Thermoelectric properties of elemental metals from first principles

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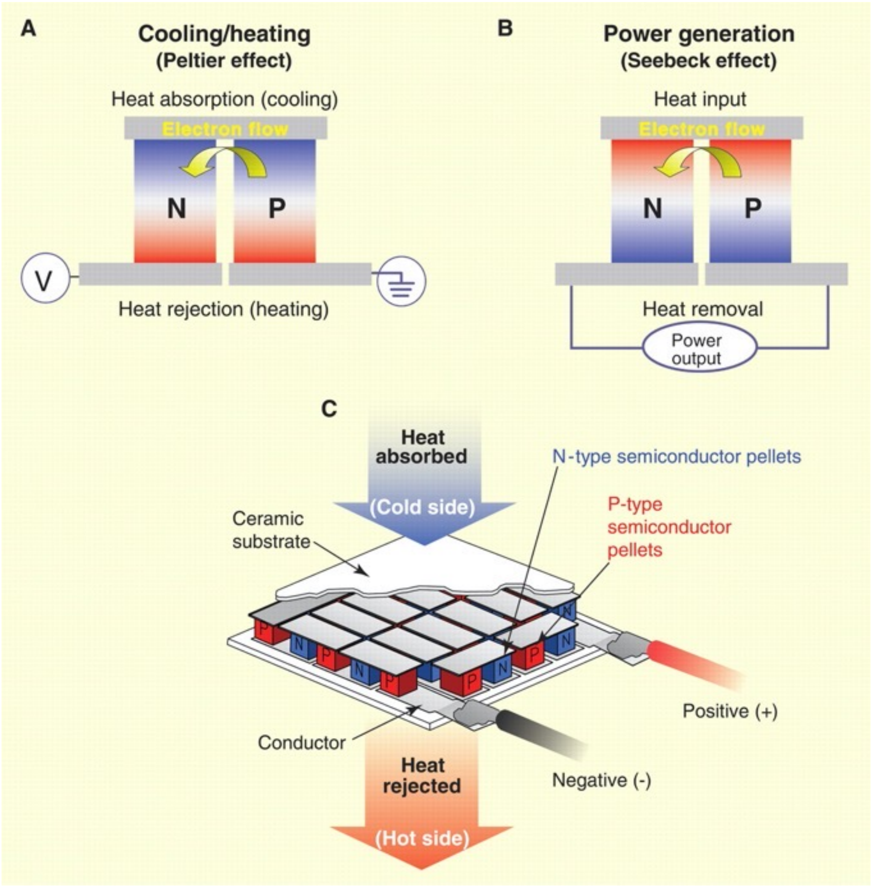
Outline

- Why elemental metals?
  - Normal *vs.* abnormal sign of Seebeck
  - Simple *vs.* complex Fermi suraface
- Two computational methods
  - Constant relaxation time approximation (CRTA)
  - Variational approach (VA)
- CRTA *vs.* VA
  - Alkali metals: Li, Na, K
  - Noble metals: Cu, Ag, Au, Pt

Thermoelectric effect



L. E. Bell, Science 321, 1457 (2008)

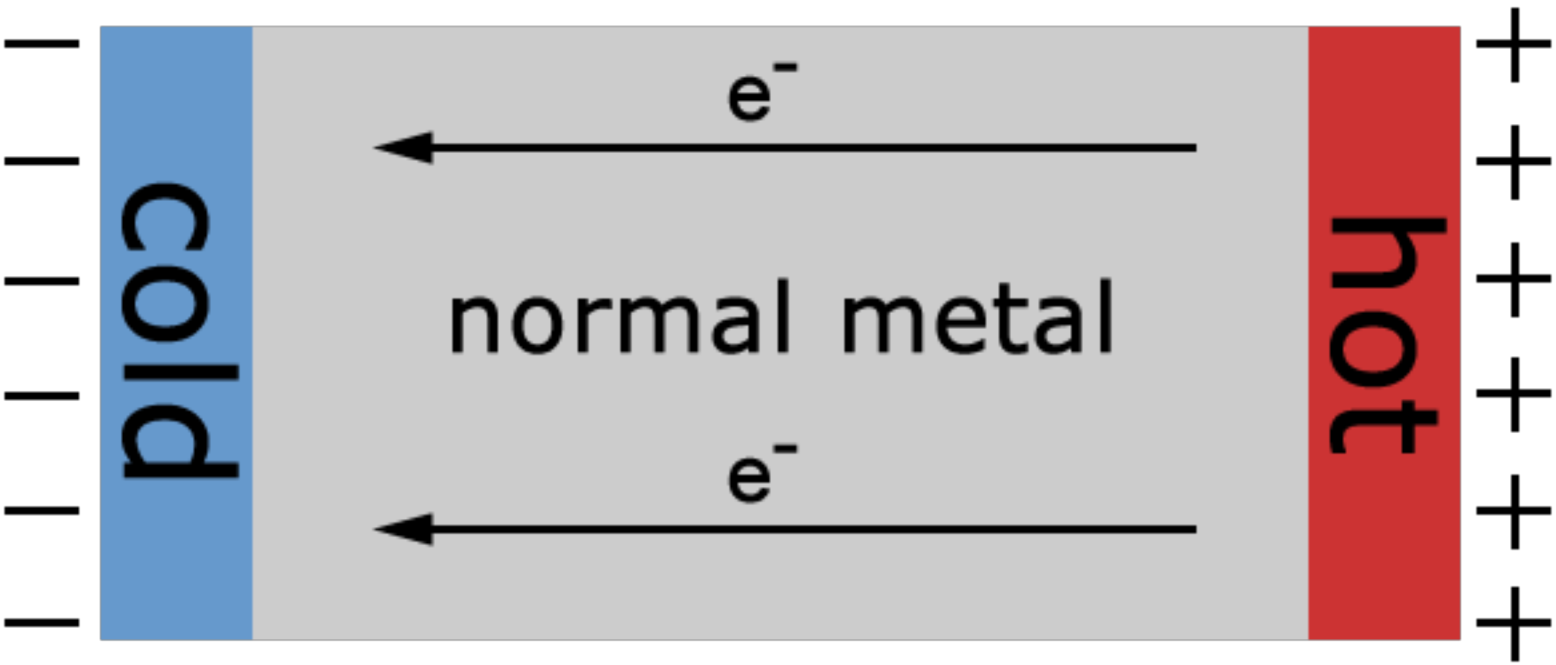
- Seebeck effect: $\vec{E} = S\vec{\nabla}T$
- Peltier effect: $\dot{Q}_P = \Pi I = STI$
- Efficiency: $\frac{T_H - T_C}{T_H}\left(\frac{\sqrt{1+ZT}-1}{\sqrt{1+ZT}+T_C/T_H}\right)$
- Figure of merit: $ZT = \frac{\sigma S^2 T}{\kappa_l + \kappa_e}$

