Ab initio Eliashberg study on anharmonicity, zero-point motion, and retardation effect in superhydrides

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References

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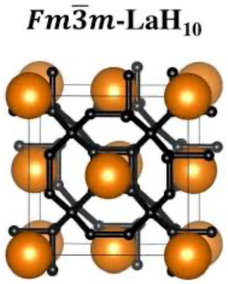
Physics Reports (2020)

I. Errea, F. Belli, L. Monacelli, A. Sanna, T. Koretsune, T. Tadano, A. R. Bianco, M. Calandra, RA, F. Mauri, J. A. Flores Livas, Nature 578 66 (2020)



W. Sano, T. Koretsune, T. Tadano R. Akashi and RA
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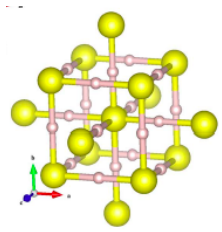
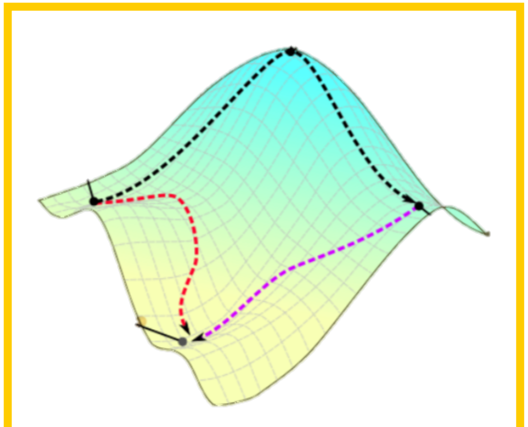


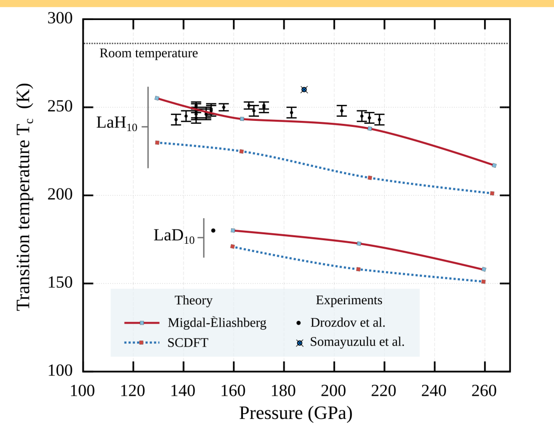
Im-3m H_3S

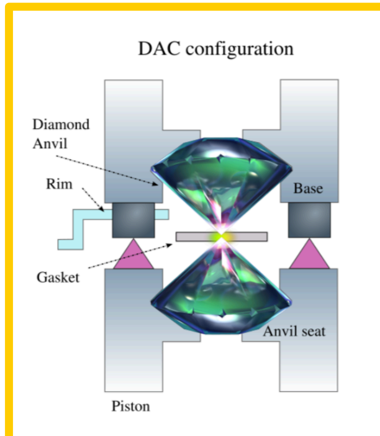
Near RT Superconductivity in High-pressure Hydrides: How did we get there ?

Physical intuition (Aschcroft PRL1968+2004)

L. Boeri







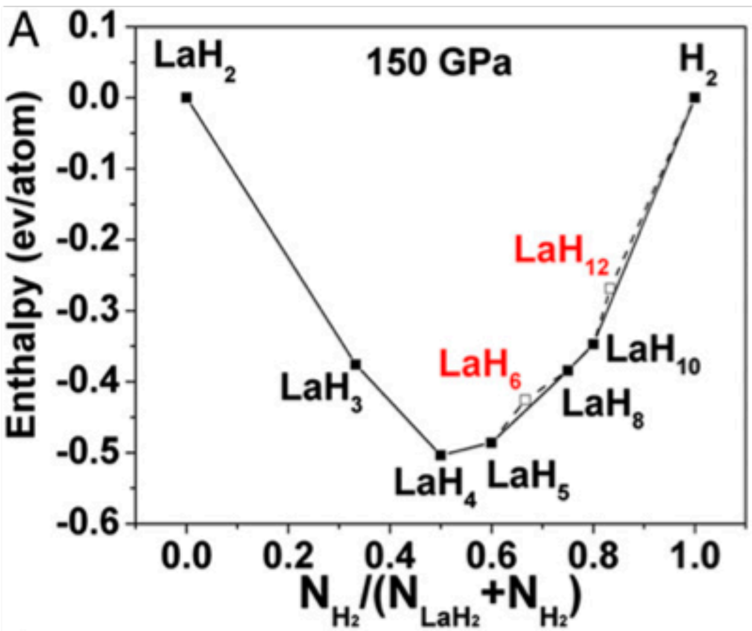
Crystal structure prediction + *Ab-initio* Superconductivity Theory + High Pressure Synthesis

