ROYAL INSTITUTE
OF TECHNOLOGY

Thermodynamic and mechanical properties at finite temperatures

Presenter: Pavel Korzhavyi

KTH – Royal Institute of Technology, Stockholm

hero-m 2i

Hero-m: Hierarchic Engineering of Industrial Materials

2nd stage (2017 – 2022): Hero-m 2 innovation

ROYAL INSTITUTE OF TECHNOLOGY

FEM
CAD-CAM

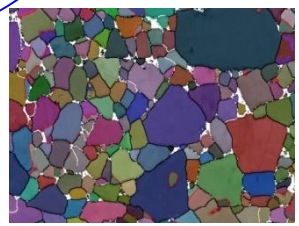
Engineering design

Thermo-Calc
DICTRA
Phase Field
Life time assessment
Many years

Continuum models

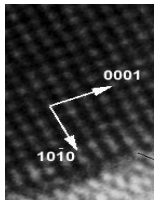
Kinetic Monte Carlo
>1 million atoms,
20 nm, long times

Phenomenological models
- Macro simulation
- Micro structure



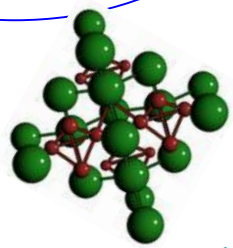
Molecular dynamics
100000 ca 10 nm 10^{-6} s

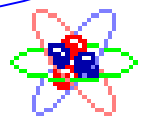
Atomic level simulation
- Statistical mechanics
- Classical dynamics
- Force field



Density functional theory:
ca 100 atoms
1 nm, 0 K

Fundamental models
- Quantum mechanics
- Quantum theory



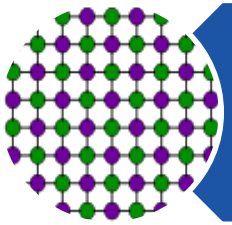


http://www.hero-m.mse.kth.se/

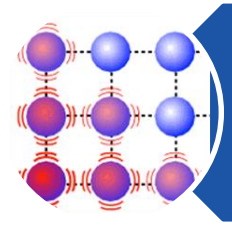
Size 1 (Å) 10 (Å) 100 (Å) 1 (μm) 1 (mm)

hero-m 2i

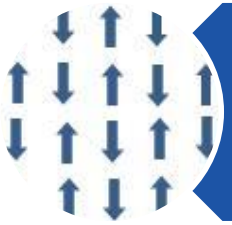
Degrees of freedom available for disorder in solids



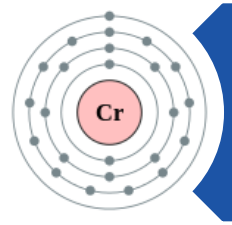
Configurational $>10^{-6}$ s



Vibrational $\sim10^{-13}$ s



Magnetic $\sim10^{-14}$ s



Electronic $\sim10^{-15}$ s

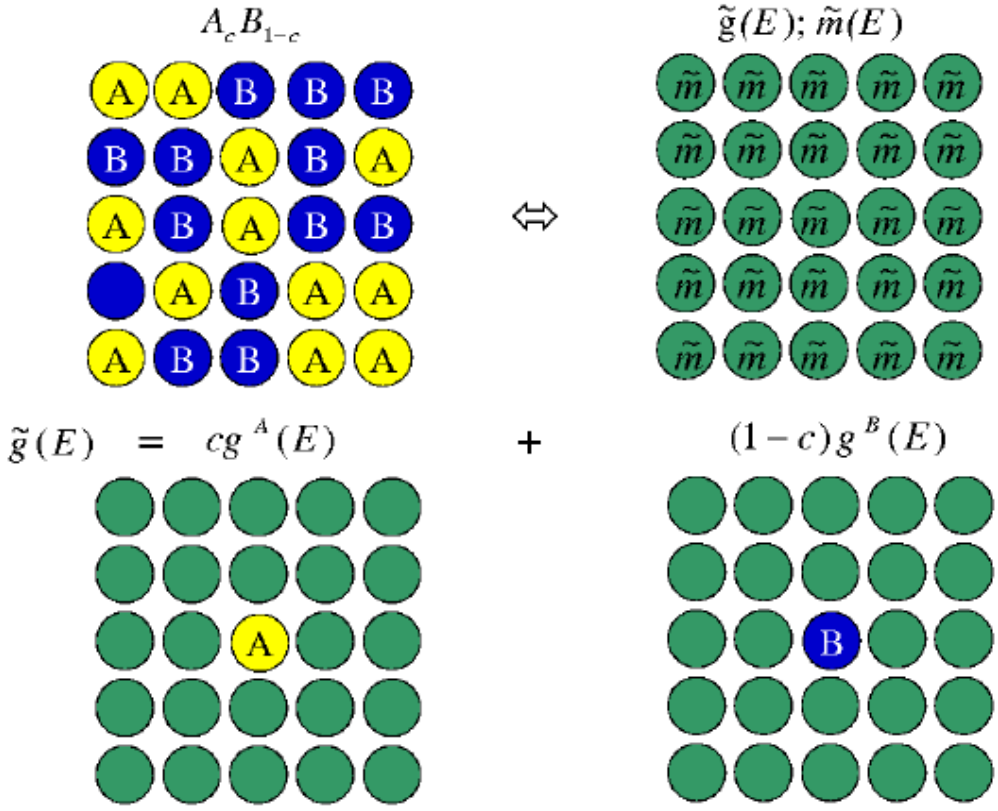
Modeling approach

- Adiabatic connection of fast and slow degrees of freedom (DOF):
  - Fast DOF are equilibrated first (at temperature T)
  - Slow DOF induce disorder (chemical, magnetic) which is treated using the coherent potential approximation (CPA)

- Self-consistent treatment of electronic (incl. magnetic) disorder

- Approximate treatment of vibrational disorder:
  - Quasi-harmonic Debye model: $\theta_D(V,T)$ - from $C_{ij}(V,T)$
  - Higher-order anharmonic effects (el.-ph.) are neglected

Random alloys: Coherent potential approximation (CPA)



Paul Soven

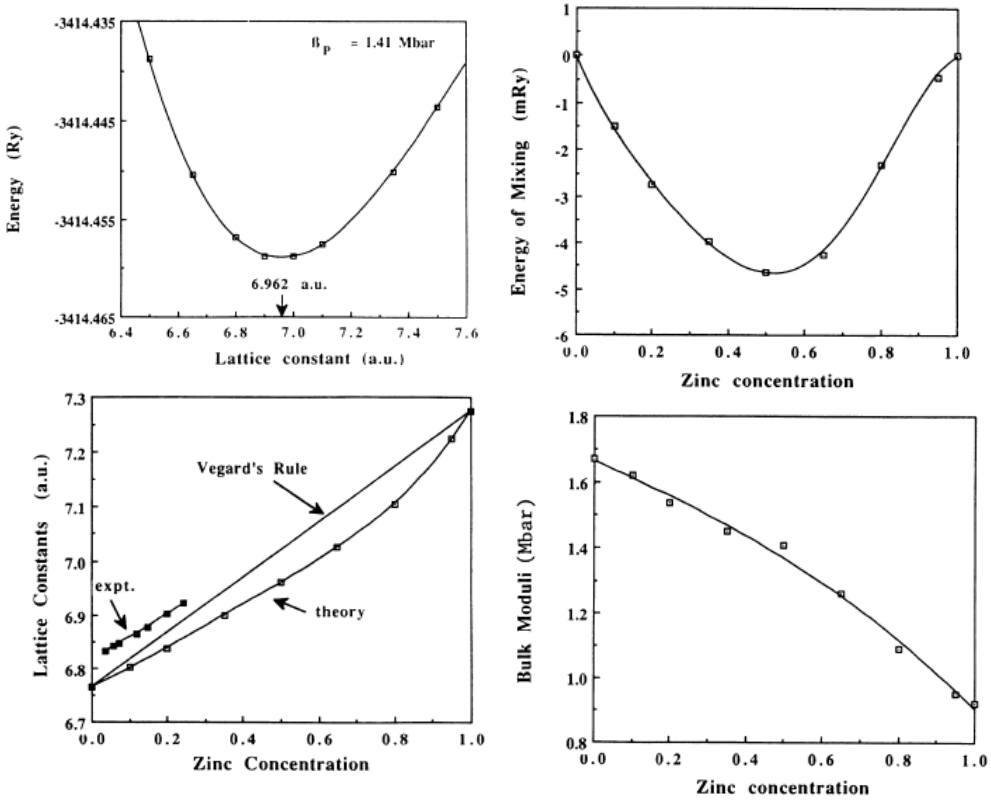
Balazs Györffy

J.S. Faulkner: *The modern theory of alloys*, Progr. Mater. Sci. **27**, 1 (1982).
A.V. Ruban, I.A. Abrikosov: *Configurational thermodynamics of alloys from first principles: effective cluster interactions*, Rep. Prog. Phys. **71**, 046501 (2008).

Total energy in the CPA

Duane Johnson

Cu-Zn fcc random alloys



For electrically neutral system, in the muffin-tin approximation:

$$E_{tot}^{CPA} = \sum_a c_a E_{tot}[\bar{\rho}_a; \bar{\rho}_0; \bar{n}_a]$$

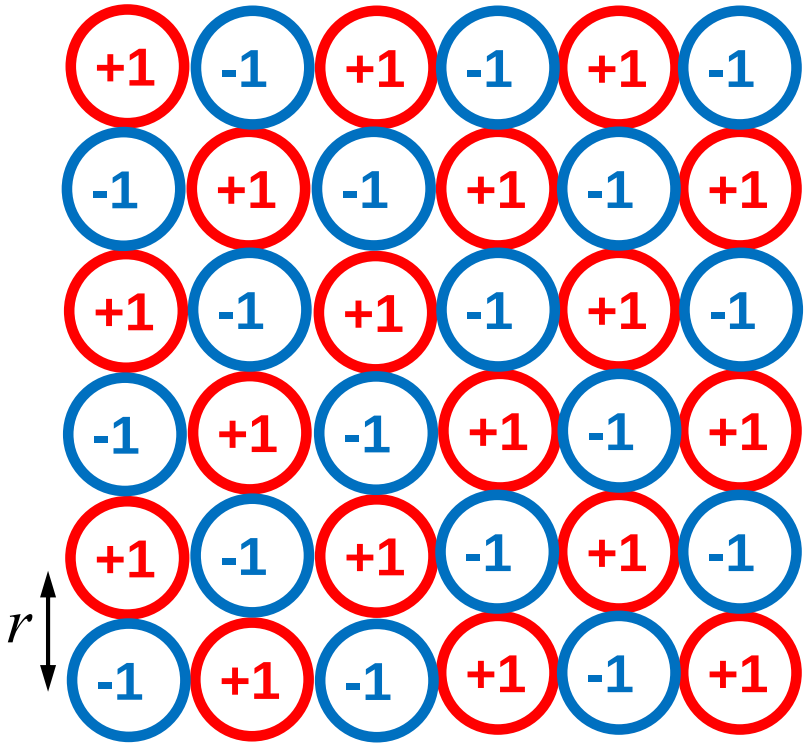
$$\rho(\boldsymbol{r}) = -\pi^{-1}\mathrm{Im}\int_{-\infty}^{\mu} d\varepsilon\, G(\boldsymbol{r},\boldsymbol{r},\varepsilon)$$

$$n(\varepsilon) = -\pi^{-1}\mathrm{Im}\int d\boldsymbol{r}\, G(\boldsymbol{r},\boldsymbol{r},\varepsilon)$$

D.D. Johnson, D.M. Nicholson, F.J. Pinski, B.L. Györffy, G.M. Stocks: *Density functional theory for random alloys: Total energy within the coherent potential approximation* Phys. Rev. Lett. 56, 2088 (1986); Phys. Rev. B **41**, 9701 (1990).

