# The 37th CMD workshop
# “Advanced study with ES-opt”

## Meta-dynamics simulation with DFT

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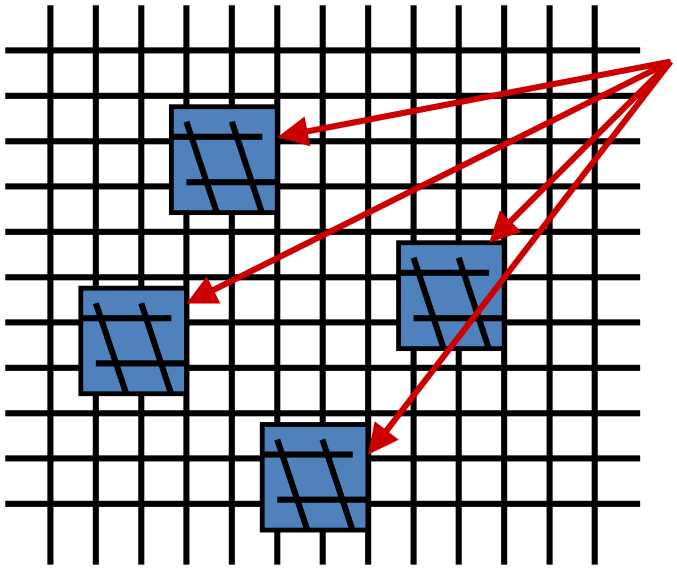
# Authors of this instruction

- Dr. Takahiro Ishikawa @ NIMS
- Prof. Hitose Nagara @ Tottori university

with contributions by K. Kusakabe.

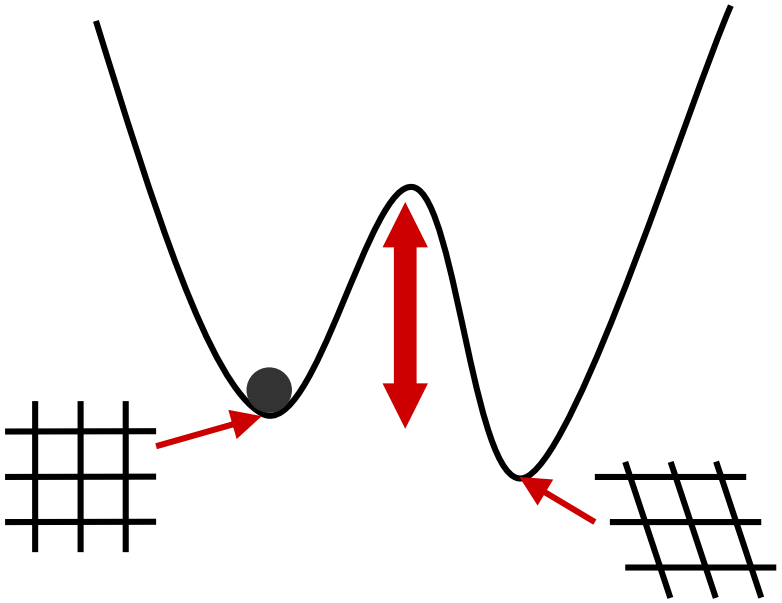
# A problem of conventional MD

## Crystal



Creation of nucleuses in a final form

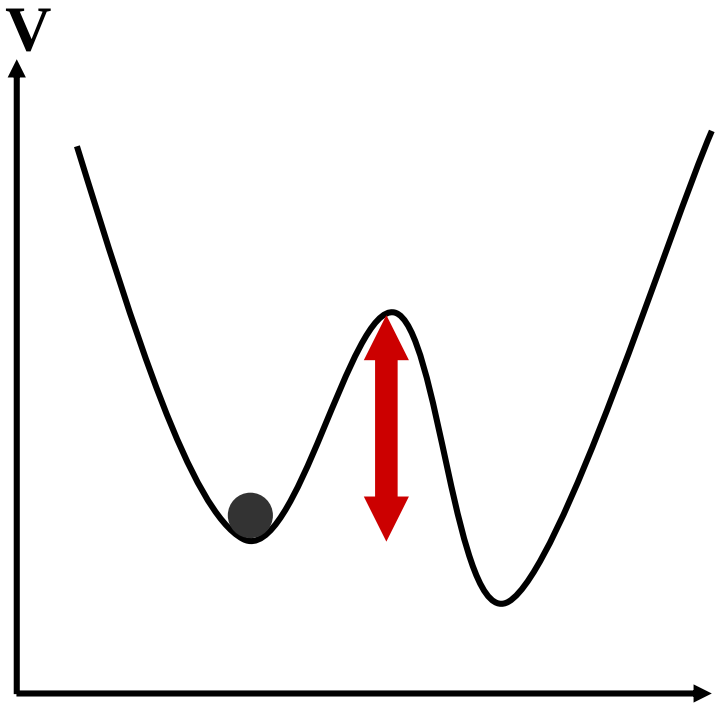
The nucleus formation cause loss in stabilization energy resulted in an energy barrier.

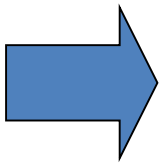


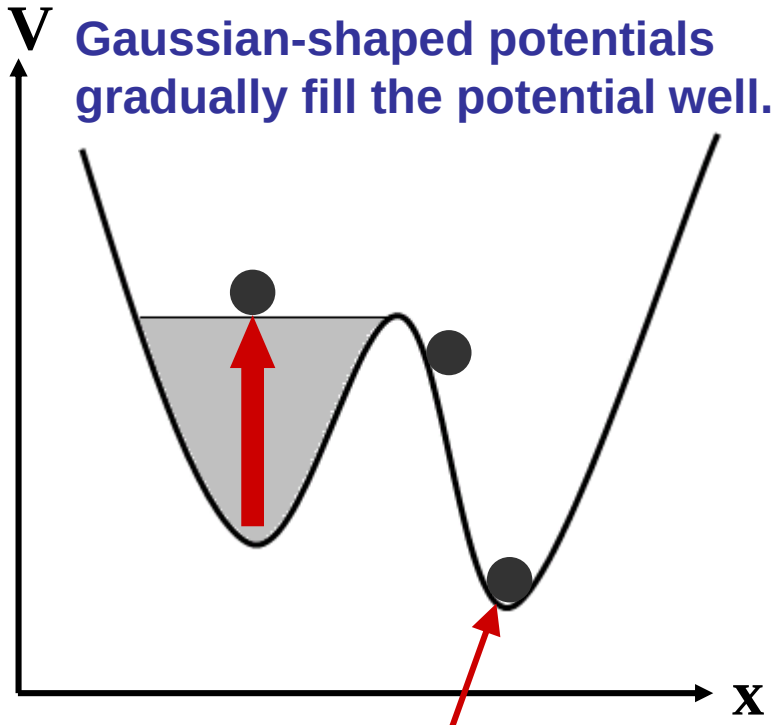
**When the barrier energy is larger than the thermal fluctuation, MD cannot search for the free energy minimum!**

