# Electron-phonon interaction under extreme pressures

## Effects on materials properties from first-principles calculations

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DocDay 2022
Mon., February 28

TU Graz

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itp cp

# Outline

## First-principles calculations / DFT

- "Schrödinger equation and the periodic table"
- computationally efficient implementation: density functional theory
- limitations in *ee* correlations
- no phonons in basic DFT, as Born-Oppenheimer is assumed

## Lattice dynamics

- give rise to topical phenomena like superconductivity (SC) and charge-density wave (CDW) formation
- affect the thermodynamic stability of a material or a certain phase

## Extreme pressure

- directly affects the lattice
- enthalpic term becomes more important
- high pressure phases largely unexplored

# Theory and methods

# Density functional perturbation theory (DFPT)

Basic idea: Taylor expansion around the equilibrium structure in terms of small atomic displacements

$$E_{\mathrm{tot}}(\Delta\tau) \approx E_{\mathrm{tot}}^{(0)} + 0 + \frac{1}{2}\sum\sum \frac{\partial E_{\mathrm{tot}}}{\partial\tau\partial\tau'}\Delta\tau\Delta\tau'$$

Harmonic approximation: Truncating the series after the second order
DFPT offers an efficient way to obtain these derivatives (= force constants) from first principles.

$$\frac{\partial E_{\mathrm{tot}}}{\partial\tau\partial\tau'} = \int \mathrm{d}\mathbf{r}\frac{\partial n(\mathbf{r})}{\partial\tau}\frac{\partial v_{\mathrm{ext}}(\mathbf{r})}{\partial\tau'} + \int \mathrm{d}\mathbf{r} n(\mathbf{r})\frac{\partial^2 v_{\mathrm{ext}}(\mathbf{r})}{\partial\tau\partial\tau'}$$

# Density functional perturbation theory (DFPT)

The Fourier transform relates the force constants to phonon frequencies by

$$D_{\tau\tau'}(\mathbf{q})e_{\tau m\mathbf{q}} = \omega^2_{m\mathbf{q}}e_{\tau m\mathbf{q}} \qquad \text{with } D_{\tau\tau'}(\mathbf{q}) \propto \mathcal{F}\left[\frac{\partial E_{\text{tot}}}{\partial\tau\partial\tau'}\right]$$

Electron-phonon coupling coefficients from interactions of the order $g \cdot c^{\dagger}_{\mathbf{k}+\mathbf{q}}c_{\mathbf{k}}\left(b_{\mathbf{q}} + b^{\dagger}_{-\mathbf{q}}\right)$ can easily be obtained by the knowledge of $\partial n(\mathbf{r})/\partial\tau$.

Important derived quantities:
Eliashberg or *ep* spectral function $\alpha^2F(\omega) \propto \sum \int g_{\mathbf{q}\nu\mathbf{k}}\delta(\epsilon_{\mathbf{q}i} - \epsilon_{\text{F}})\delta(\epsilon_{\mathbf{k}+\mathbf{q}j} - \epsilon_{\text{F}})$
*ep* coupling strength $\lambda = 2\int \text{d}\omega\alpha^2F(\omega)/\omega$

# Thermodynamics

Setting: crystalline solids in the ground state with applied external pressure: isothermal-isobaric ensemble with $T = 0\,\mathrm{K} \rightarrow$ isoenthalpic-isobaric ensemble minimizing the enthalpy $H = U + pV$.
Different compositions: thermodynamically stable phases $\pi_{x,y}$ are determined via their enthalpy of formation

$$\Delta H(\pi_{x,y}) = H(\pi_{x,y}) - \frac{xH(\pi_{1,0}) + yH(\pi_{0,1})}{x+y}$$

with respect to the pure elemental phases $\pi_{1,0}$ and $\pi_{0,1}$, where

$$H(\pi_{x,y}) = \frac{E_{\mathrm{tot}}(\pi_{x,y})}{N} + p\frac{V(\pi_{x,y})}{N}.$$

The sets of phases that are additionally stable against decomposition into neighbouring phases form so-called *convex hulls*.