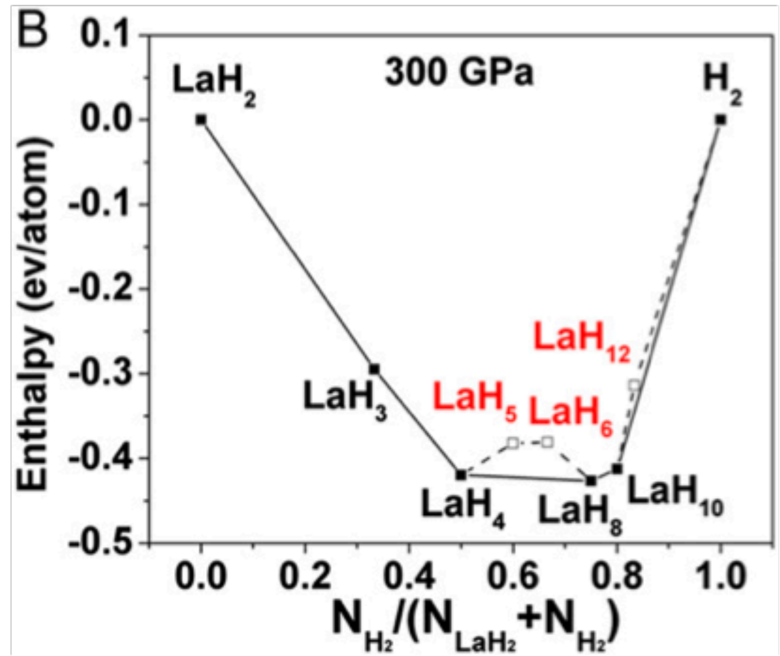
New Superconductors can be predicted (chemical formula, stoichiometry, synthesis pressure) and synthesized!

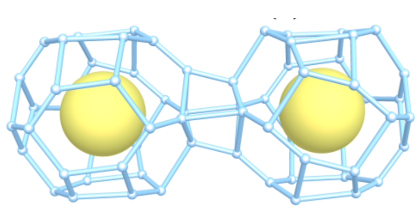
Ab initio theormodynamics

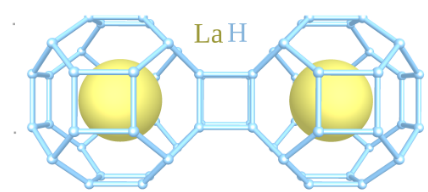
H. Liu et al., PNAS (2017)
I.A. Kruglov et al., PRB (2020)