# The Meta Dynamics

R. Martoňák *et al.*, Phys. Rev. Lett. 90, 75503 (2003)






**Gaussian-shaped potentials gradually fill the potential well.**

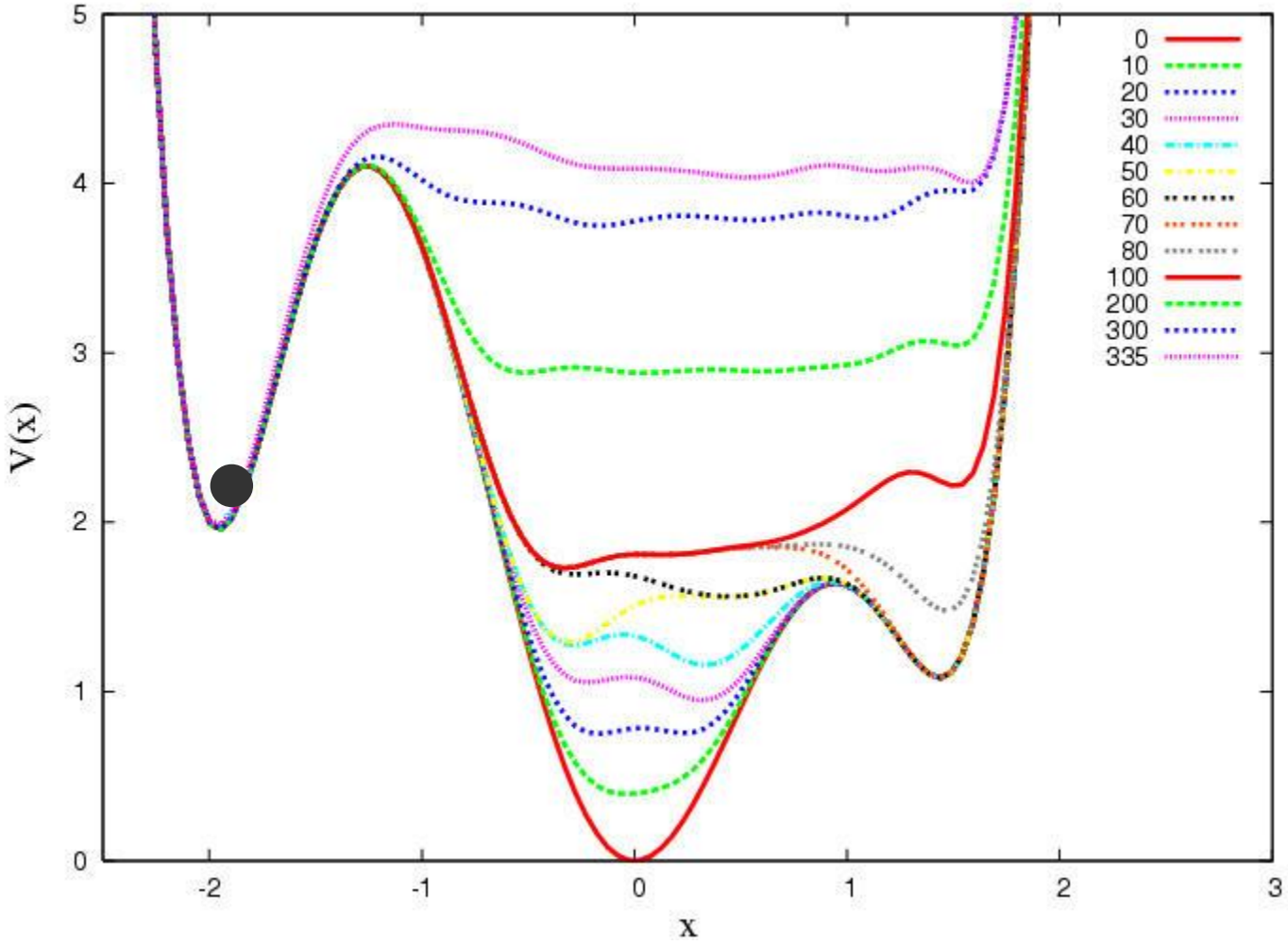
$$V_g(x) = \sum_{t_i<t} W \exp(-\left|x(t) - x(t_i)\right|^2 / 2\delta h^2)$$

$\delta h$ : **Stepping parameter**

$W$ : **Weight of a Gaussian**

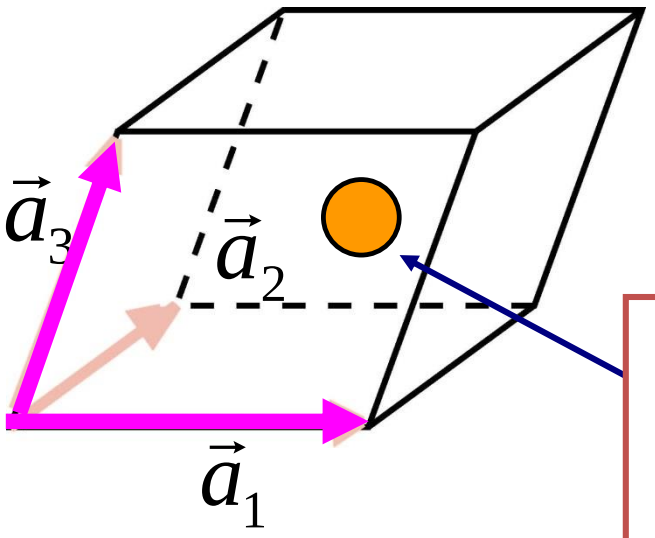
**The motion allows the system fall into the minimum.**

# The Meta Dynamics



# Application of the meta-dynamics for a simulation of the pressure induced structural transformation

Simulation cell




Action of the simulation cell makes the system escape from the potential well. (A step of this action is called a meta-step.)

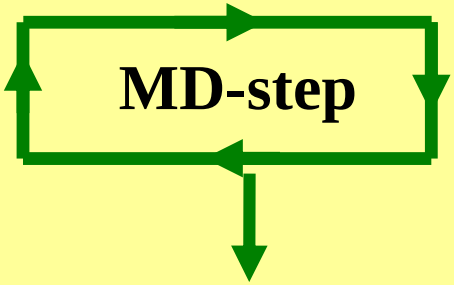
Between adjacent meta-steps, the system moves following the conventional MD.

As a result, search of the free-energy minimum is done on a nine-dimensional phase space (reduced to six-dimensional space by utilizing a symmetric matrix representation) specified by ($\vec{a}_1$, $\vec{a}_2$, $\vec{a}_3$).

# Flowchart of Meta-dynamics

Starting from a minimal as a potential well.

① Constant $\underline{h}$ MD




・New atomic position
・Pressure tensor

② Driving force $\underline{F}_o^t$

⑥ Total driving force

③ Update of $\underline{h}$

**Filling the FES**

Already visited $\underline{h}$

④ Filling the FE well

⑤ Driving force $\underline{F}_g^t$

By adding Gauss potentials, the system goes out of the potential well.