Electronic transport: σ, S, κ_e

Phonon transport: κ_l

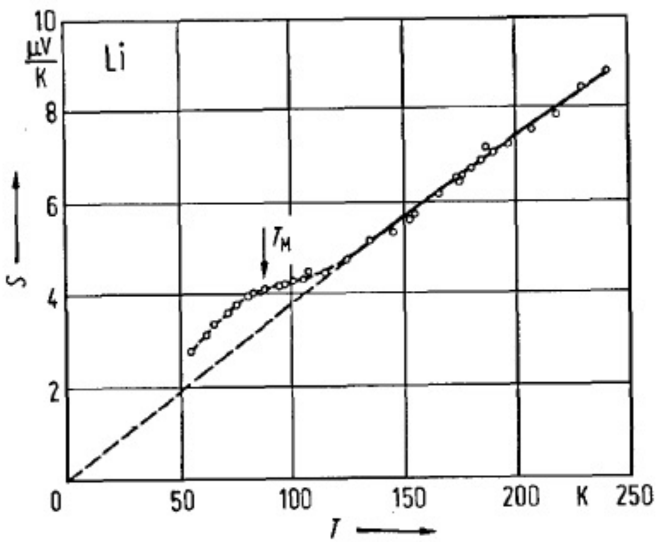
Seebeck effect in a “normal” metal

$$\vec{E} = S\vec{\nabla}T$$

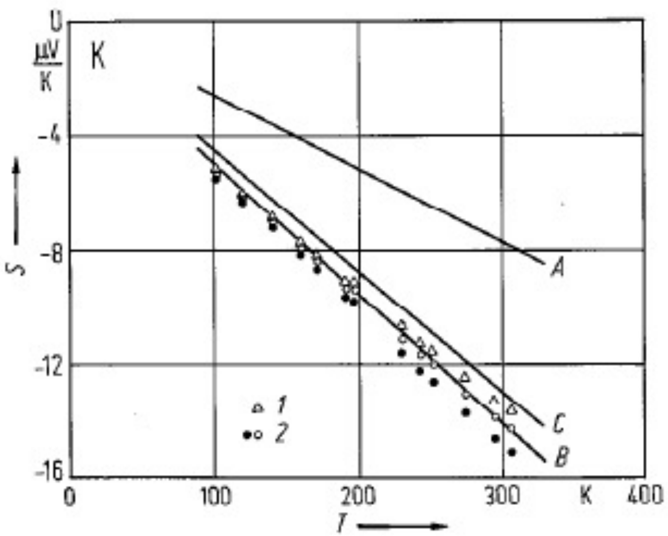


$$S < 0$$

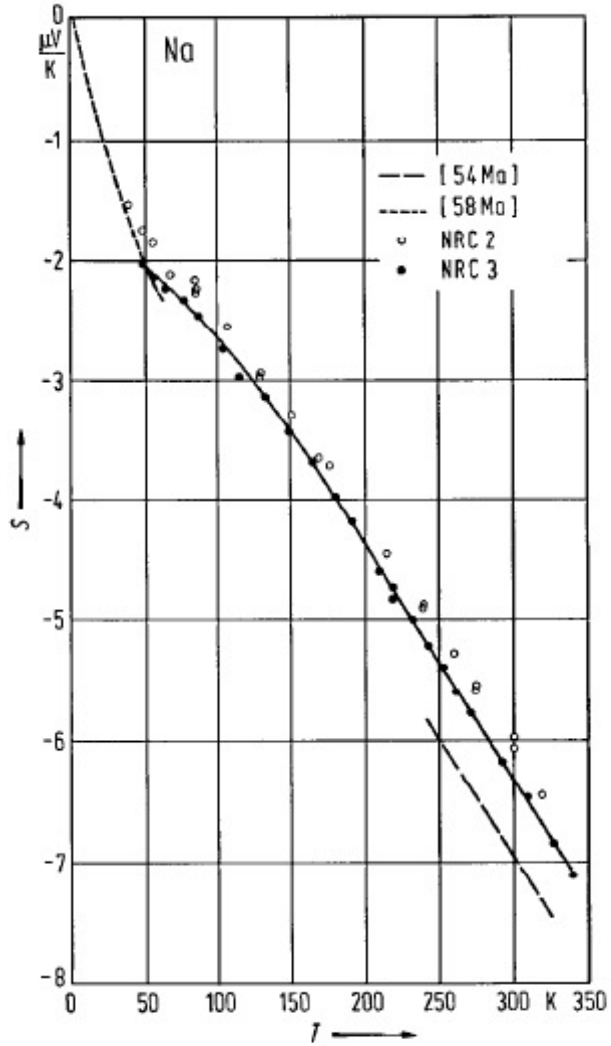
S in alkali metals



S>0



S<0

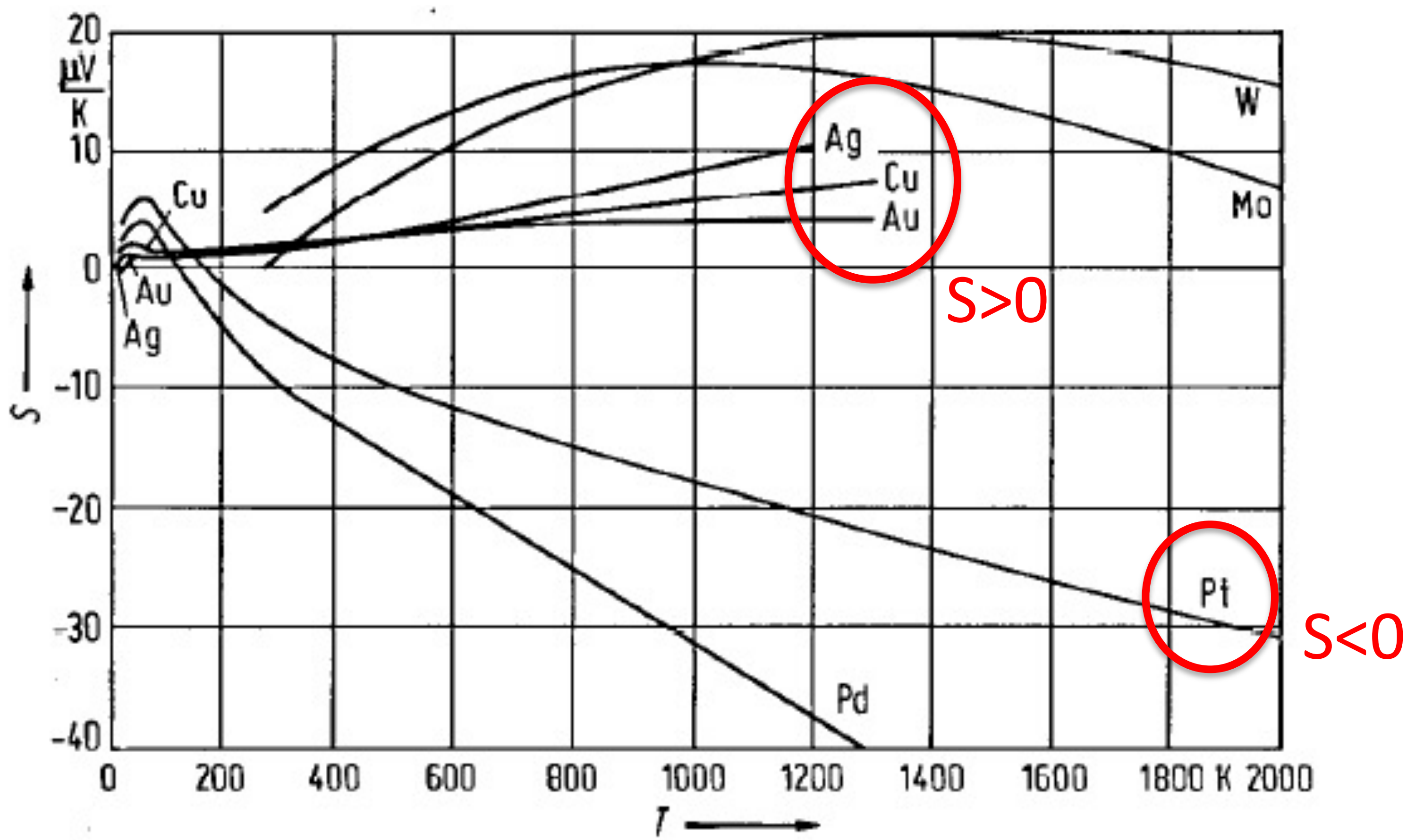


S<0

Nearly-free-electron (NFE) conduction