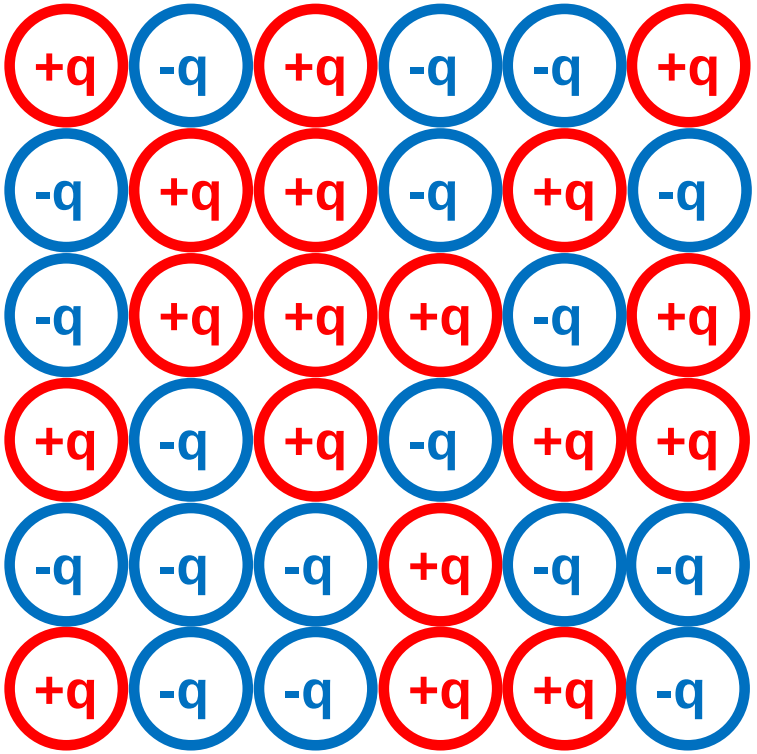
Madelung energy in the CPA

Ordered 50-50 alloy



$$E_M = -\alpha_M \frac{e^2}{r}$$

Random 50-50 alloy

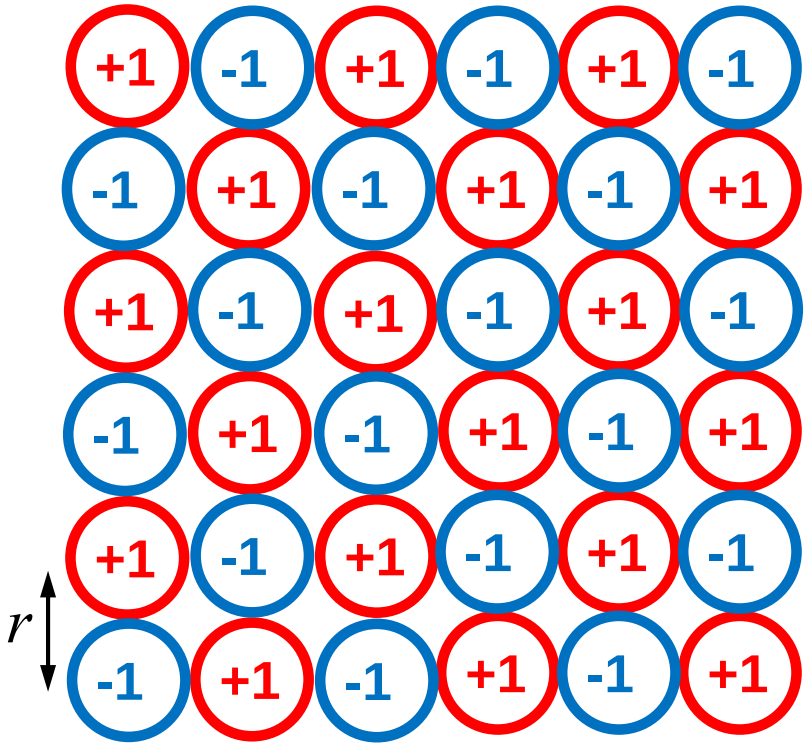


$$E_M = 0 \quad ?$$

Energy per pair of ions, α_M = 1.7476 (NaCl)

Madelung energy in the CPA

Ordered 50-50 alloy



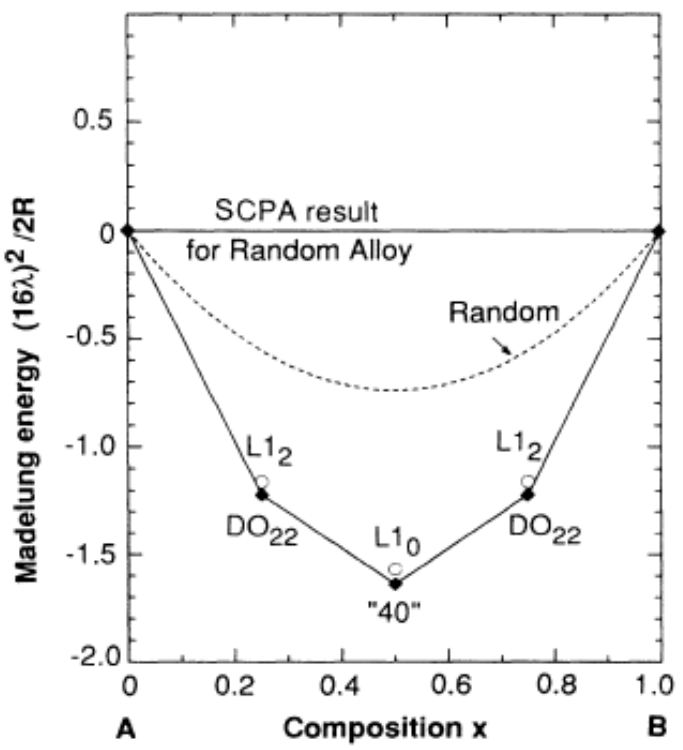
$$E_M = -\alpha_M \frac{e^2}{r}$$

Energy per pair of ions, α_M = 1.7476 (NaCl)

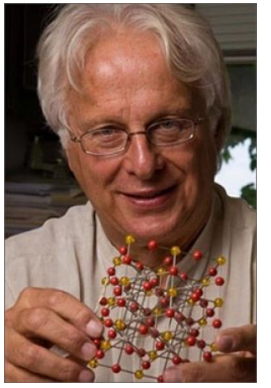
PHYSICAL REVIEW B VOLUME 42, NUMBER 17 15 DECEMBER 1990-I

Ground-state structures and the random-state energy of the Madelung lattice

R. Magri, S.-H. Wei, and Alex Zunger
Solar Energy Research Institute, Golden, Colorado 80401
(Received 22 August 1990)



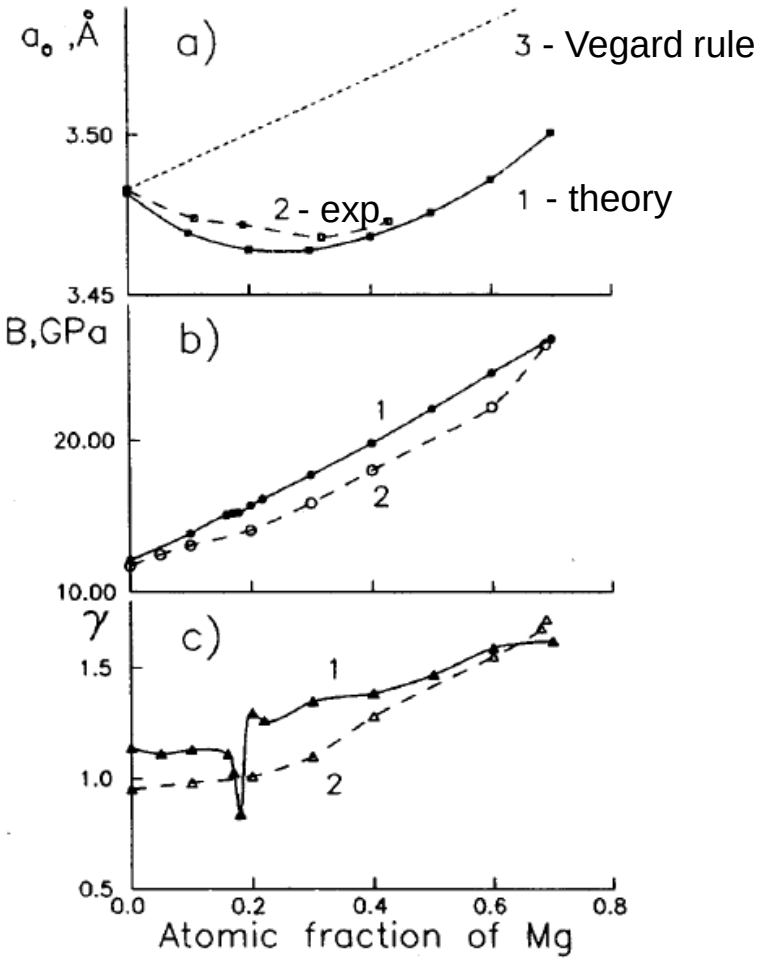
Random	$A_{0.5}B_{0.5}$	· · ·	0.739 52	0.738 65



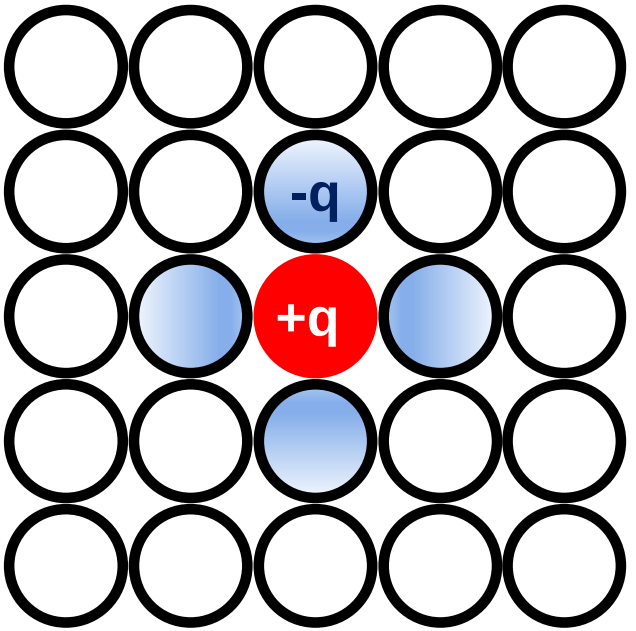
$$E_M^{rand} = -c(1-c)e^2\alpha_M \frac{q^2}{r}$$

Madelung energy in the CPA

Li–Mg bcc



Screened impurity model



$$v_{scr}^{a} = -e^2 \frac{q_a}{r}$$

$$E_M \approx -c(1-c)e^2 \frac{(q_A - q_B)^2}{r}$$

I.A. Abrikosov, Yu.Kh. Vekilov, P. A. Korzhavyi, A.V. Ruban, L.E. Shilkrot, Solid State Commun. **83**, 867 (1992).

Charge correlations in alloys

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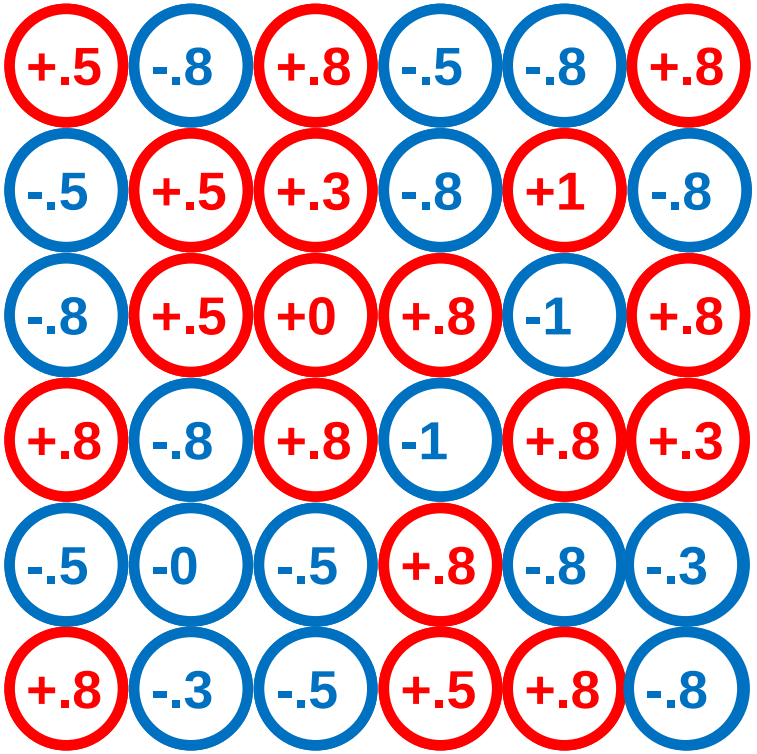
Screened impurity model

$$v_{scr}^{a} = -e^2 \alpha_{scr} \frac{q_a}{r_{ws}}$$

$$E_M = -\frac{\beta_{scr}}{2} e^2 \alpha_{scr} \sum_a c_a \frac{{q_a}^2}{r_{ws}}$$

Screening parameters α_{scr} and β_{scr} are to be found from supercell and/or "embedded cluster" calculations.

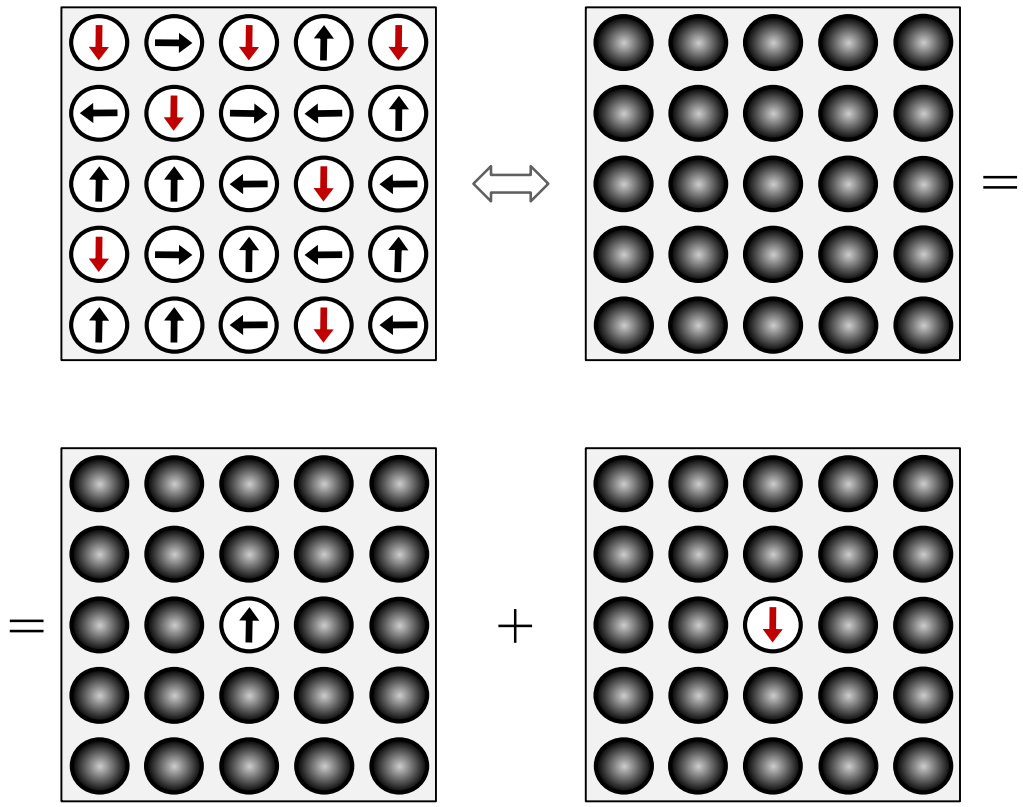
Random 50-50 alloy



D.D. Johnson, F.J. Pinski, Phys. Rev. B **48**, 11553 (1993).
P.A. Korzhavyi, A.V. Ruban, S.I. Simak, Yu.Kh. Vekilov, Phys. Rev. B **49**, 14229 (1994).
P.A. Korzhavyi, A.V. Ruban, I.A. Abrikosov, H.L. Skriver, Phys. Rev. B **51** (1995).
A.V. Ruban, S.I. Simak, P.A. Korzhavyi H.L. Skriver, Phys. Rev. B **66**, 024202 (2002).