# Metadynamics Algorithm

**R. Mortonak *et al.*, Phys. Rev. Lett. 90, 75503 (2003)**

② $\underline{\mathrm{F}}^{t}_{o\,ij} = -\partial G^{t}_{o} \big/ \partial \underline{\mathrm{h}}^{t}_{ij}$

$\underline{\mathrm{p}}^{t}$ : Internal pressure tensor

$$\underline{\mathrm{F}}^{t}_{o\,ij} = -\partial G^{t}_{o} \big/ \partial \underline{\mathrm{h}}^{t}_{ij} = \Omega^{t}\{[(\underline{\mathrm{p}}^{t} - p_{\mathrm{ext}})\underline{\mathrm{h}}^{t\,-1}]_{ij} + [(\underline{\mathrm{p}}^{t} - p_{\mathrm{ext}})\underline{\mathrm{h}}^{t\,-1}]_{ji}\}\left(1 - \frac{1}{2}\delta_{ij}\right)$$

⑥ $\underline{\mathrm{F}}^{t} = \underline{\mathrm{F}}^{t}_{o} + \underline{\mathrm{F}}^{t}_{g}$

$\underline{\mathrm{F}}^{t}_{o}$ : Driving force from original G

$\underline{\mathrm{F}}^{t}_{g}$ : Driving force from Gaussian

③ $\underline{\mathrm{h}}^{t+1} = \underline{\mathrm{h}}^{t} + \delta h\, \underline{\mathrm{F}}^{t} \big/ \left|\underline{\mathrm{F}}^{t}\right|$

$t$ : Number of metasteps

$\delta h$ : Stepping parameter

⑤ $G^{t}_{g}(\underline{\mathrm{h}}^{t}) = \sum_{t(i)<t} We^{-\left|\underline{\mathrm{h}}^{t} - \underline{\mathrm{h}}^{t(i)}\right|^{2} \big/ 2\delta h^{2}}$

$W$ : Height of a Gaussian

⑥ $\underline{\mathrm{F}}^{t}_{g\,ij} = -\partial G^{t}_{g} \big/ \partial \underline{\mathrm{h}}^{t}{}_{\mathrm{ij}} = \sum_{t(i)<t} \frac{W}{\delta h^{2}} (\underline{\mathrm{h}}^{t} - \underline{\mathrm{h}}^{t(i)}) e^{-\left|\underline{\mathrm{h}}^{t} - \underline{\mathrm{h}}^{t(i)}\right|^{2} \big/ 2\delta h^{2}}$

# Metadynamics simulation method in ESopt

Metadynamics parts are written in
UNIX shell scripts and perl scripts.

Ab-initio MD part uses ESopt.

How to run the examples
on the workshop machines
will be given in separate documents.
(This time, it is not distributed, because it is under reconstruction.)

# Very Simple Example

## Impurity migration

- H in Silicon

Si ---- 8 atoma in a cube and
on diamond latice points

H ----- 1

→ escape from a minimum energy point

1) Try a run with default parameters

2) Try runs with diffrent parameters

# More Complicate Example

Pressure induced structural phase transition

- **Si ---- 8 atoms in a cube on diamond lattice points**
- **Apply the pressure**

→ **Unit cell shape will change**

# Predicting Crystal Structures

- Very simple equation of motion

$$G(\mathbf{h}) = F(\mathbf{h}) + PV$$

where $G(\mathbf{h})$ is the Gibbs free energy
and $F(\mathbf{h})$ is the Helmholtz free enrgy
as functions of $\mathbf{h} = (\mathbf{a}, \mathbf{b}, \mathbf{c})$ with $V = \det(\mathbf{h})$.

Driving force for the change of $\mathbf{h}$

$$-\frac{\partial G}{\partial h_{ij}} = V\{[(\mathbf{p}^t - p)\mathbf{h}^{-1}]_{ij} + [(\mathbf{p}^t - p)\mathbf{h}^{-1}]_{ji}\}(1 - \frac{1}{2}\ \delta_{ij})$$

$$\mathbf{F}^t = -\frac{\partial G}{\partial \mathbf{h}} \quad , \qquad \mathbf{h}^{t+1} = \mathbf{h}^t + \delta h \frac{\mathbf{F}^t}{\left|\mathbf{F}^t\right|}$$

**Internal stress $P^t$ are calculated by an ab-initio MD pacckage**

In metadynamics, history dependent Gaussian potential is added to get $G^t(\mathbf{h})$,

where

$$G^t(\mathbf{h}) = G(\mathbf{h}) + \sum_{t'<t} We^{-\left|\mathbf{h}-\mathbf{h}^{t'}\right|^2/2(d\mathbf{h})^2}$$

between t +1and t, MD run at constant **h**, $P$, and $T$ long enough to allow reluxation.

- Using metadynamics to get information how to synthesize new materials
- High pressure is one of those methods
- Nanoscience

**→Large sample size simulation is necessary (pararell computor)**

CMD-WS 13 @ IIAS
2008.9.10

# Determining the structure of compressed calcium in phase V by the ab-initio molecular dynamics simulation

Graduate School of Engineering Science, Osaka University
T. Ishikawa, A. Ichikawa, H. Nagara, K. Kusakabe and N. Suzuki

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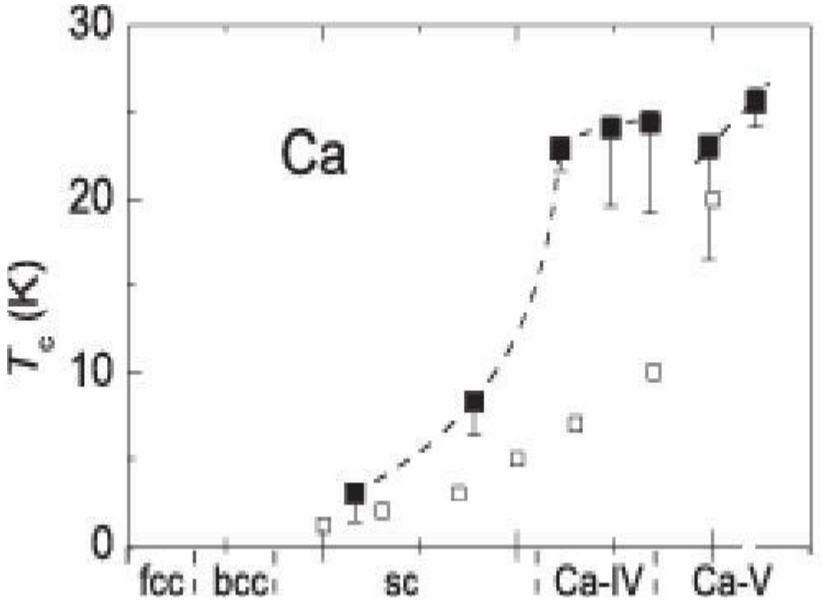
# Superconductuvity in Ca at high Pressures