Foiles, Landolt–Börnstein (1985)

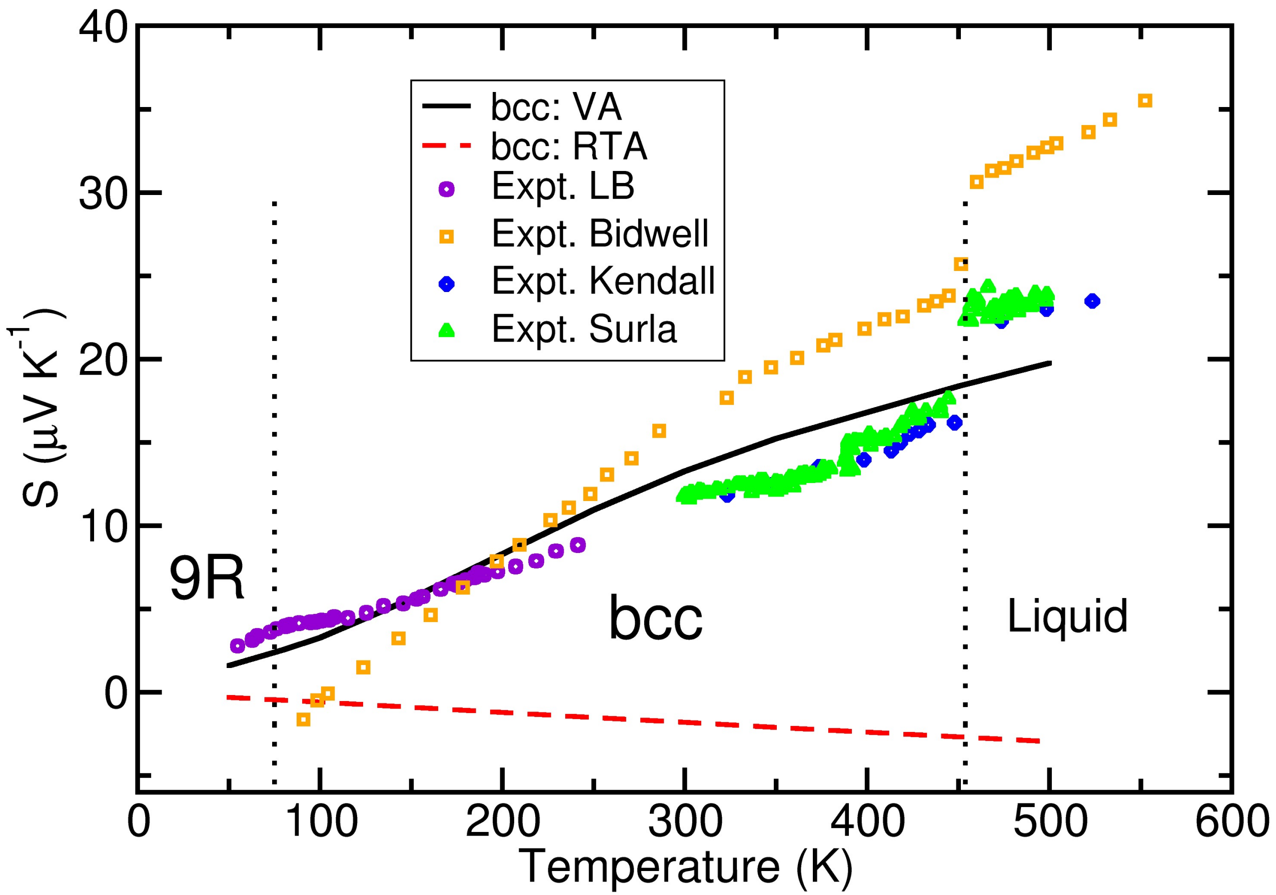
S in noble metals



- Cu/Ag/Au: filled d bands; *s*-electron conduction
- Pt: ϵ_F crosses with *s* and *d* bands; more complex Fermi surface

Foiles, Landolt–Börnstein (1985)

Positive Seebeck in bcc lithium



- CRTA predicts the wrong sign!
- What about other elemental metals?