Disordered local moment (DLM) model of paramagnetic state

Alloy analogy



Fe(DLM) = 50% Fe↑+ 50% Fe↓

"Equivalence" theorem:

A.J. Pindor, J. Staunton, G.M. Stocks and H. Winter, *J. Phys. F: Met. Phys.* 13, 979 (1983);

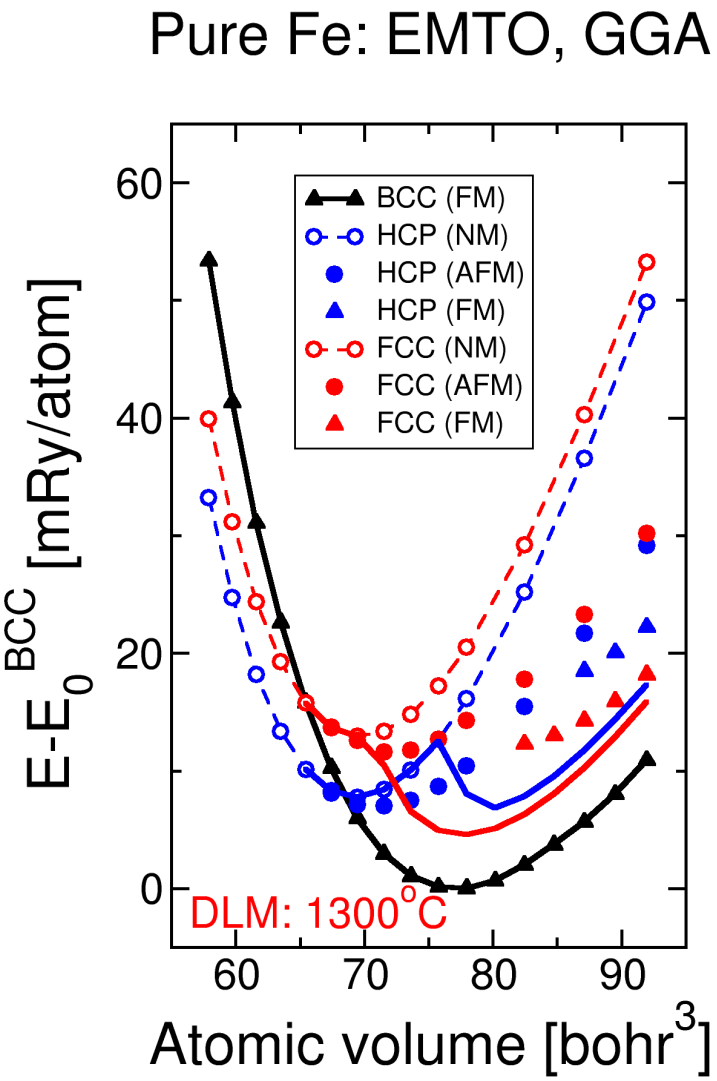
B. L. Gyorffy, A. J. Pindor, J. Staunton, G.M. Stocks and H. Winter*: J. Phys. F: Met. Phys.* 15, 1337 (1985).

Magnetic entropy:

$$S_{\mathrm{magn}} = k_{\mathrm{B}} \ln(M_s + 1)$$

P. Korzhavyi *et al.*, *MRS Proc.* **842** 185-190 (2005), art. S4.10.

Electronic structure calculations: EMTO-CPA code




Levente Vitos


Hans Skriver

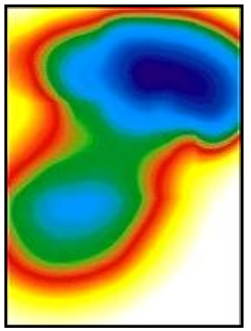

Andrei Ruban


Igor Abrikosov

Exact Muffin-Tin Orbitals theory

(O.K. Andersen 1994, L. Vitos, H.L. Skriver 2000)

Coherent Potential Approximation -chemical and magnetic disorder



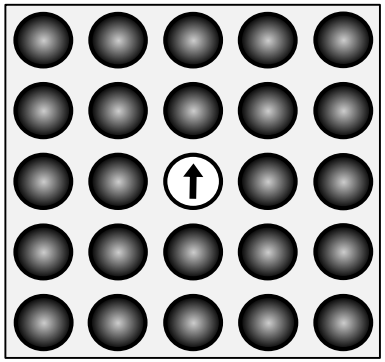
EMTO-CPA method

L. Vitos, I.A. Abrikosov, B. Johansson, Phys. Rev. Lett. 87, 156401 (2001).

Spin fluctuations in a self-consistent DLM model

- Rigid spin moment orientations:

$$S_{\mathrm{magn}} = k_{\mathrm{B}} \ln(M_s + 1)$$



- Transverse spin moment fluctuations: mean-field contributions to one-electron potential

$$\Delta V_{\uparrow\downarrow} = \mp k_{\mathrm{B}} T / (M_s + 1)$$

- The moment M_S is treated as localized but non-integer and calculated self-consistently at any temperature T

Methodology (summary)

- **Configurational disorder:** coherent potential approximation (CPA) with charge correlations
- **Magnetic disorder:** paramagnetic state represented by the disordered local moment (DLM) model
- **Electronic disorder:** partial filling of electron states according to Fermi function $f(\epsilon) = [\exp\left\{\frac{\epsilon-\epsilon_F}{k_B T}\right\} + 1]^{-1}$

$$F_{\mathrm{CPA}}(V,T) = E_{\mathrm{CPA}} - T\left(S_{\mathrm{el}} + S_{\mathrm{magn}} + S_{\mathrm{conf}}\right)$$

- **Lattice vibrations:** post-processing of partial free energy $F_{\mathrm{CPA}}(V,T)$ using quasi-harmonic Debye model:

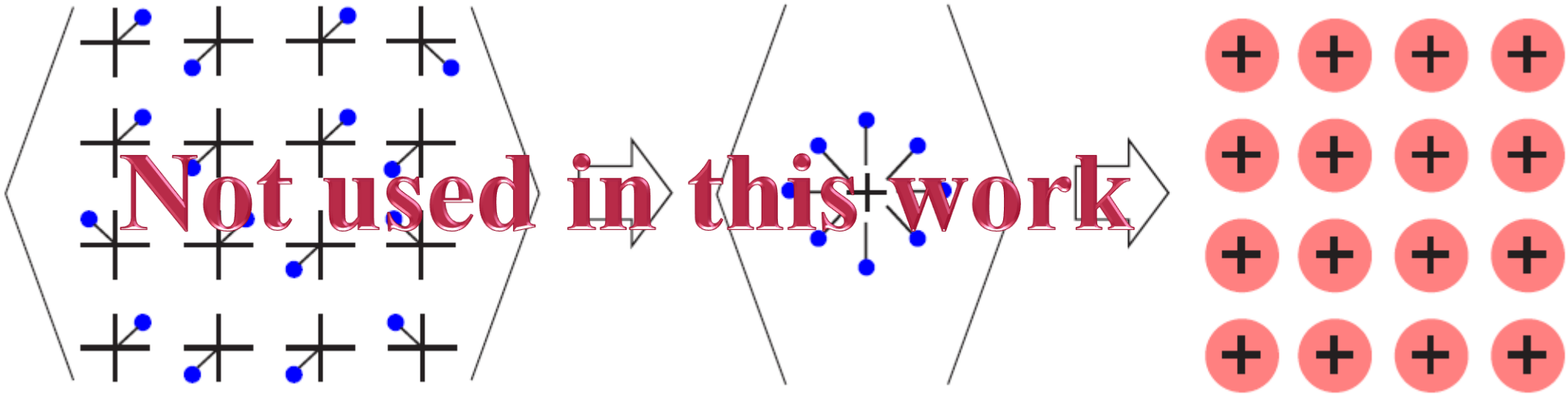
$$F_{\mathrm{Debye}}(V,T) = \frac{9}{8} k_{\mathrm{B}} \theta_{\mathrm{D}} + k_{\mathrm{B}} T\left\{\left[1 - \exp(-\frac{\theta_{\mathrm{D}}}{T})\right] - D(\frac{\theta_{\mathrm{D}}}{T})\right\}$$

$$F(V,T) = F_{\mathrm{CPA}}(V,T) + F_{\mathrm{Debye}}(V,T)$$

Grimvall, G. Thermophysical Properties of Materials; Elsevier Science: Amsterdam, The Netherlands, 1999.

CPA-based model of atomic vibrations

Compatible with Einstein model

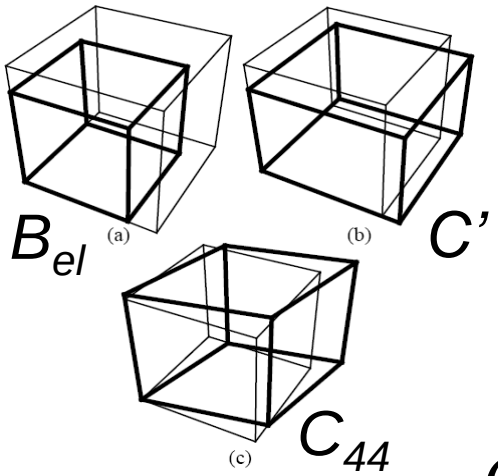


Implemented in SPR-KKR package by:

H. Ebert, S. Mankovsky, K. Chadova, S. Polesya, J. Minár, D. Ködderitzsch, *Phys. Rev. B* **91**, 165132 (2015).

Calculations of elastic stiffness constants of steels

Elastic moduli



Bulk modulus B – from the equation of state (Birch-Murnaghan):

$$F(V) - F(V_0) = \frac{BV}{B'}\left[\frac{(V_0/V)B'}{B'-1} + 1\right] - \frac{BV_0}{B'-1}$$

Shear constants C' and C_{44} – volume-conserving distortions:

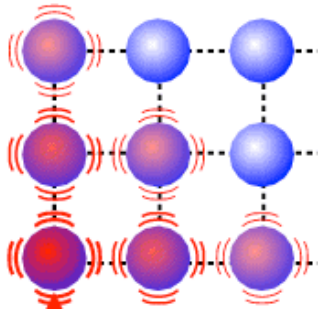
$$\begin{pmatrix} a'_x \\ a'_y \\ a'_z \end{pmatrix} = (\mathbf{1}+\boldsymbol{\varepsilon}) \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$$

$$C': \quad \mathbf{1}+\boldsymbol{\varepsilon} = \begin{pmatrix} 1+\delta & 0 & 0 \\ 0 & 1-\delta & 0 \\ 0 & 0 & 1/(1-\delta^2) \end{pmatrix} \qquad F - F_0 = 2V_0 C' \delta^2 + O(\delta^4)$$

$$C_{44}: \quad \mathbf{1}+\boldsymbol{\varepsilon} = \begin{pmatrix} 1 & \delta & 0 \\ \delta & 1 & 0 \\ 0 & 0 & 1/(1-\delta^2) \end{pmatrix} \qquad F - F_0 = 2V_0 C_{44} \delta^2 + O(\delta^4)$$

R. Sandström and P. Korzhavyi, *Canadian Metallurgical Quarterly* **53**, 282 (2014).
T. Hammerschmidt et al., *Phys. Status Solidi B* 251, 81 (2014).