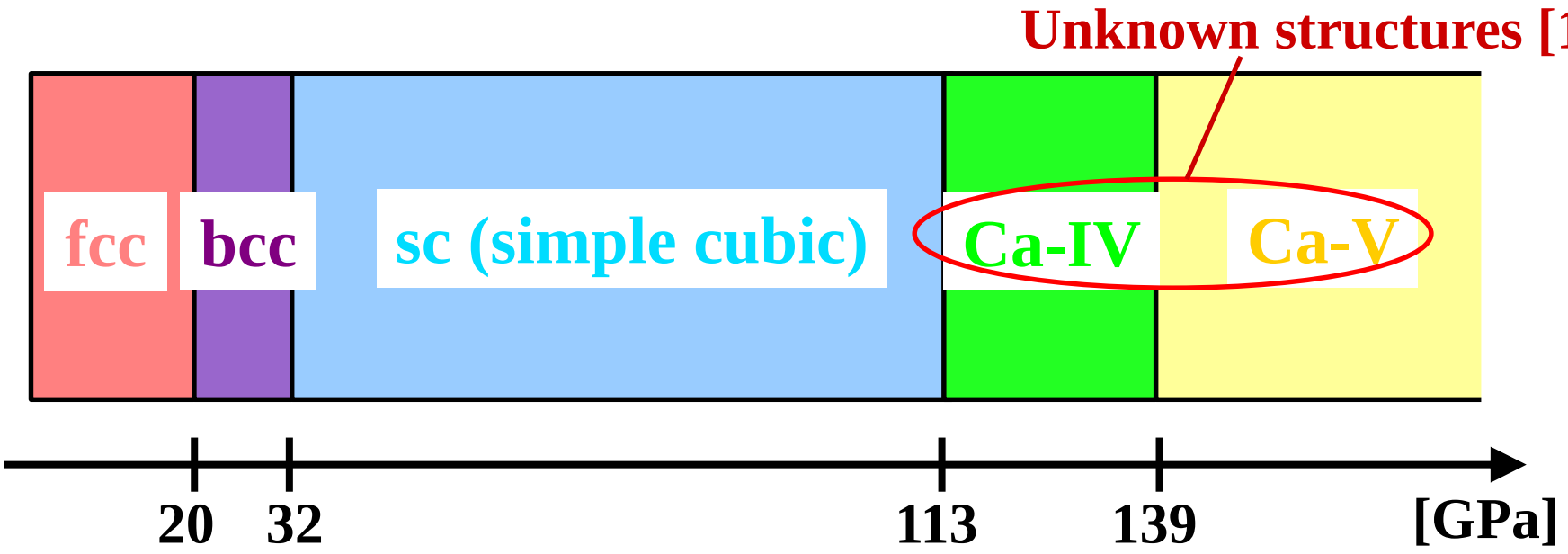
- High $T_c$ : 25K at 161GPa
- Highest record in elements

(2nd is Li 20 K at 48GPa)




T.Yabuuchi,T.Matsuoka,
Y.Nakamoto, and K. Shimizu,
J.Phys.Soc.JPN, 75, 83703(2006)

# Previous research of compressed calcium




- Decrease of the coordination number with increase of pressure.
  12(fcc)→8(bcc)→6(sc)
- The simple cubic structure can exist in wide pressure range.
- Superconducting transition temperature Tc linearly increases with increase of pressure. → 25K at 161GPa [2]


[1] T. Yabuuchi et al., J. Phys. Soc. Jpn. 74, 2391 (2005).
[2] T. Yabuuchi et al., J. Phys. Soc. Jpn. 75, 83703 (2006).

# Computational details

- Metadynamics code + PWscf code
- Ultrasoft pseudopotential, GGA(Perdew-Wang 91)
- Valence electron → 3s, 3p, 4s
- k-space integration → 8×8×8, Cut-off energy →24Ry

- Update of the cell by the steepest descent method (Meta-step)

$$\mathbf{h}_{ij}^{t+1} = \mathbf{h}_{ij}^{t} + \delta h \mathbf{F}_{ij}^{t} / |\mathbf{F}_{ij}^{t}| \qquad \mathbf{h} = (\vec{a}, \vec{b}, \vec{c})$$

$\delta h$ : Stepping parameter

- Driving force

$$\mathbf{F}_{ij}^{t} = \mathbf{F}_{\mathbf{o}ij}^{t} + \mathbf{F}_{\mathbf{g}ij}^{t} \qquad \mathbf{F}_{\mathbf{o}ij}^{t} = -\partial G_o(\mathbf{h}^t)/\partial \mathbf{h}_{ij}$$

$G_o$ : Gibbs free energy

$$\mathbf{F}_{\mathbf{g}ij}^{t} = -\partial G_g(\mathbf{h}^t)/\partial \mathbf{h}_{ij}$$

- Guassian potential

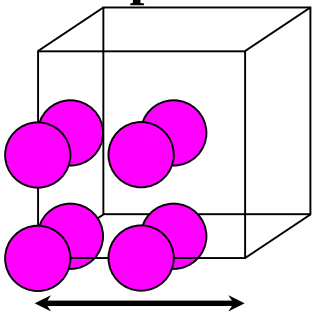
$$G_g(\mathbf{h}^t) = \sum_{t'<t} \prod_{i,j} W \exp(-[\mathbf{h}^t - \mathbf{h}^{t'}]_{ij}^2 / 2\delta h^2)$$