Xu and Verstraete, PRL 112, 196603 (2014)

Methodologies

- Boltzmann's transport equation (BTE)

$$-\boldsymbol{v}_{\boldsymbol{k}} \cdot \frac{\partial f_{\boldsymbol{k}}}{\partial T} \boldsymbol{\nabla} T - \boldsymbol{v}_{\boldsymbol{k}} \cdot \mathrm{e} \frac{\partial f_{\boldsymbol{k}}}{\partial \epsilon_{\boldsymbol{k}}} \boldsymbol{E} = - \frac{\partial f_{\boldsymbol{k}}}{\partial t}\bigg|_{\mathrm{scatt}}$$

  – The relaxation time approximation (RTA)

$$-\frac{\partial f_{\boldsymbol{k}}}{\partial t}\bigg|_{\mathrm{scatt}} = \frac{f_{\boldsymbol{k}} - f_{\boldsymbol{k}}^{0}}{\tau_{\boldsymbol{k}}}$$

    - First-principles RTA
    - Constant RTA (CRTA)

  – The variational approach (VA)

$$-\frac{\partial f_{\boldsymbol{k}}}{\partial t}\bigg|_{\mathrm{scatt}} = \sum_{\boldsymbol{k}'} Q_{\boldsymbol{k}\boldsymbol{k}'} \phi_{\boldsymbol{k}'} \qquad \left(f_{\boldsymbol{k}} \equiv f_{\boldsymbol{k}}^{0} - \phi_{\boldsymbol{k}} \frac{\partial f_{\boldsymbol{k}}^{0}}{\partial \epsilon_{\boldsymbol{k}}} \right)$$

P. Allen, Phys.Rev.B 17, 3725 (1978)

Constant RTA (CRTA)

- Energy-dependent conductivity tensor

$$\sigma_{\alpha\beta}(\epsilon) = N_s e^2 \sum_{\boldsymbol{k}} \tau_{\boldsymbol{k}} v_\alpha(\boldsymbol{k}) v_\beta(\boldsymbol{k}) \delta(\epsilon - \epsilon_{\boldsymbol{k}})$$

$$\rightarrow N_s e^2 \tau \sum_{\boldsymbol{k}} v_\alpha(\boldsymbol{k}) v_\beta(\boldsymbol{k}) \delta(\epsilon - \epsilon_{\boldsymbol{k}})$$

- Transport coefficients

$$\sigma_{\alpha\beta} = \frac{1}{V_{\text{cell}}} \int \sigma_{\alpha\beta}(\epsilon)\, (-\frac{\partial f}{\partial \epsilon}) d\epsilon$$

$\sigma_{\alpha\beta}/\tau$

$$S_{\alpha\beta} = \frac{1}{eT} \frac{\int \sigma_{\alpha\beta}(\epsilon)(\epsilon - \epsilon_F)(-\frac{\partial f}{\partial \epsilon}) d\epsilon}{\int \sigma_{\alpha\beta}(\epsilon)\, (-\frac{\partial f}{\partial \epsilon}) d\epsilon}$$

τ cancelled out

- Adopted by BoltzTrap and BoltzWann

The variatonal approach (VA)

$$-\frac{\partial f_{\boldsymbol{k}}}{\partial t}\bigg|_{\text{scatt}} = \sum_{\boldsymbol{k}'} Q_{\boldsymbol{k}\boldsymbol{k}'}\phi_{\boldsymbol{k}'}$$

- Ansatz
  - Basis functions: product of Fermi-surface harmonics (FSH) and energy polynomial
  - Only need 0$^{\text{th}}$ (constant) and 1$^{\text{st}}$ order (linear) polynomials
- Scattering operator

P. Allen, Phys.Rev.B 17, 3725 (1978)

$$(Q_{nn'})_{\alpha\beta} = \frac{2\pi V_{\text{cell}} N(\epsilon_F)}{\hbar k_B T}\int d\epsilon d\epsilon' d\omega \sum_{s,s'=\pm 1} f(\epsilon)[1-f(\epsilon')]$$

$$\times\{[n(\omega)+1]\delta(\epsilon-\epsilon'-\hbar\omega)+n(\omega)\delta(\epsilon-\epsilon'+\hbar\omega)\}$$

$$\times\alpha^2_{\text{Allen}}F(s,s',\alpha,\beta,\epsilon,\epsilon',\omega)\times J(s,s',n,n',\epsilon,\epsilon')$$

$$\alpha^2_{\text{Allen}}F(s,s',\alpha,\beta,\epsilon,\epsilon',\omega) = \frac{1}{2N(\epsilon_F)}\sum_{\boldsymbol{k}\boldsymbol{k}'}\left|g^{q\nu}_{\boldsymbol{k}\boldsymbol{k}'}\right|^2\delta(\epsilon_{\boldsymbol{k}}-\epsilon)\delta(\epsilon_{\boldsymbol{k}'}-\epsilon')\,\delta(\omega_{\boldsymbol{q}}-\omega)$$

$$\times[F_\alpha(\boldsymbol{k})-sF_\alpha(\boldsymbol{k}')][F_\beta(\boldsymbol{k})-s'F_\beta(\boldsymbol{k}')]$$

Transport coefficients from VA

$$\rho_{\alpha\beta} = \frac{1}{2e^2 (Q_{00}^{-1})_{\alpha\beta}} \approx \frac{1}{2e^2} (Q_{00})_{\alpha\beta}$$

$$S_{\alpha\beta} = -\frac{\pi k_B}{\sqrt{3}e} \frac{(Q_{01}^{-1})_{\alpha\beta}}{(Q_{00}^{-1})_{\alpha\beta}} \approx \frac{\pi k_B}{\sqrt{3}e} \sum_{\gamma} (Q_{01})_{\alpha\gamma} (Q_{11}^{-1})_{\gamma\beta}$$

- *Ab-initio* electron-phonon coupling (EPC) matrix
- With both intra- and inter-band transitions
- Fermi smearing

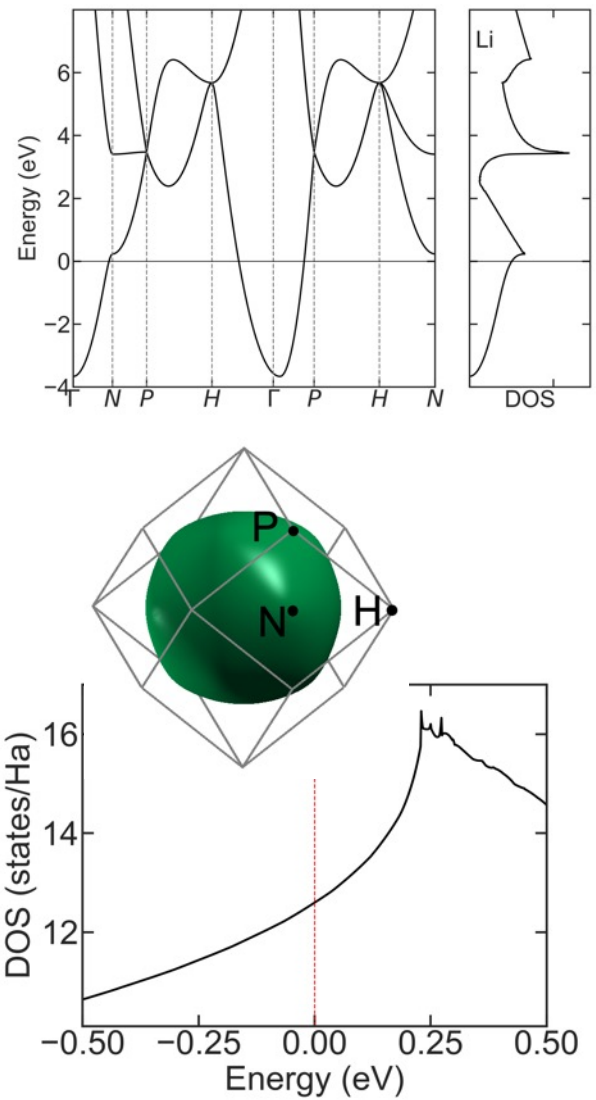
$$\boldsymbol{k}' - \boldsymbol{k} = \boldsymbol{q} + \boldsymbol{g}$$