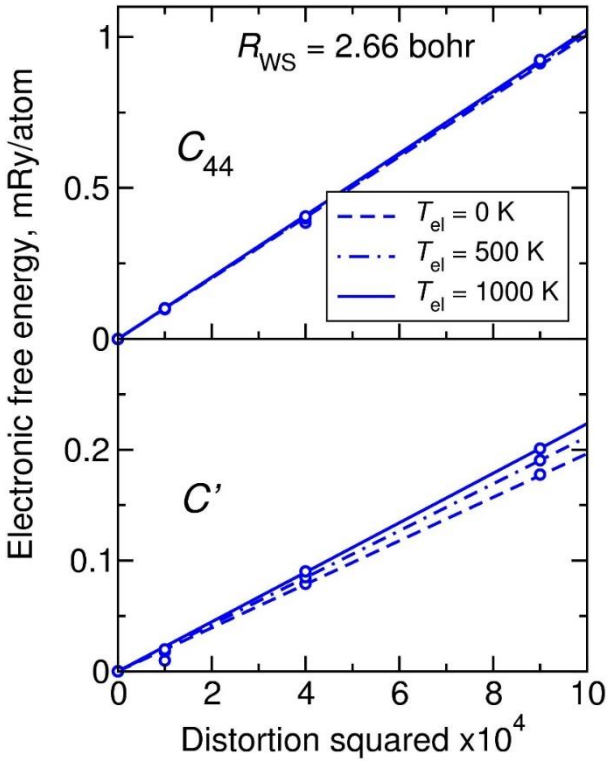
Quasi-harmonic Debye model

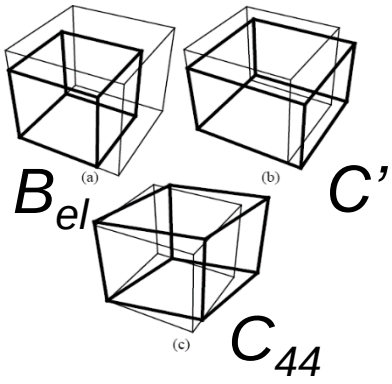


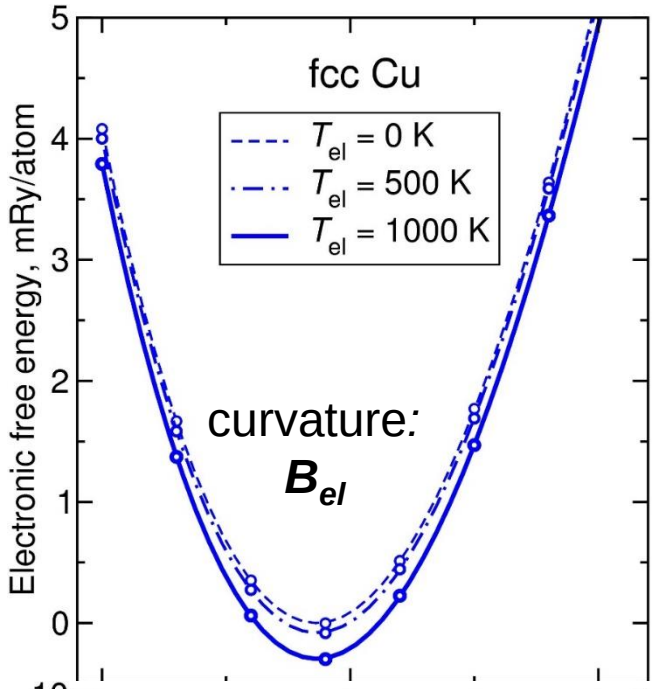
- Calculated partial free energy (containing electronic and magnetic contributions) for a number of distortions is used to set up the Debye model
- Longitudinal constant: $\langle L \rangle = B_{el} + \frac{4}{3}\langle S \rangle$
- Shear constant: $\langle S \rangle = \frac{G_V + G_R}{2}$; $G_V = \frac{2C' + 3C_{44}}{5}$; $G_R = \frac{5C'C_{44}}{2C' + 3C_{44}}$
- Average stiffness: $\langle K \rangle = \left[\frac{1}{3}\langle L \rangle^{-3/2} + \frac{2}{3}\langle S \rangle^{-3/2}\right]^{-2/3}$
- Debye temperature (volume-dependent): $\Theta_D = 67.48[\langle K \rangle R_{WS}/M]^{1/2}$

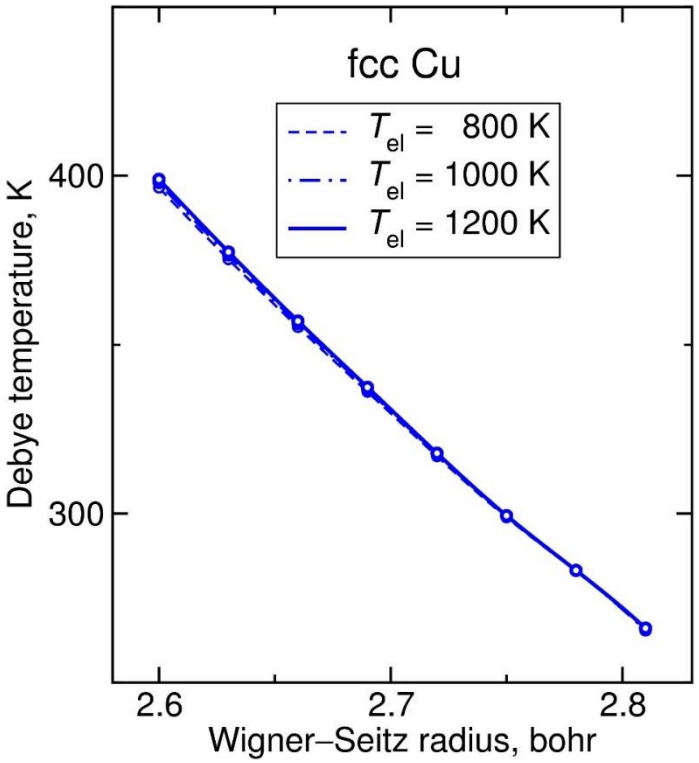
O. L. Anderson, *J. Phys. Chem. Solids* **24**, 909-917 (1963).
V. L. Moruzzi, J. F. Janak, K. Schwarz, *Phys. Rev. B* **37**, 790 (1988).

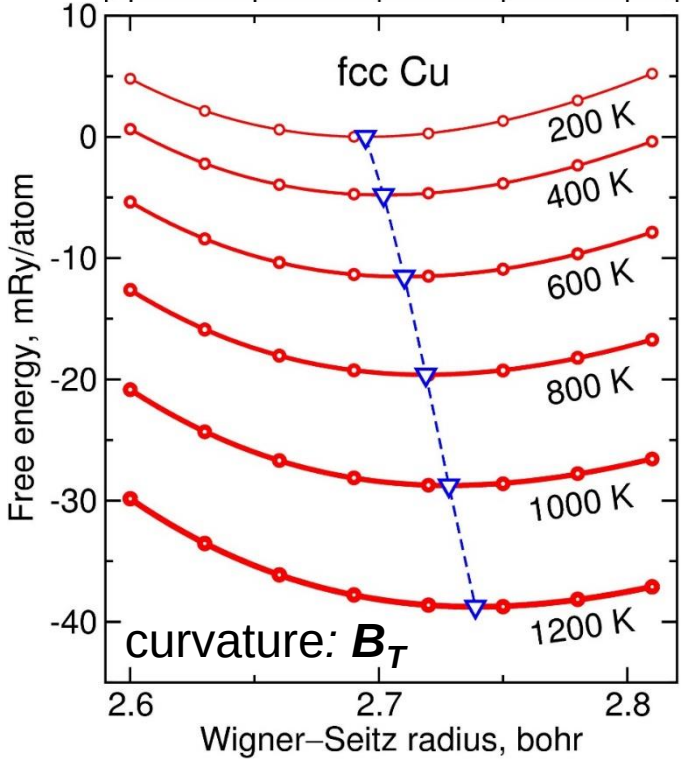
Case studies: fcc Cu







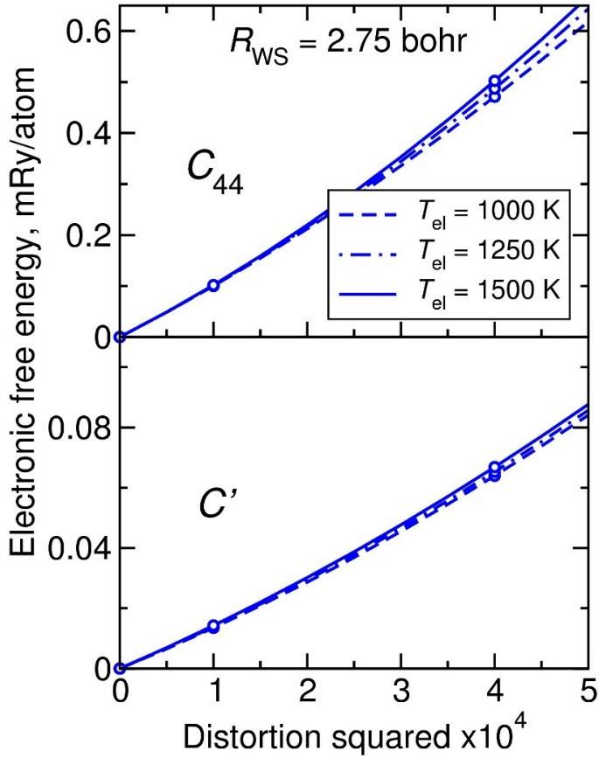


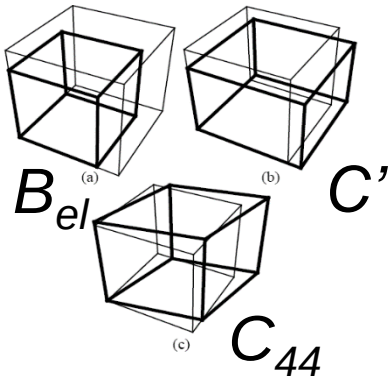


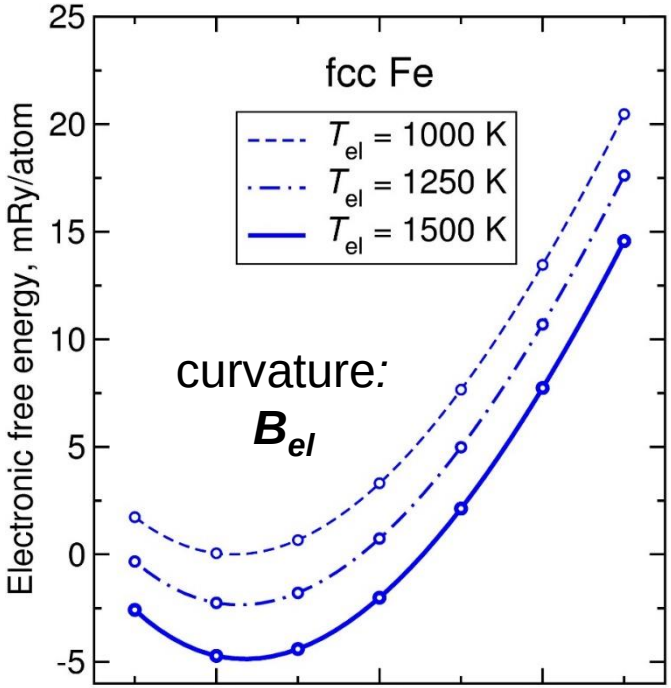
Wigner–Seitz radius

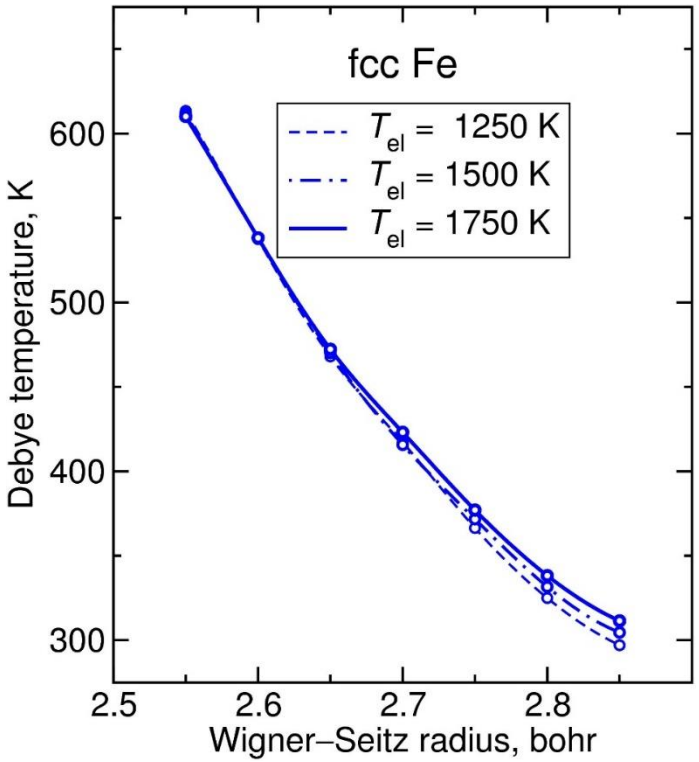
R_{WS}: $V = \frac{4\pi}{3} R_{\mathrm{WS}}^3$