# Strategy and computational methods

**Evolutionary structure search**[1,2]

- generate possible candidates
- thermodynamic stability via fast DFT calculations

**High accuracy DFT**[3]

- verify phase diagram
- equilibrium crystal structures
- electronic properties

**Advanced DFT-based methods**

- DFPT[3], ME theory[4], multidim. fully anharmonic phonon analysis
- phononic properties, *ep* coupling, SC

[1] USPEX, A. R. Oganov and C. W. Glass, J. Chem. Phys. 124, 244704 (2006)

[2] A. O. Lyakhov et al., Comput. Phys. Commun. 184, 1172 (2013)

[3] QE, P. Giannozzi et al., J. Phys. Condens. Matter 21, 395502 (2009)

[4] EPW, S. Poncé et al., Comput. Phys. Commun. 209, 116 (2016)

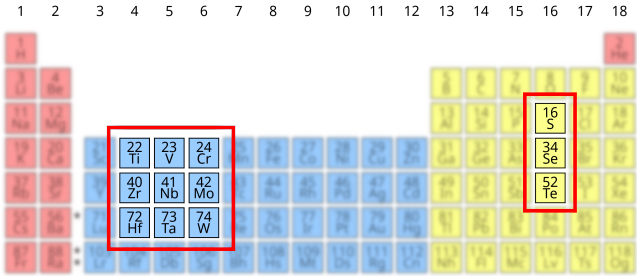
# Transition metal chalcogenides (TMC)[1]

[1] The following results were published in
R. Lucrezi and C. Heil, J. Phys.: Condens. Matter, (2021), "Superconductivity and strong anharmonicity in novel Nb-S phases"
or taken from ongoing unpublished research.

# Motivation for TMCs

**TMC**

Compounds consisting of a transition metal and a chalcogen ($TM_xC_y$, C = S, Se, Te)



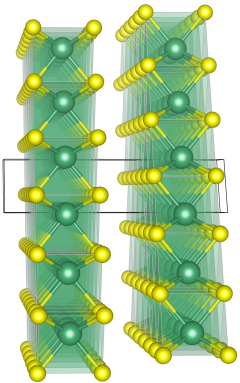

## A diverse material class

- group-4/6 TMCs: semiconducting phases used in photovoltaics and electronics, indirect-to-direct band gap transition
- group-5 TMCs: metallic phases exhibiting SC and CDW order

# Motivation for TMCs

## Known phases

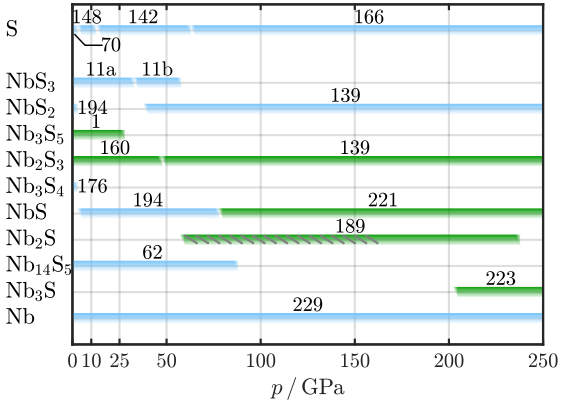
- many layered structures
- mainly TMDs in group 4 and 5
- 1D and 2D materials (beyond graphene)
- changing properties with intercalation, stacking order, doping (cathodes, solid lubricants, electrocatalysts)
- geometric constraint promoting *ep* processes like SC and CDW ($NbS_2$, $NbSe_2$, $NbSe_3$)
- pressure significantly affects layers
- complete phase diagrams largely unexplored for high pressures



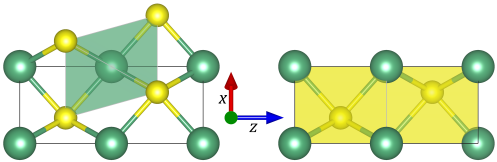
# Phase diagram of the Nb-S system

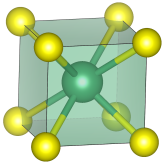
## Insights

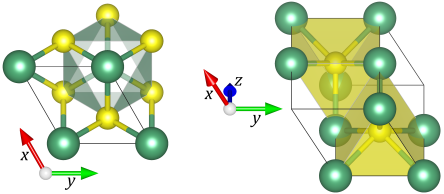
- many different phases and stoichiometries
- stable pressures for known phases (shown in sky blue)
- new material discoveries (in green)
- metallic binary phases with low *ep* coupling
- distinct geometric building blocks