Convex hull of LaH_x

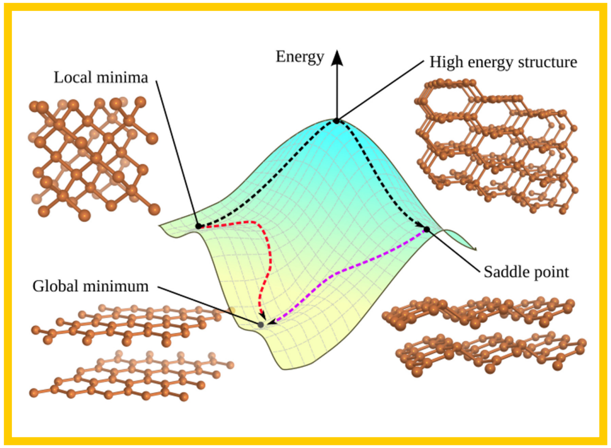


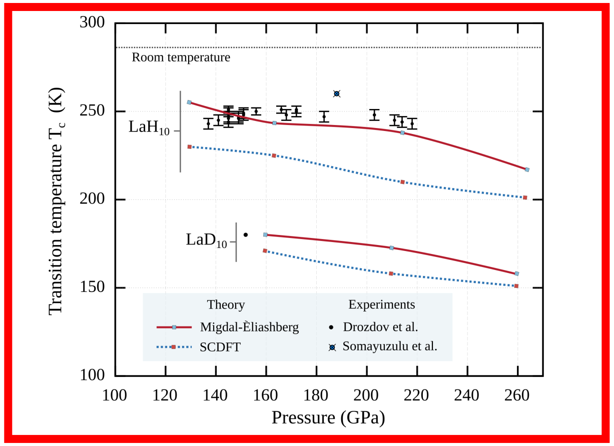


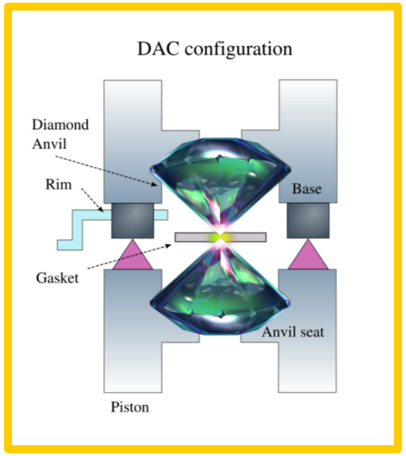




Near RT Superconductivity in High-pressure Hydrides: How did we get there ?







Crystal structure prediction + *Ab-initio* Superconductivity Theory + High Pressure Synthesis

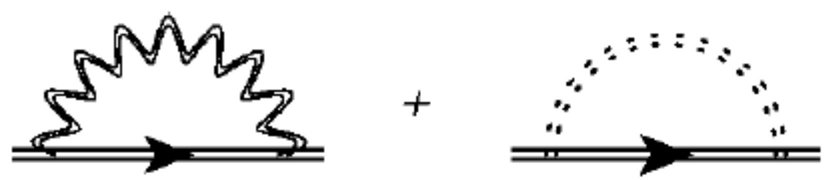
1) Retardation effect 2) Phonon anharmonicity 3) Zero point motion

Migdal-Eliashberg Theory

Self-consistent perturbation theory:
lowest-order dressed-phonon and dressed Coulomb contribution to Σ retained

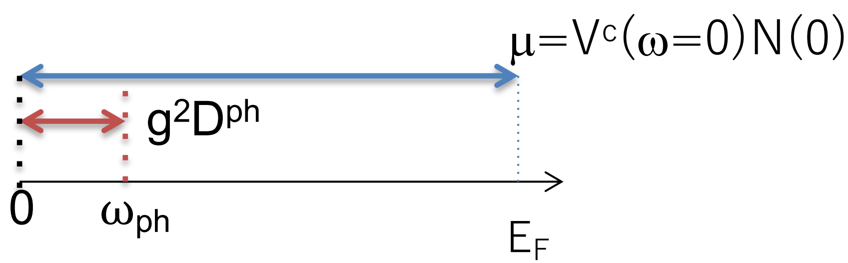
(Nambu-Gor'kov formalism)

$$\overline{\Sigma}(\mathbf{k}, i\omega_n) = -k_B T \sum_{\mathbf{k}',n'} \overline{\tau_3}\,\overline{G}(\mathbf{k}', i\omega_{n'})\overline{\tau_3}\left[\sum_\lambda \left\{g_{\mathbf{kk}'\lambda}\right\}^2 D_\lambda(\mathbf{k}-\mathbf{k}', i\omega_n - i\omega_{n'}) + V_c(\mathbf{k}-\mathbf{k}')\right]\frac{d^4 p'}{(2\pi)^4}$$



Retardation Effect

$$\boxed{\Delta_j(\boldsymbol{p}, i\omega_n) = -\frac{T}{N}\sum\{V_{jl}^{\mathrm{ph}}(\boldsymbol{q}, i\omega_m) + V_{jl}^{\mathrm{c}}(\boldsymbol{q}, i\omega_m)\}|G_l(\boldsymbol{p}+\boldsymbol{q}, i\omega_m + i\omega_n)|^2\Delta_l(\boldsymbol{p}+\boldsymbol{q}, i\omega_n + i\omega_m)}$$



Morel-Anderson Phys. Rev. 125 1263 (1962)

Coulomb pseudo potential $\mu^* = \dfrac{\mu}{1 + \mu \ln\left(\dfrac{E_F}{\omega_{ph}}\right)}$ (empirical parameter)

introduces substantial uncertainty in the calculation of T_c

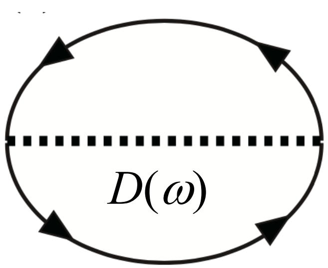
Superconducting DFT

M. Lüders et al, PRB 72, 024545 (2005)
M. Marques et al, PRB 72, 024546 (2005)

$$\boxed{\Delta_i = -\mathcal{Z}_i \Delta_i - \frac{1}{2}\sum_j \mathcal{K}_{ij} \frac{\tanh[\beta/2E_j]}{E_j}\Delta_j} \qquad \mathcal{K} = \frac{\delta^2(E_H + F_{\mathrm{xc}})}{\delta\chi^*\delta\chi}$$

Kohn-Sham perturbation theory (F, D, V_c are obtained from first-principles calc.)

