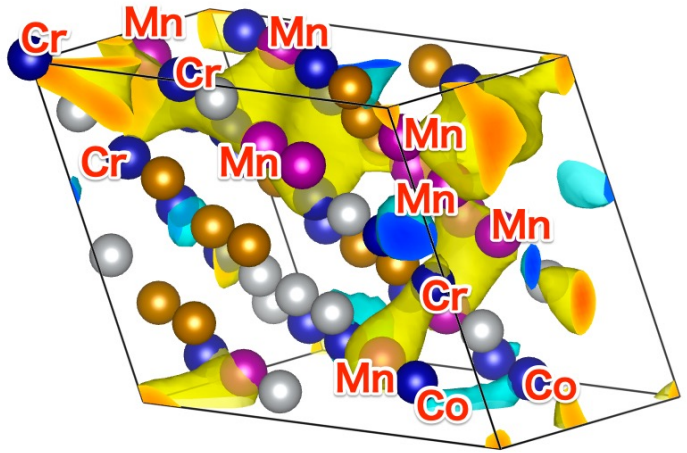
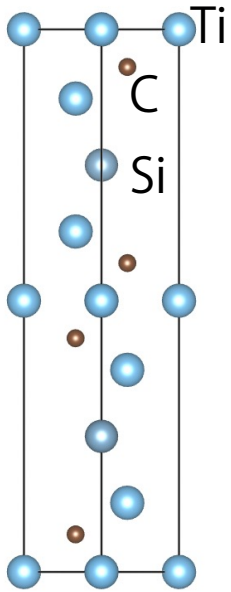
Atomic Stress Calculation in OpenMX





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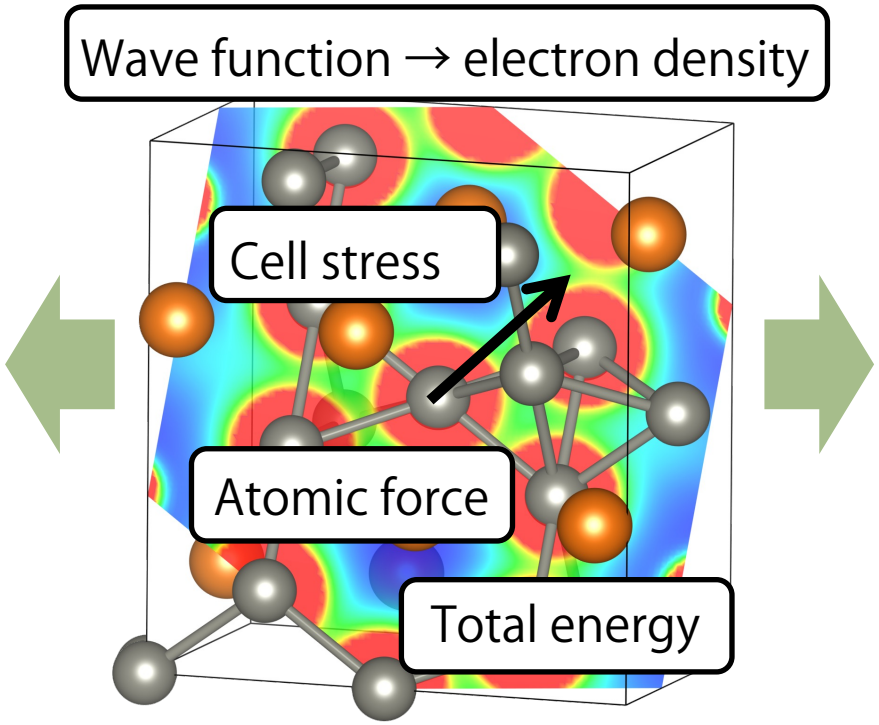
Overview

- Background
- Atomic stress: formulation and Implementation in OpenMX
- Applications
  - Atomic stress distribution in multicomponent alloys and its origins
  - Elastic heterogeneity in hetero-nanostructures

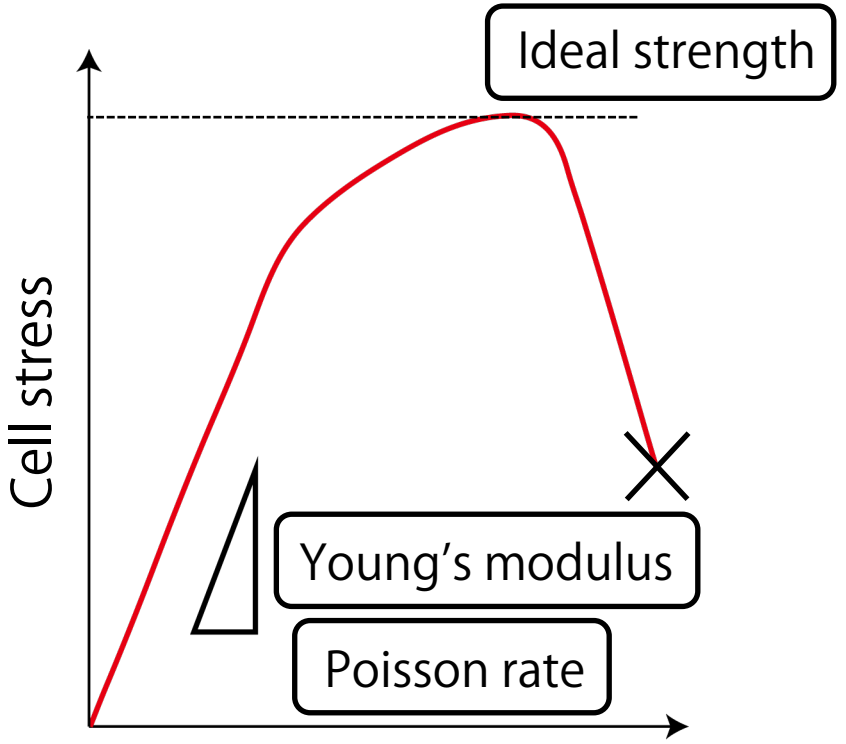
Background

Materials Mechanics from ab initio

Ab initio calculation gives energy, force and stress based on quantum mechanics.



Atomic structure of $MgZn_2$
(periodic boundary condition)



Stress-strain curve on cell

Stress distribution is not available in conventional methods.

Why atomic stress?

Elastic interaction between dislocation and solute atom

$$U_{\mathrm{el}}(x,y) = -p(x,y)\,\mathrm{d}V$$

Strain energy by dislocation

Pressure

Volume change by dislocation

Pressure by dislocation

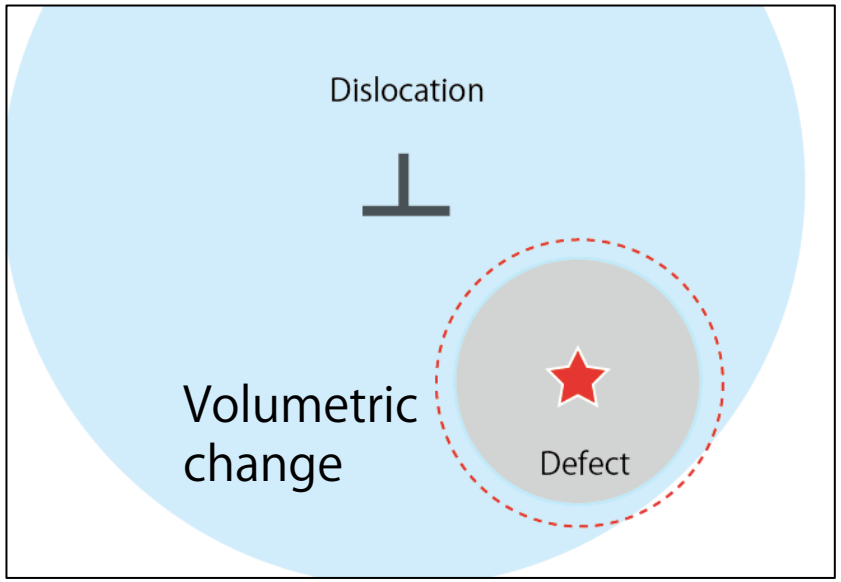
$$p_{\mathrm{d}}(x,y) = K\varepsilon_v = \frac{\mathrm{d}V}{V}$$

Bulk modulus, Volumetric strain

Pressure by dislocation

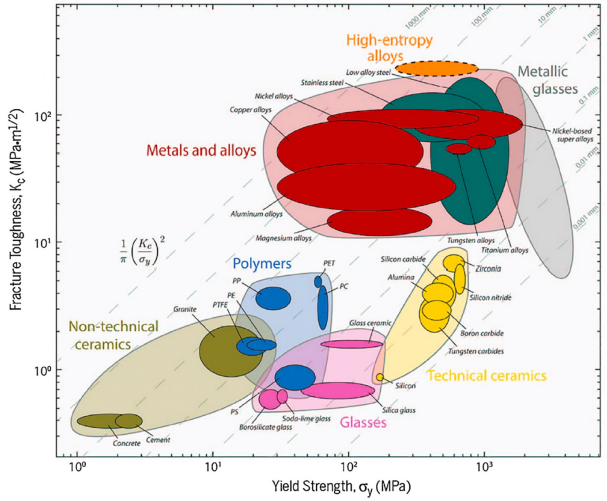
$$U_{\mathrm{el}}(x,y) = -p(x,y)\,p_{\mathrm{d}}(x,y)\,\frac{V}{K} = -\left(p_{\mathrm{D}}(x,y) + p_{\mathrm{d}}(x,y)\right)p_{\mathrm{d}}(x,y)\,\frac{V}{K}$$

Pressure by defect



reflecting characterisity of defect

Elastic interaction can be understood based on the electronic structure.



Stress in continuum mechanics

Momentum conservation laws

Stress vector $\mathbf{t}_n = \boldsymbol{\sigma}(\mathbf{r}) \cdot \mathbf{n}$ Surface normal

Stress tensor

$$\int_V \rho \mathbf{a} \mathrm{d}V = \int_V \rho \mathbf{g} \mathrm{d}V + \int_S \mathbf{t}_S \mathrm{d}S$$

Density acceleration Body force Surface force

$$\int_V \rho \mathbf{r} \times \mathbf{a} \mathrm{d}V = \int_V \rho \mathbf{r} \times \mathbf{g} \mathrm{d}V + \int_S \mathbf{r} \times \mathbf{t} \mathrm{d}S$$

$$\rho \mathbf{a} = \mathrm{div}\boldsymbol{\sigma}(\mathbf{r}) + \rho \mathbf{g}$$

$$\boldsymbol{\sigma}^{\mathrm{T}}(\mathbf{r}) = \boldsymbol{\sigma}(\mathbf{r})$$

$$\mathbf{f}(\mathbf{r}) = \mathrm{div}\boldsymbol{\sigma}(\mathbf{r})$$

Divergence of stress is equal to the forve acting on a material point.