Computational details

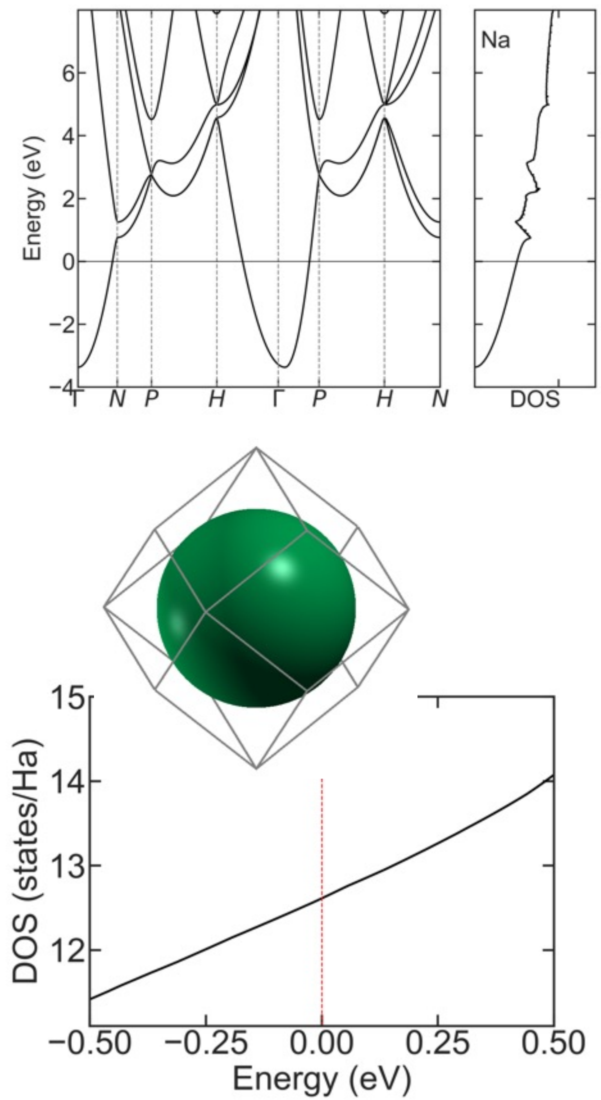
- Alkali metals: Li, Na, K (bcc)
- Noble metals: Cu, Ag, Au, Pt (fcc)
- CRTA: ABINIT + BoltzTrap
- VA: ABINIT
  - EPC (DFPT):
    - 24×24×24 *k*-grid (Unshifted)
    - 12×12×12 *q*-grid
  - ANADDB: `ifltransport 2`

Band structures (alkali metals)