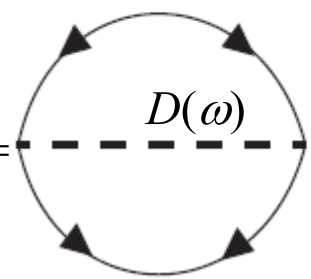
G (Green fn.)



$$D^{s}_{\lambda,q}(\nu_n) = -\frac{2\Omega_{\lambda,q}}{\nu_n^2 + \Omega_{\lambda,q}^2}$$

F (anomalous Green fn.)

$F_{xc}{}^{e\text{-}ph} =$



$$D^{s}_{\lambda,q}(\nu_n) = -\frac{2\Omega_{\lambda,q}}{\nu_n^2 + \Omega_{\lambda,q}^2}$$

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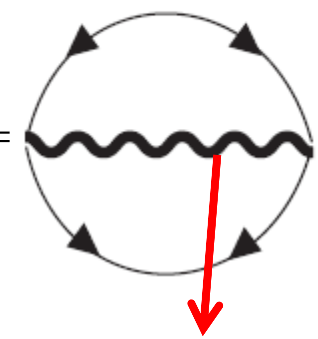
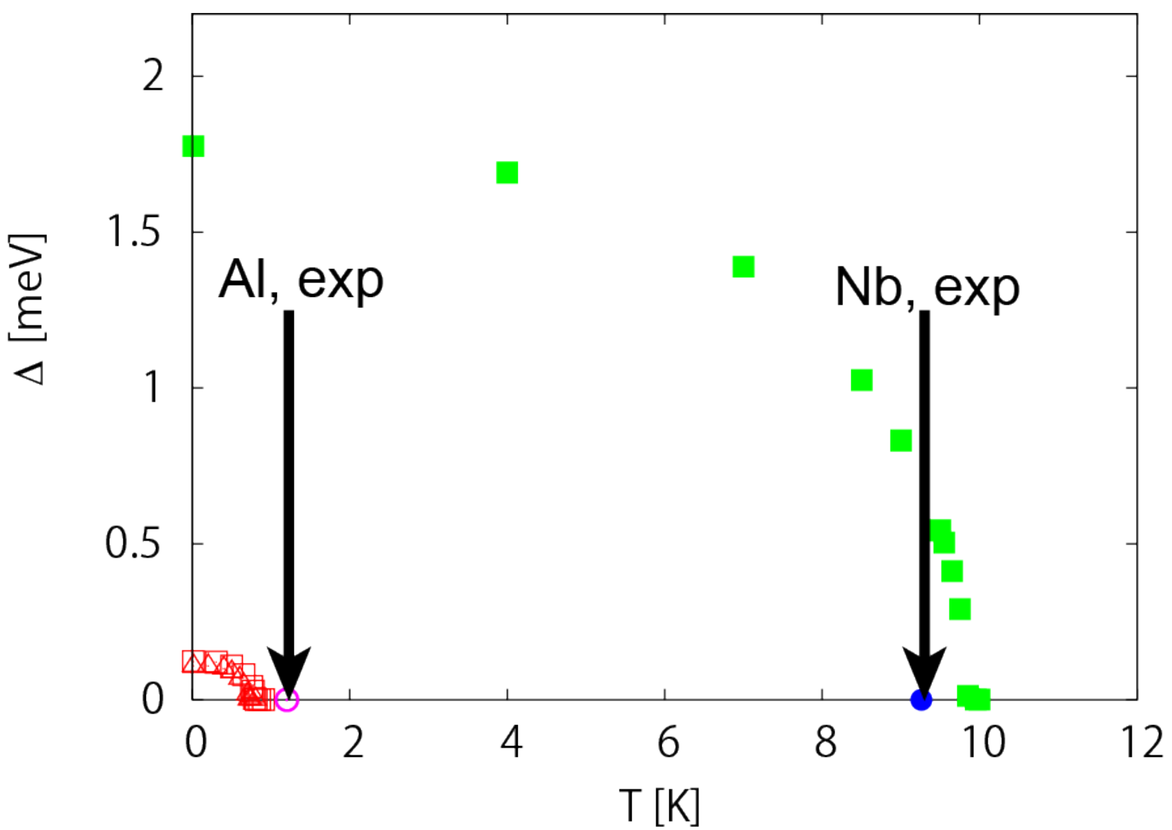