Energy conservation law

Force Deformation

$$\int \delta R(\mathbf{r}) \mathrm{d}V = \int \mathbf{f}(\mathbf{r}) \cdot \delta \mathbf{u}(\mathbf{r}) \mathrm{d}V = \int \mathrm{div}\boldsymbol{\sigma}(\mathbf{r}) \cdot \delta \mathbf{u}(\mathbf{r}) dV$$

Work

$$\boldsymbol{\sigma}(\mathbf{r}) = \left(\frac{\partial F(\mathbf{r})}{\partial \boldsymbol{\varepsilon}(\mathbf{r})} \right)_T$$

Stress field: strain derivative of free energy density

Stress in atomic level

Momentum conservation law

Discretization

$$\mathrm{div}\boldsymbol{\sigma}(\mathbf{r}) = \sum_i \mathbf{f}_i \delta(\mathbf{r} - \mathbf{r}_i)$$

Fourier transformation

$$i\mathbf{k}\hat{\boldsymbol{\sigma}}(\mathbf{k}) = -\sum_i \mathbf{f}_i \exp(i\mathbf{k}\cdot\mathbf{r}_i)$$

Two-body force

$$= -\sum_i \sum_{i\neq j} \mathbf{f}_{ij} \exp(i\mathbf{k}\cdot\mathbf{r}_i)$$

Inverse Fourier transformation

$$\boldsymbol{\sigma}(\mathbf{r}) = \frac{1}{2}\sum_i \sum_{i\neq j} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij} \delta(\mathbf{r} - \mathbf{r}_i)$$

Integrate and average

$$\bar{\boldsymbol{\sigma}} = \frac{1}{V}\int_V \boldsymbol{\sigma}(\mathbf{r})d\mathbf{r} = \frac{1}{2V}\sum_i \sum_{j\neq i} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij}$$

Cell stress

$$\boldsymbol{\sigma}_i = \frac{1}{2V_i}\sum_{j\neq i} \mathbf{r}_{ij} \otimes \mathbf{f}_{ij}$$

Atomic stress

Basically, two-body force is not defined in ab initio calculation

Energy conservation law：

Cell stress

Total energy

$$\bar{\boldsymbol{\sigma}} = \frac{1}{V}\frac{\partial E_{\mathrm{tot}}}{\partial \boldsymbol{\varepsilon}}$$

Cell strain

Atomic energy

$$\boldsymbol{\sigma}_i = \frac{1}{V_i}\frac{\partial E_{\mathrm{i}}}{\partial \boldsymbol{\varepsilon}}$$

Atomic stress

Inconsistent with the definition by internal force?

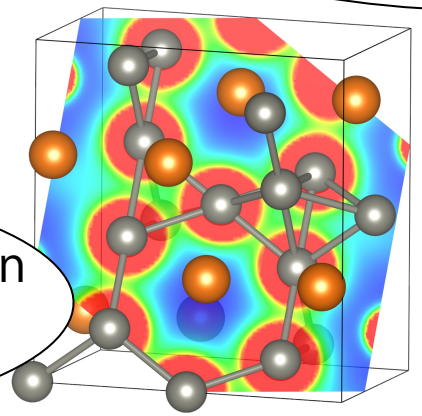


Fig: Periodic boundary condition cell

Definition of ab initio atomic level stress

Cell-strain derivative of atomic energy

Cell stress （Nielsen-Martin）

Total energy of cell

$$\bar{\sigma}_{\alpha\beta} = \frac{1}{\Omega}\frac{\partial E}{\partial \varepsilon_{\alpha\beta}}$$

Cell volume　　Cell strain

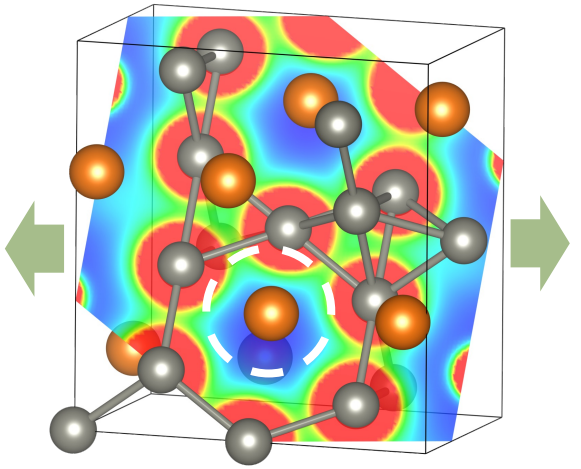
Atomic stress

Depending on atomic energy

Atom-wise decomposed total energy

$$\sigma_{\alpha\beta,i} = \frac{1}{\Omega_i}\frac{\partial E_i}{\partial \varepsilon_{\alpha\beta}}$$

Atomic volume　　Cell strain



Decomposed energy's response against cell strain

Practical implementation of atomic stress

LSMS- based method (ORNL)	QMAS (AIST)	OpenMX (Univ. Tokyo)
Voronoi	Bader	Atomic orbital

Stress decomposition should solve the non-uniqueness of decomposed stress.

Problem: Non-uniqueness of energy/stress density

Total stress and total energy on DFT (under periodic boundary condition)

Total stress $\sigma_{\alpha\beta} = \frac{\partial E_{\mathrm{tot}}}{\partial \varepsilon_{\alpha\beta}} = \int_{\Omega_c} \underline{\sigma_{\alpha\beta}(\mathbf{r})}\mathrm{d}\mathbf{r} = \int_{\Omega_c} \sigma_{\alpha\beta}(\mathbf{r}) + g(\mathbf{r})\mathrm{d}\mathbf{r}$

Stress density*1

Total energy $E_{\mathrm{tot}} = \int_{\Omega_c} \underline{\varepsilon_{\mathrm{tot}}(\mathbf{r})}\mathrm{d}\mathbf{r} = \int_{\Omega_c} \varepsilon_{\mathrm{tot}}(\mathbf{r}) + f(\mathbf{r})\mathrm{d}\mathbf{r}$

Energy density*2

Any function integrates to zero can be added to the total stress/energy.

$$\int_{\Omega_c} g(\mathbf{r})\mathrm{d}\mathbf{r} = 0 \qquad \int_{\Omega_c} f(\mathbf{r})\mathrm{d}\mathbf{r} = 0$$

➡ "Gauge-dependent problem" *1,2

*1Filippetti, et al., PRB, 61, 8433 (2000).
*2Chetty, et.al, PRB, 45, 6074 (1992).

Ex. Kinetic energy density

Symmetric KED $t_s(\mathbf{r}) = \frac{\hbar^2}{2m}\sum_i f_i \nabla\psi_i^*(\mathbf{r})\cdot\nabla\psi_i(\mathbf{r})$ ➡ Generalized KED*1: $t(\mathbf{r}) = t_s(\mathbf{r}) + \gamma\nabla^2\rho(\mathbf{r})$

Stress component $\frac{\partial}{\partial r_\alpha}\frac{\partial\rho(\mathbf{r})}{\partial r_\beta}$

Problem: find partial region where the gauge-dependent term integrates to zero.

$$\int_{\Omega'} \frac{\partial}{\partial r_\alpha}\frac{\partial\rho(\mathbf{r})}{\partial r_\beta} = 0$$

Solution: Stress decomposition based on atomic orbital

Locality can avoid the non-uniqueness problem.

In LCAO,

Ab initio atomic stress in LCAO formulation

Electron density matrix

Hamiltonian operator

$$\sigma_{\gamma\eta,\mathrm{cell}} = \frac{1}{V_{\mathrm{cell}}} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \rho_{i\alpha j\beta} \sum_{i\alpha, j\beta} \left\langle \phi_{i\alpha} \middle| \hat{h} \middle| \phi_{j\beta} \right\rangle$$

$$\sigma_{\gamma\eta,i} = \frac{1}{V_i} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \rho_{i\alpha j\beta} \sum_{j\beta,\alpha} \left\langle \phi_{i\alpha} \middle| \hat{h} \middle| \phi_{j\beta} \right\rangle$$