$W$ : Weight of a Gaussian

- 120GPa, 100 MD-steps/1 meta-step

# Result of the conventional MD

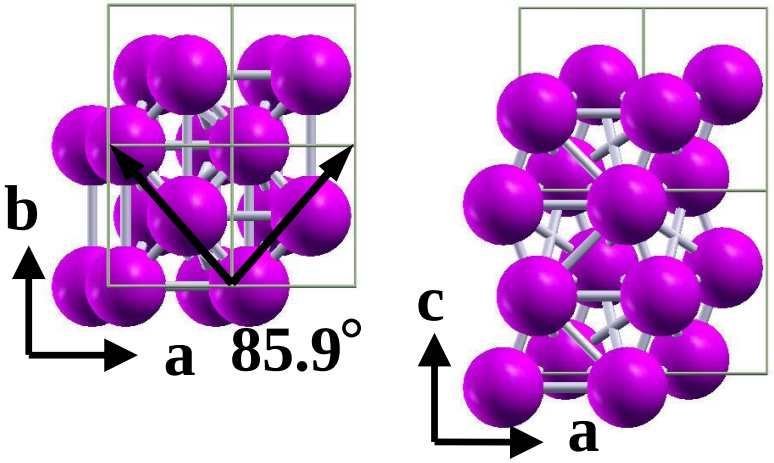
Simple cubic



8 atoms

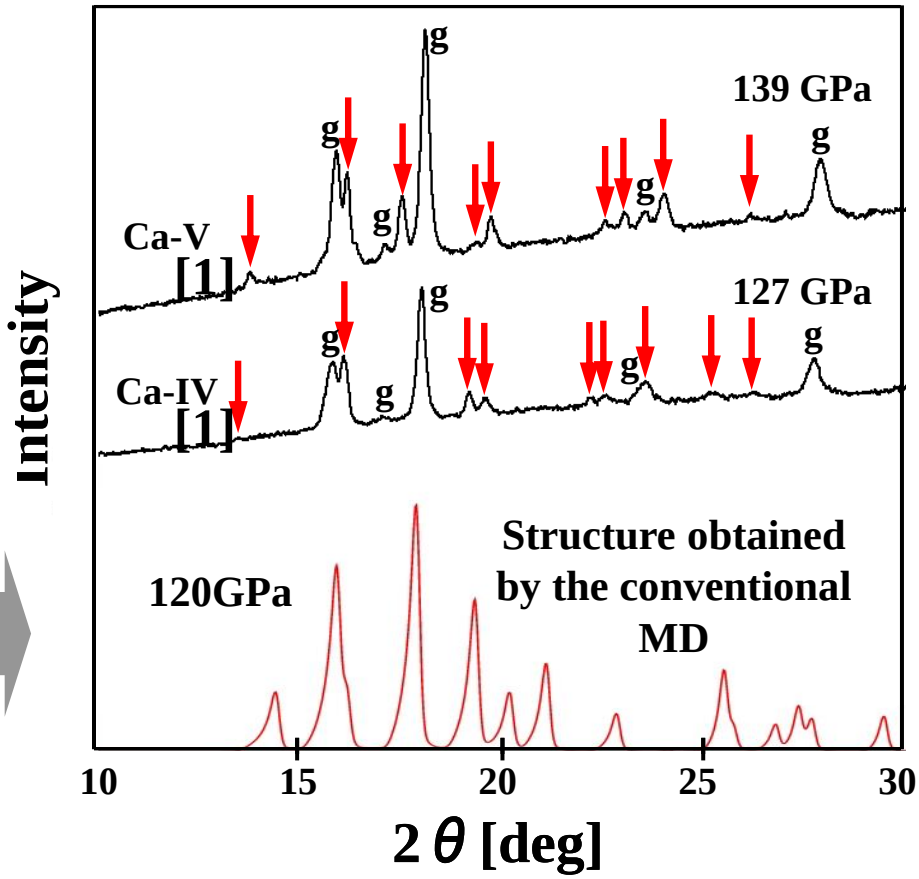
4.5Å

Structure obtained
by the conventional MD



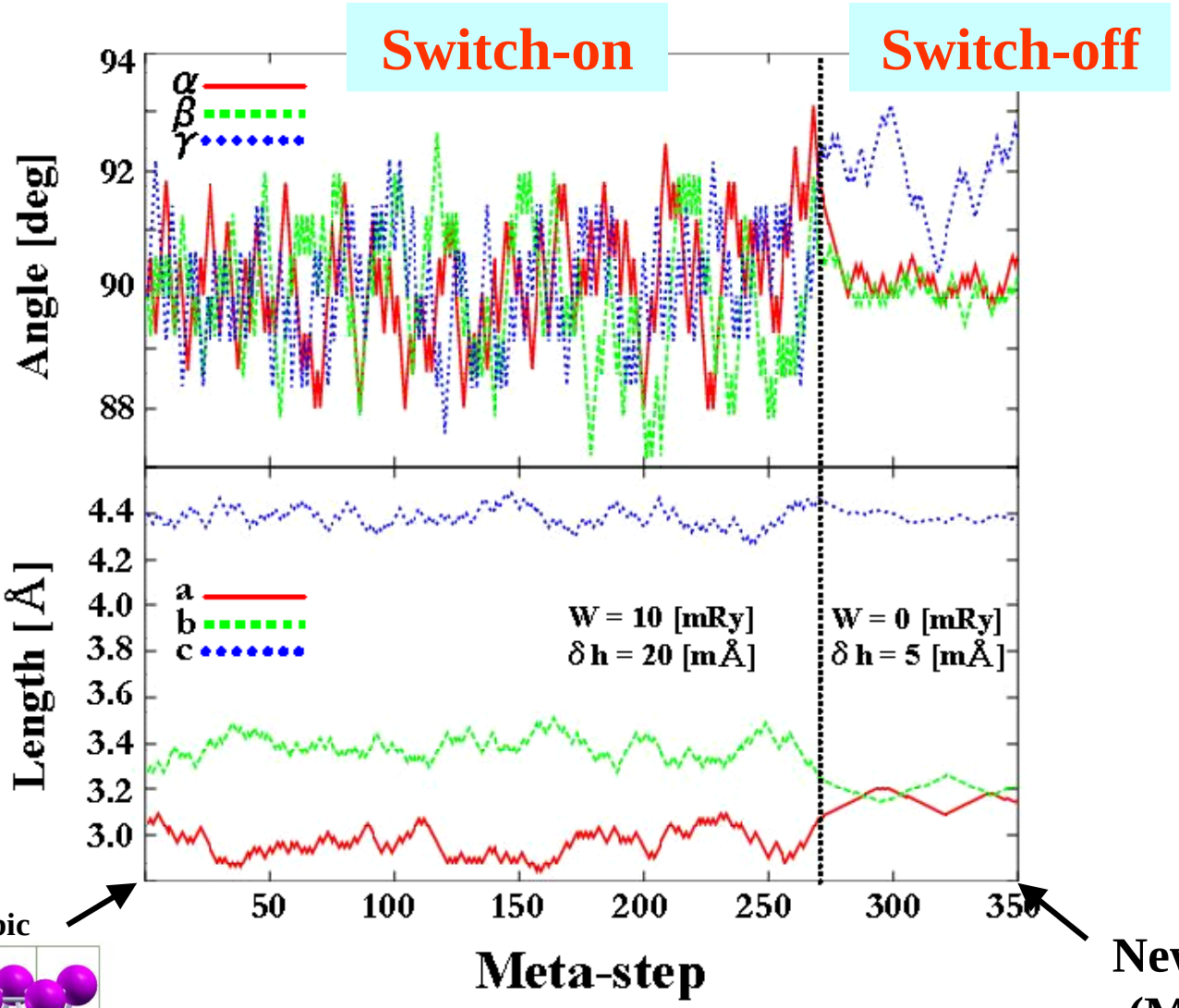

a=3.05Å, b/a=1.08, c/a=1.44

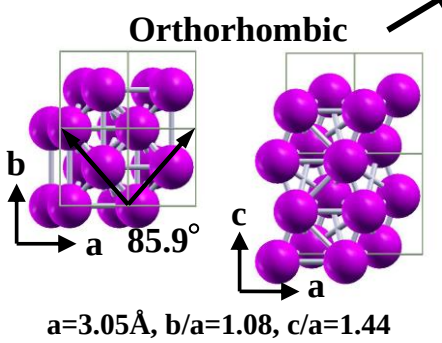
[1] T. Yabuuchi et al.,
J. Phys. Soc. Jpn. 74, 2391 (2005)




The diffraction pattern does not match the experimental patterns!

