Introduction to the Theory of Lattice Vibrations and their Ab Initio Calculation

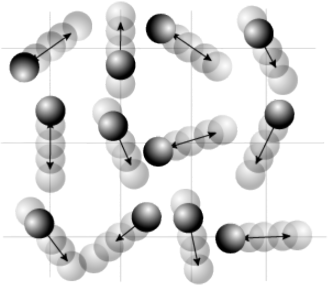
Lecture 10: CDW and Ferroelectric Transitions

Ion Errea

Dept. Applied Physics, University of the Basque Country (UPV/EHU),
San Sebastian, Spain

Centro de Fśica de Materiales (CSIC-UPV/EHU), San Sebastian, Spain

Donostia International Physics Center,
San Sebastian, Spain



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Universidad del País Vasco Euskal Herriko Unibertsitatea

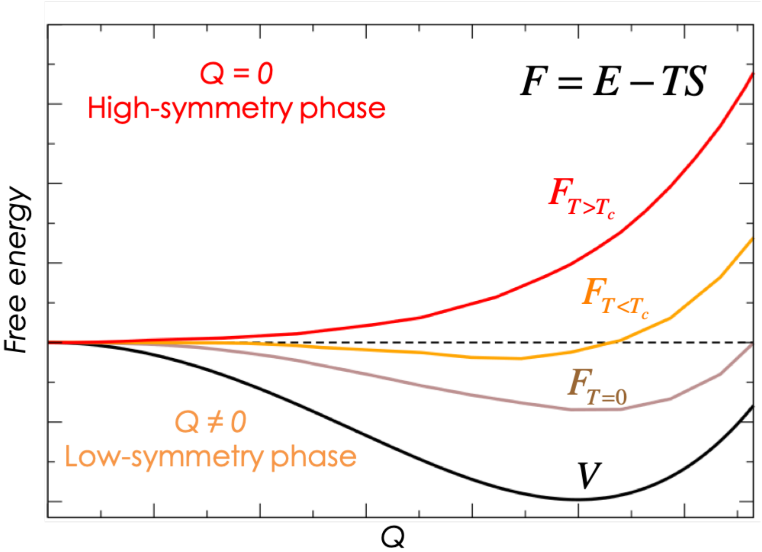
Materials Physics Center
Centro de Física de Materiales

Donostia International Physics Center

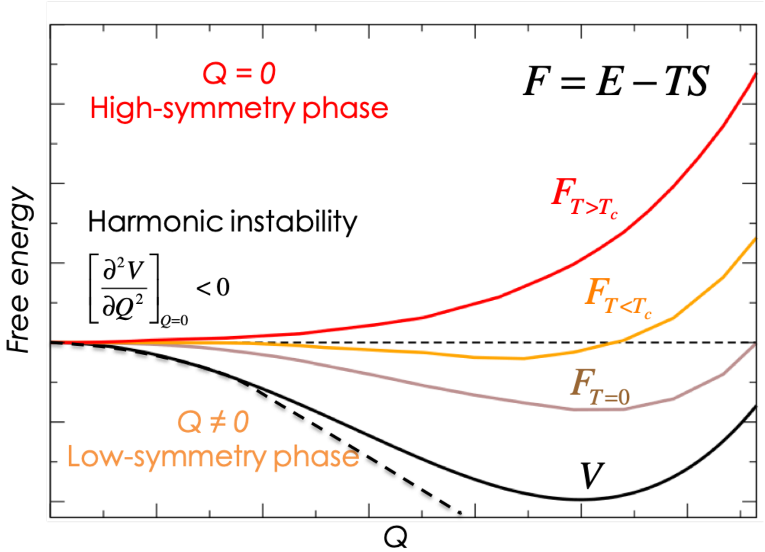
Outline

1. Displacive second-order phase transitions
2. CDW transitions in transition metal dichalcogenides
3. Structural transitions in ferroelectric and thermoelectric materials
4. Conclusions