screened Coulomb V_c

Application to elemental Al and Nb



Ab initio Migdal-Eliashberg calculation

$$\Delta_j(\boldsymbol{p}, i\omega_n) = -\frac{T}{N}\sum\{V^{\mathrm{ph}}_{jl}(\boldsymbol{q}, i\omega_m) + V^{\mathrm{c}}_{jl}(\boldsymbol{q}, i\omega_m)\}|G_l(\boldsymbol{p}+\boldsymbol{q}, i\omega_m + i\omega_n)|^2\Delta_l(\boldsymbol{p}+\boldsymbol{q}, i\omega_n + i\omega_m)$$

$$\Sigma_{j\mathbf{p}}(i\omega_n) = -\frac{1}{N\beta}\sum_{l\mathbf{q}m} V^{\mathrm{ph}}_{jl}(\mathbf{q}, i\omega_m) G_{l\mathbf{p}+\mathbf{q}}(i\omega_m + i\omega_n)$$

Convolution of the V and G, Δ

Efficient Fourier transformation $i\omega_n \rightleftarrows \tau$

Intermediate representation of the Green's fn

Shinaoka et al., Phys. Rev. B **96**, 035147 (2017)

Spectral representation of the Green's function

$$G(\tau) = \int_{-\omega_{\mathrm{max}}}^{\omega_{\mathrm{max}}} d\omega K_{\pm}(\tau, \omega)\rho(\omega)$$

$$K_{\pm}(\tau, \omega) = \frac{e^{-\tau\omega}}{1 \pm e^{-\beta\omega}}$$

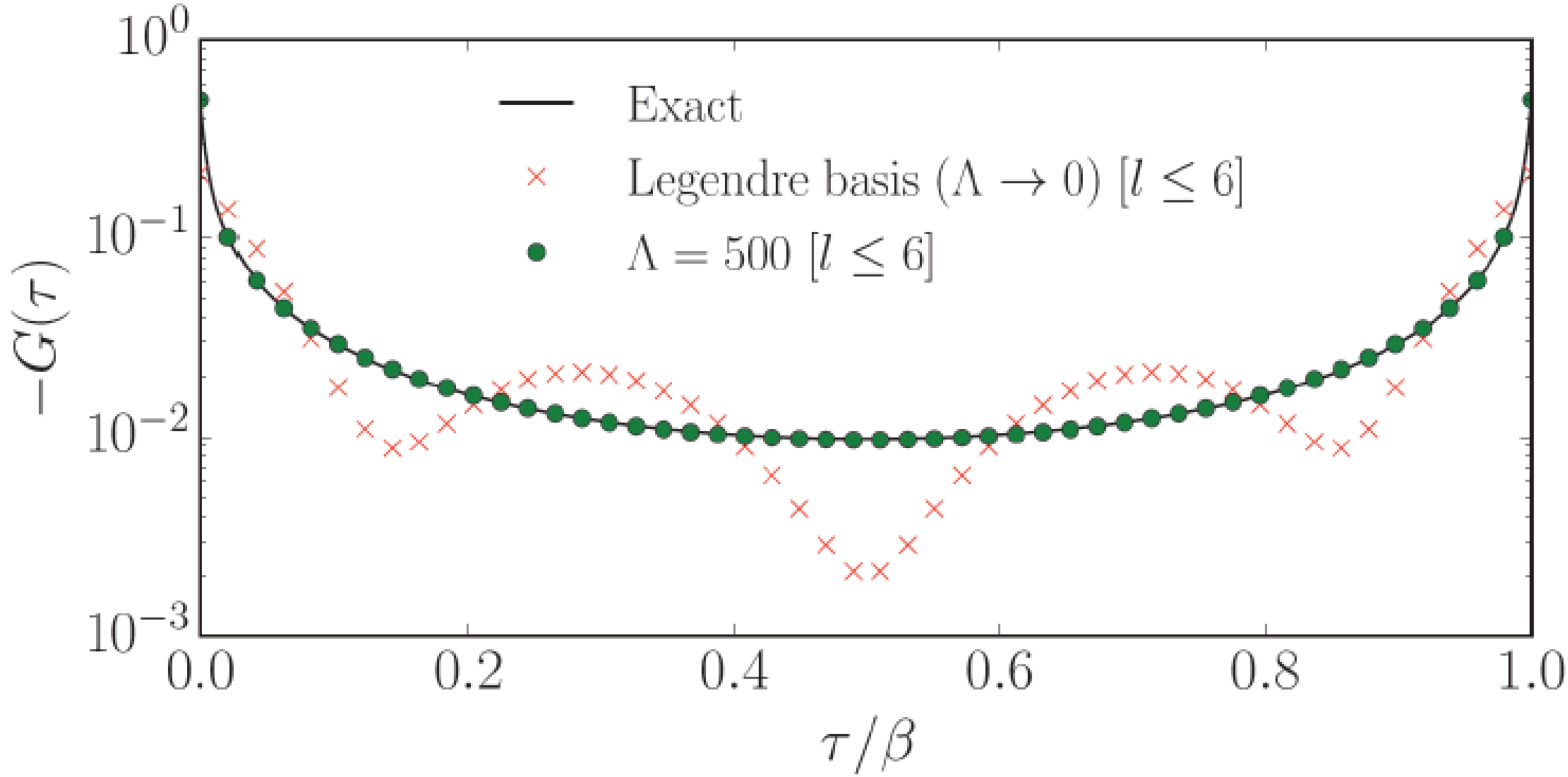
$$\boldsymbol{G} = \boldsymbol{K}\boldsymbol{\rho} \qquad K = USV^{\mathrm{t}}$$ Singular value decomposition