Voronoi volume of atom i

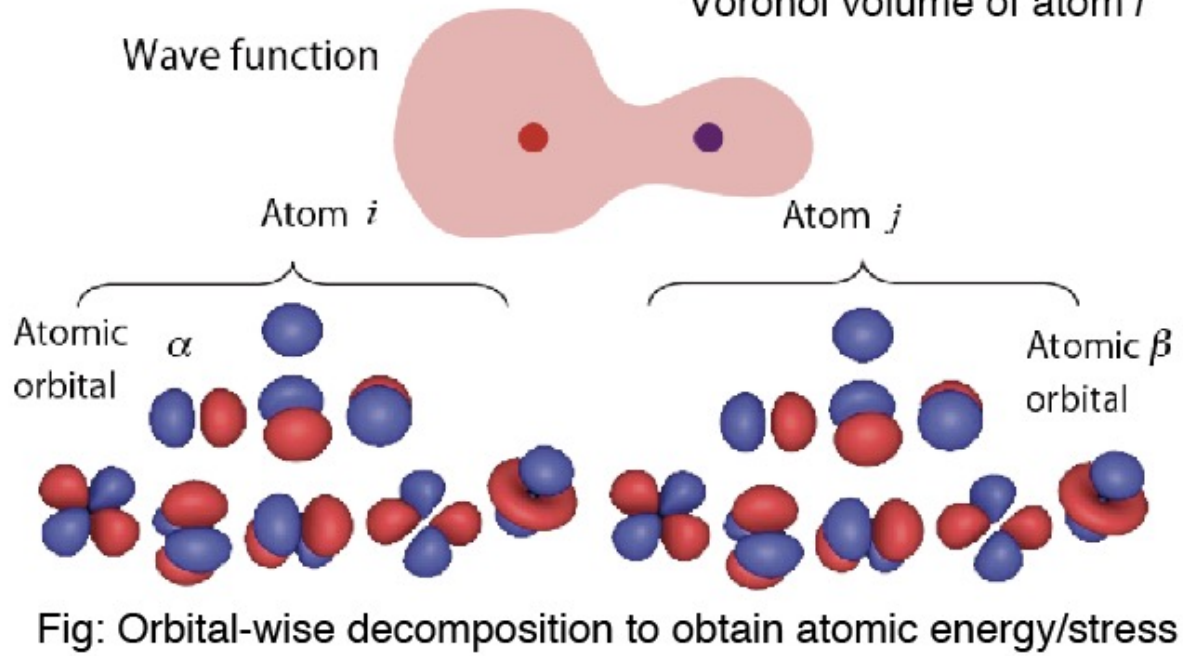
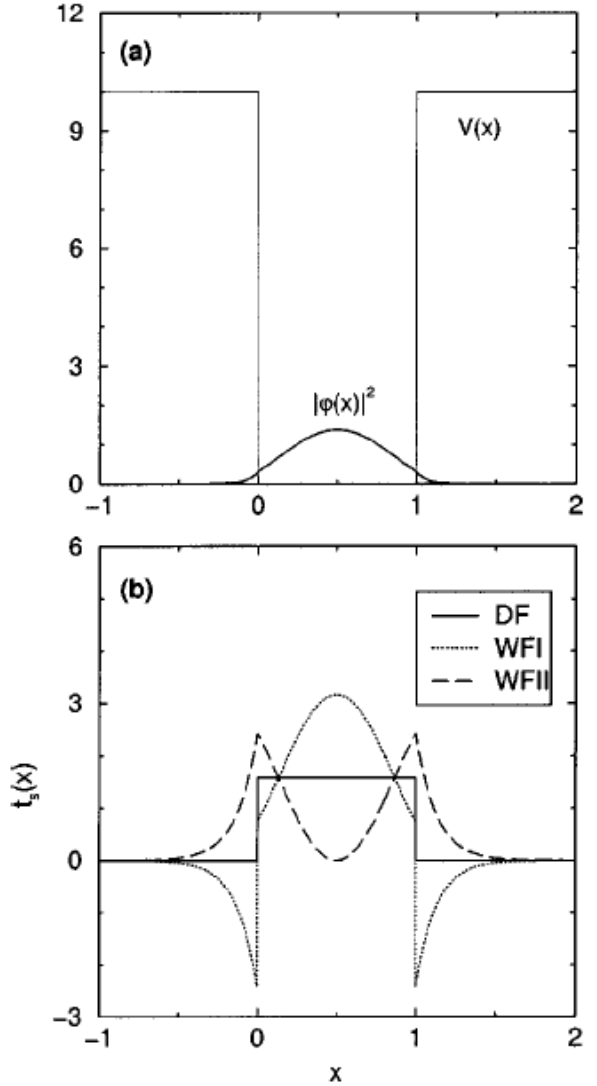


Fig: Orbital-wise decomposition to obtain atomic energy/stress



Two KED distributions on potential-well model

Sim et al., JCP, (2003)

Formulation and Implementation in OpenMX

Formulation of stress decomposition in OpenMX

Atomic stress is decomposition of total stress.

➡ Almost same formulation

Stress calculation is like force calculation.

Atomic coordinate derivative w.r.t η axis

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} = \frac{\partial t^{\eta}}{\partial \varepsilon_{\gamma\eta}} \frac{\partial}{\partial t^{\eta}} = t^{\gamma} \frac{\partial}{\partial t^{\eta}}$$

Strain derivative w.r.t $\gamma\eta$ component

➡ Stress formulation is similar to that of atomic force.

See https://www.openmx-square.org/tech_notes/tech23-1_0.pdf

Stress formulation in OpenMX

Yoshinori Shiihara* and Taisuke Ozaki

January 7, 2017

1 References

In this formulation, we referred to the following documents:

[1] OpenMX web site, Technical notes, "Total energy and forces"
http://www.openmx-square.org /tech_notes /tech1-1_2.pdf
[2] Stress formulation on LCAO-based DFT by P. J. Feibelman
P. J. Feibelman, PRB 44, 3916 (1991).
[3] Stress formulation in SIESTA code
J. M. Soler, et al., J. Phys.: Conden. Matter, 14, 2745 (2002).
[4] Stress formulation in plane-wave-based PAW-DFT by M. Kohyama (in Japanese, not published)
[5] GGA stress formulation in LCAO method by J. M. Solar, et al.
L. C. Balbas, J. L. Martins, J. M. Soler, PRB 64, 165110 (2001).

2 Total energy, wave function, and electron density matrix in LCAO formulation

Denisty functional total energy E_{tot} considered in this document is

$$E_{\mathrm{tot}} = E_{\mathrm{kin}} + E_{\mathrm{na}} + E_{\mathrm{ec}}^{(\mathrm{NL})} + E_{\delta\mathrm{ee}} + E_{\mathrm{XC}} + E_{\mathrm{SCC}}, \quad (1)$$

Formulation of stress decomposition in OpenMX

This energy component represents the electrostatic interaction between difference charge δn given by

$$\delta n(\mathbf{r}) = n(\mathbf{r}) - \sum_I n_I^{(\mathrm{a})}(\mathbf{r} - \mathbf{t}_I), \tag{33}$$

where $n_I^{(a)}$ is an atomic charge density evaluated by a confinement atomic calculations associated with the site i. δV_{H} is the electrostatic potential coming from δn. Considering Eq. (13), we have the following strain derivative of this electrostatic energy:

$$\frac{\partial E_{\delta \mathrm{ee}}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\gamma\eta} \int_\Omega \delta n(\mathbf{r}) \delta V_{\mathrm{H}} \mathbf{dr} + \frac{1}{2} \int_\Omega \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_{\mathrm{H}} \mathbf{dr} + \frac{1}{2} \int_\Omega \delta n(\mathbf{r}) \frac{\partial \delta V_{\mathrm{H}}}{\partial \varepsilon_{\gamma\eta}} \mathbf{dr} \tag{34}$$

Note that the first term of the right-hand side is a strain derivative of the volume term shown in Eq. (9). Here, we expand the second term:

$$\begin{aligned}
&\frac{1}{2} \int_\Omega \frac{\partial \delta n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} \delta V_{\mathrm{H}} \mathbf{dr} = \frac{1}{2} \int_\Omega \delta V_{\mathrm{H}} \frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left(n(\mathbf{r}) - \sum_I n_I^{(\mathrm{a})}(\mathbf{r} - \mathbf{t}_I) \right) \mathbf{dr} \\
&= \frac{1}{2} \int_\Omega \delta V_{\mathrm{H}} \left(\frac{\partial n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} - \sum_I \frac{\partial}{\partial \varepsilon_{\gamma\eta}} n_I^{(\mathrm{a})}(\mathbf{r} - \mathbf{t}_I) \right) \mathbf{dr} \\
&= \frac{1}{2} \int_\Omega \delta V_{\mathrm{H}} \left(\frac{\partial n(\mathbf{r})}{\partial \varepsilon_{\gamma\eta}} - \sum_I \nabla_\gamma n_I^{(\mathrm{a})}(\mathbf{r} - \mathbf{t}_I)(r^\eta - t_I^\eta) \right) \mathbf{dr},
\end{aligned} \tag{35}$$

where we used the following equation,

$$\partial n_I^{(\mathrm{a})}(\mathbf{r} - \mathbf{t}_I) / \partial \varepsilon_{\gamma\eta} = \nabla_\gamma n_I^{(\mathrm{a})}(\mathbf{r} - \mathbf{t}_I)(r^\eta - t_I^\eta). \tag{36}$$

Stress formulation: two-center integral (1)

Two-center integral: Kinetic energy, etc.

AO center　Cell vector

$$\rho^{(\mathbf{R}_n)}_{s,i\alpha,j\beta}\left\langle \phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{V}\middle|\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\right\rangle$$

Density matrix　Potential operator　Basis function

Strain derivative $\dfrac{\partial}{\partial\varepsilon_{\gamma\eta}}\rho^{(\mathbf{R}_n)}_{s,i\alpha,j\beta}\left\langle \phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{V}\middle|\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\right\rangle$

$$=\frac{\partial\rho^{(\mathbf{R}_n)}_{s,i\alpha,j\beta}}{\partial\varepsilon_{\gamma\eta}}\left\langle \phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{V}\middle|\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\right\rangle$$

Overlap term

$$+\rho^{(\mathbf{R}_n)}_{s,i\alpha,j\beta}\frac{\partial}{\partial\varepsilon_{\gamma\eta}}\left\langle \phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{V}\middle|\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\right\rangle$$

$$\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n\rightarrow\mathbf{r}$$

$$\left\langle \phi_{i\alpha}(\mathbf{r}-\mathbf{t}_i)\middle|\hat{V}\middle|\phi_{j\beta}(\mathbf{r}-\mathbf{t}_j-\mathbf{R}_n)\right\rangle$$

$$\mathbf{t}_{ji,n}=\mathbf{t}_j+\mathbf{R}_n-\mathbf{t}_i$$

$$\rightarrow\left\langle \phi_{i\alpha}(\mathbf{r})\middle|\hat{V}\middle|\phi_{j\beta}(\mathbf{r}+\mathbf{t}_i-\mathbf{t}_j-\mathbf{R}_n)\right\rangle$$

$$\mathbf{t}_{ji,n}{}^{\varepsilon}=(\mathbf{I}+\boldsymbol{\varepsilon})\cdot\mathbf{t}_{ji,n}$$

$$=\left\langle \phi_{i\alpha}(\mathbf{r})\middle|\hat{V}\middle|\phi_{j\beta}(\mathbf{r}-\mathbf{t}_{ji,n})\right\rangle$$

Stress formulation: two-center integral (2)