Second-order displacive phase transitions

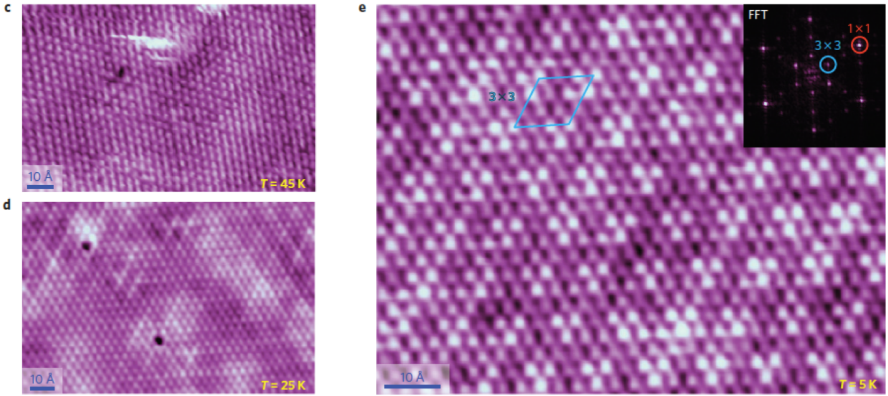


Second-order displacive phase transitions

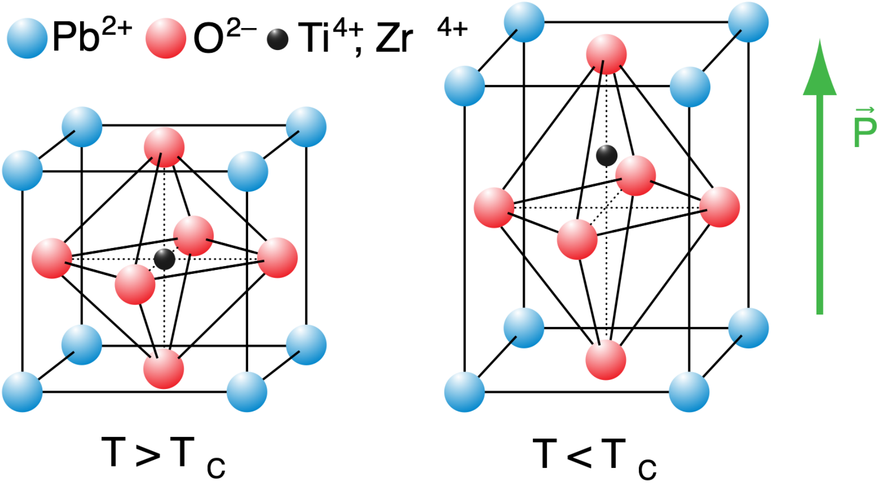


CDW transitions in metals

The electronic charge modulates as the lattice distorts



A polarization is created when the lattice distors



The free energy curvature allows to calculate these transition in the SSCHA

$$\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} = \Phi_{ab} + \sum_{cdefgh} \overset{(3)}{\Phi}_{acd} \Lambda_{cdef}[0][\mathbf{1} + \overset{(4)}{\boldsymbol{\Phi}} \boldsymbol{\Lambda}[0]]^{-1}_{efgh} \overset{(3)}{\Phi}_{ghb}$$

where

- $\boldsymbol{\Phi}$ are the SCHA auxiliary force-constants
- The non-perturbative force constants are

$$\overset{(3)}{\Phi}_{abc} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

$$\overset{(4)}{\Phi}_{abcd} = \left\langle \frac{\partial^4 V(\mathbf{R})}{\partial R_a \partial R_b \partial R_c \partial R_d} \right\rangle_{\tilde{\rho}_{\boldsymbol{\mathcal{R}},\boldsymbol{\Phi}}}$$

- The $\boldsymbol{\Lambda}$ tensor is

$$\Lambda[0]^{abcd} = \sum_{\mu\nu} \frac{\hbar}{4 \mathtt{w}_\nu \mathtt{w}_\mu} e^a_\nu e^b_\mu e^c_\nu e^d_\mu \begin{cases} \frac{dn_B(\mathtt{w}_\mu)}{d\mathtt{w}_\mu} - \frac{2n_B(\mathtt{w}_\mu)+1}{2\mathtt{w}_\mu} & , \mathtt{w}_\nu = \mathtt{w}_\mu \\ \frac{n_B(\mathtt{w}_\mu)-n_B(\mathtt{w}_\nu)}{\mathtt{w}_\mu - \mathtt{w}_\nu} - \frac{1+n_B(\mathtt{w}_\mu)+n_B(\mathtt{w}_\nu)}{\mathtt{w}_\mu + \mathtt{w}_\nu} & , \mathtt{w}_\nu \neq \mathtt{w}_\mu \end{cases}$$

The free energy phonons are needed to describe displacive phase transitions

Different dynamical matrices:

- Harmonic dynamical matrix:

$$D_{ab}^{har} = \frac{1}{\sqrt{M_a M_b}} \left[\frac{\partial^2 V(\mathbf{R})}{\partial R_a \partial R_b} \right]_{\mathbf{R}=\mathbf{R}_0} = \frac{1}{\sqrt{M_a M_b}} \phi_{ab}$$

- SCHA dynamical matrix calculated at $\boldsymbol{\mathcal{R}}_0$:

$$D_{ab}^{S} = \frac{1}{\sqrt{M_a M_b}} \Phi_{ab}$$

- Dynamical matrix based on SCHA free energy curvature:

$$D_{ab}^{F} = \frac{1}{\sqrt{M_a M_b}} \left[\frac{\partial^2 \mathcal{F}(\boldsymbol{\mathcal{R}})}{\partial \mathcal{R}_a \partial \mathcal{R}_b} \right]_{\boldsymbol{\mathcal{R}}=\boldsymbol{\mathcal{R}}_0}$$

Plotting the phonons as a function of temperature coming from D^F displacive phase transitions can be predicted

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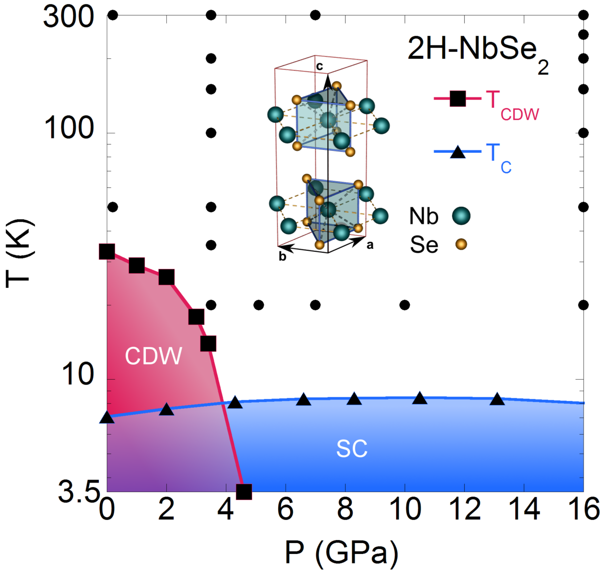
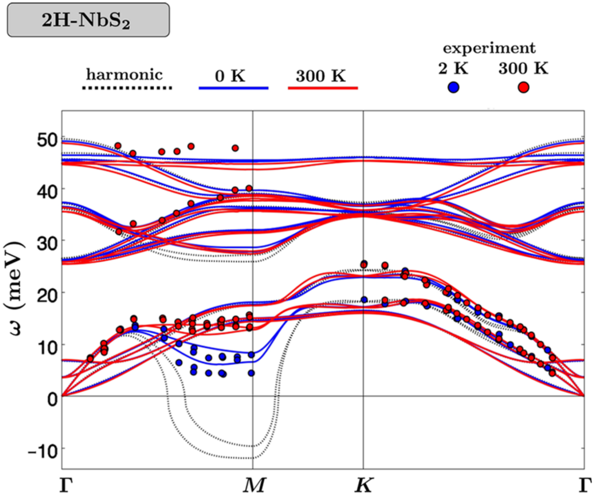
CDWs in transition metal dichalcogenides

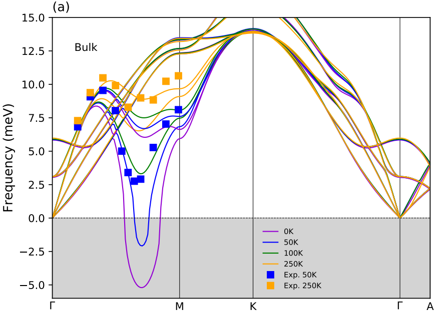


Absence of CDW transition in NbS_2



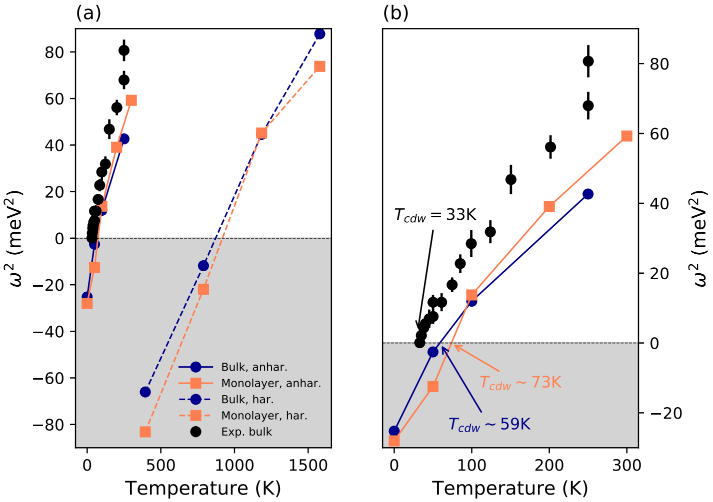
Bianco *et al.*, Nano Lett. (2019)