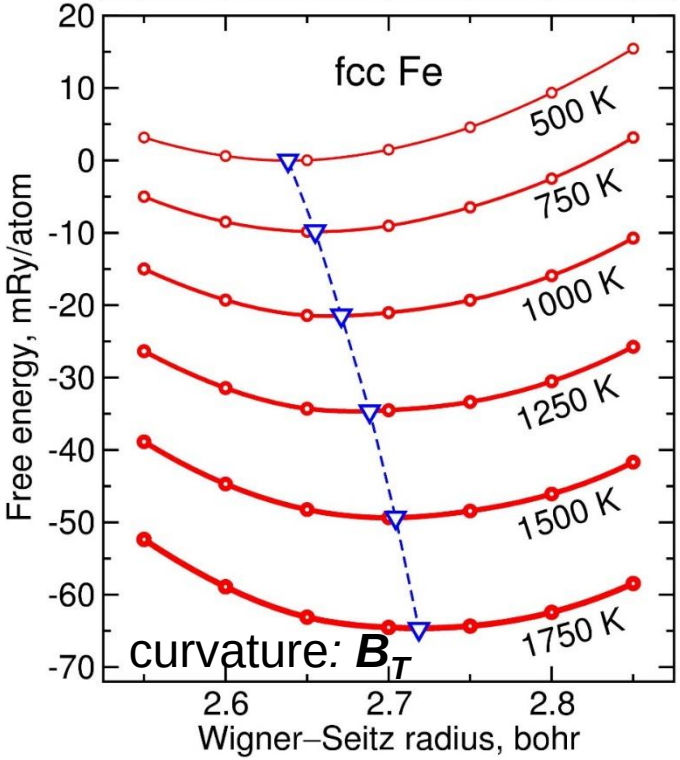
Case studies: fcc Fe







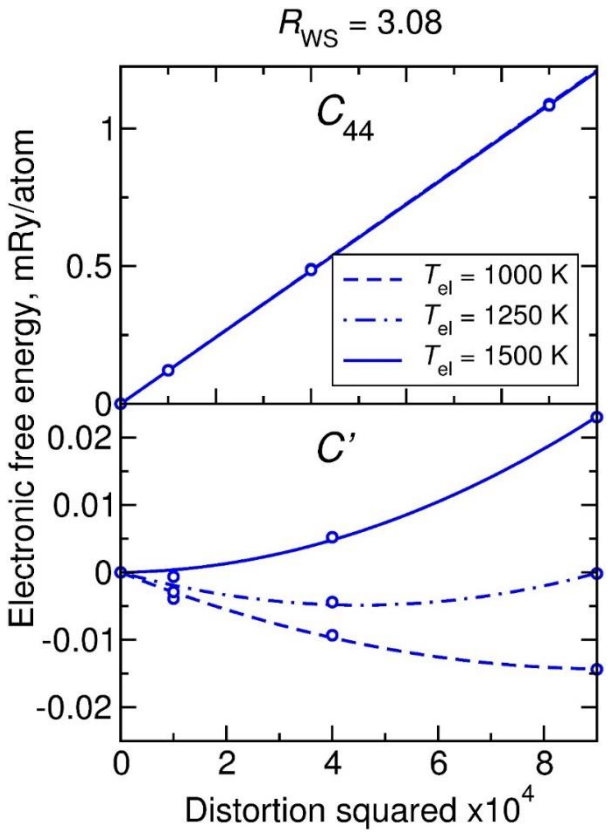


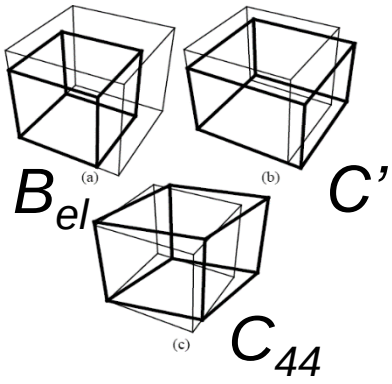


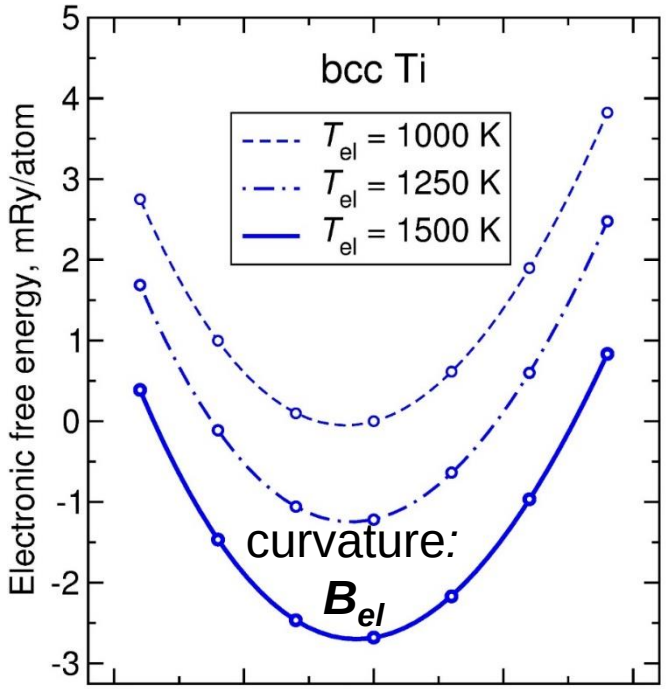
Wigner–Seitz radius

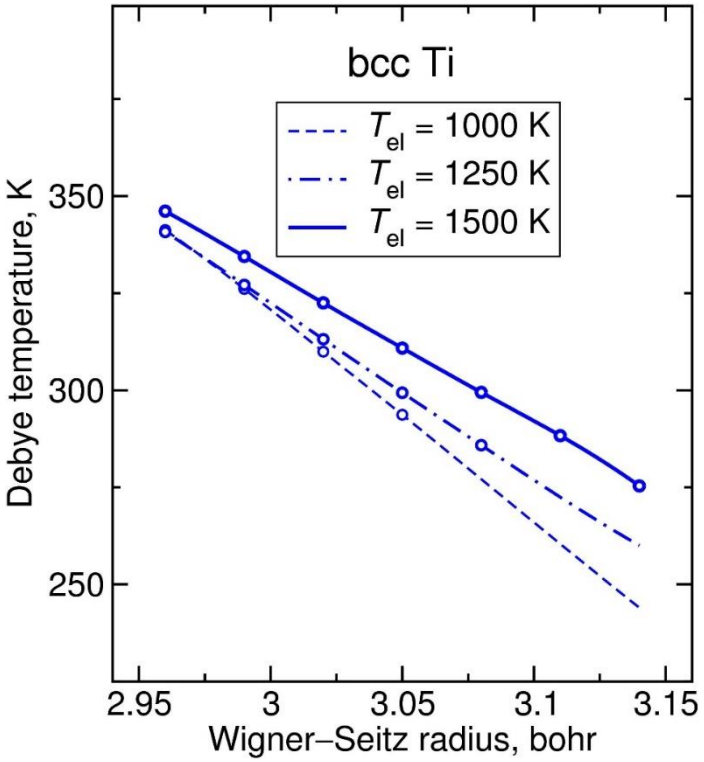
R_{WS}: $V = \frac{4\pi}{3} R_{\mathrm{WS}}^3$

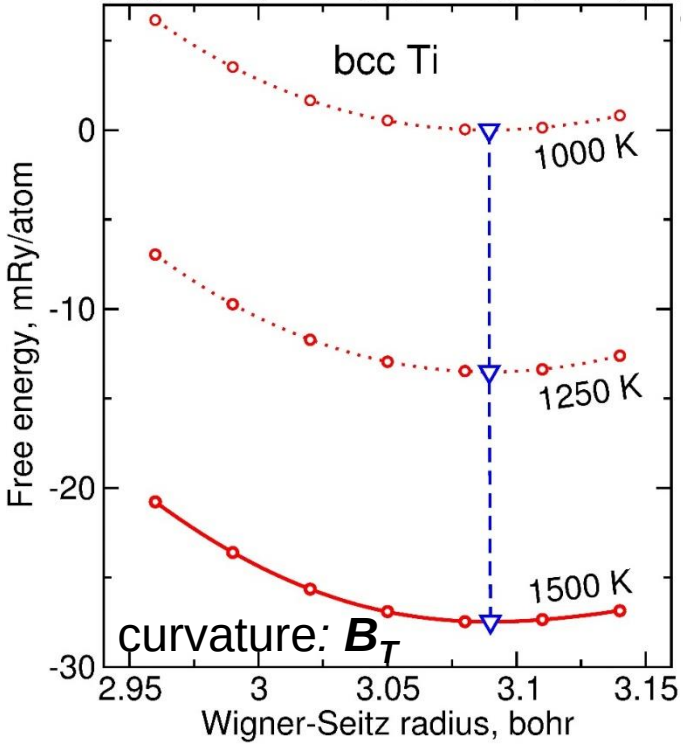
Case studies: bcc Ti











Wigner–Seitz radius

R_{WS}: $V = \frac{4\pi}{3} R_{\mathrm{WS}}^3$

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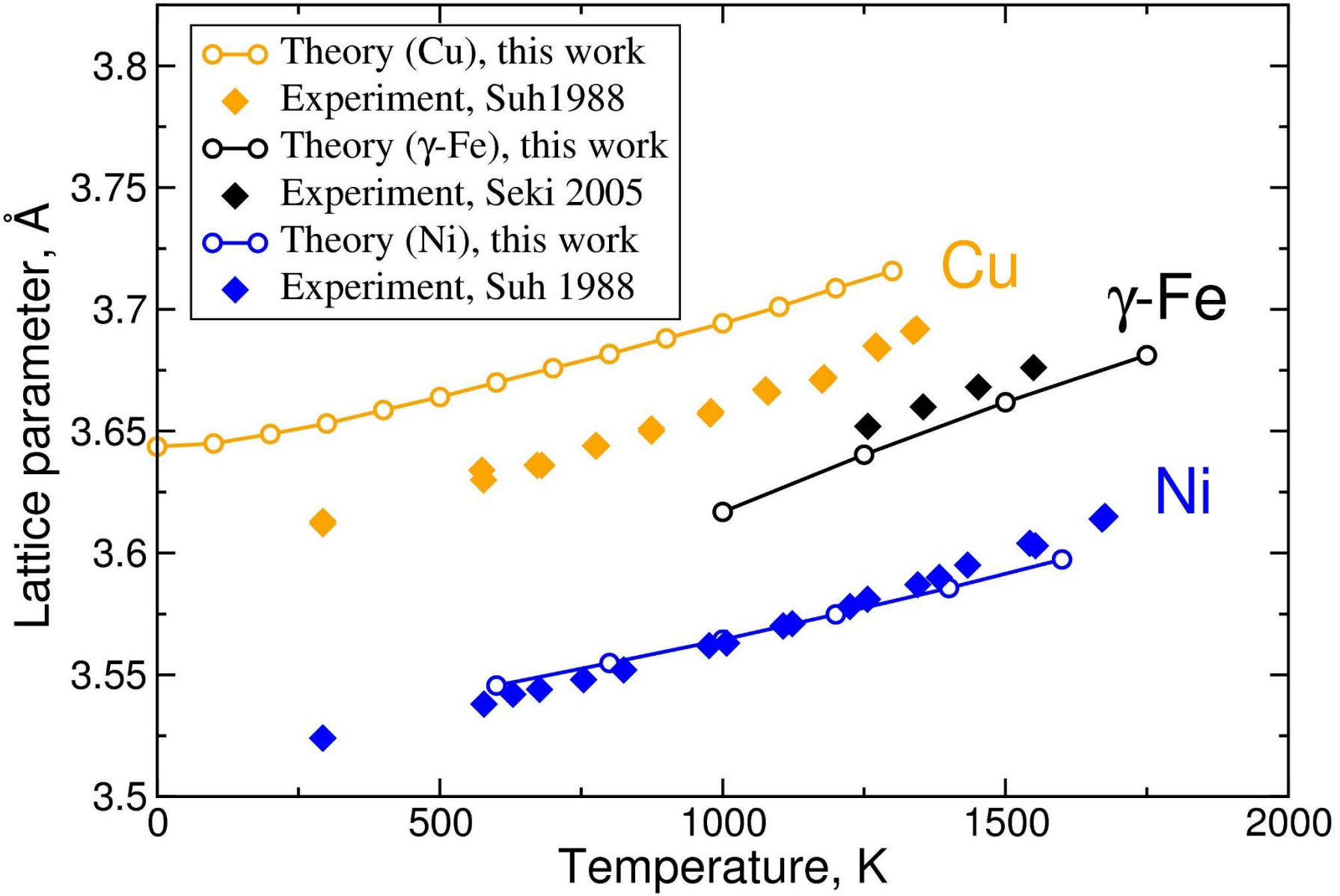
Calculated lattice parameters and bulk moduli of selected cubic metals