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \phi_{i\alpha}(\mathbf{r}) \middle| \hat{V} \middle| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{ji,n}) \right\rangle$$

$$= \left(\frac{\partial}{\partial t^{\gamma}_{ji,n}} \left\langle \phi_{i\alpha}(\mathbf{r}) \middle| \hat{V} \middle| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{ji,n}) \right\rangle \right) t^{\eta}_{ji,n}$$

$$\mathbf{t}_{ji,n}{}^{\varepsilon} = (\mathbf{I} + \boldsymbol{\varepsilon}) \cdot \mathbf{t}_{ji,n}$$

$$\frac{\partial t_{\iota}}{\partial \varepsilon_{\gamma\eta}} = \delta_{\iota\eta} t_{\eta}$$

$$\frac{\partial}{\partial \varepsilon_{\gamma\eta}} \left\langle \phi_{i\alpha}(\mathbf{r}) \middle| \hat{V} \middle| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{ji,n}) \right\rangle$$

$$= \left(\frac{\partial}{\partial t^{\gamma}_{i}} \left\langle \phi_{i\alpha}(\mathbf{r} - \mathbf{t}_{i}) \middle| \hat{V} \middle| \phi_{j\beta}(\mathbf{r} - \mathbf{t}_{j} - \mathbf{R}_{n}) \right\rangle \right) t^{\eta}_{ij,n}$$

$$\mathbf{t}_{ij,n} = \mathbf{t}_{i} - \mathbf{t}_{j} - \mathbf{R}_{n}$$

Force component acting on atom *i*

Decomposition rule

Stress between atom *i* and *j*: σ

- 1/2 σ for atom i
- 1/2 σ for atom j

Stress formulation: integral over cell

Stress components from Hartree energy, exchange-correlation energy, etc.

$$\int_{V_\mathrm{B}} n(\mathbf{r})V(\mathbf{r})\mathrm{d}\mathbf{r}$$

Strain derivative $\dfrac{\partial}{\partial\varepsilon_{\gamma\eta}}\int_{V_\mathrm{B}} n(\mathbf{r})V(\mathbf{r})\mathrm{d}\mathbf{r}$

$$= \delta_{\gamma\eta}\int_{V_\mathrm{B}} n(\mathbf{r})V\mathrm{d}\mathbf{r} + \int_{V_\mathrm{B}} \frac{\partial n(\mathbf{r})}{\partial\varepsilon_{\gamma\eta}}V(\mathbf{r})\mathrm{d}\mathbf{r} + \int_{V_\mathrm{B}} n(\mathbf{r})\frac{\partial V(\mathbf{r})}{\partial\varepsilon_{\gamma\eta}}\mathrm{d}\mathbf{r}$$

Product rule

(in GGA) $\int_{V_\mathrm{B}} f_\mathrm{XC}[n,|\nabla n|,n_\mathrm{pcc}]\mathrm{d}\mathbf{r}$

Force-like terms appear as well

Strain derivative $\dfrac{\partial}{\partial\varepsilon_{\gamma\eta}}\int_{V_\mathrm{B}} f_\mathrm{XC}[n,\nabla n,n_\mathrm{pcc}]\mathrm{d}\mathbf{r}$

$$= \delta_{\gamma\eta}\int_{V_\mathrm{B}} f_\mathrm{XC}\mathrm{d}\mathbf{r} + \int_{V_\mathrm{B}} \frac{\partial f_\mathrm{XC}}{\partial n(\mathbf{r})}\frac{\partial n(\mathbf{r})}{\partial\varepsilon_{\gamma\eta}}\mathrm{d}\mathbf{r} + \int_{V_\mathrm{B}} \frac{\partial f_\mathrm{XC}}{\partial\nabla n(\mathbf{r})}\cdot\frac{\partial\nabla n(\mathbf{r})}{\partial\varepsilon_{\gamma\eta}}\mathrm{d}\mathbf{r}$$

Product & chain rules

Applications

- **Atomic stress distribution in multicomponent random alloys and its origins**

  Y. Shiihara, Y. Itai, I. Lobzenko, T. Tsuru, Frontiers in Materials, 9, 895626 (2022).

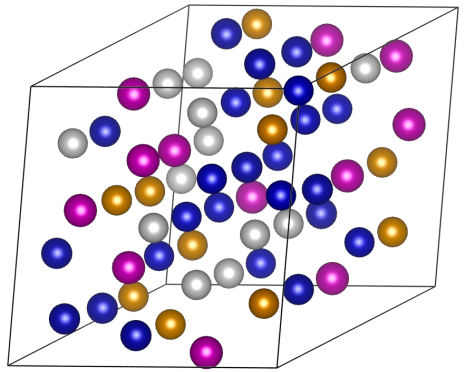
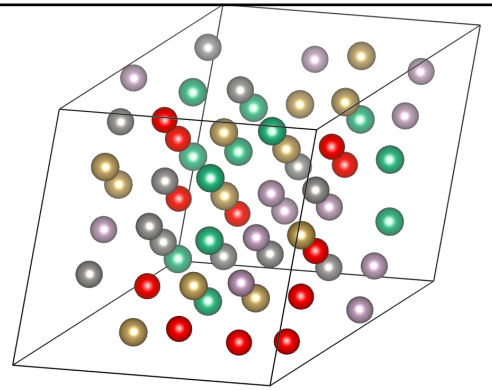
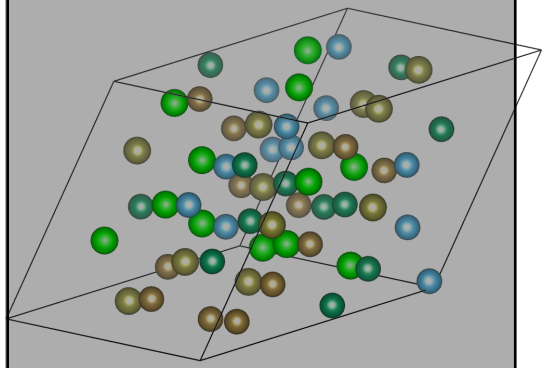
- **Elastic heterogeneity in hetero-nanostructures**

  Partly, R. Hossain, H. Kimizuka, Y. Shiihara, and S. Ogata, Comput. Mater. Sci., 209, 111366 (2022).

Computational models

Y. Shiihara, Y. Itai, I. Lobzenko, T. Tsuru, Frontiers in Materials, 9, 895626 (2022).

Atomic structures

fcc	bcc	
CrMnFeCoNi types	VNbTaMoW types	TiZrHfNbTa + α types
 CrMnFeCoNi 60 atoms	 VNbTaMoW 60 atoms	 TiZrHfNbTa 60 atoms
# of atoms: bi: 60, ter: 60, qua: 60 , qui: 60, sep: 60 (10 variants × 5 cases)	# of atoms: bi: 60, ter: 60, qua 60: , qui: 60, sep: 60 （10 variants × 5 cases）	# of atoms: bi: 60, ter: 60, qua 60: , qui: 60, sep: 60

# of elements bi: binary, ter: ternary, qua: quarternary, qui: quinary, sep: septenary

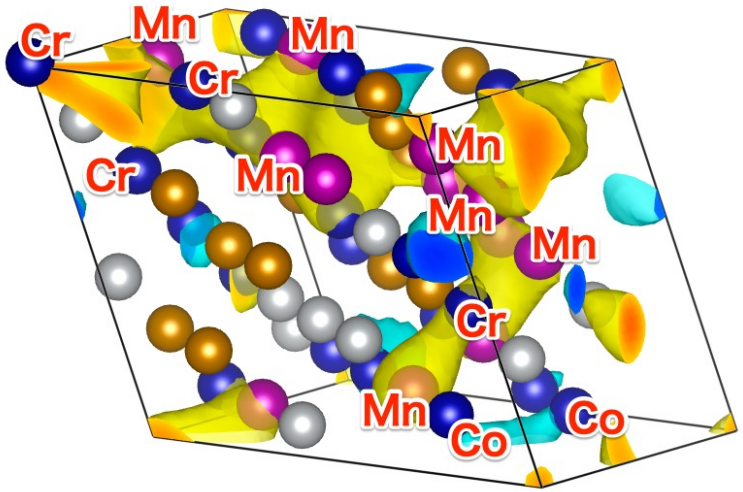


Fig.: Atomic stress in CrFeMnCoNi

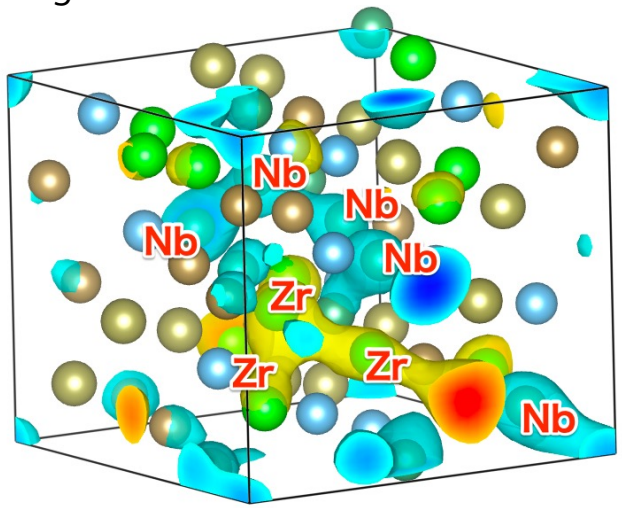


Fig.: Atomic stress in VNbTaMoW

Ab initio calculation

OpenMX, Spin-polarized DFT , Norm-conserving pseudo potential, PBE-GGA,
k-grid: 0.022 Å, Electronic Temp.: 1500 K, FFT grid: 400 Ry

Yield stress vs atomic stress dispersion

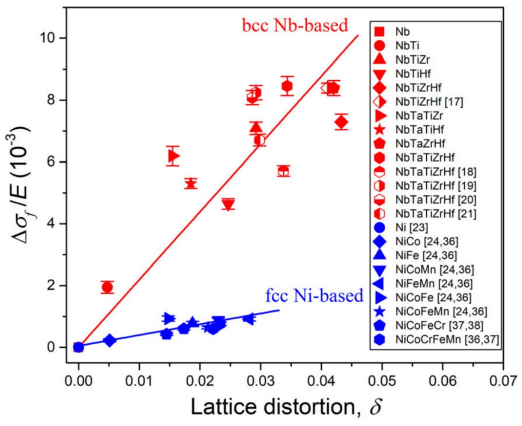


Fig.: Friction stress vs lattice distortion. Zhao et al. (2019)

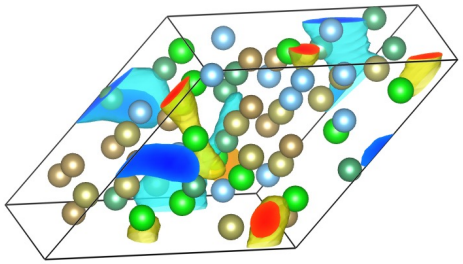


Fig.: Pressure distribution in a random alloy

Oh, et al., Nature commun. (2019).