# Characteristic crystal structures






## Main geometric building blocks

- octahedra
- trigonal prisms

} low $p$

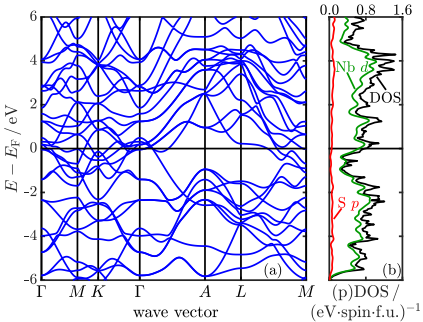
- CsCl-like cubes

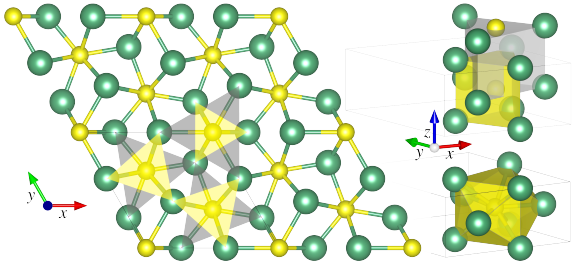
high $p$

# An interesting new material: $Nb_2S$

## Electronic properties

- strong 3D character
- high Nb *d* contribution around $E_F$

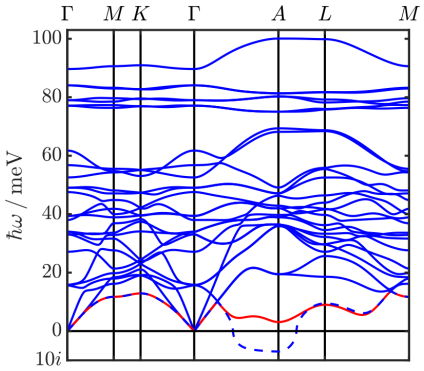


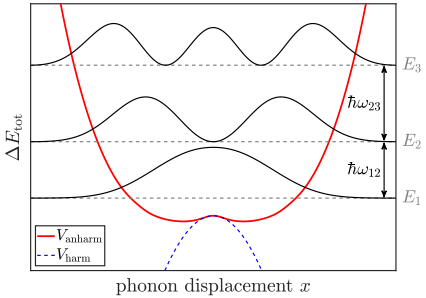



# Phonons and *ep* coupling in $Nb_2S$

## Harmonic DFPT

indicates lattice instability (dashed mode)




## Fully anharmonic analysis

- dynamic stability from 175 to 250 GPa
- strong *ep* coupling ($\lambda \approx 2.5$)
- SC up to 25 K (aniso. ME)

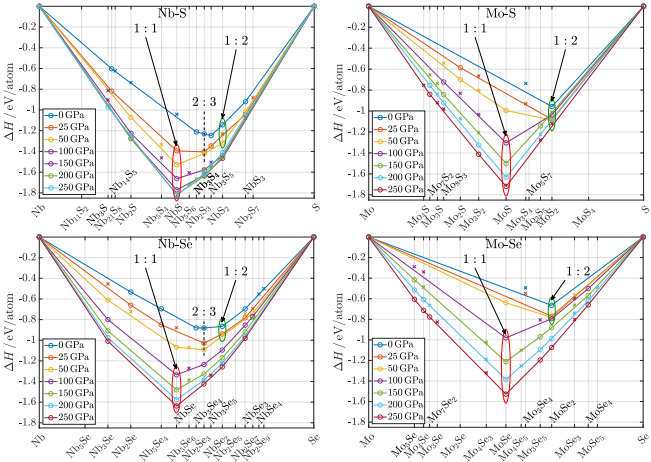
# Ongoing work in the systems Mo-S, Mo-Se, Nb-S, Nb-Se

## Convex hull

Convex hulls of enthalpy of formation show stable (circles) and metastable (crosses) phases

## Insights

- LP focus on 1:2, prismatic/octahedral bonding
- HP focus on 1:1, cubic bonding
- TM governs the overall trend