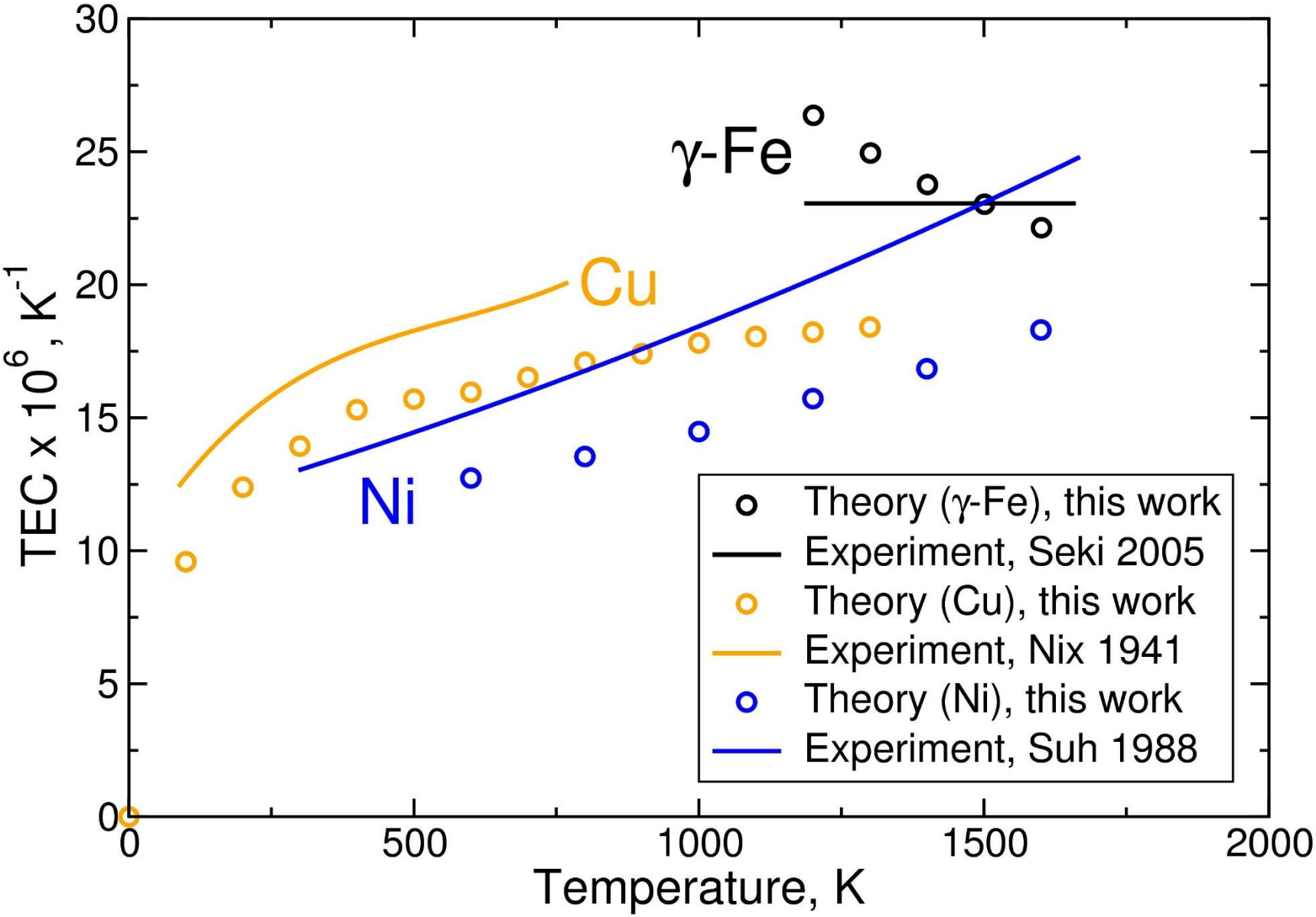
Metal	T, K	Lattice Parameter, Å			Bulk Modulus, GPa		
		a_{el}	a_T	a_{exp} [1]	B_{el}	B_T	B_{exp} [1]
Cu	800	3.638	3.682	3.646	140.0	118.0	124.8
% error, Reference		−0.2	+1.0	[51]	+12.2	−5.4	[53]
Ni	800	3.526	3.555	3.550	194.1	174.4	171.0
% error, Reference		−0.7	+0.1	[51]	+13.5	+2.0	[55]
γ-Fe	1250	3.540	3.640	3.652	136.7	103.1	102.7
% error, Reference		−3.0	−0.3	[52]	+33.1	+0.4	[56]
β-Ti	1250	3.27	3.32	3.31	106.2	90.9	87.7
% error, Reference		−1.3	+0.3	[49]	+21.0	+3.6	[57]
Cr	1000	2.851	2.871	2.901	249.7	229.6	190
% error, Reference		−1.7	−1.0	[58]	+31.4	+20.8	[59]
Mo	1000	3.164	3.181	3.159	249.1	231.5	247.5
% error, Reference		+0.2	+0.7	[60]	+0.6	−6.5	[61]
W	1000	3.192	3.206	3.175	294.2	275.9	298.3
% error, Reference		+0.5	+1.0	[62]	+12.2	−5.4	[63]

Pavel A. Korzhavyi, Jing Zhang, *Metals* **11**, 195 (2021).

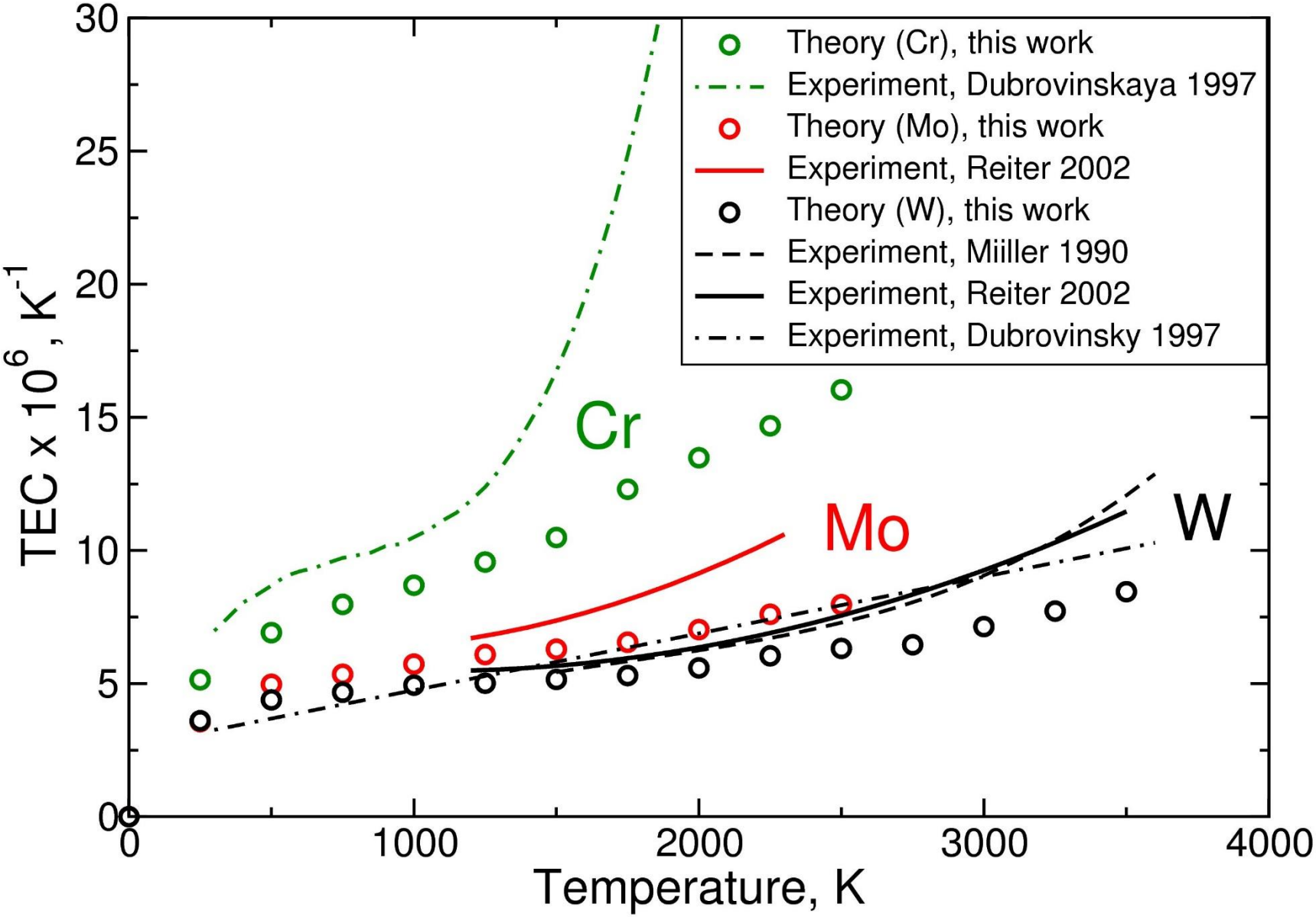
Lattice parameters of fcc Cu, Fe, and Ni



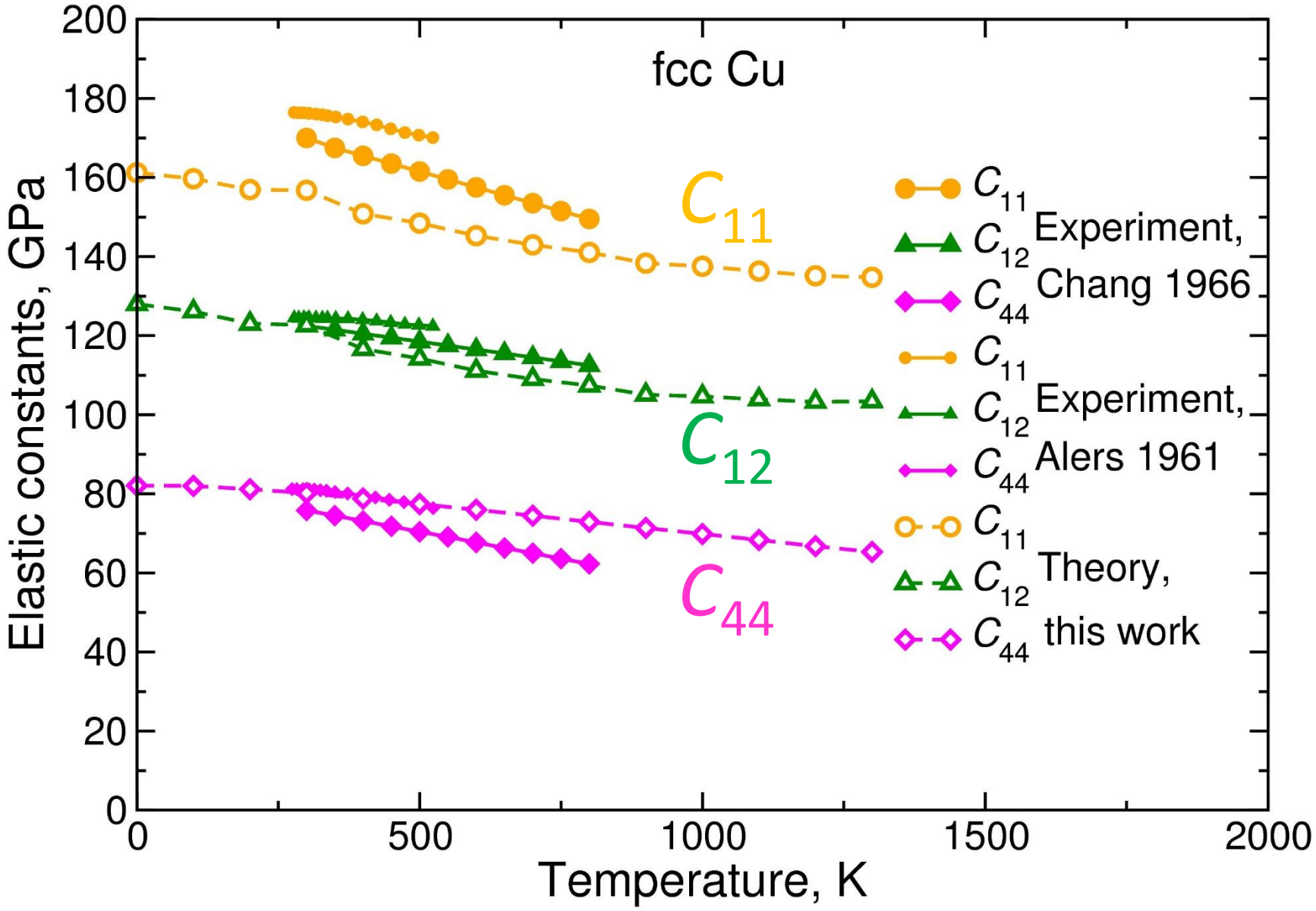
Thermal expansion coefficient of fcc Cu, Fe, and Ni



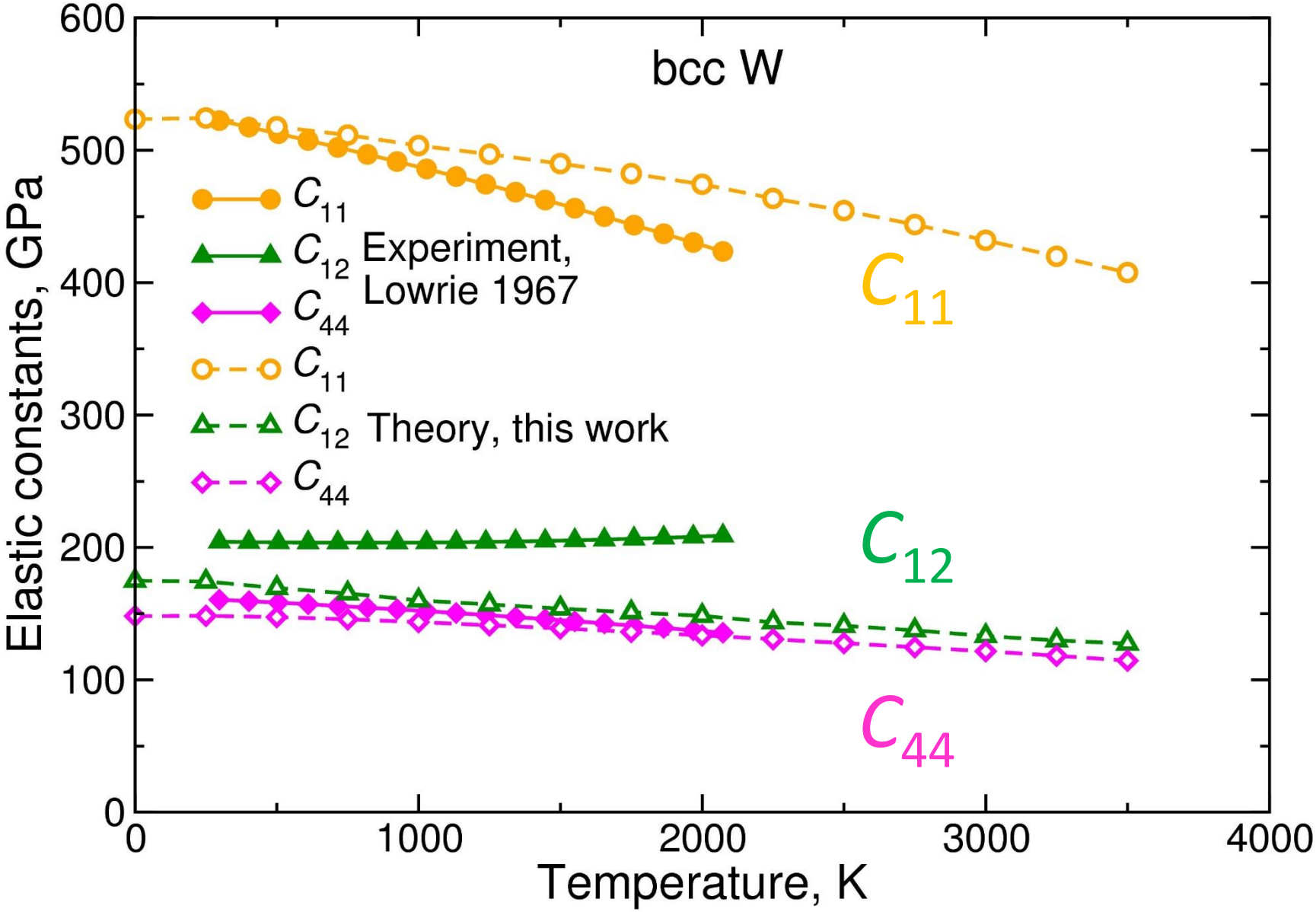
Thermal expansion coefficient of bcc Cr, Mo, and W