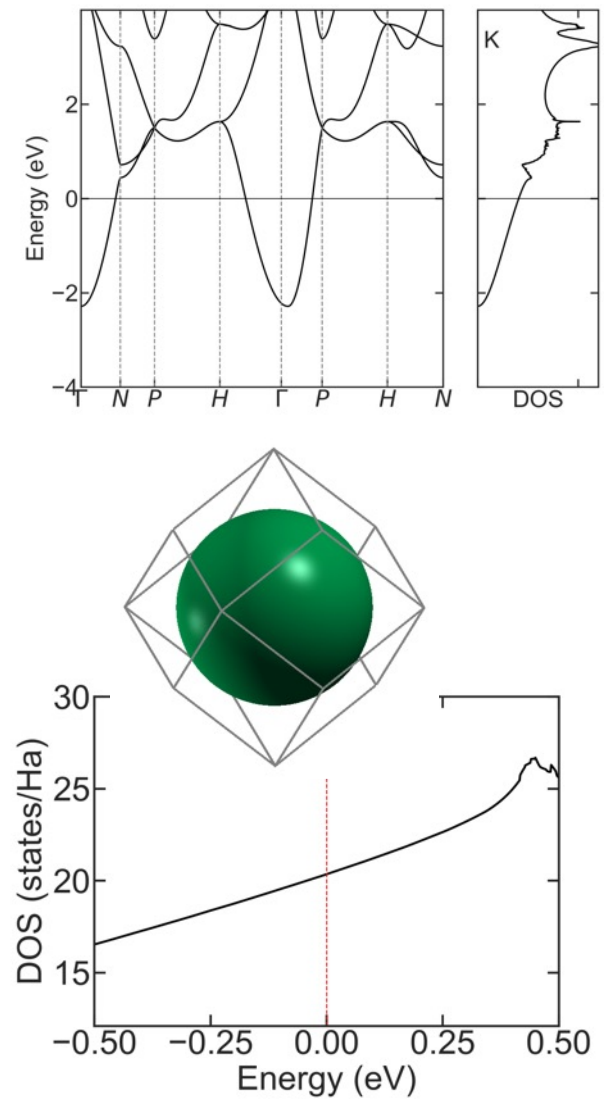
Li



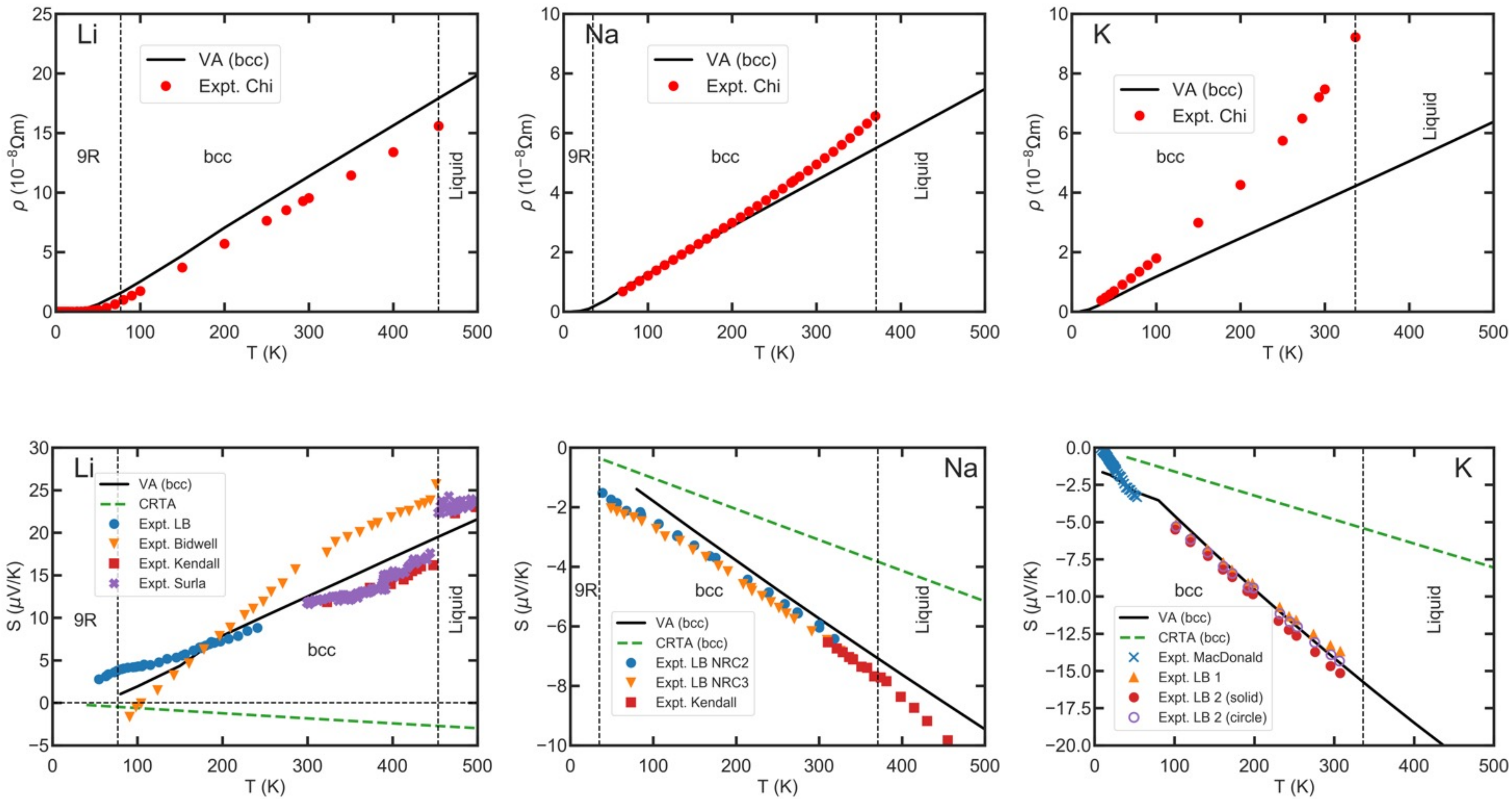
Na



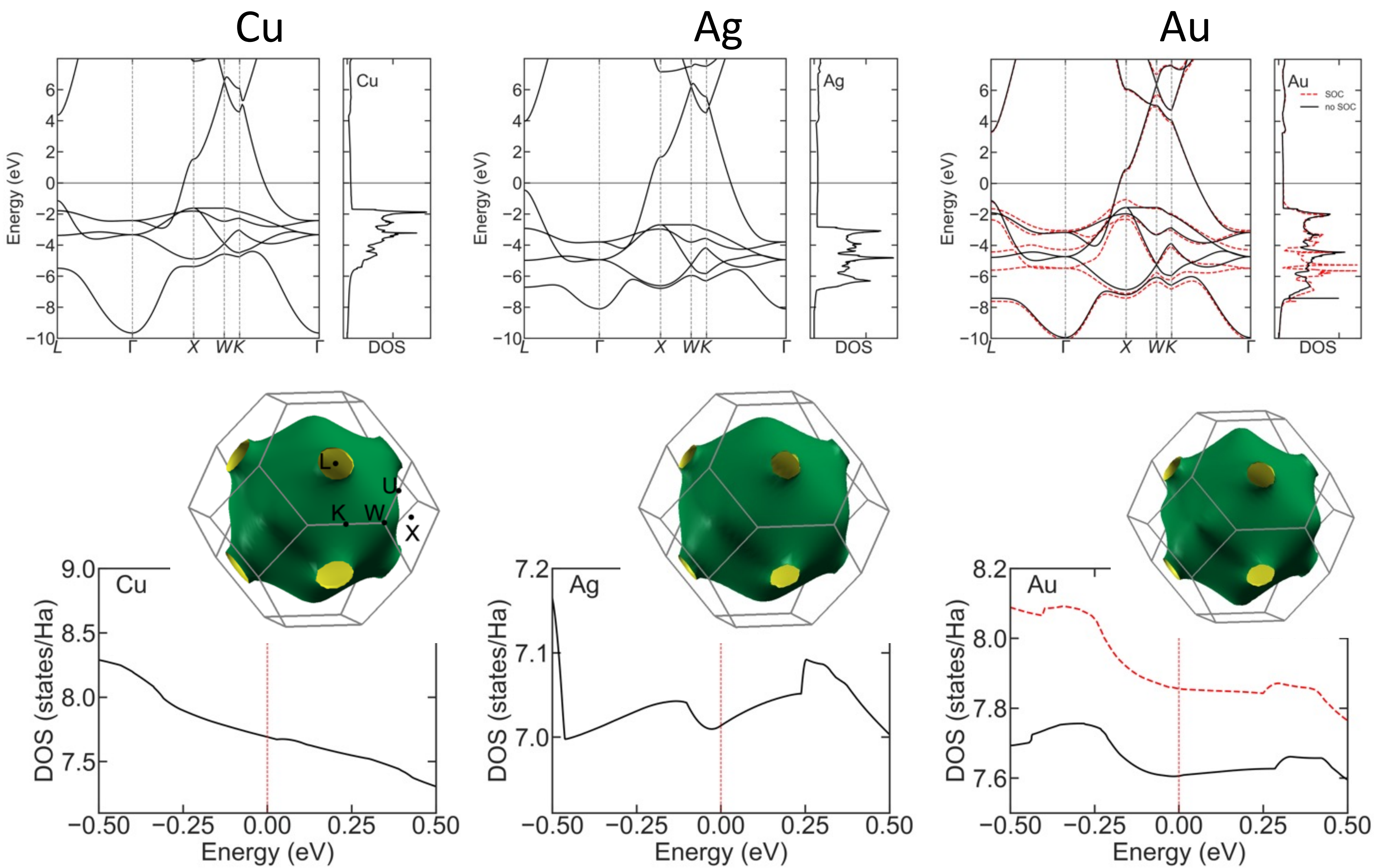
K