$$K(\tau, \omega) = \sum_{l=0}^{\infty} s_l u_l(\tau) v_l(\omega) \qquad \Lambda \equiv \beta\omega_{\mathrm{max}}$$

Expansion of G with the IR basis

Shinaoka et al., Phys. Rev. B **96**, 035147 (2017)

$$G(\tau) = \sum_{l=0}^{l_{\max}} G_l^{\mathrm{IR}} u_l(\tau)$$



Fourier transformation with the IR basis

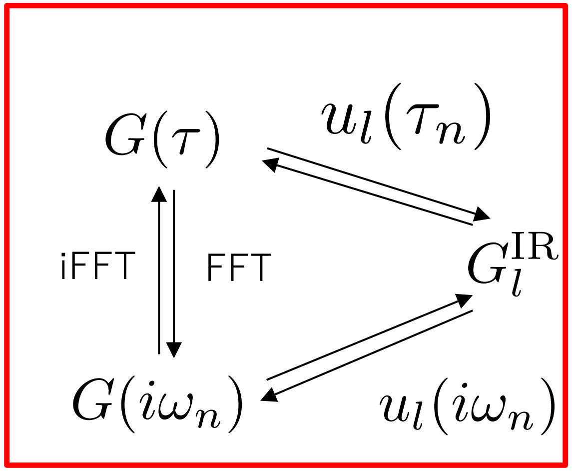
For given $G(i\omega_n)$ and $u_l(i\omega_n)$, G_l^{IR} can be calculated by linear least square fitting procedure

