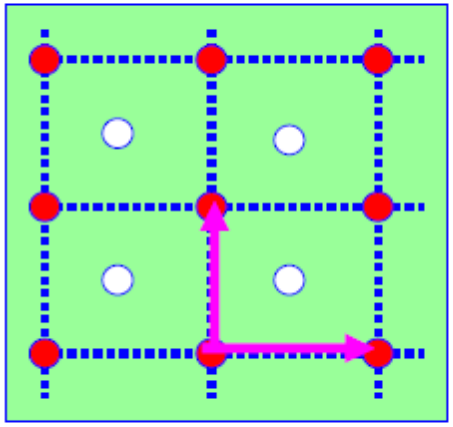
BCC (001) surface



x= $\frac{1}{2}a$

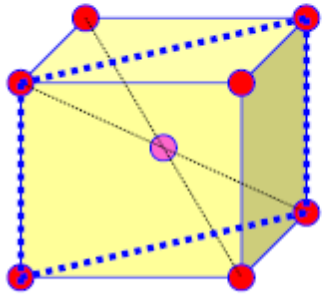
$$\vec{a}_1 = a(1 \quad 0 \quad 0)$$
$$\vec{a}_2 = a(0 \quad 1 \quad 0)$$
$$\vec{a}_3 = a(0 \quad 0 \quad C)$$

?	?	mx
....	....	....
0.0	0.0	$2x$
0.5	0.5	x
0.0	0.0	0
0.5	0.5	$-x$
0.0	0.0	$-2x$
....	....	....
?	?	$-mx$



C=slab thickness
+10A

BCC (110) surface

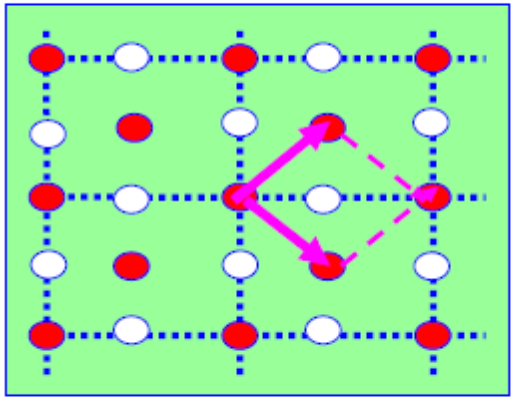


$x = \frac{\sqrt{2}}{2}a$

$$\vec{a}_1 = a(\frac{\sqrt{2}}{2} \quad -\frac{1}{2} \quad 0)$$

$$\vec{a}_2 = a(\frac{\sqrt{2}}{2} \quad \frac{1}{2} \quad 0)$$

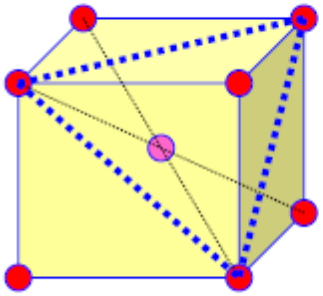
$$\vec{a}_3 = a(0 \quad 0 \quad C)$$



C=slab thickness
+10A

?	?	mx
....	....	....
0.0	0.0	$2x$
0.5	0.5	x
0.0	0.0	0
0.5	0.5	$-x$
0.0	0.0	$-2x$
....	....	....
?	?	$-mx$

BCC (111) surface (HEX)