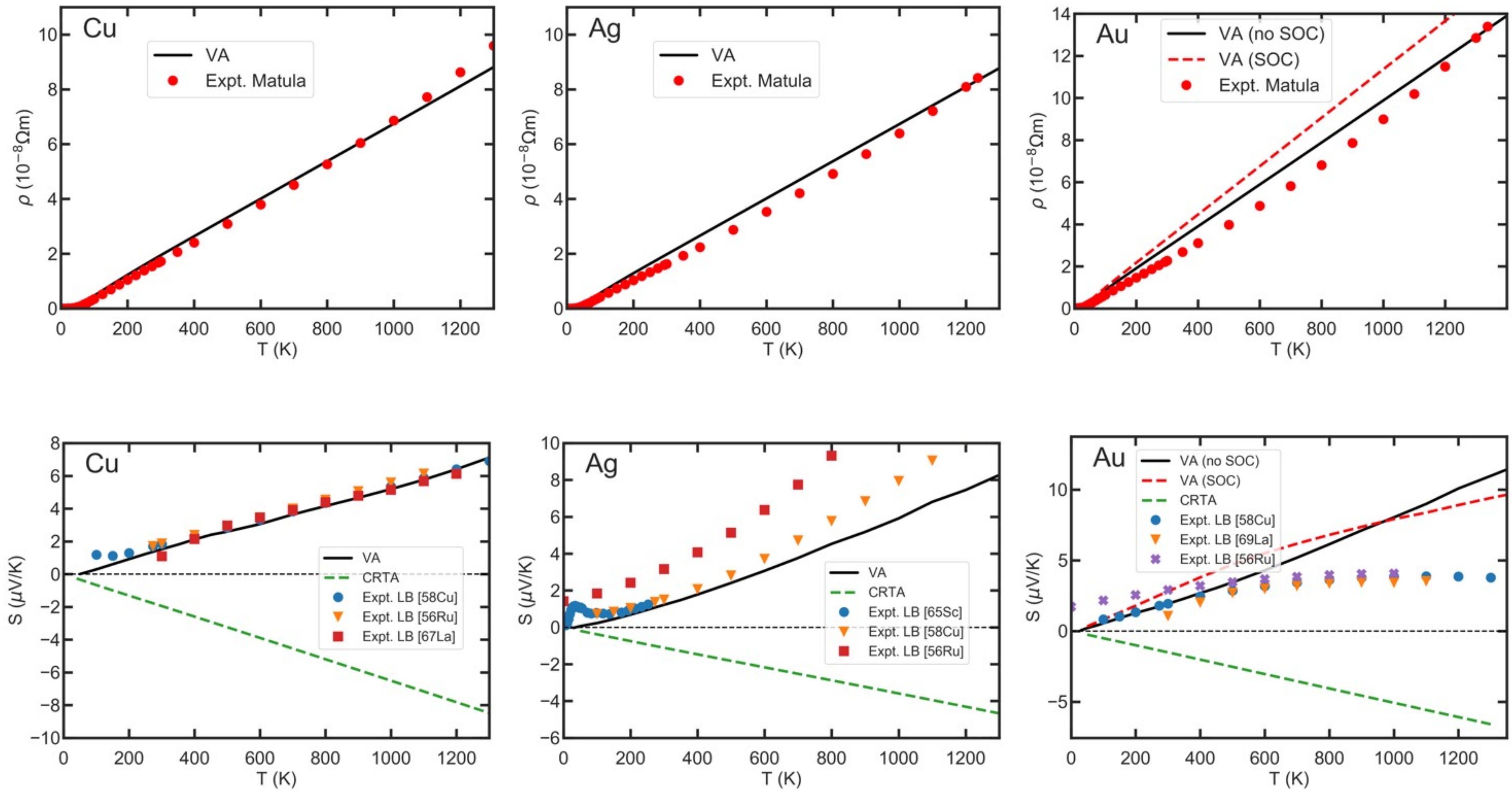
Electrical resistivity and Seebeck (alkali metals)



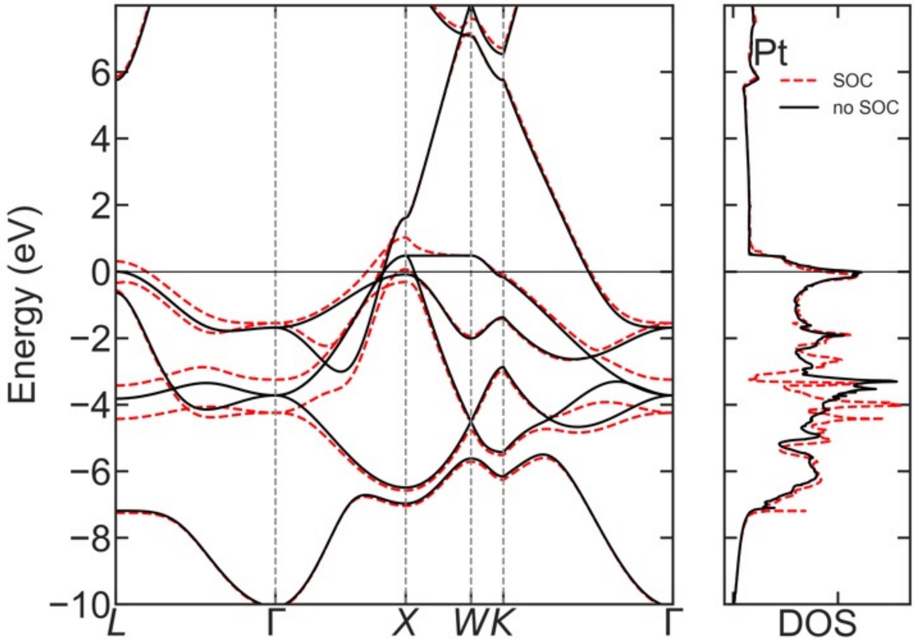
Band structures (noble metals)