$$G(i\omega_n) = \sum_{l=0}^{l_{\max}} G_l^{\mathrm{IR}} u_l(i\omega_n)$$

$$u_l(i\omega_n) = \int_0^\beta d\tau u_l(\tau) \exp(i\omega_n \tau)$$

$$G(\tau) = \frac{1}{\beta} \sum_n \exp(-i\omega_n \tau) G(i\omega_n)$$

$$G(\tau) = \sum_{l=0}^{l_{\max}} G_l^{\mathrm{IR}} u_l(\tau)$$

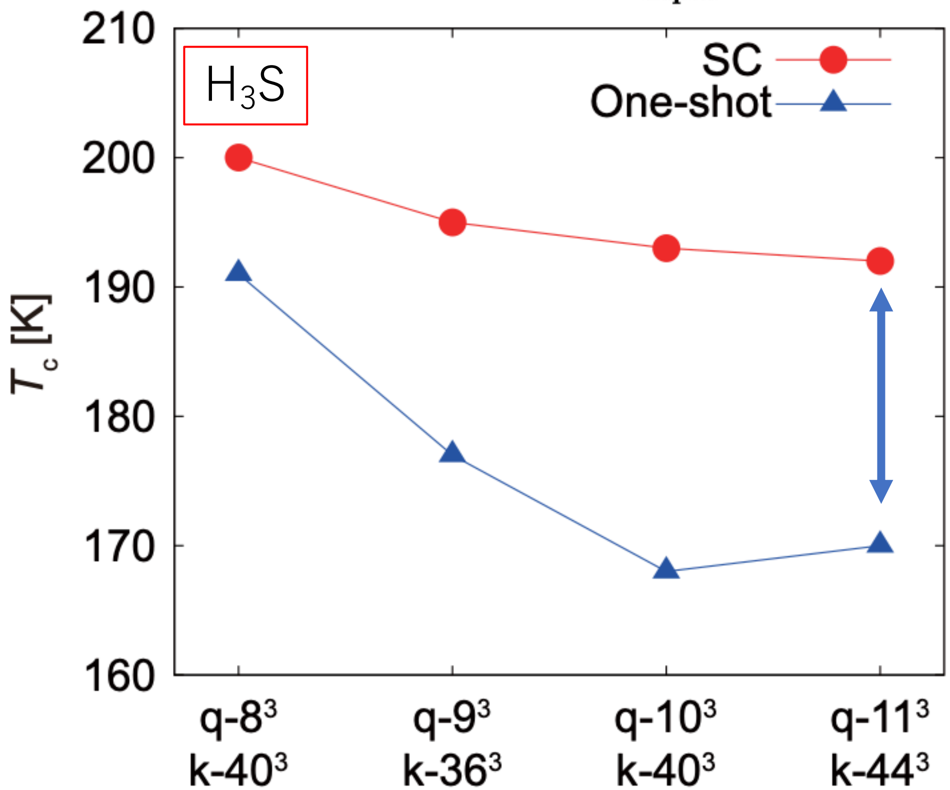


$u_l(i\omega_n)$ can be pre-computed, and stored in a library as a matrix

Self-consistent Migdal-Eliashberg calculation

$$\Delta_j(\boldsymbol{p}, i\omega_n) = -\frac{T}{N}\sum\{V^{\rm ph}_{jl}(\boldsymbol{q}, i\omega_m) + V^{\rm c}_{jl}(\boldsymbol{q}, i\omega_m)\}|G_l(\boldsymbol{p}+\boldsymbol{q}, i\omega_m + i\omega_n)|^2\Delta_l(\boldsymbol{p}+\boldsymbol{q}, i\omega_n + i\omega_m)$$

$$\Sigma_{j\mathbf{p}}(i\omega_n) = -\frac{1}{N\beta}\sum_{l\mathbf{q}m} V^{\rm ph}_{jl}(\mathbf{q}, i\omega_m) G_{l\mathbf{p}+\mathbf{q}}(i\omega_m + i\omega_n)$$



One-shot calculation overestimate the mass-enhancement effect (T_c underestimated)

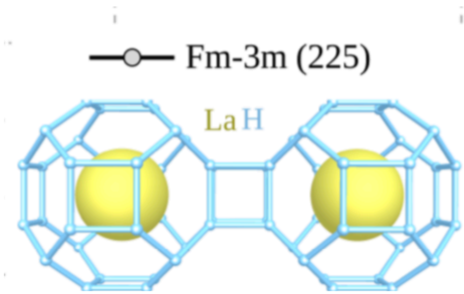
W. Sano, RA et al., PRB2016
T. Wang, RA, et al., in prep.