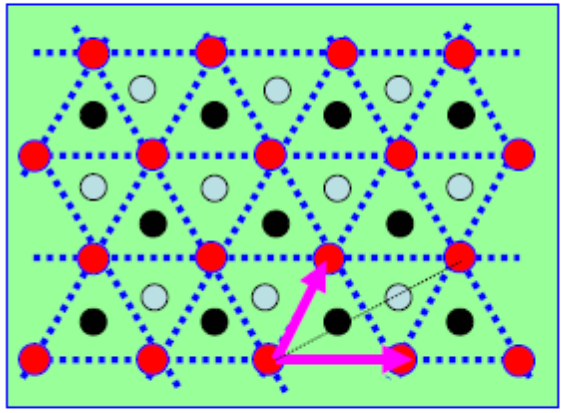


$x = \frac{\sqrt{3}}{6} a$

$$\vec{a}_1 = \sqrt{2}a(1 \quad 0 \quad 0)$$

$$\vec{a}_2 = \sqrt{2}a(\frac{1}{2} \quad \frac{\sqrt{3}}{2} \quad 0)$$

$$\vec{a}_3 = a(0 \quad 0 \quad C)$$



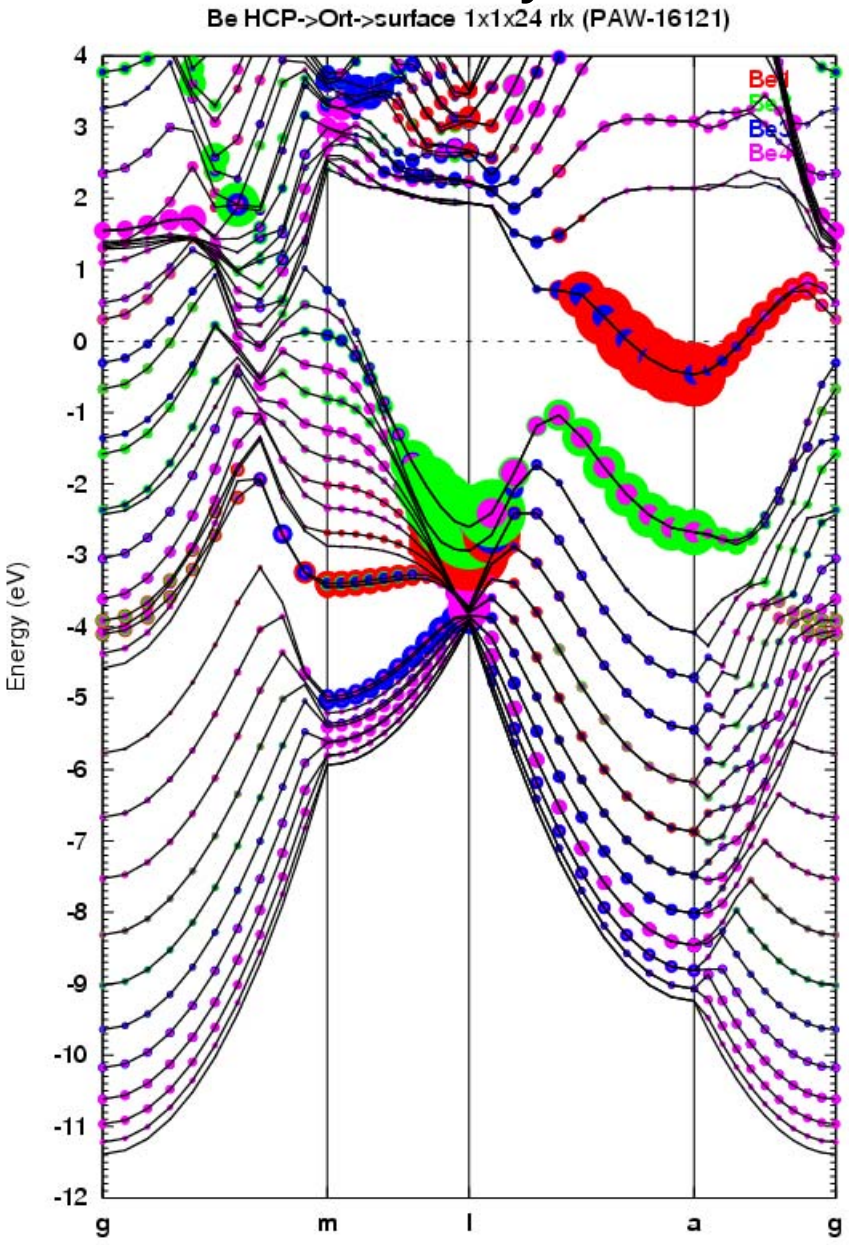
C=slab thickness
+10A

?	?	mx
....	....	....
2/3	2/3	$2x$
1/3	1/3	x
0.0	0.0	0
–1/3	–1/3	$-x$
–2/3	–2/3	$-2x$
....	....	....
?	?	$-mx$