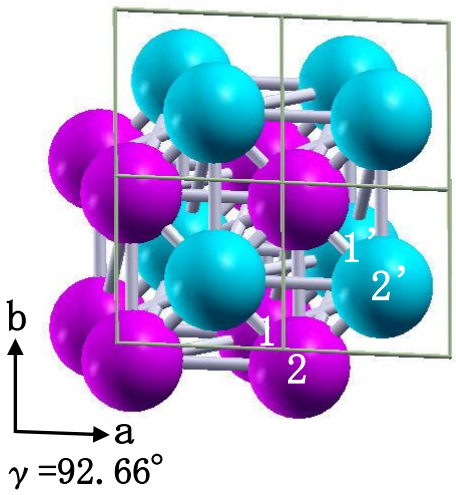
# Result of the metadynamics simulation

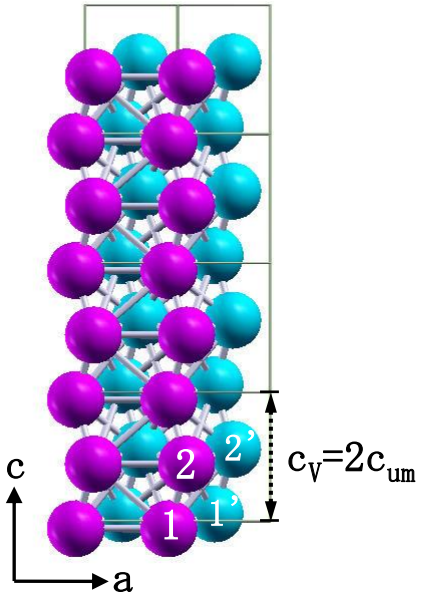


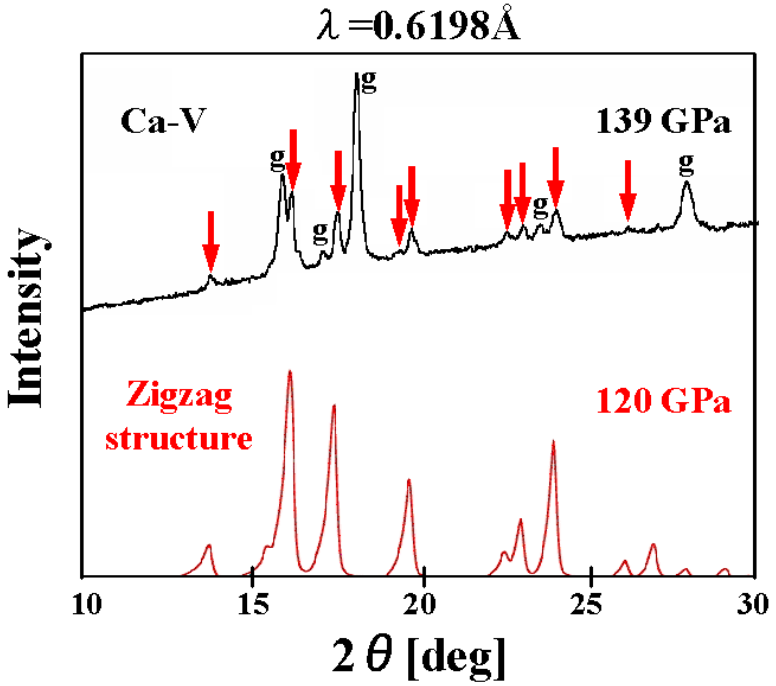




$$G_g(\mathbf{h}^t) = \sum_{t'<t} \prod_{i,j} W \exp(-[\mathbf{h}^t - \mathbf{h}^{t'}]^2_{ij}/2\delta h^2)$$

# New structure obtained by the metadynamics




- **Interpenetrating structure of two monoclinic lattices**
- **Zigzag pattern along c axis**

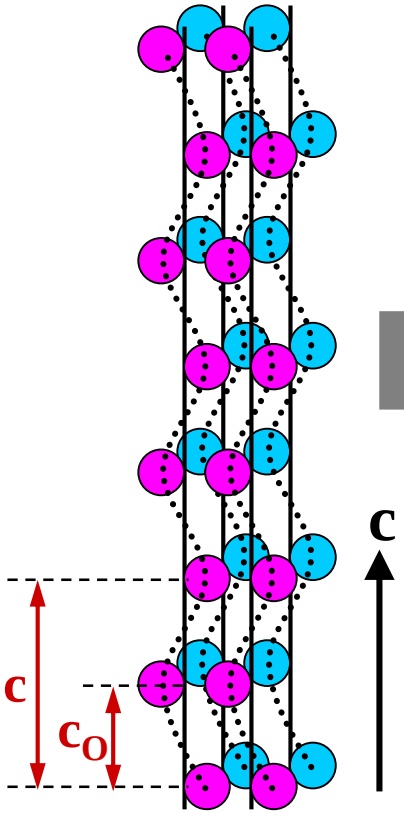
**g : Peaks from a metal gasket**
**↓: Diffraction peaks from the sample**