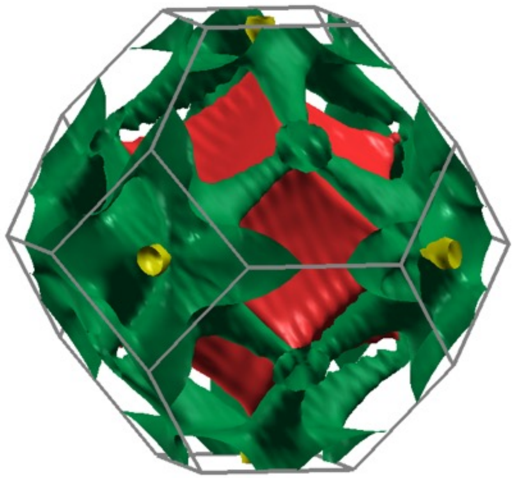


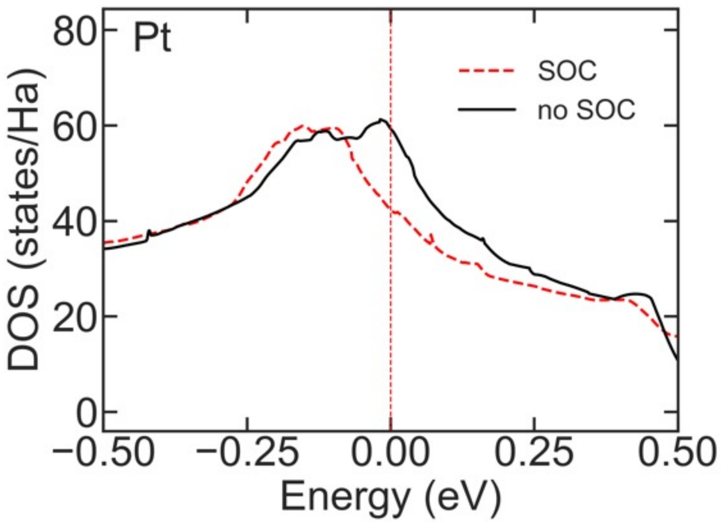
Electrical resistivity and Seebeck (noble metals)



Band structure (Pt)



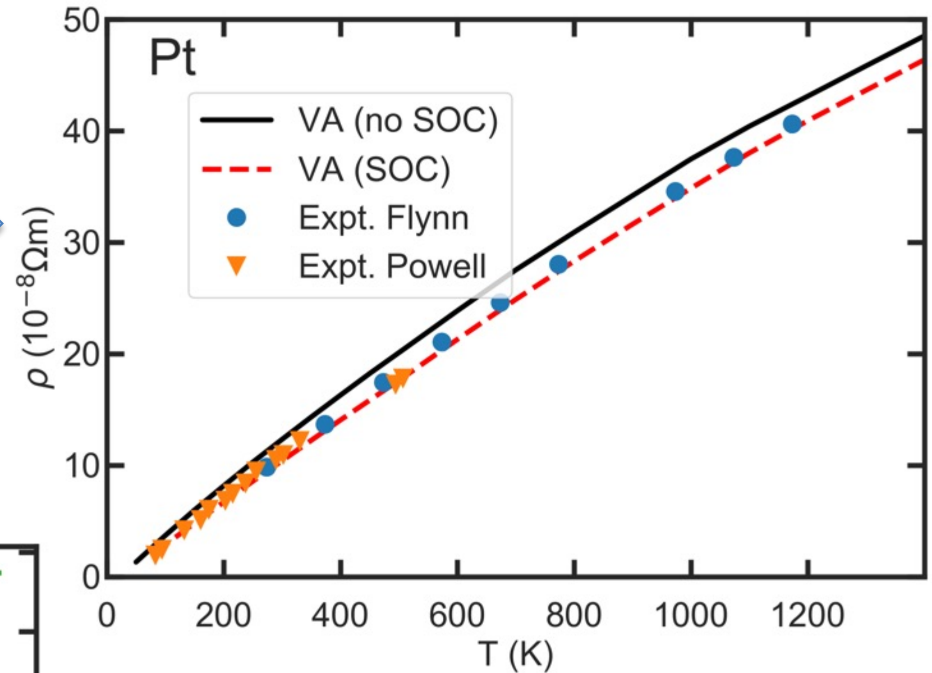


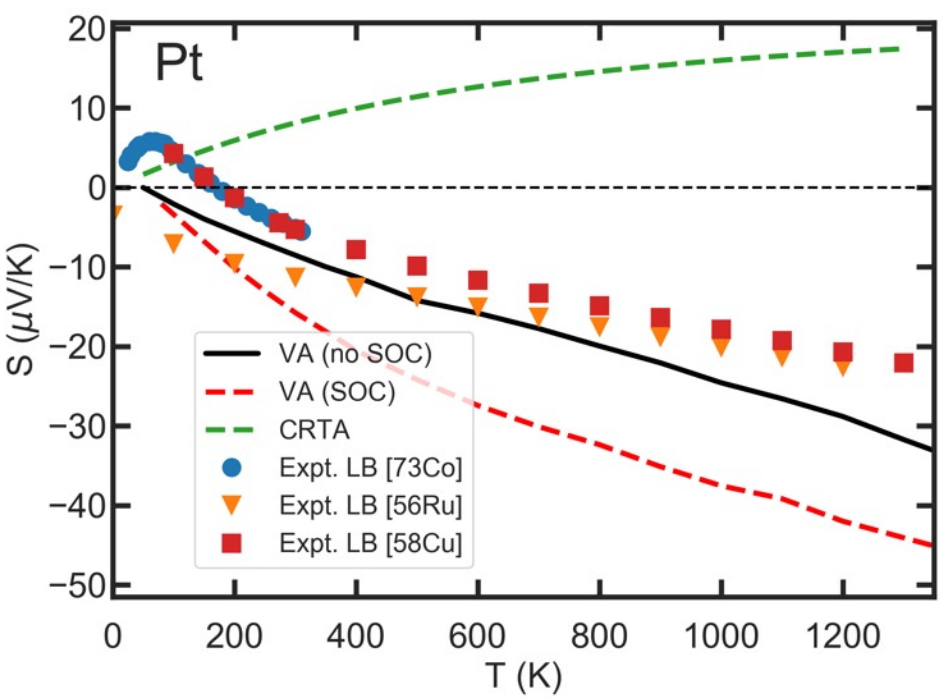


- Fermi energy crossing both the *d* and *s* bands
- DOS at ϵ_{F} close to a maximum
- Complex Fermi surface
  - Non-spherical (*s*-electron)
  - Hole-like (*d*-electron)

Electrical resistivity and Seebeck (Pt)

Good agreement for Pt with complex Fermi surface





- VA predicts negative S (no phonon drag)
- CRTA predicts wrong sign
- SOC effect
  - Slightly improves ρ
  - Overestimates |S|

Conclusions

- Variational approach
  - Resistivity and Seebeck coefficients
  - Quantitative agreement for alkali metals and noble metals
  - A few exceptions: underestimation of ρ for Na and K
- Constant RTA
  - Seebeck coefficients
  - Wrong sign of S for Li, Cu, Ag, Au (S>0), and Pt (S<0)
  - Significant underestimation of $|S|$ for Na and K
- Outlook: Fe (FM with possible spin flips)

Thank you!

Xu, Di Gennaro and Verstraete, PRB 102, 155128 (2020)