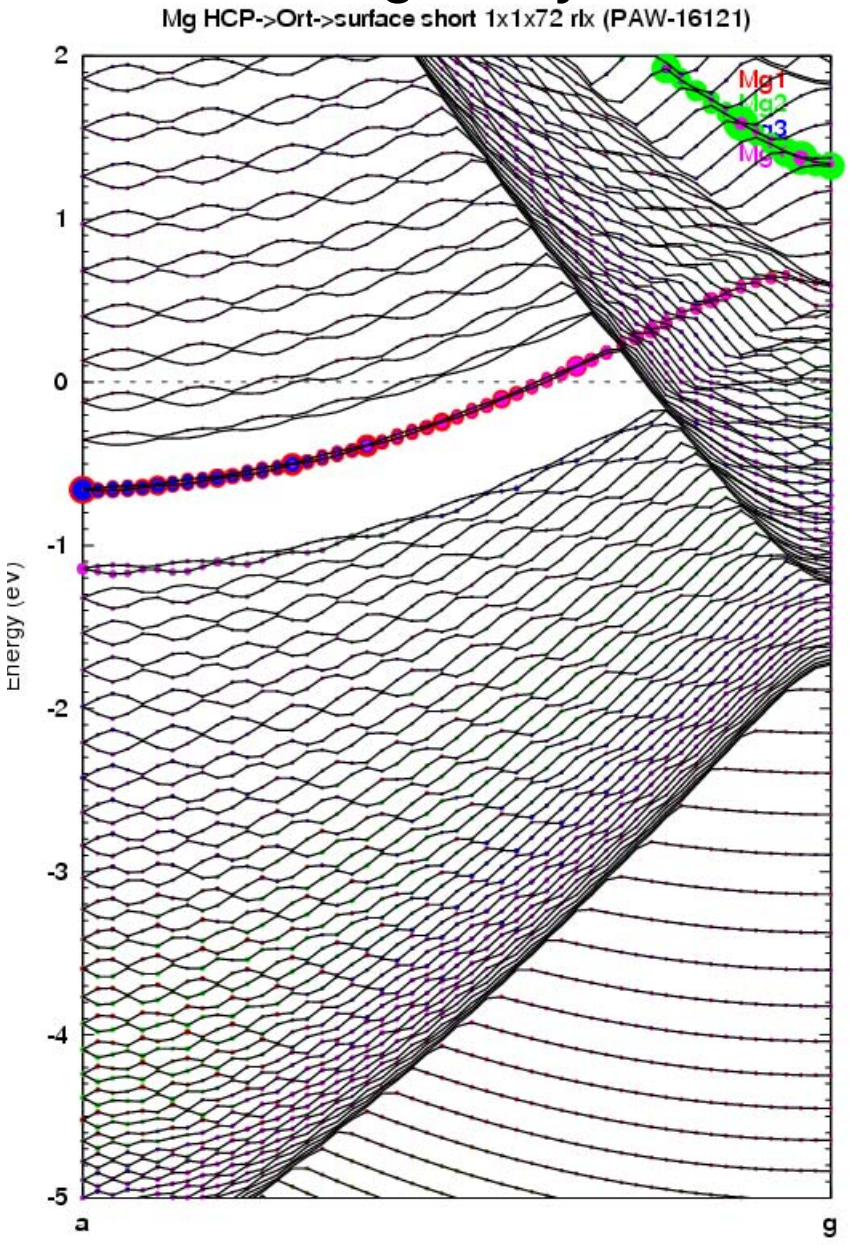
Be(1010) and Mg(1010) surface

($10\bar{1}0$)	1st layer relaxation	1st layer thermal contraction	SS decay length	Energy shift (relaxation)	Energy shift (thermal contraction)	EP coupling constant λ
Mg(1010)	-14.5%[a]	$\Delta d_{12}/\Delta T$ = -0.015% (1/K)[c]	S1 20 ML[e] S2 52 ML[e]	S1 5.5 meV[e] S2 6.0 meV[e]	S1 ($\Delta E/\Delta T$) -0.364×10^{-4} eV/K[e] S2 ($\Delta E/\Delta T$) 0.969×10^{-4} eV/K[e]	S1 0.304[e] S2 0.391[e]
Be(1010)	-25%[b]	$\Delta d_{12}/\Delta T$ = -0.019% (1/K)[d]	S1 4 ML[f] S2 6 ML[f]	S1 29 meV[f] S2178 meV[f]	S1($\Delta E/\Delta T$) -0.61×10^{-4} eV/K[f] S2 ($\Delta E/\Delta T$) 1.71×10^{-4} eV/K[f]	S1 0.646[f] S2 0.491[f]

Be 24layer

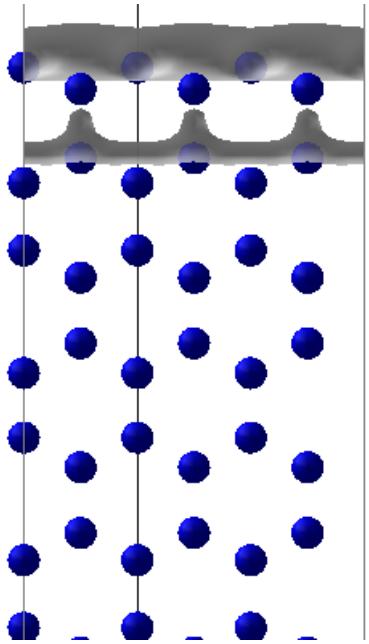


Mg 72layer



Be(1010)

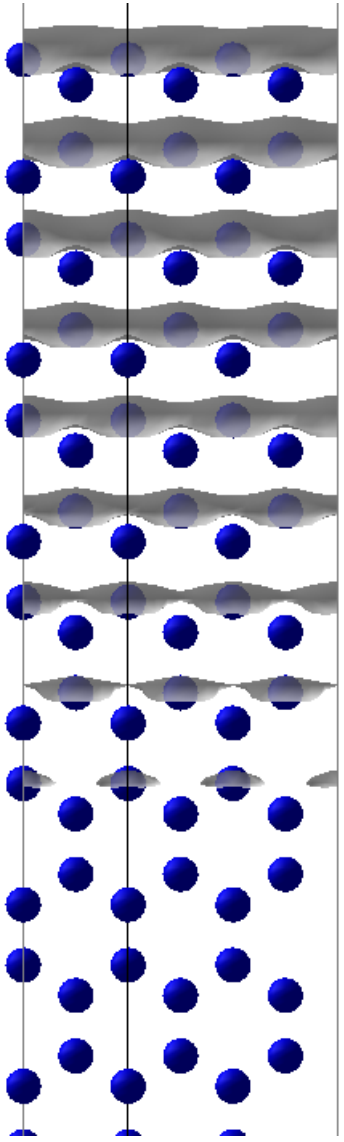
010



S2
K55
B16

Mg(1010)

010



S2
K1
B71

Table 1 Relaxation of topmost interlayer spacing at unreconstructed clean metal surfaces

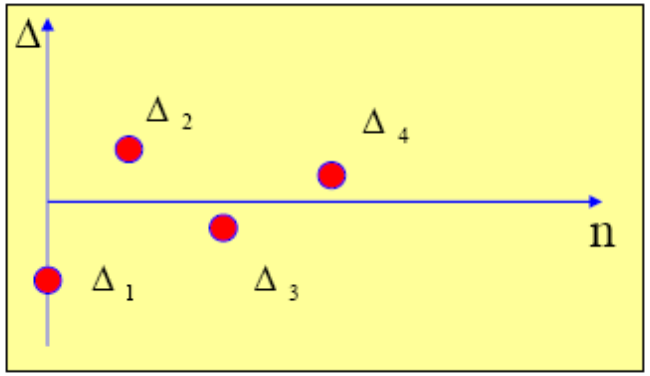
Each entry consists of:
Chemical symbol (interlayer spacing change from bulk value).
[After F. Jona and P. M. Marcus, in "The Structure of Surfaces II," eds. J. F. van der Veen and M. A. Van Hove, Springer-Verlag (Heidelberg, 1988), p. 90]

hcp(0001)	Re (−5%), Sc (−2%), Ti (−2%), Zr (−1%)
fcc(111)	Al (+1%), Ag (0%), Cu (−0.7%), Pt (+1%), Rh (0%)
bcc(110)	Fe (+0.5%), Na (0%), V (−0.3%), W (0%)
fcc(100)	Al (0%), Cu (−1%), Rh (0%)
bcc(100)	Fe (−5%), Mo (−9.5%), Ta (−11%), V (−7%), W (−8%)
fcc(110)	Al (−8.5%), Ag (−8%), Cu (−8.5%), Ni (−8.5%), Pb (−16%), Rh (−3%)
hcp(10-10)	Re (−17%)
bcc(211)	Fe (−10%), W (−12%)
fcc(311)	Al (−13%), Ni (−16%), Cu (−5%)
bcc(310)	Fe (−16%)
fcc(331)	Al (−12%)
fcc(210)	Al (−15.5%)
bcc(111)	Fe (−17%)
bcc(210)	Fe (−22%)