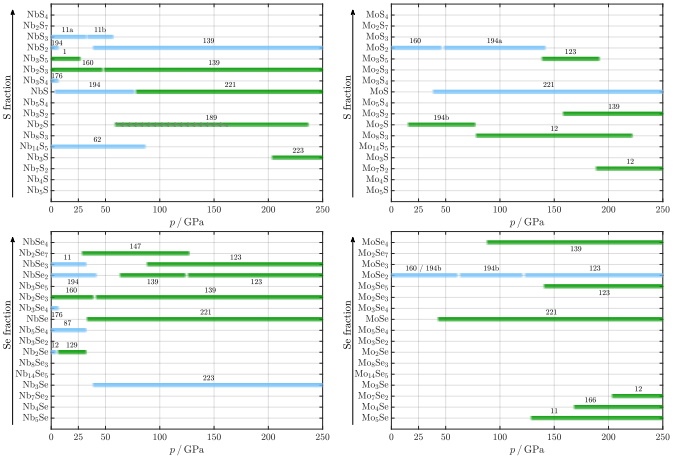
# Ongoing work in the systems Mo-S, Mo-Se, Nb-S, Nb-Se

## Phase diagram

$p - x$ phase diagrams show all thermodynamically stable phases indicating the symmetry

## Insights

- known phases in sky blue
- new discoveries in green
- HP Nb: simple cubic stacking
- HP Mo: complex stacking



# Ternary hydride systems[1]

[1] The following results were taken from the work
R. Lucrezi, S. Di Cataldo, et al., subm. to Npj Comput. Mater. (2022), "In-silico synthesis of novel lowest-pressure high-$T_c$ ternary superhydrides" preprint available at arXiv: 2112.02131 [cond-mat.supr-con], (2021).

# The hydride rush

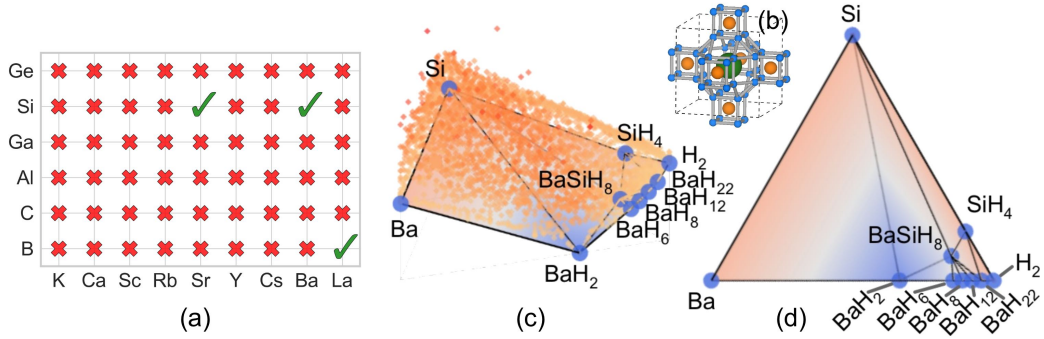
**Superhydrides**

Materials incorporating a huge amount of hydrogen in their crystal structure


## Background

- Conventional high-$T_c$ SC like $H_3S$ and $LaH_{10}$ started a hydride rush
- $T_c > 200\,K$ but pressure $> 150\,GPa$
- (thermo)dynamically unstable at lower pressures due to light H atoms
- binary hydrides mostly explored

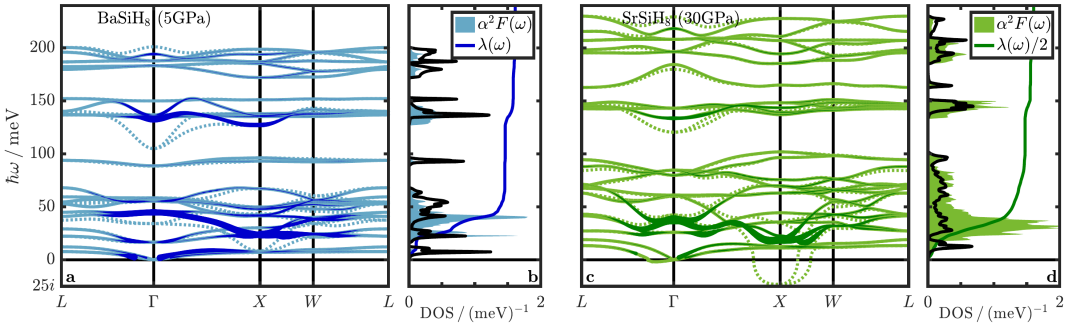
# The $XYH_8$ template: inspired by $LaBH_8$