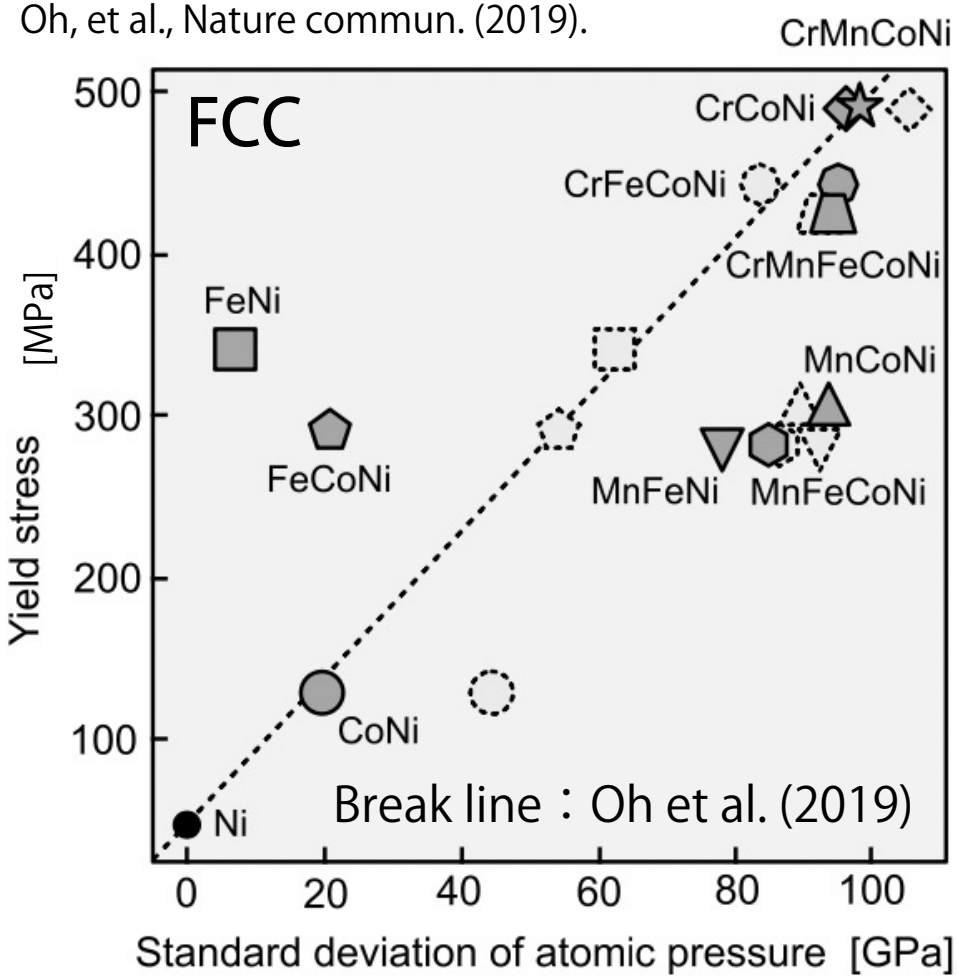


Fig: Standard deviation of atomic pressure vs experimentally estimated friction stress (0K) in fcc random alloys.

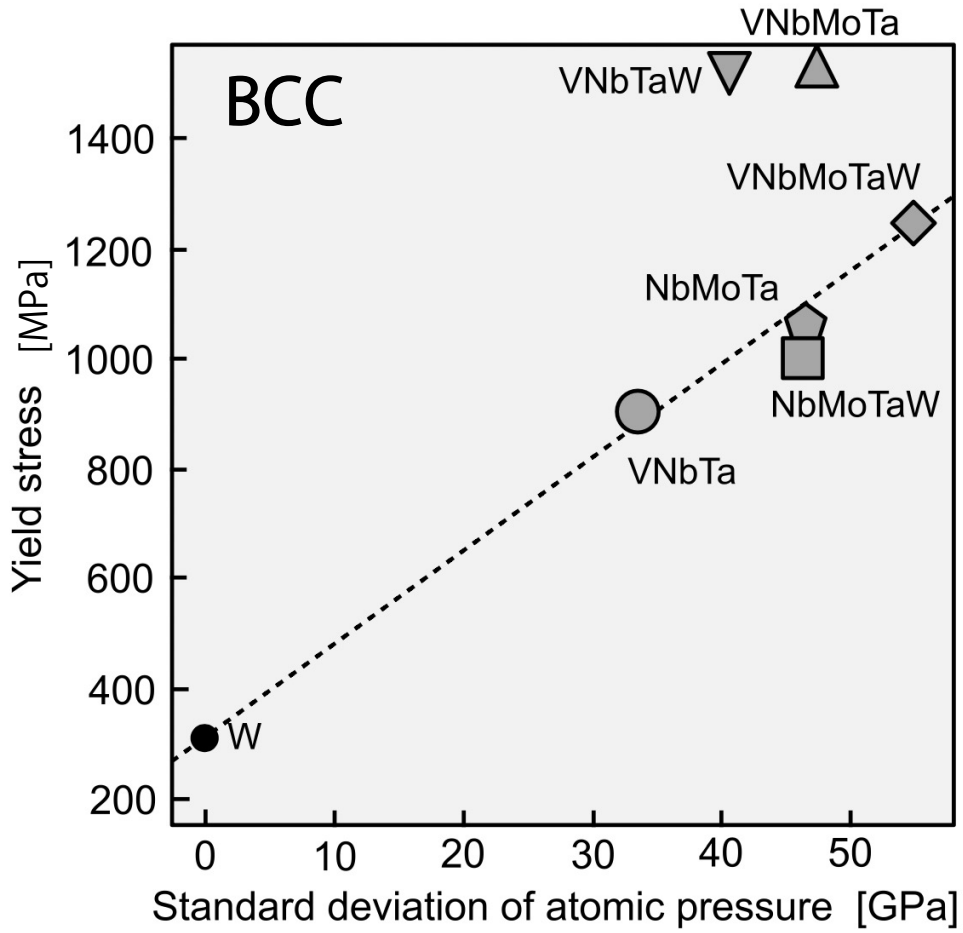


Fig: Standard deviation of atomic pressure vs yield stress (experiment, room temp.) in bcc random alloys.

How can tensile/compressive atomic stress appear?

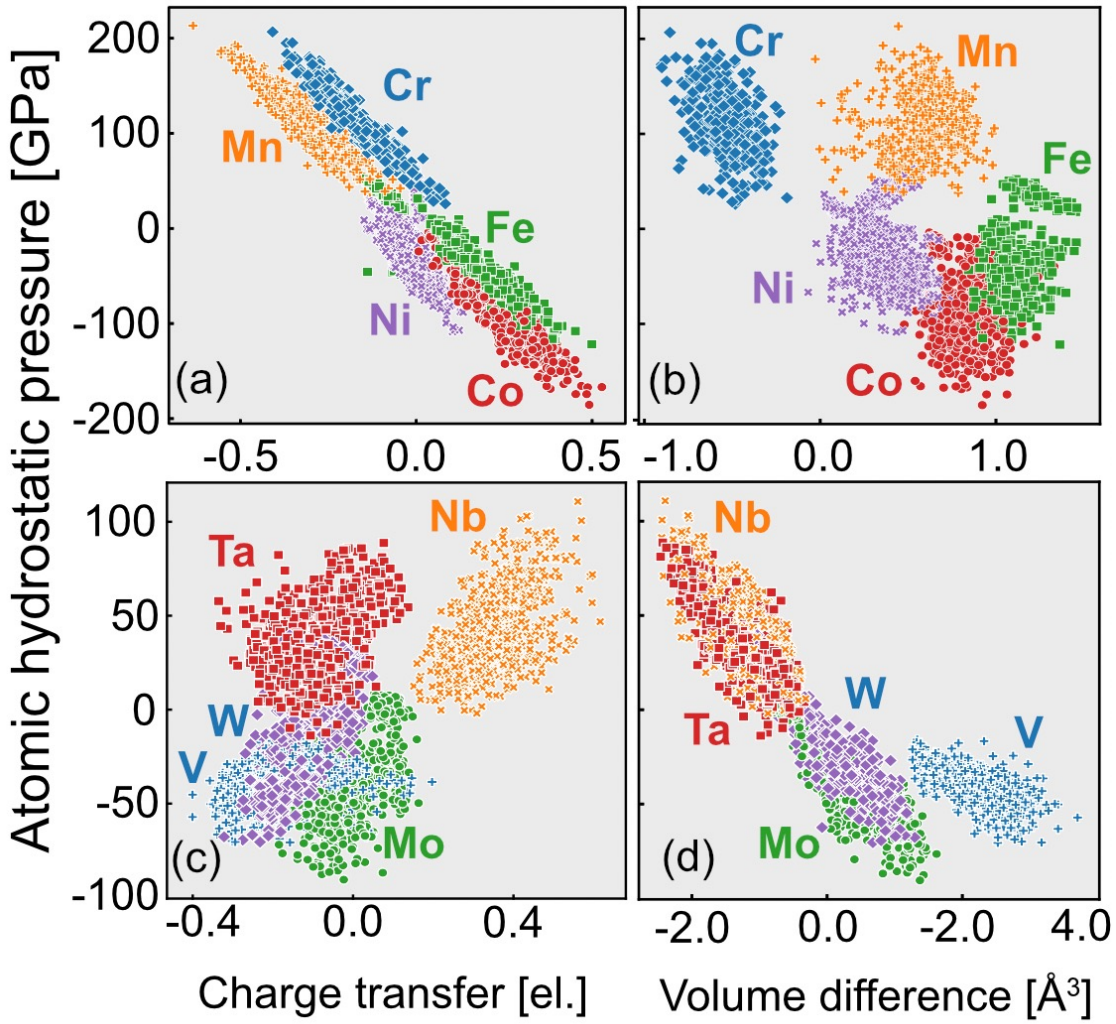


Fig: Atomic pressure vs atomic quantities (charge transfer/volume difference)