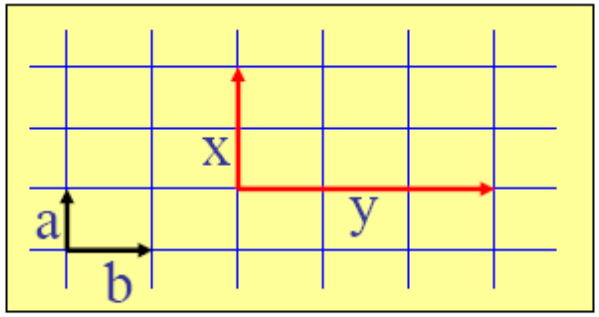
Relaxation and reconstruction

(i) Contraction (metal)

$$\Delta_i = \frac{d_i - d_{o(ideal)}}{d_{o(ideal)}}$$



(ii) Reconstruction

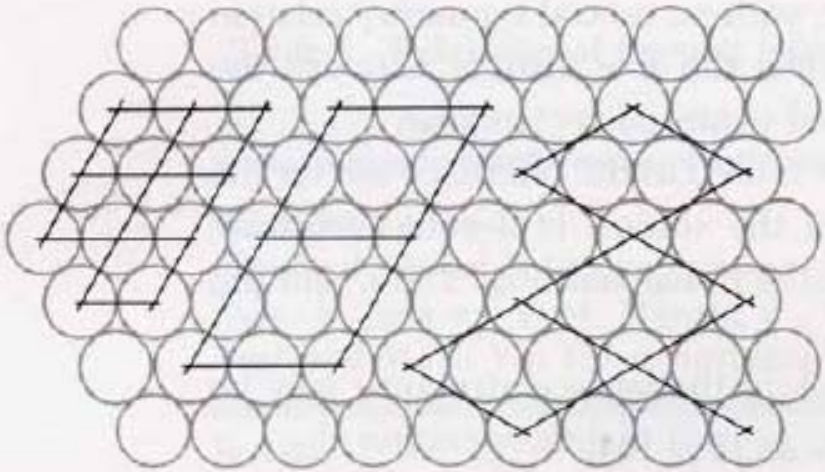


$$\vec{x} = n\vec{a}$$

$$\vec{y} = m\vec{b}$$

$$\Rightarrow \quad p(n \times m)$$

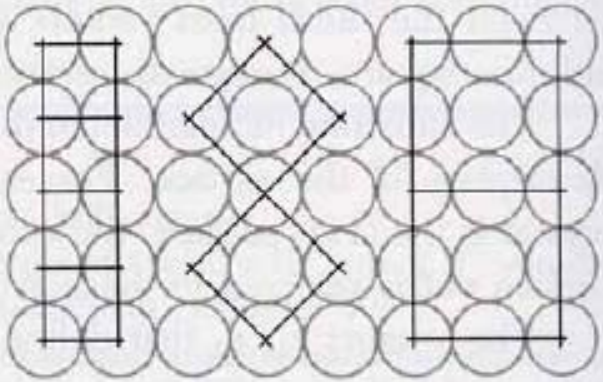
P(2x3) or *(2x3)*



p(1 × 1) p(2 × 2) $(\sqrt{3} \times \sqrt{3})$R30°

fcc(111), hcp(0001)

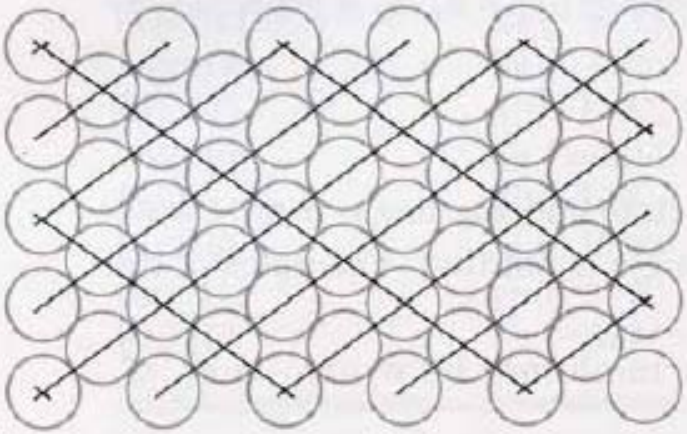
(a)



p(1 × 1) c(2 × 2) p(2 × 2)

fcc(100), bcc(100)

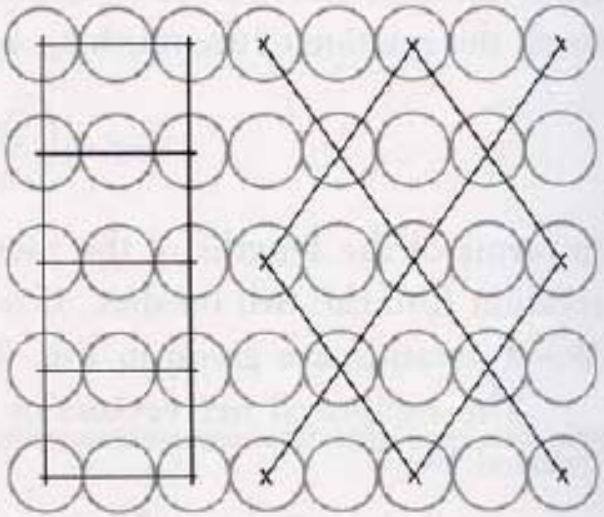
(b)



p(2 × 1)

bcc(110)

(c)