**The zigzag structure is the candidate structure of Ca-V!**

# Exploration of the structure of Ca-IV

**Final structure of Ca-V**

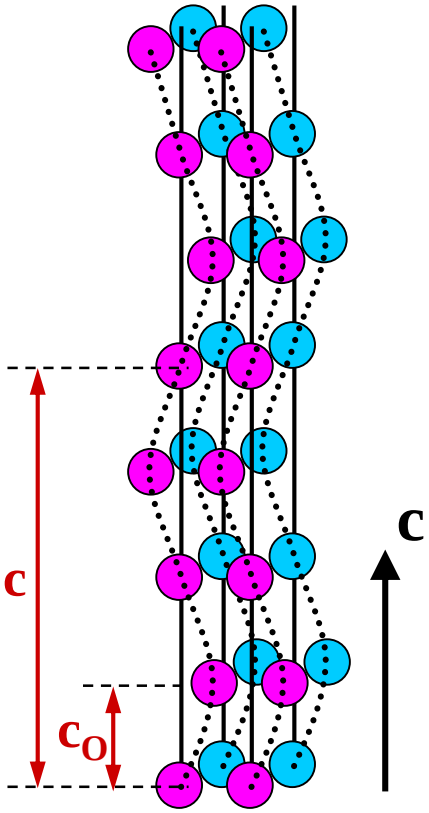
$\vec{q} = (0,0,0.5)$




$c/c_O=2$

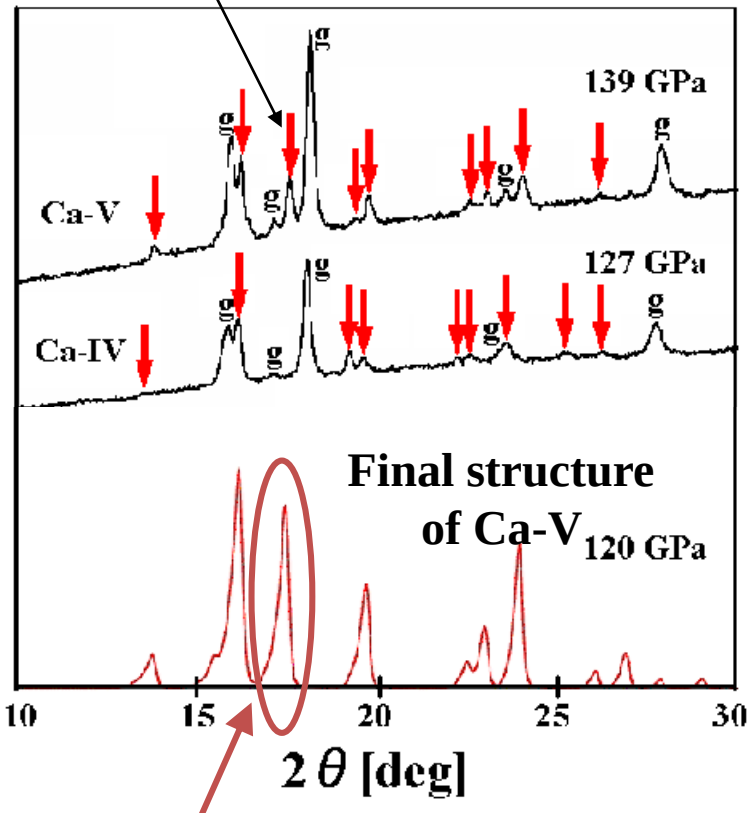
**Predicted structure of Ca-IV**

$\vec{q} = (0,0,0.25)$




$c/c_O=4$

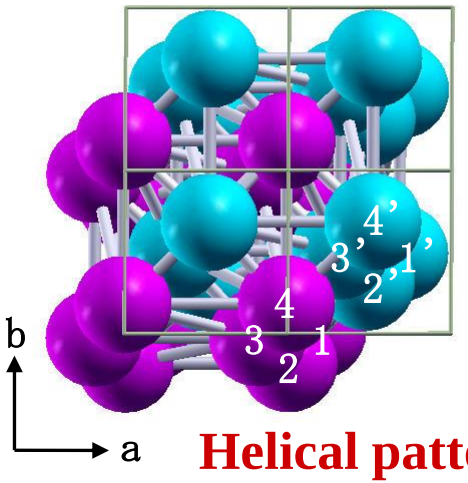
**Most distinct change at the transition from Ca-IV to Ca-V!**