CDW temperature in bulk and monolayer $NbSe_2$



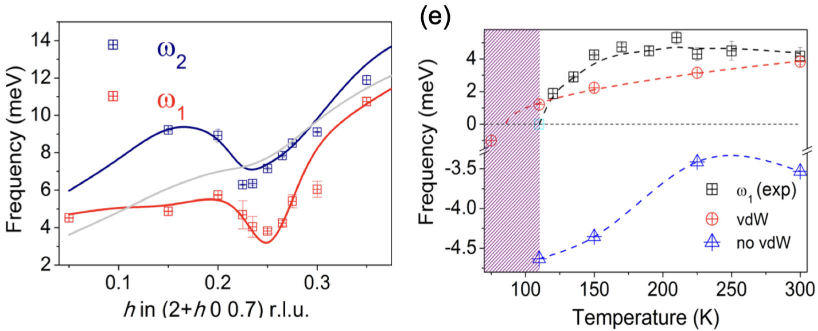
Bianco *et al.*, PRL (2020)

CDW temperature in bulk and monolayer $NbSe_2$



Bianco *et al.*, PRL (2020)

CDW temperature in bulk VSe_2



Diego *et al.*, Nat. Commun. (2021)

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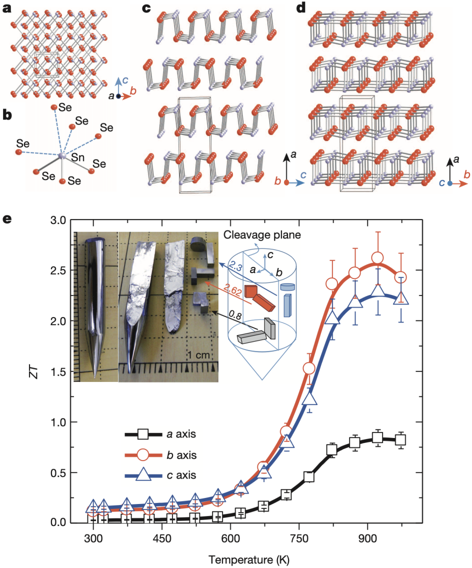
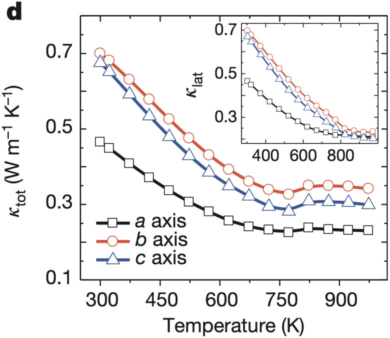
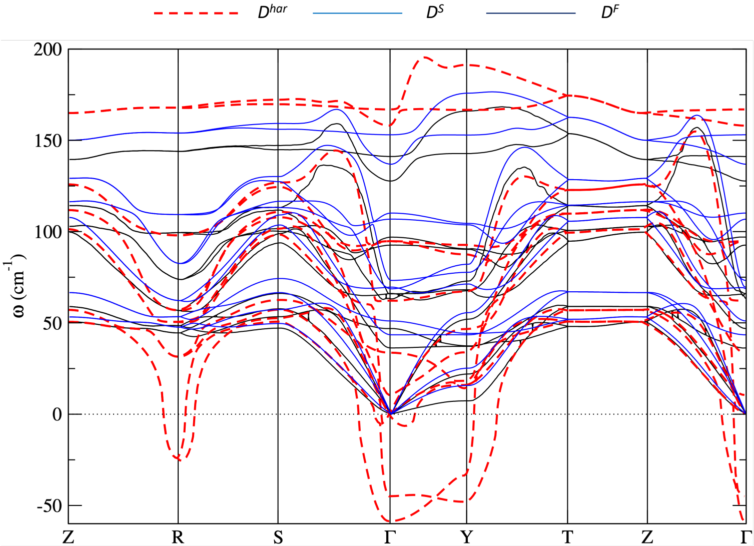
Record thermoelectric figure of merit in SnSe