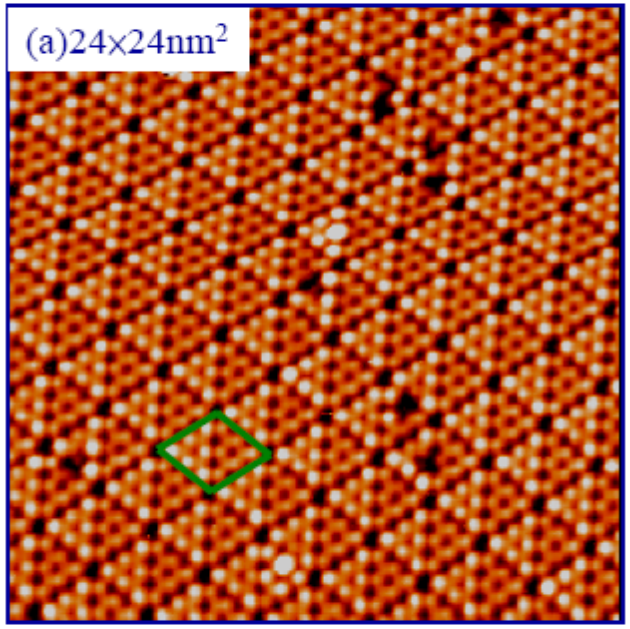
p(2 × 1) c(2 × 2)

fcc(110)

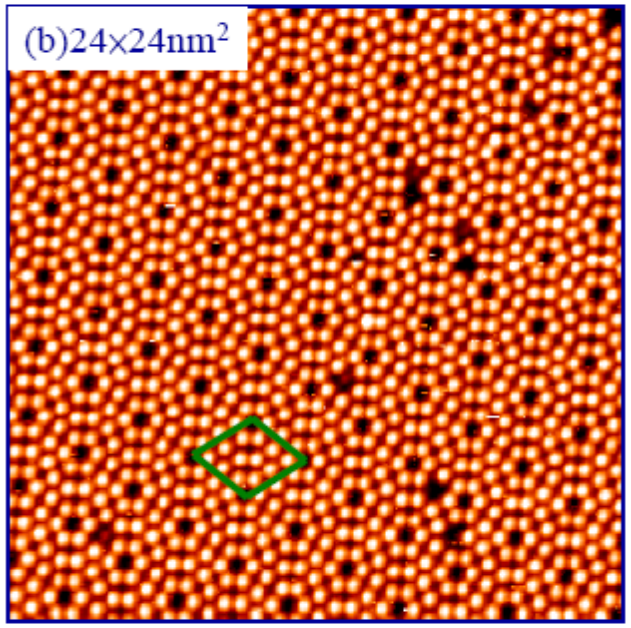
(d)

Si(111) 7x7 surface reconstruction measured by STM under positive and negative bias

施加正負樣品偏壓下所得之7x7重構圖像



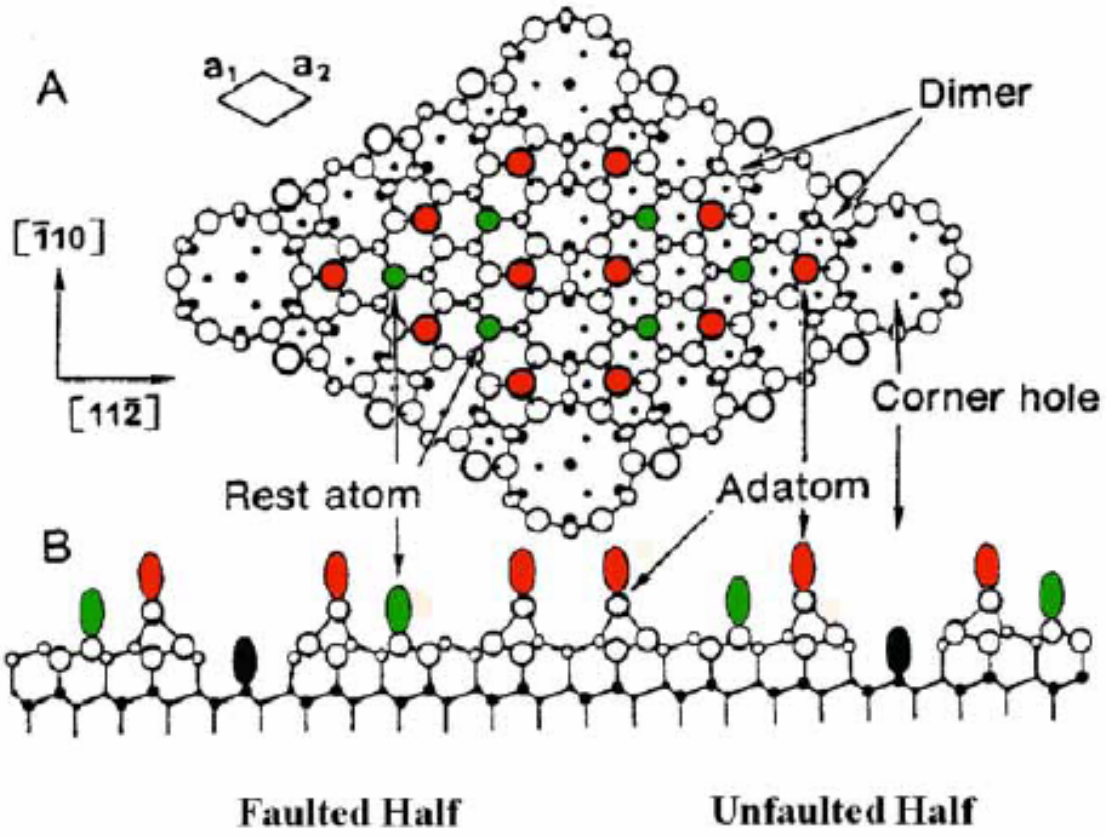
樣品偏壓：-1.5V
bias



樣品偏壓：+1.5V
bias

Reconstruction model

Si（111）-7×7重構DAS模型



D： 9 dimers

A：12 adatoms

S： 1 Stacking fault

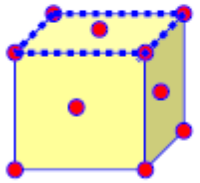
19 Dangling bonds

Surface energy

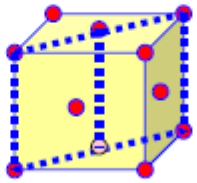
Energy required to create the surfaces from bulk