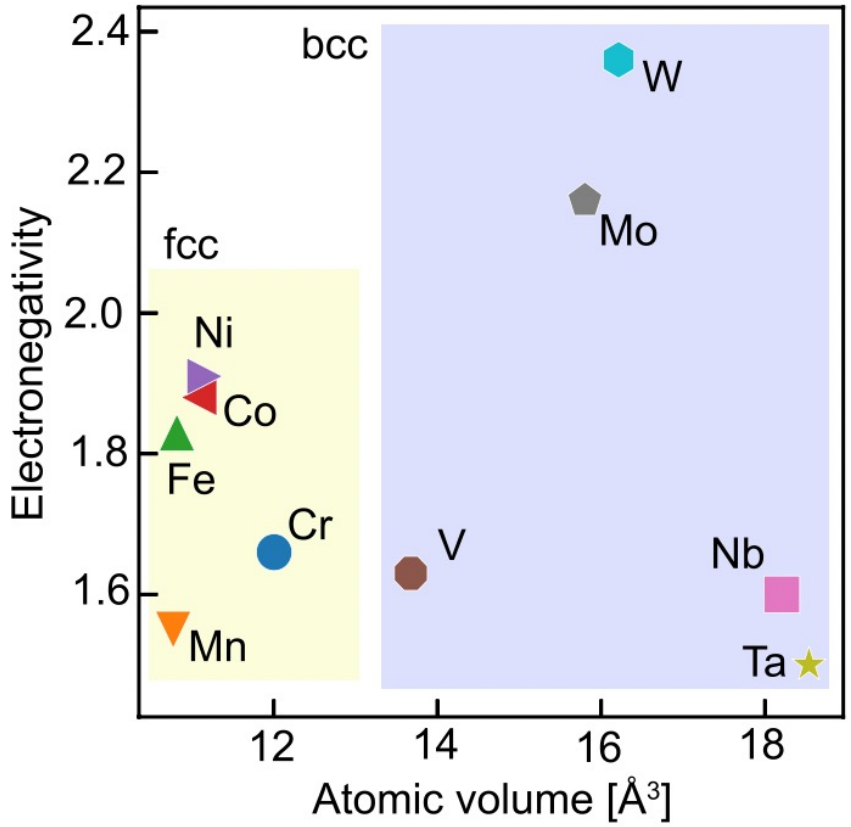


Fig: Electronegativity and atomic volume of each element

- Fcc: charge transfer, bcc: volume difference
- Both should simultaneously affect!

Regression by atomic-level quantities

Red bar: charge-related, blue bar: volume-related

fcc

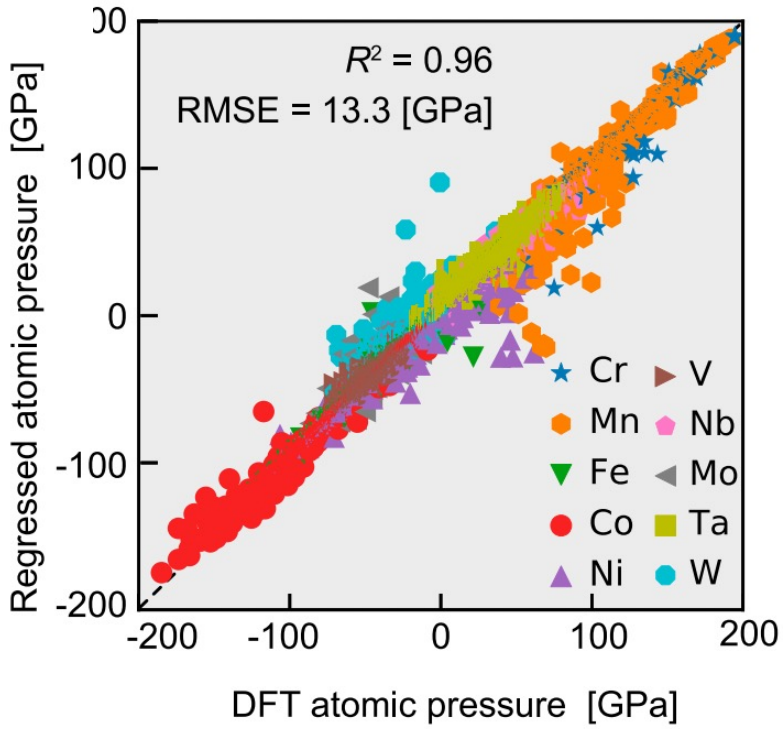


Fig: Regression accuracy of atomic pressure for fcc and bcc alloys.

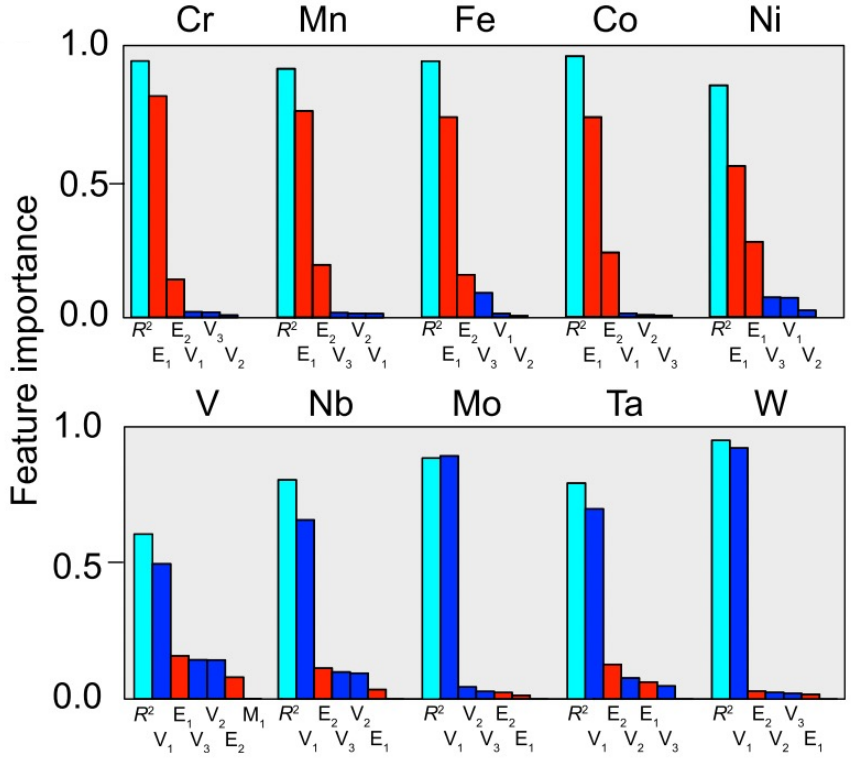


Fig: Feature importance of regression for fcc and bcc alloys

Features：

E1: Charge transfer from the bulk

E2: Charge diff. from 1st NN ave

V1: Vol. diff. from the bulk

V2: Vol. diff. from 1st NN ave.

V3: Vol. diff. from cell ave.

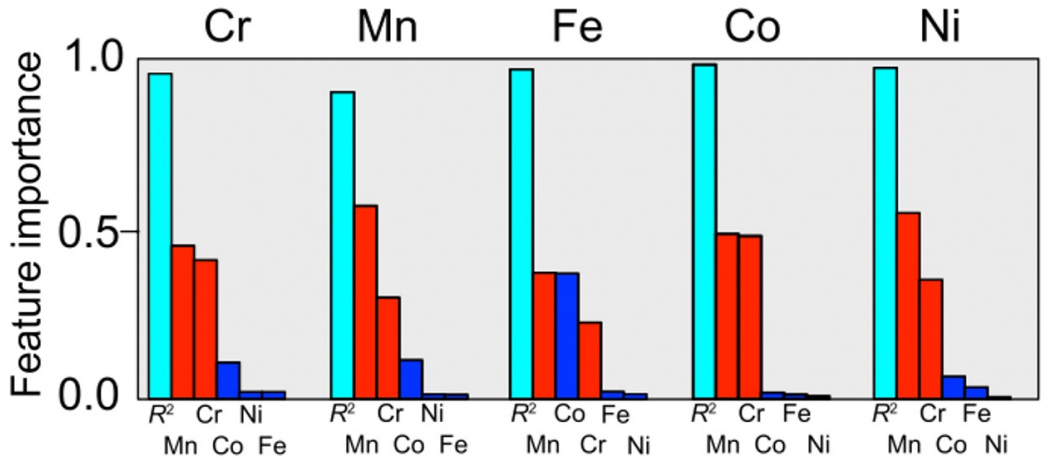
fcc

Clear difference: charge transfer (fcc), volume change(bcc)

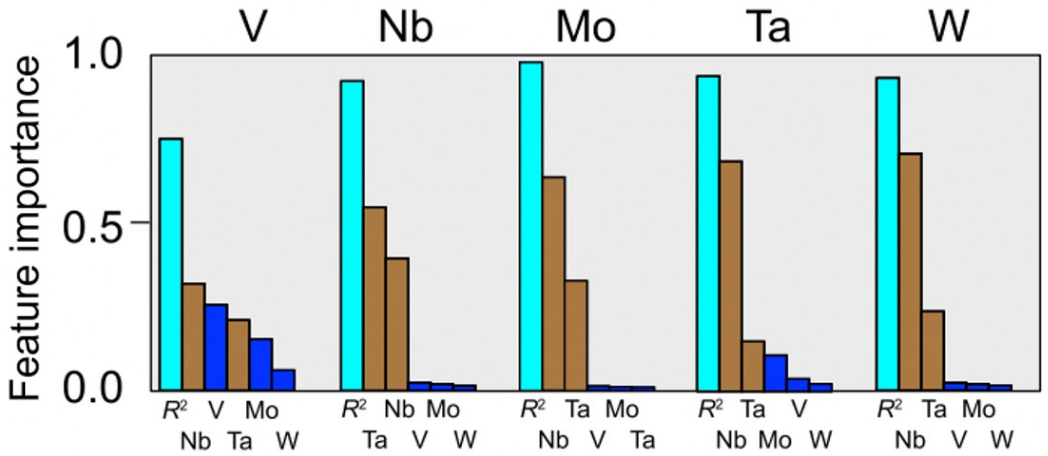
Atomic stress determined by 1st neighbors