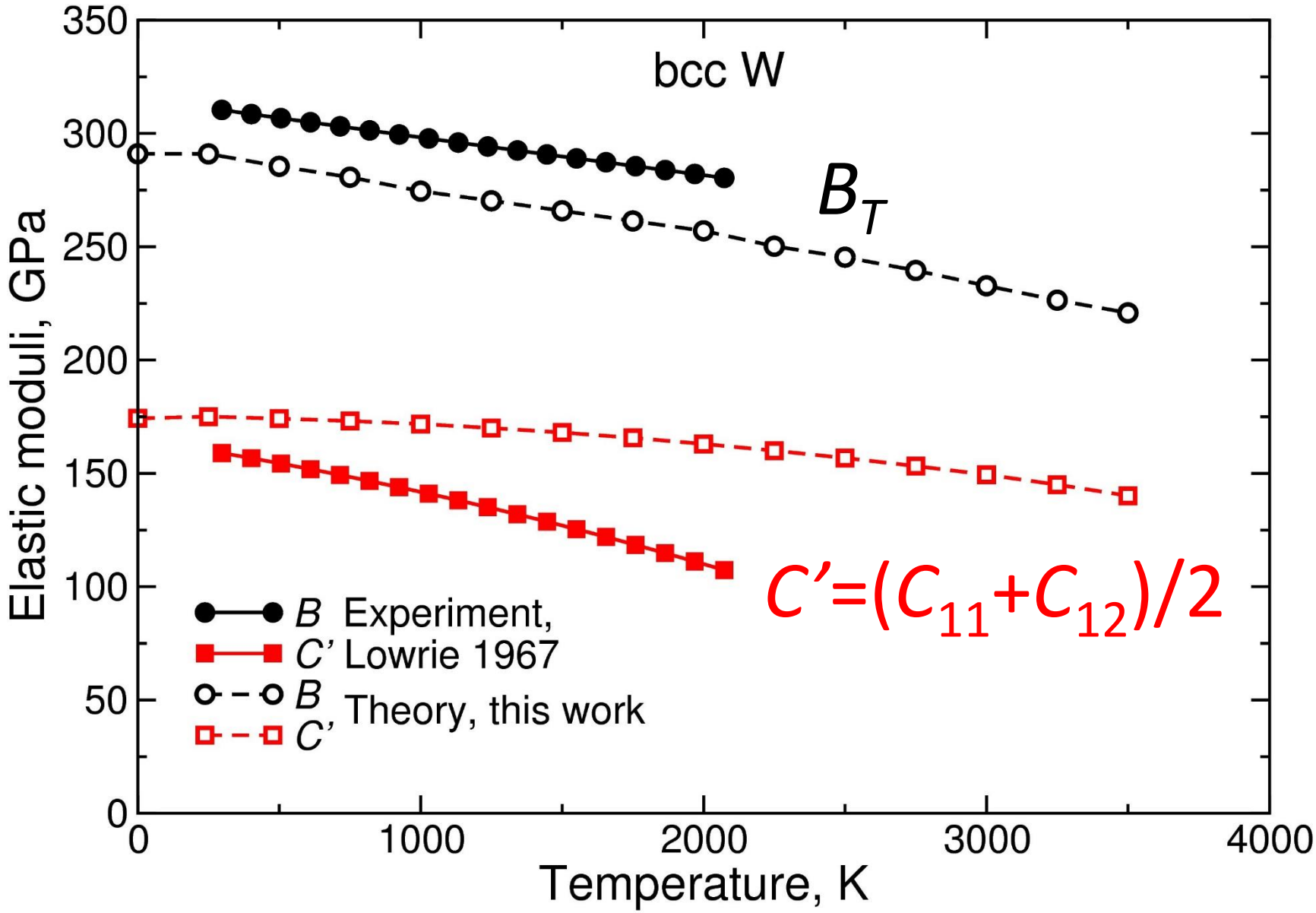
Temperature dependence of elastic constants for fcc Cu



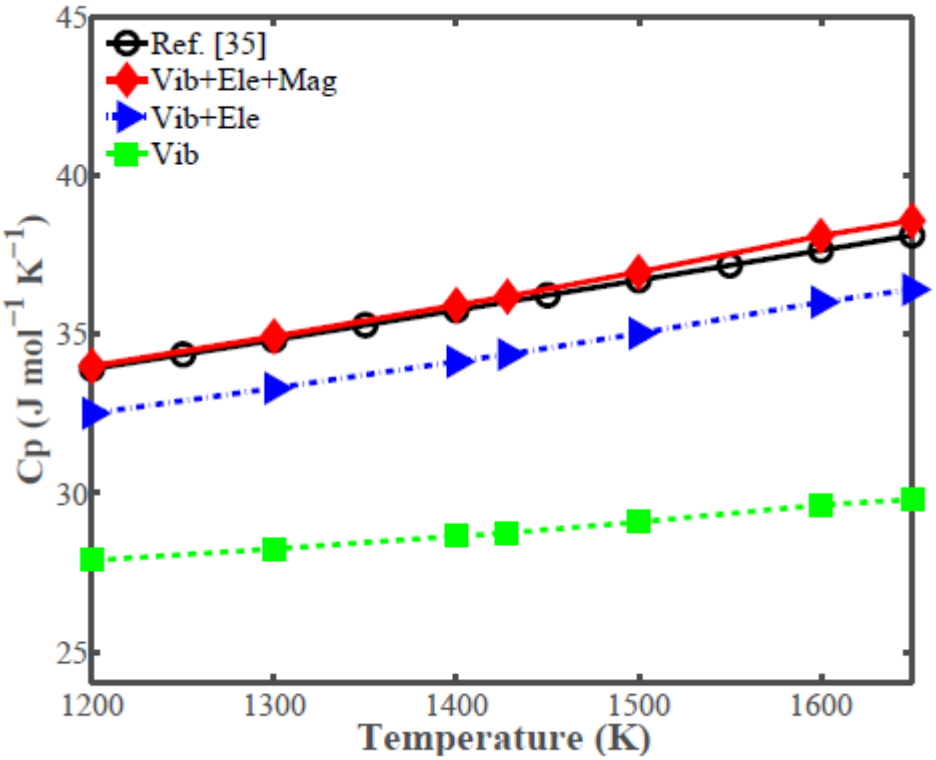
Temperature dependence of elastic constants for bcc W



Temperature dependence of elastic moduli for bcc W



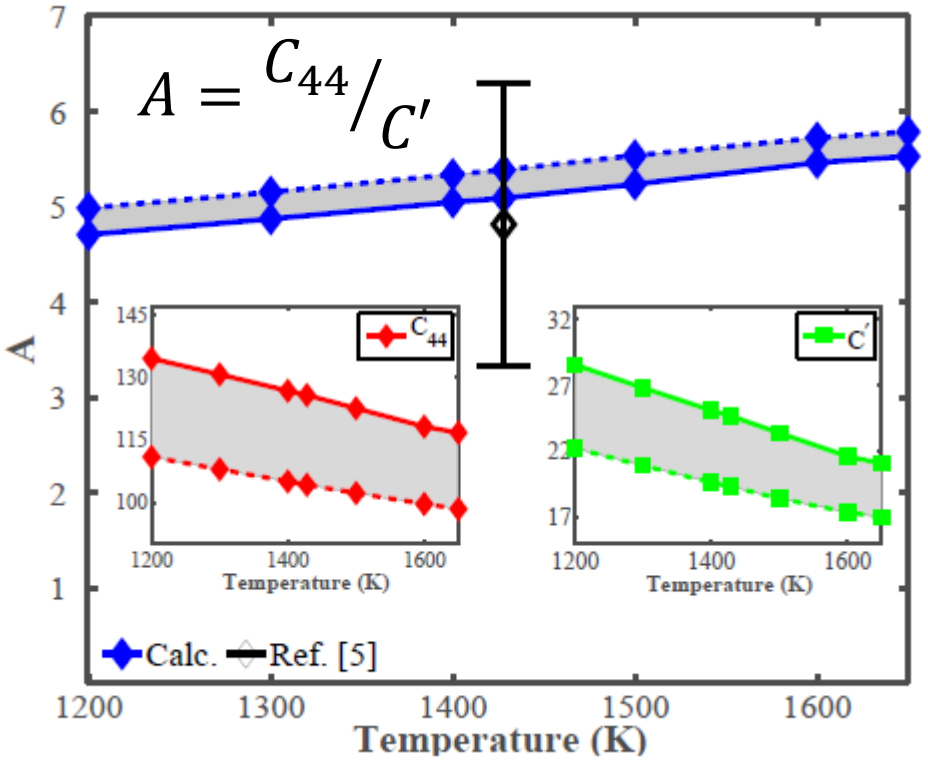
Heat capacity of fcc Fe

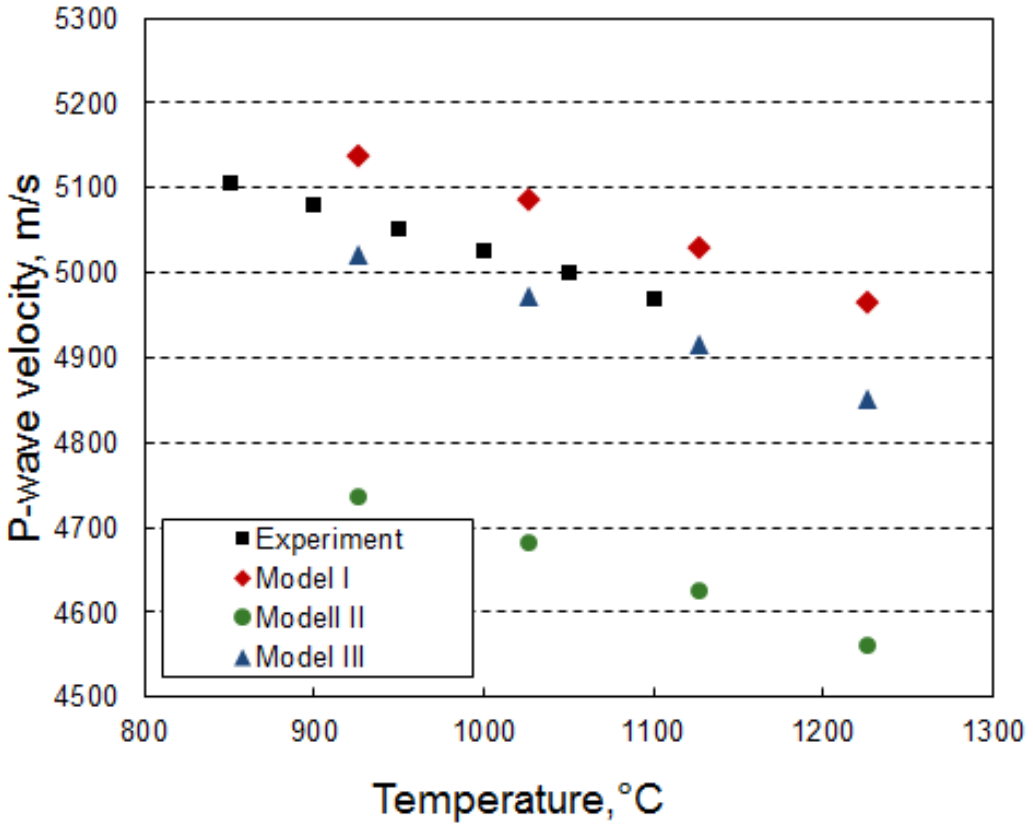


- Desai has critically assessed available experiments.
- Around 80% of C_p is due to the lattice contributions.
- The rest is due to the electronic and magnetic contributions.

H. Ehteshami and P. Korzhavyi, Thermophysical properties of paramagnetic Fe from first principles, Phys. Rev. B 96, 224406 (2017).

Elastic anisotropy and sound velocity for fcc Fe





Comparison with Laser Ultrasonics method:
B. Hutchinson *et al.* *Ultrasonics* **87**, 44–47 (2018).