## Strategy

- browse the periodic table in the neighbourhood of La and B
- determine dynamically stable phases, calculate thermodynamic and SC behaviour

# Phonons



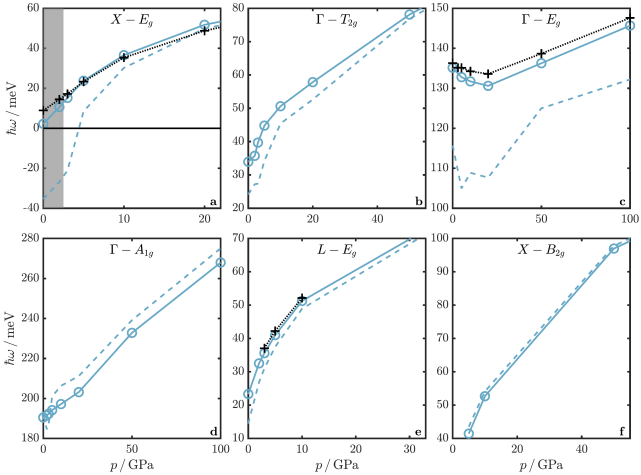

## Phononic behaviour

- high electron-phonon coupling
- strong anharmonicity in many modes

# Anharmonic corrections

## Frozen phonon approach

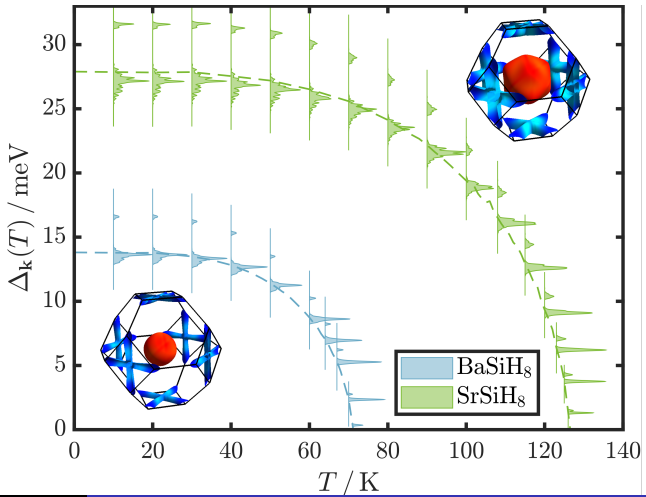
- harmonic (DFPT) result as dashed lines
- PES for each mode as $V(x)$ in the SEQ (solid lines)
- 2D and 3D checks if approach is appropriate (crosses)



# Superconducting gap $\Delta(T)$

## Migdal-Eliashberg theory

- SC state from many-body calculations
- two-gap superconductors
  $BaSiH_8$: $\sim 70\,K$, $\sim 3\,GPa$
  $SrSiH_8$: $\sim 125\,K$, $\sim 30\,GPa$
- distinct distribution on the Fermi surface



# Summary

## Theory

- DFPT: phonons and *ep* quantities
- thermodynamics and enthalpy of formation
- computational methods and strategy

## TMCs

- layered structures
- distinct buildings blocks
- new phase discoveries
- superconductivity up to 25 K

## Ternary hydrides

- $XYH_8$ template
- low-pressure stability search
- two new compounds $BaSiH_8$, $SrSiH_8$
- strong anharmonicity
- low-$p$ and high-$T$ superconductivity

# Thank you for your attention

Related publications

R. Lucrezi and C. Heil, J. Phys.: Condens. Matter, (2021)
"Superconductivity and strong anharmonicity in novel Nb-S phases" available at doi.org/10.1088/1361-648X/abda7a

R. Lucrezi, S. Di Cataldo, et al., subm. to Npj Comput. Mater. (2022)
"In-silico synthesis of novel lowest-pressure high-$T_c$ ternary superhydrides", preprint available at arXiv: 2112.02131 [cond-mat.supr-con], (2021).

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