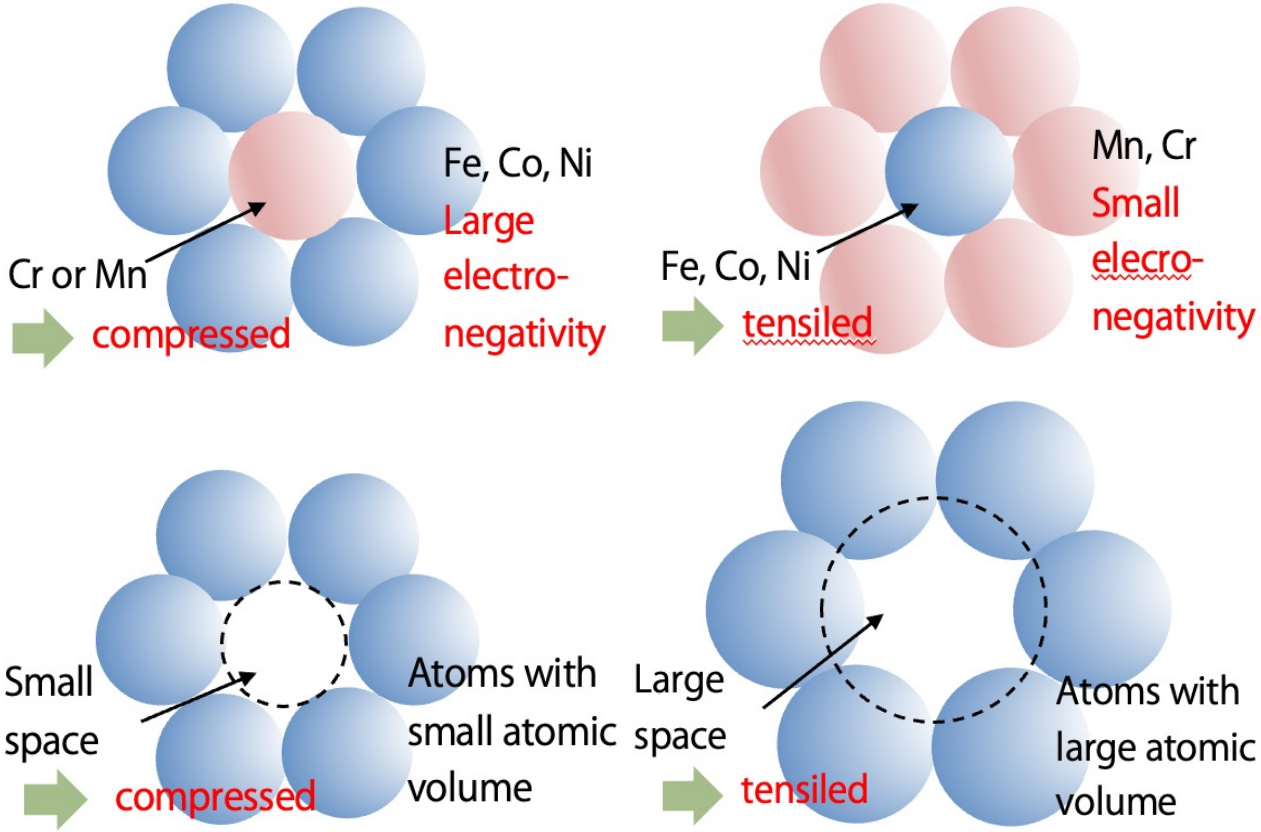
Regressed by # of atoms for each element in 1st shell

fcc



bcc

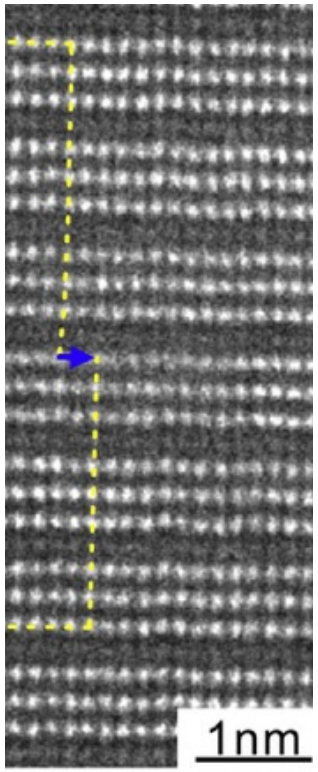


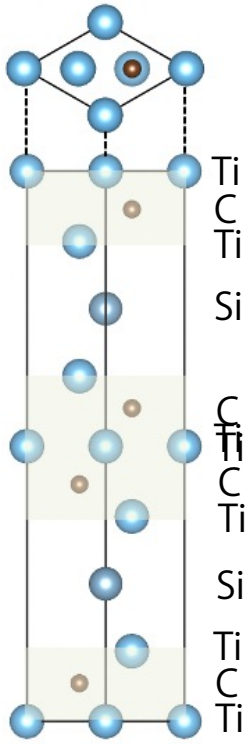


We obtained rational explanation for the origin of atomic stress.

Local elasticity calculation in hetero-nano structures

Hetero-nano struct.





MAX phase: Ti_3SiC_2

M. Higashi, et al., Acta Materialia 161 (2018) 161-170

Elastic constants:

Stress = Elastic constant matrix × Strain

$$\begin{bmatrix}\sigma_{11}\\ \sigma_{22}\\ \sigma_{33}\\ \sigma_{23}\\ \sigma_{31}\\ \sigma_{12}\end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & \mathrm{sym} & & C_{44} & 0 \\ & & & & & \frac{C_{11}-C_{12}}{2} \end{bmatrix} \begin{bmatrix}\varepsilon_{11}\\ \varepsilon_{22}\\ \varepsilon_{33}\\ \gamma_{23}\\ \gamma_{31}\\ \gamma_{12}\end{bmatrix}$$

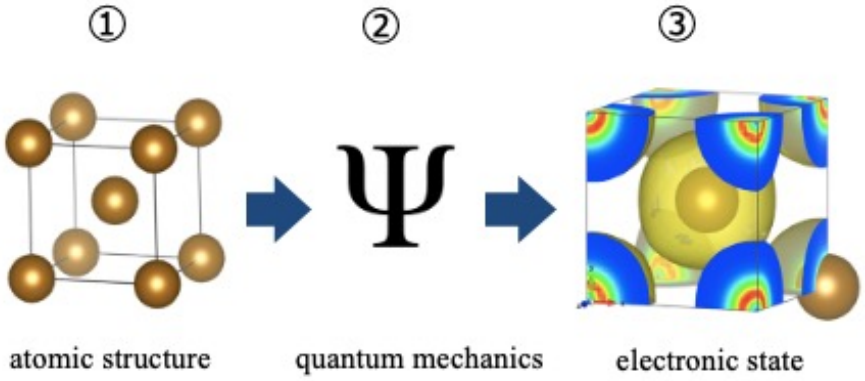
Cell elastic constant = Change in cell stress / Given cell stress

$$C_{ijkl} = \frac{\Delta\sigma_{ij}}{\Delta\varepsilon_{kl}}$$

Local elastic constant = Change in local stress / Change in local strain

$$C_{ijkl} = \frac{\Delta\sigma_{ij}}{\Delta\varepsilon_{kl}}$$

First-principles method:



- Total energy - OK
- Atomic force - OK
- Cell stress - OK
- Cell elastic constant - OK
- Local stress - NG
- Local elastic constant - NG

To calculate local elasticity, we need local stress and local strain.

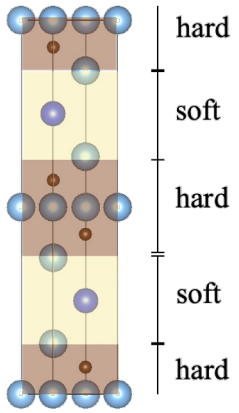
Local elastic constant calculation

Local elastic constants

$$C_{\gamma\eta\iota\kappa,V_A} = \frac{\sum_{i\in V_A} V_i \Delta\sigma_{\gamma\eta,i}}{\sum_{i\in V_A} V_i \Delta E_{\iota\kappa,i}}$$

Local volume

Voronoi decomposition



Atomic stress

In LCAO,

Electron density matrix

$$\sigma_{\gamma\eta,\mathrm{cell}} = \frac{1}{V_{\mathrm{cell}}}\frac{\partial}{\partial\varepsilon_{\gamma\eta}}\rho_{i\alpha j\beta}\sum_{i\alpha,j\beta}\left\langle\phi_{i\alpha}\middle|\hat{h}\middle|\phi_{j\beta}\right\rangle$$

Hamiltonian operator

Ab initio atomic stress in LCAO formulation

$$\sigma_{\gamma\eta,i} = \frac{1}{V_i}\frac{\partial}{\partial\varepsilon_{\gamma\eta}}\rho_{i\alpha j\beta}\sum_{j\beta,\alpha}\left\langle\phi_{i\alpha}\middle|\hat{h}\middle|\phi_{j\beta}\right\rangle$$

Voronoi volume of atom i

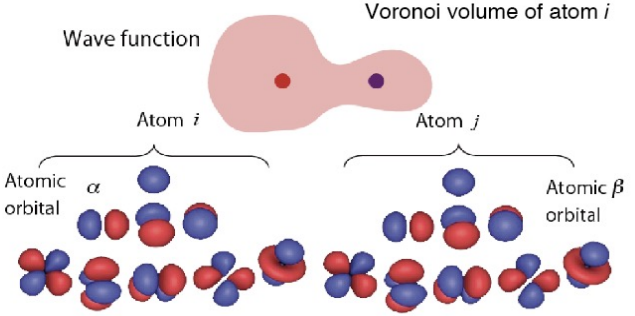


Fig: Orbital-wise decomposition to obtain atomic energy/stress

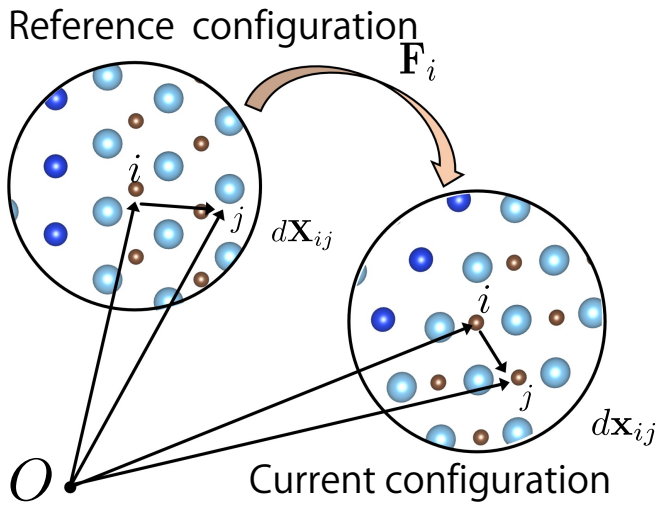
Atomic strain*

Atomic deformation gradient: minimize

$$\phi_i = \sum_j w_j(\Delta\mathbf{x}_{ij} - \mathbf{F}_i\cdot\Delta\mathbf{X}_{ij})^{\mathrm{T}}(\Delta\mathbf{x}_{ij} - \mathbf{F}_i\cdot\Delta\mathbf{X}_{ij})$$