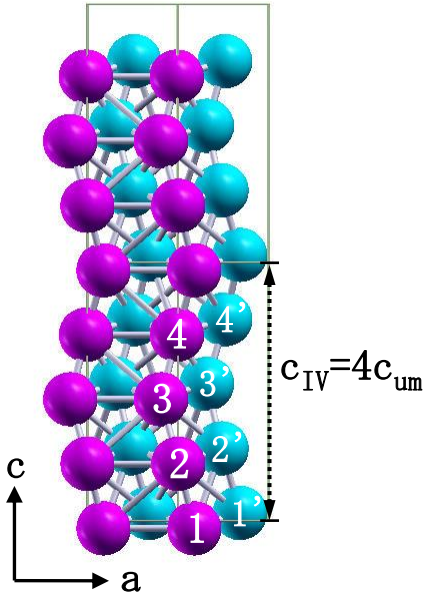

**The peak around 17° disappears by changing q from (0,0,0.5) to (0,0,0.25)!**

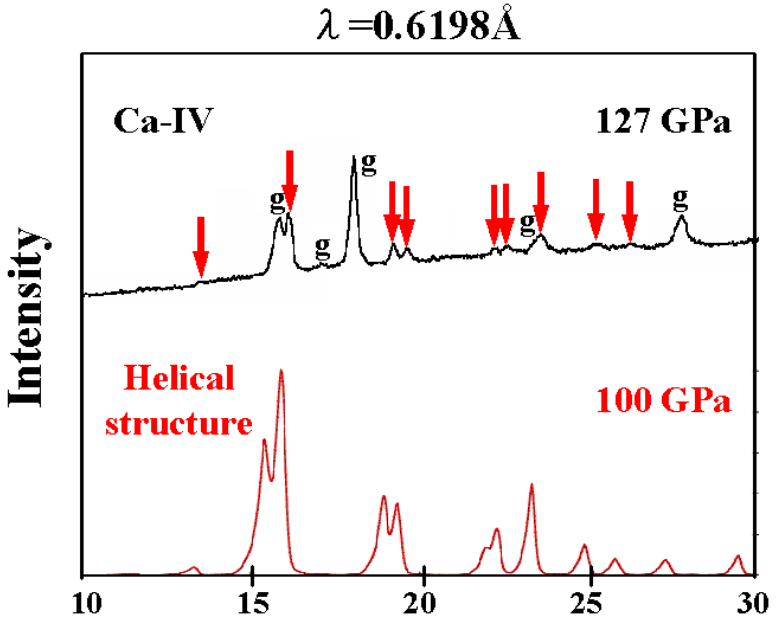
# Structures of Ca-IV and Ca-V

## Candidate of Ca-IV

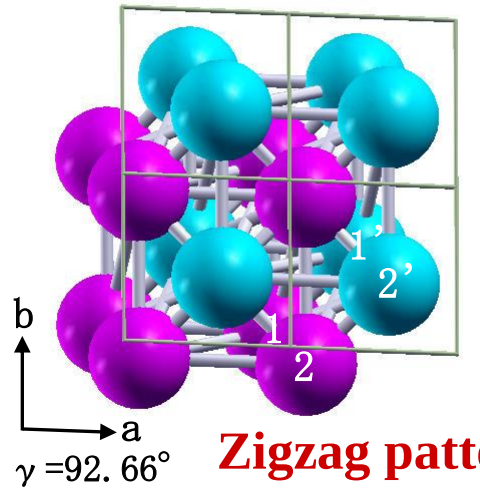



Helical pattern

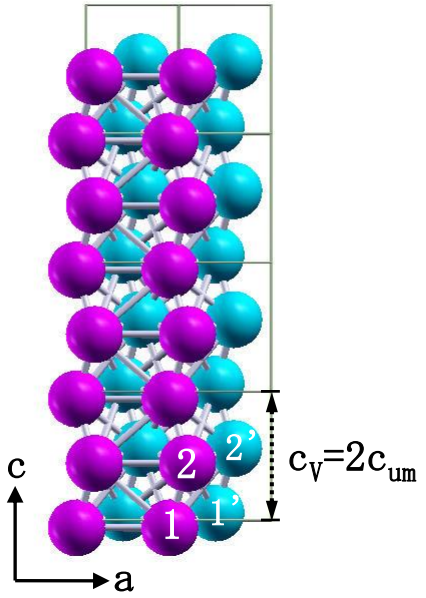


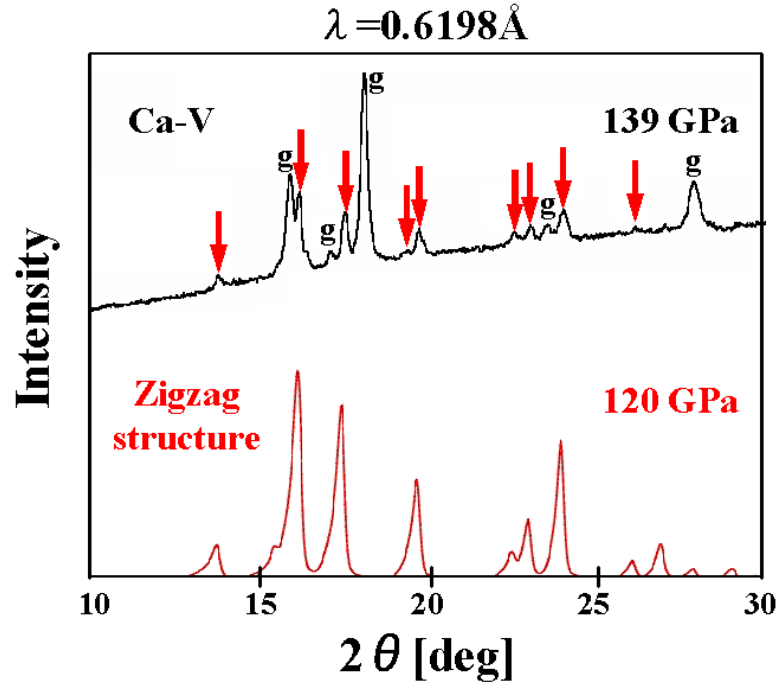




## Candidate of Ca-V

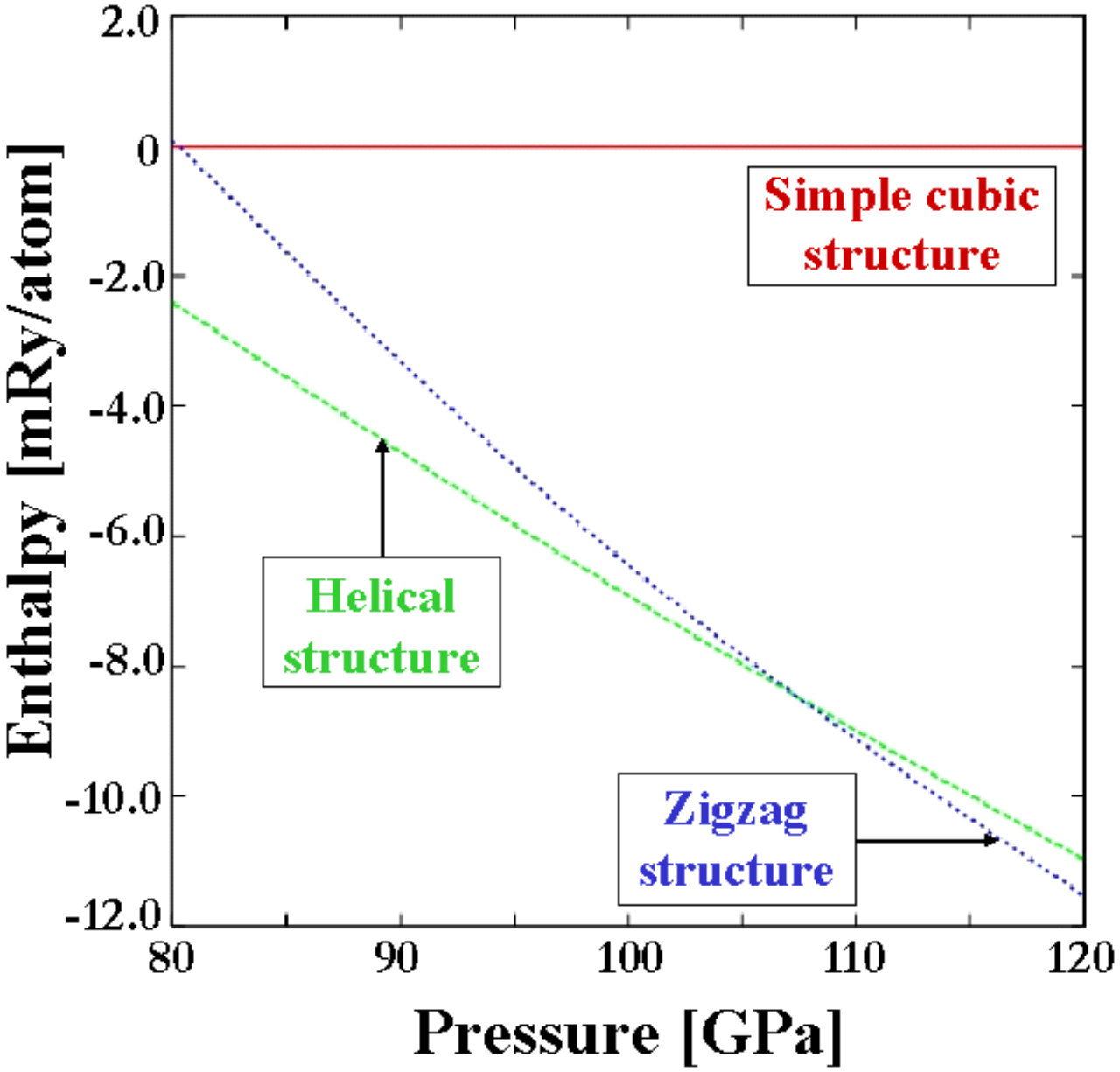



Zigzag pattern



# Comparison of the enthalpy curves



# Calculated Tc for the zigzag structure

**μ*=0.1, k-points=(32,32,32), q-points=(4,4,4)**

| P[GPa] | λ | $\omega_{log}$[K] | Tc[K] |
|---|---|---|---|
| 100 | 1.1113 | 245.07 | 19.87 |
| 110 | 1.0524 | 240.01 | 18.04 |
| 120 | 0.9909 | 250.87 | 17.23 |
| 130 | 0.9149 | 294.35 | 17.74 |
| 140 | 0.8932 | 314.79 | 18.19 |

# Summary

- **The predicted structure of Ca-IV is the interpenetrating structure of two tetragonal lattices with the helical distortion.**

- **The predicted structure of Ca-V is the interpenetrating structure of two monoclinic lattices with the zigzag distortion.**

- **We calculated Tc for the zigzag structure and obtained high values which are almost equal to the experimental data.**