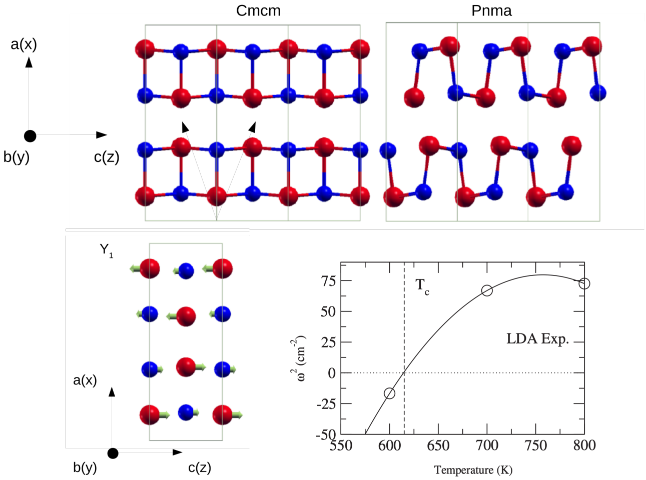
Zhao *et al.*, Nature (2014)

Phonon spectra in SnSe at 800 K



Aseginolaza *et al.*, PRL (2019)

Displacive second order phase transition in SnSe



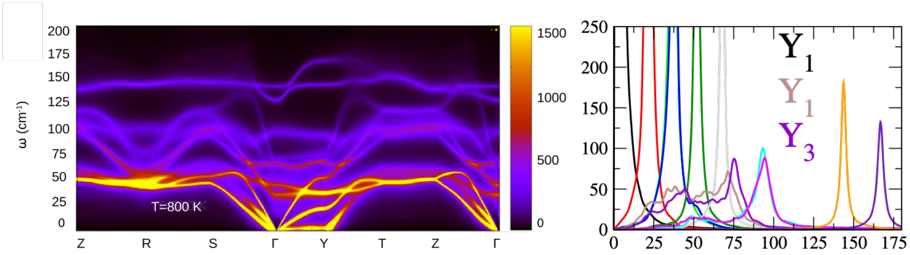
Aseginolaza *et al.*, PRL (2019)

Physical phonons in SnSe

$$\sigma(\boldsymbol{q},\omega) = \frac{1}{2\pi}\sum_{\mu}\left[\frac{-\mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)]}{(\omega - \mathrm{Re}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)])^2 + \mathrm{Im}[\mathcal{Z}_\mu(\boldsymbol{q},\omega)]^2}\right]$$

where

$$\mathcal{Z}_\mu(\boldsymbol{q},\omega) = \sqrt{\mathtt{w}_\mu^2(\boldsymbol{q}) + \Pi_\mu(\boldsymbol{q},\omega + i\eta)}$$



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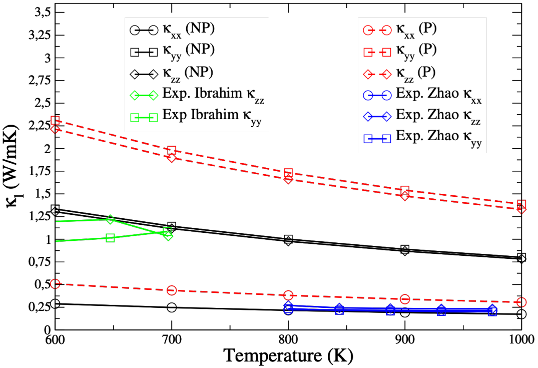
Lattice thermal conductivity with non-perturbative 3rd order force constants



Non-perturbative 3rd order force constants

$$\overset{(3)}{\Phi}_{abc} = \left\langle \frac{\partial^3 V(\mathbf{R})}{\partial R^a \partial R^b \partial R^c} \right\rangle_{\rho_{\mathcal{H}}}$$

Perturbative 3rd order force constants

$$\overset{(3)}{\phi}_{abc} = \left[\frac{\partial^3 V(\mathbf{R})}{\partial R^a \partial R^b \partial R^c} \right]_{\mathbf{R}_0}$$

Aseginolaza *et al.*, PRL (2019)

Conclusions

1. The SSCHA allows to determine the temperature at which 2nd order displacive phase transition occur, such as CDW in metals and ferroelectric transitions
2. Thermal conductivity can be calculated in systems with unstable harmonic phonons, including high-order anharmonic effects in the lifetimes