Depend on (i) temperature (decreases as T increases)
(ii) material (cohesive energy)
(iii) orientation : number of bond cut

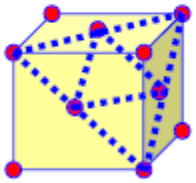
Surface energy $\gamma \sim$ area of the surface unit cell



FCC(001)



FCC(110)



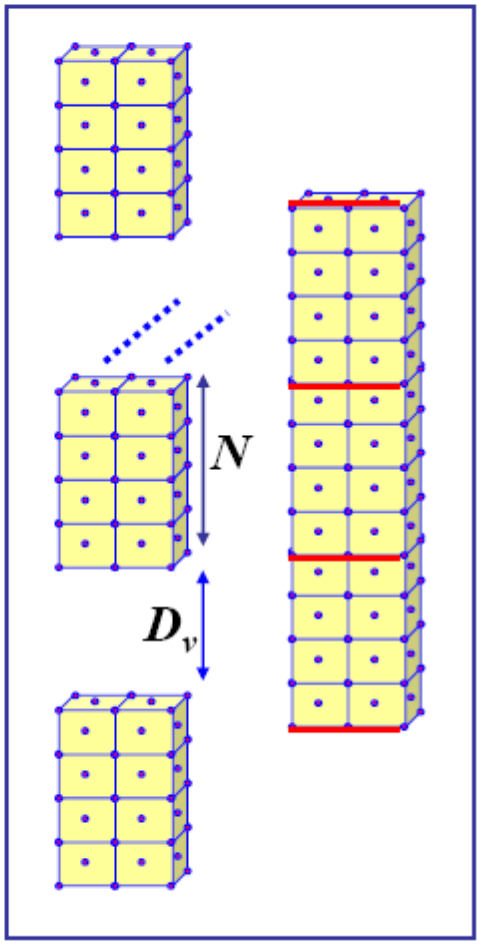
FCC(111)