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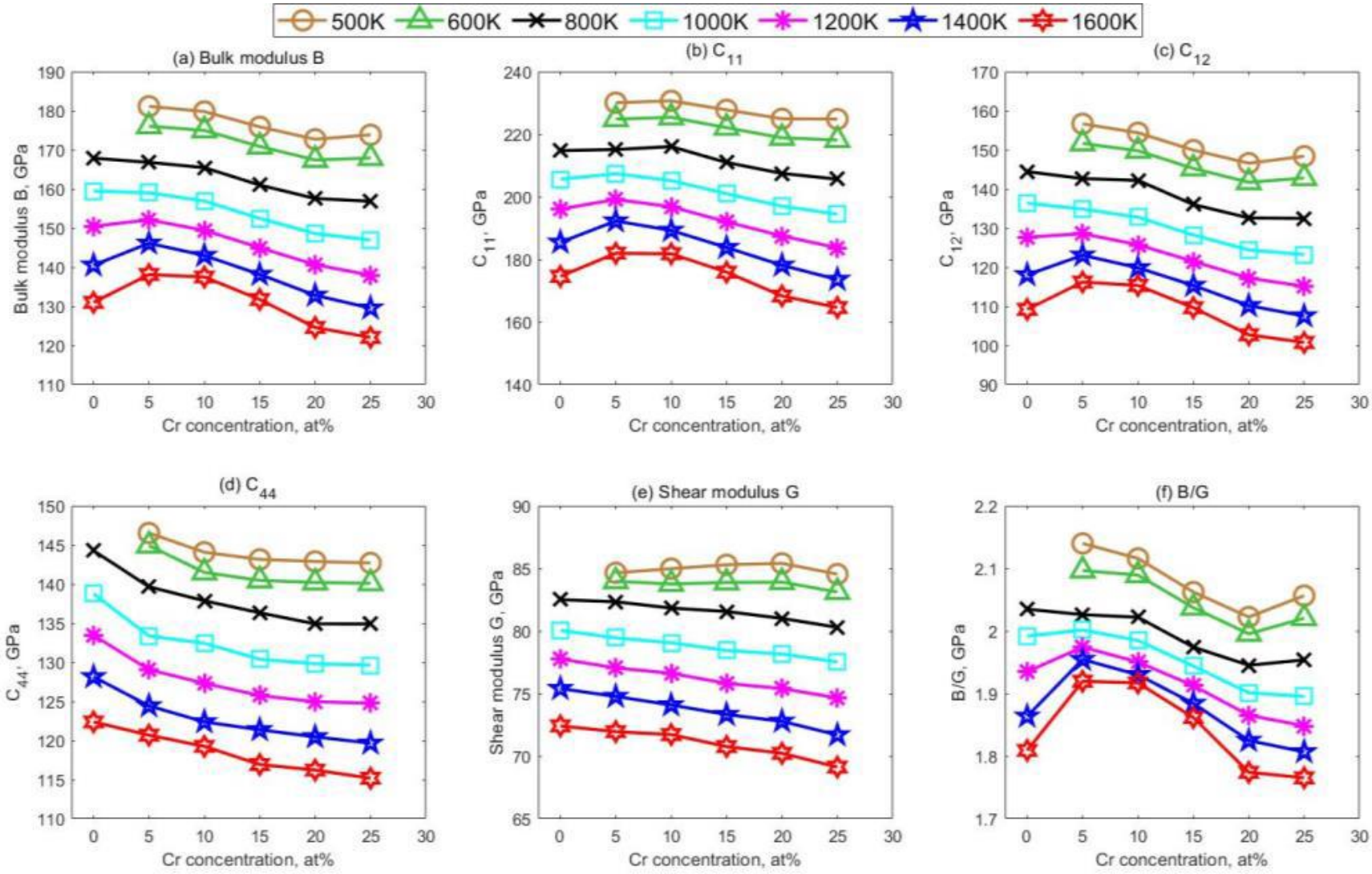
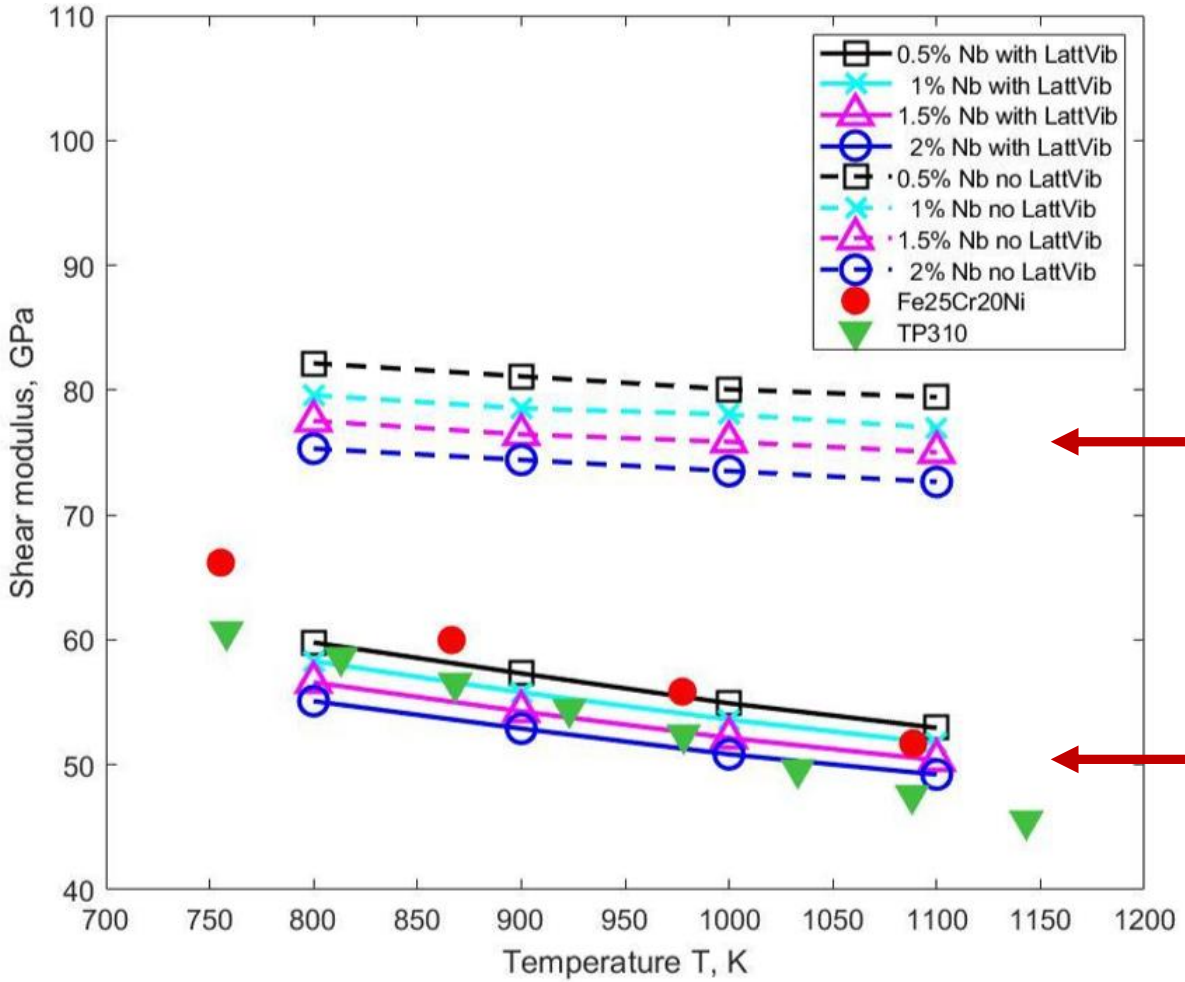
Elastic properties of fcc Ni-Cr alloys



J. Zhang, P.A. Korzhavyi, J. He, Materials Today Commun. **28**, 102551 (2021).

hero-m 2i

Shear modulus of austenitic steel: Fe25Cr20Ni+xNb



EMTO-CPA
(electronic+magnetic disorder)

EMTO-CPA
+ QH Debye

J. Zhang, P. Korzhavyi, and J. He, *Comput. Mater. Sci.* **85**, 109973 (2020).

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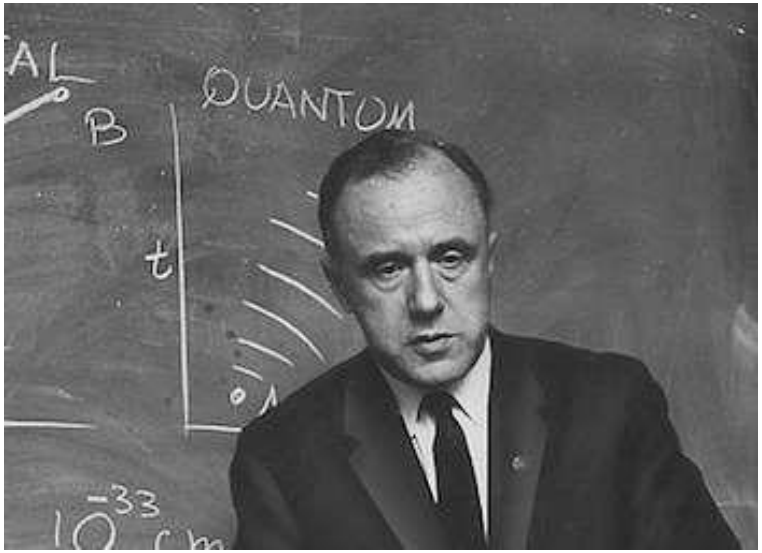
Conclusions:

- Thermal properties of selected transition metals have been evaluated with the help of *ab initio* informed, quasi-harmonic Debye model
- Quasi-harmonic treatment is computationally simple and is a good approximation in many cases
- Performance of DFT approximations is crucial for the accuracy of *ab initio* thermal property modelling
- Anharmonic effects are important in some cases, and generally at high temperatures. Atomic displacements must be included into electronic structure calculations

Pavel A. Korzhavyi, Jing Zhang, *Metals* **11**, 195 (2021).

Take-home quote: *Never make a calculation until you know the answer*



Never make a calculation until you know the answer. Make an estimate before every calculation, try a simple physical argument (symmetry! invariance! conservation!) before every derivation, guess the answer to every puzzle. Courage: no one else needs to know what the guess is. Therefore make it quickly, by instinct. A right guess reinforces the instinct. A wrong guess brings the refreshment of surprise. In either case, life as a spacetime expert, however long, is more fun.

–John Archibald Wheeler, *Spacetime Physics*

Contributors

- Jing Zhang, Andrei Ruban (KTH, Stockholm)
- Mariyal Jebasty (Anna University, Chennai, India)
- Junjing He (Hangzhou Dianzi University, China)

Thank you for your attention!

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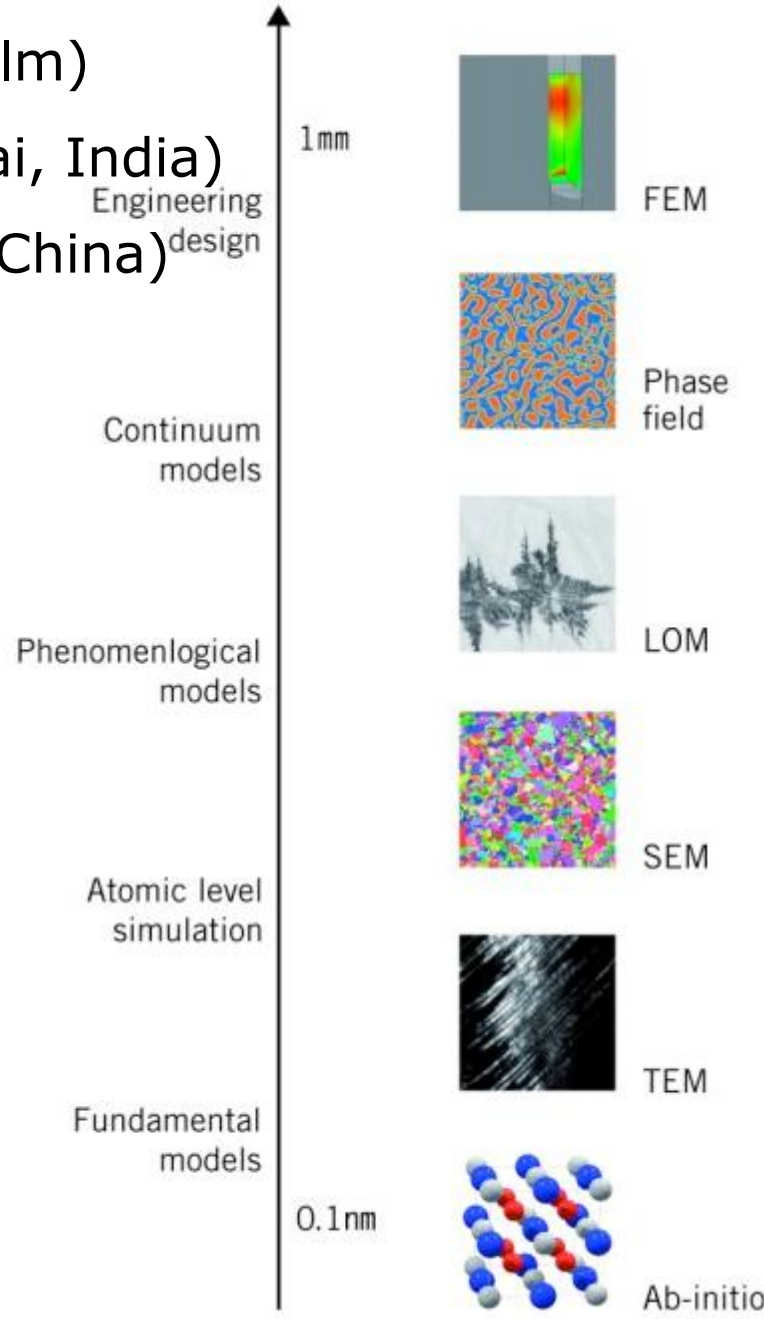

Case studies: bcc Ti