Atomic Green-Lagrange strain of atom i

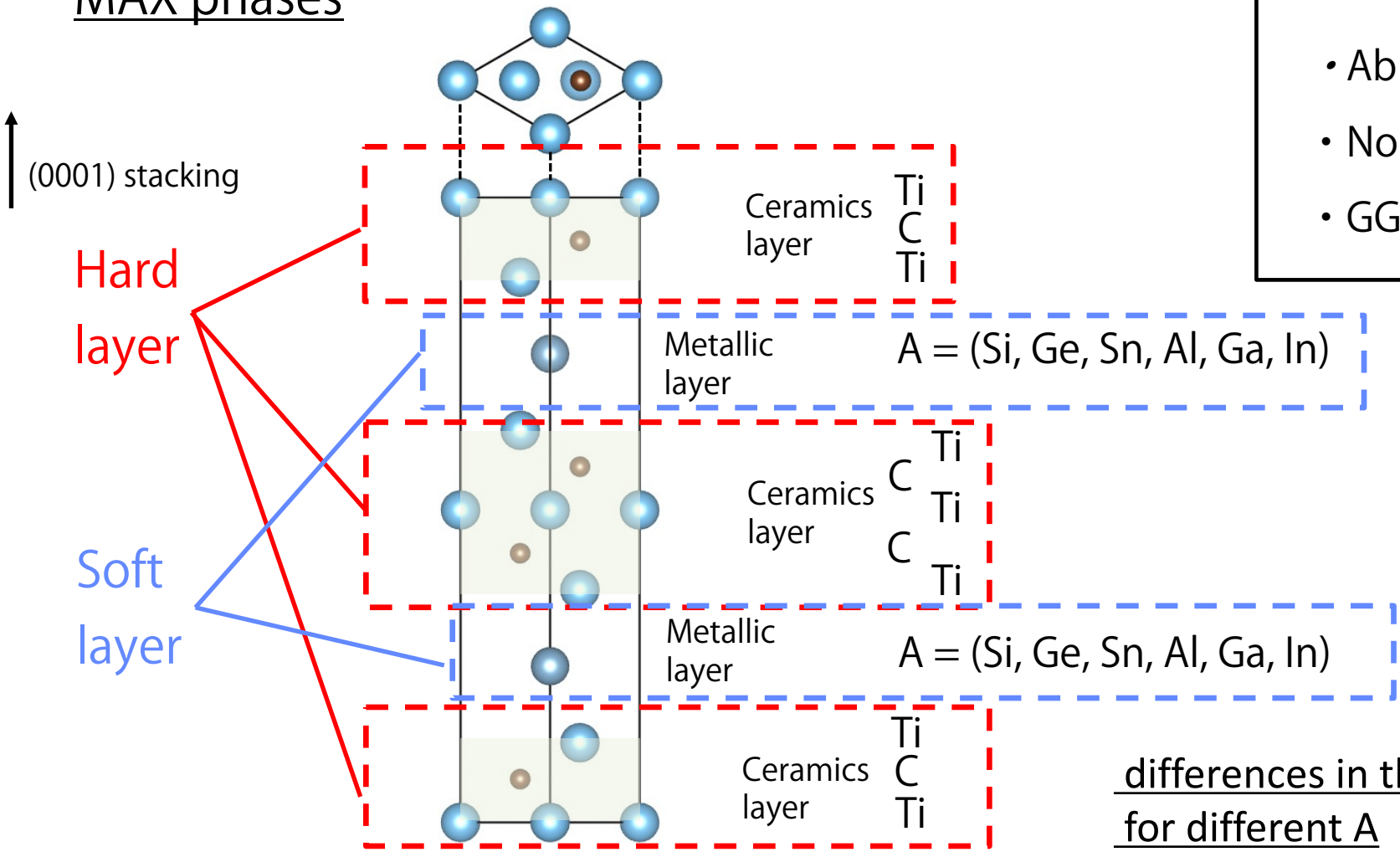
$$\mathbf{E}_i = \frac{1}{2}\left(\mathbf{F}_i{}^{\mathrm{T}}\mathbf{F}_i - \mathbf{I}\right)$$



*P. M. Gullet, Model. Simul. Mater. Sci. Eng., 16, 015001 (2008)

Computational settings

MAX phases



- Ab initio software: OpenMX
- Norm conserving pseudopotential
- GGA

differences in the local elastic constants for different A

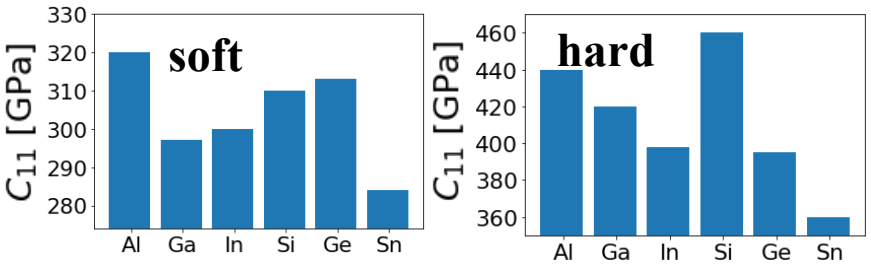
MAX phases : Local elastic constants

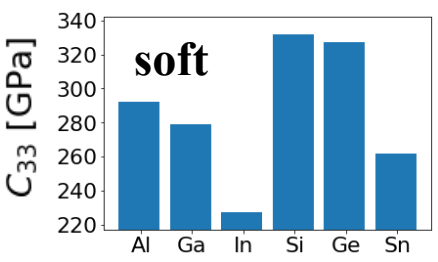
Partly, R. Hossain, H. Kimizuka, Y. Shiihara, and S. Ogata, Comput. Mater. Sci., 209, 111366 (2022).

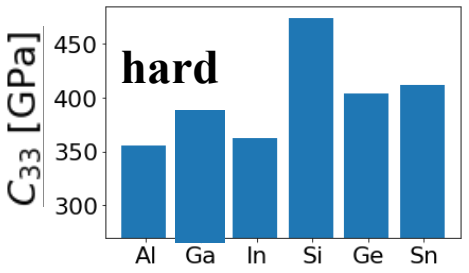
[GPa]

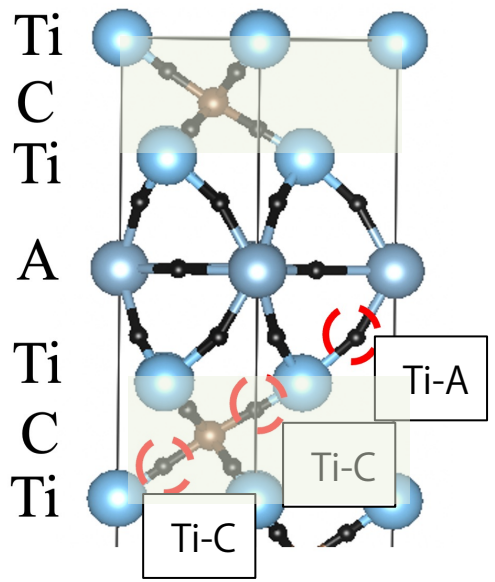
A	layer	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Al	soft	320	42	46	292	127
	hard	440	78	76	355	148
Ga	soft	297	51	54	279	116
	hard	420	76	27	380	138
In	soft	300	55	45	227	97
	hard	398	82	62	362	137

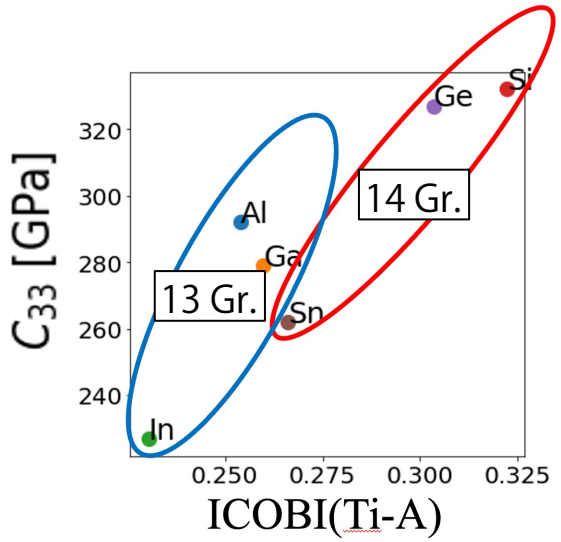
A	layer	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}
Si	soft	310	57	86	332	167
	hard	460	100	148	474	195
Ge	soft	313	49	65	327	143
	hard	395	60	79	404	151
Sn	soft	284	67	55	262	108
	hard	360	74	86	412	149











We obtained local elasitic constants correlating bond property.

Summary and future plans

Summary

- The formulation of atomic stress was shown and discussed.
  - Orbital decomposition can avoid the non-uniqueness problem in atomic stress.
- In multicomponent random alloys, reasonable atomic stress was obtained.
- The local elasticity calculation is demonstrated in the case of MAX phases.

Future plans

- Prepare papers describing the formulation
  (collaborative work with Prof. Shimada in Kyoto Univ.)
- Publish my subroutines in Github as unofficial function of OpenMX.
- Revise the formulation based on pair interaction.

Thank you for your attention!