$$\gamma_{111} < \gamma_{100} < \gamma_{110}$$

Repeated slab model

D_v: Vacuum thickness *(10 A°)*

N: Slab thickness *(5 ~ 13 layers)*



Surface energy per surface atom

$$\gamma = \frac{1}{2}\left(E_{slab} - NE_{bulk}\right)$$

E_{bulk} : Energy of an atom in bulk

Surface energy of Li(001) calculated using different slab thickness

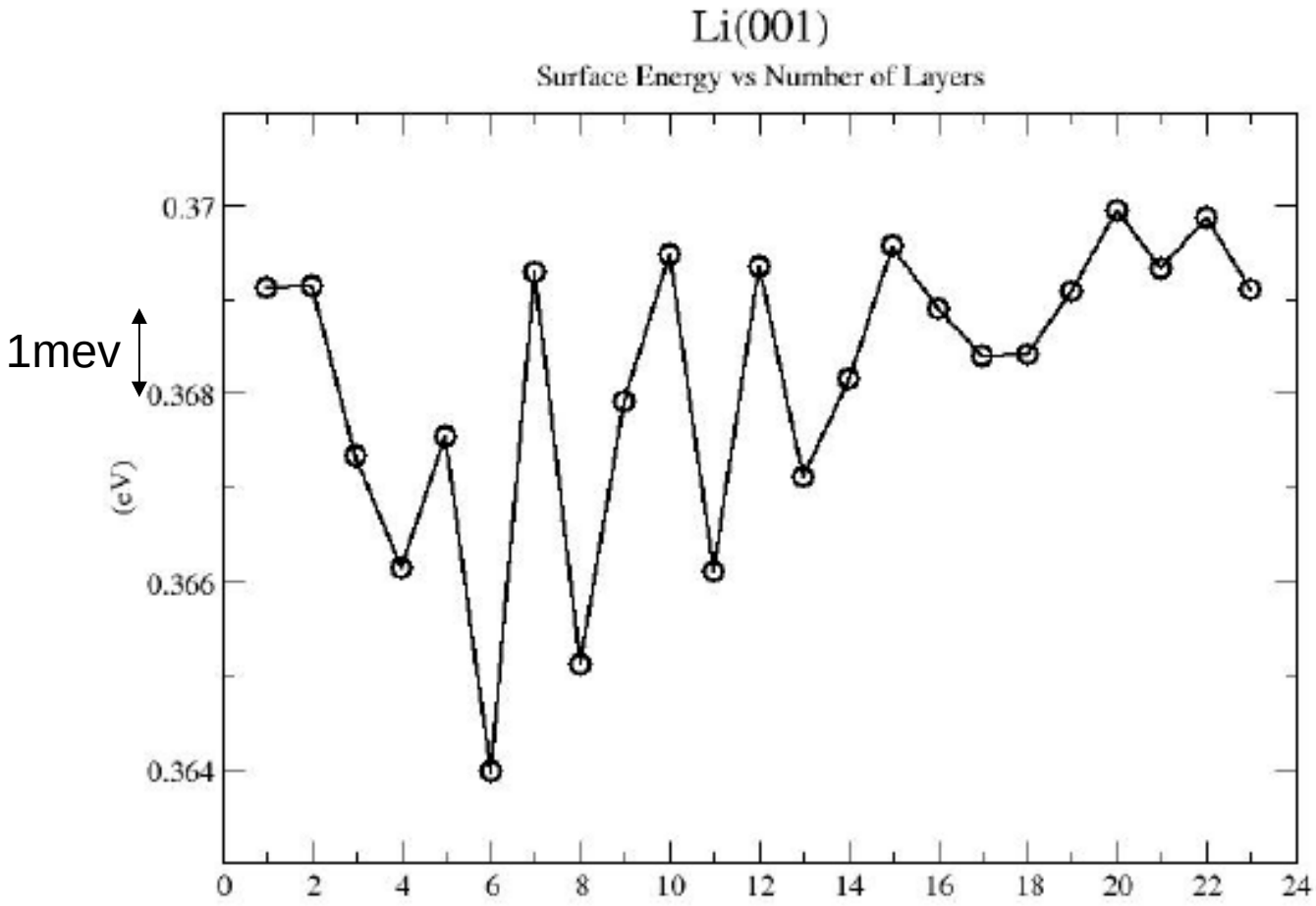


Table 2 Electron work functions[a]

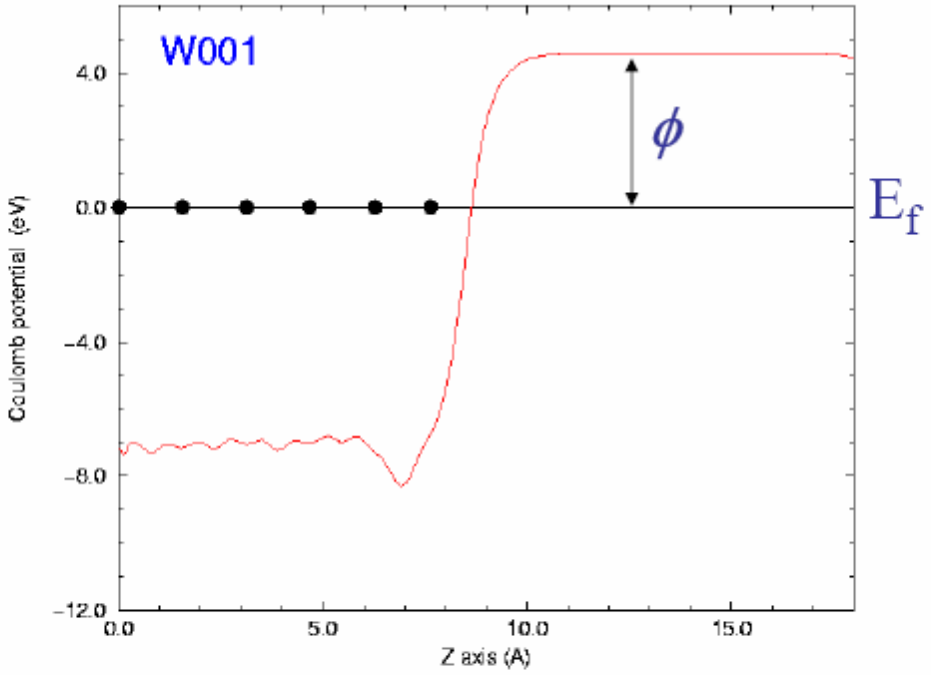
(Values obtained by photoemission, except tungsten obtained by field emission.)

Element	Surface plane	Work function, in eV
Ag	(100)	4.64
	(110)	4.52
	(111)	4.74
Cs	polycrystal	2.14
Cu	(100)	4.59
	(110)	4.48
	(111)	4.98
Ge	(111)	4.80
Ni	(100)	5.22
	(110)	5.04
	(111)	5.35
W	(100)	4.63
	(110)	5.25
	(111)	4.47

[a]After H. D. Hagstrum

Work function for W(001) surface

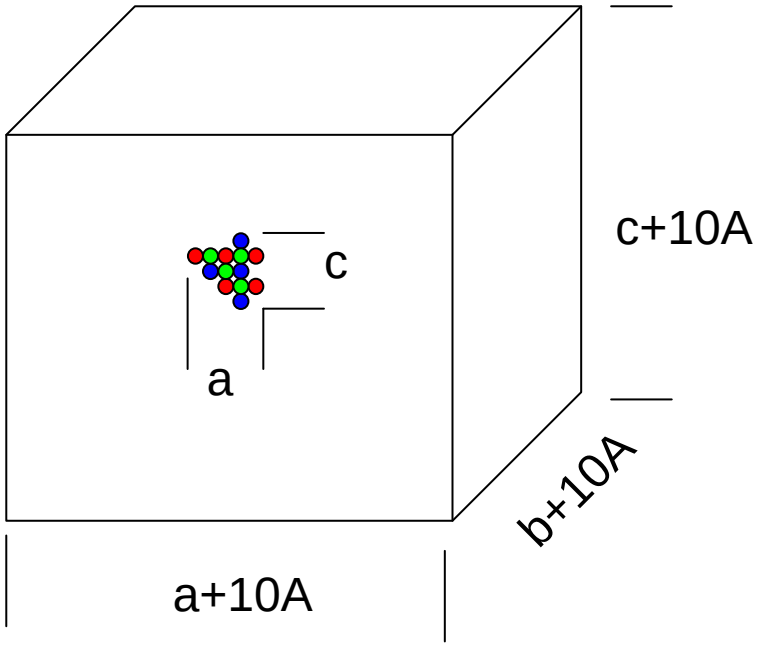
$$V(z) = \frac{1}{A}\iint V(\vec{r})\,dx\,dy$$



Model for molecule calculation

Super cell model

No dispersion
along x,y,z direction



CMS II-8 Hands-on: surface and molecule calculation

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Work list

- Calculate DOS of W(BCC)(111) surface
- Calculate O2 bond length

W(BCC)(111) surface

INCAR:

SYSTEM = W BCC

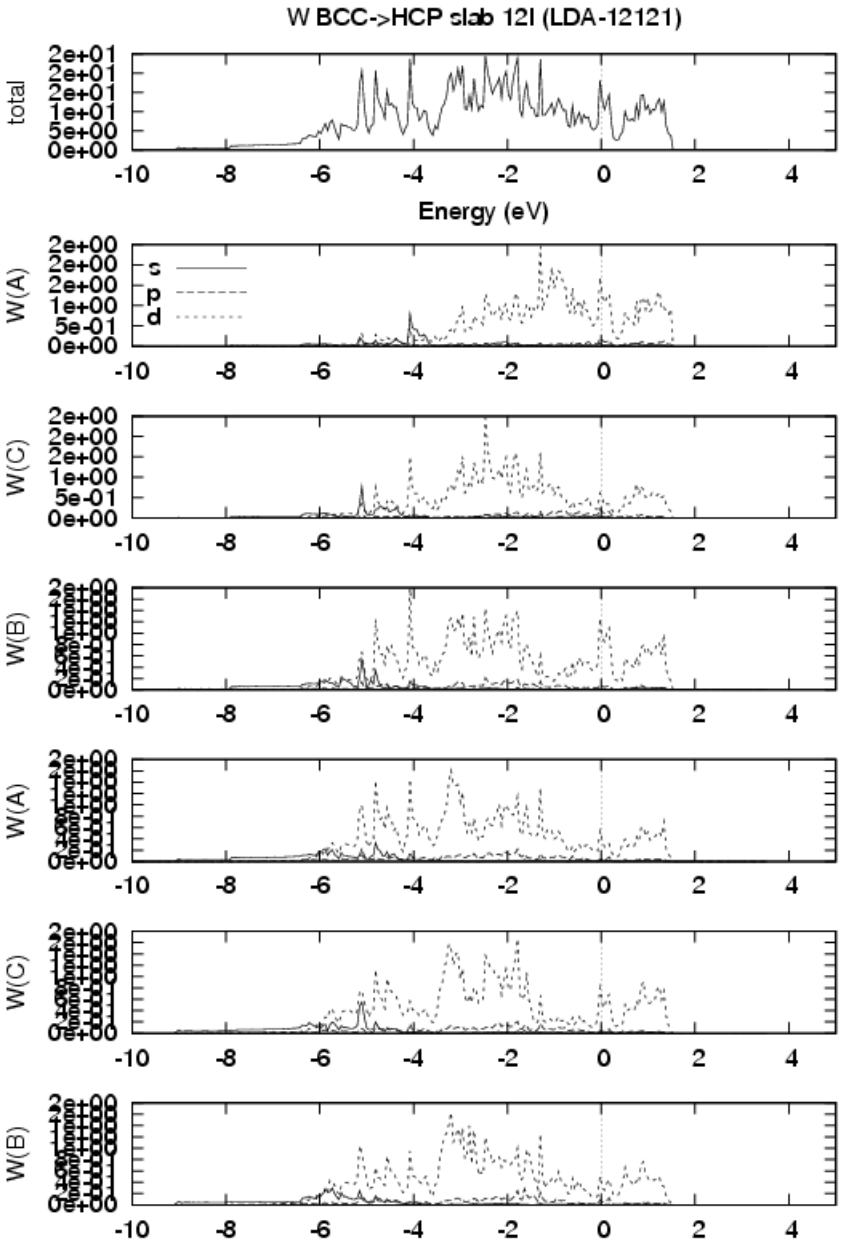
DOS related values
 ISMEAR = -5
 RWIGS = 1.45

KPOINTS:

W
0
GMonkhorst-Pack
12 12 1
0 0 0

POSCAR:

W BCC->HCP
 1.0
 4.47 0.0 0.0
-2.235 3.871133555 0.0
 0.0 0.0 20.0
12
Cartesian
0.0 0.0 0.0 ! W(A)
0.0 2.58077 0.91243 ! W(C)
2.23502 1.29036 1.82480 ! W(B)
0.0 0.0 2.73722 ! W(A)
0.0 2.58077 3.64965 ! W(C)
2.23502 1.29036 4.56202 ! W(B)
0.0 0.0 5.47445 ! W(A)
0.0 2.58077 6.38688 ! W(C)
2.23502 1.29036 7.29925 ! W(B)
0.0 0.0 8.21167 ! W(A)
0.0 2.58077 9.12410 ! W(C)
2.23502 1.29036 10.0365 ! W(B)


W BCC->HCP slab 12l (LDA-12121)
total
W(A)
W(C)
W(B)
W(A)
W(C)
W(B)
s
p
d
Energy (eV)

O2 bond length

INCAR:

SYSTEM = O2

DOS related values
 ISMEAR = 0
 SIGMA = 0.01
 RWIGS = 0.8
 NSW = 50
 ISIF = 2
 IBRION = 2
 POTIM = 0.1

KPOINTS:

O2
0
Monkhorst-Pack
1 1 1
0 0 0

POSCAR:

O2
 1.0
10.0 0.0   0.0
 0.0 10.0 0.0
 0.0 0.0   10.0
 2
Cartesian
 0.0   0.0   0.0 ! O
 0.0   0.0   1.0 ! O

Maximum number of ionic step
Relax atoms only
Ionic relaxation method (conjugate gradient)
Step size

Homework

please Email to jeng@phys.sinica.edu.tw

- Find optimized lattice structure of W(111) surface using ISIF=2 and compare the PDOS of each layer with unrelaxed ones
- Find the optimized bond length of O2 molecule using ISIF=2