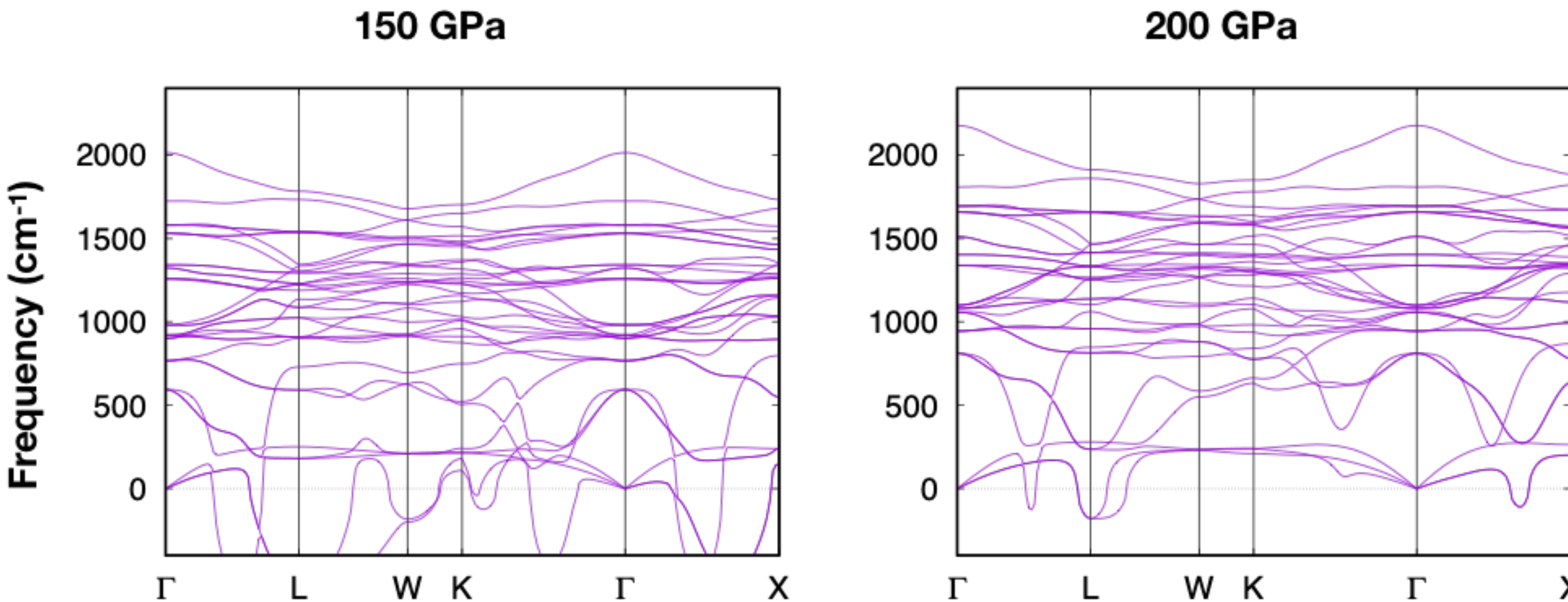
Intermediate representation of the Green's fn →Self-consistent calculation considering the retardation effect can be performed efficiently

Phonon anharmonicity

I. Errea, RA et al., Nature2020

LaH_{10}





Harmonic approximation: many negative modes

Anharmonic Hamiltonian

Tadano-Tsuneyuki, JPSJ 87 041015(2018)

$$H = T + U_2 + U_3 + U_4$$

$$U_n = \frac{1}{n!} \sum_{\{\ell,\kappa,\mu\}} \Phi_{\mu_1 \ldots \mu_n}(\ell_1\kappa_1; \ldots; \ell_n\kappa_n) u_{\mu_1}(\ell_1\kappa_1) \cdots u_{\mu_n}(\ell_n\kappa_n)$$

nth-order force constant (FC)

Transform by normal coordinate

$$u_\mu(\ell\kappa) = \frac{1}{\sqrt{NM_\kappa}} \sum_{\boldsymbol{q},j} Q_{\boldsymbol{q}j} e_\mu(\kappa; \boldsymbol{q}j) e^{i\boldsymbol{q}\cdot\boldsymbol{r}(\ell)}$$

$$U_n = \frac{1}{n!} \sum_{\{\boldsymbol{q},j\}} \Delta(\boldsymbol{q}_1 + \cdots + \boldsymbol{q}_n) \Phi(\boldsymbol{q}_1 j_1; \ldots; \boldsymbol{q}_n j_n) Q_{\boldsymbol{q}_1 j_1} \cdots Q_{\boldsymbol{q}_n j_n}$$

reciprocal form of nth-order FC

Anharmonic Hamiltonian

Tadano-Tsuneyuki, JPSJ 87 041015(2018)

Second quantization $Q_{\boldsymbol{q}j} = \sqrt{\frac{\hbar}{2\omega_{\boldsymbol{q}j}}}\hat{A}_{\boldsymbol{q}j}$

Displacement operator

$$\hat{A}_{\boldsymbol{q}j} = \hat{b}_{\boldsymbol{q}j} + \hat{b}^{\dagger}_{-\boldsymbol{q}j}$$

$$\hat{H} = \underbrace{\sum_{\mathbf{q}j} \hbar\omega_{\mathbf{q}j}\left(n_{\mathbf{q}j} + \frac{1}{2}\right)}_{\hat{H}_0} + \underbrace{\hat{U}_3 + \hat{U}_4}_{\hat{H}'}$$

$$\hat{U}_n = \frac{1}{n!}\left(\frac{\hbar}{2}\right)^{\frac{n}{2}} \sum_{\{\boldsymbol{q},j\}} \Delta(\boldsymbol{q}_1 + \cdots + \boldsymbol{q}_n) \frac{\Phi(\boldsymbol{q}_1 j_1; \ldots ; \boldsymbol{q}_n j_n)}{\sqrt{\omega_{\boldsymbol{q}_1 j_1} \cdots \omega_{\boldsymbol{q}_n j_n}}} \hat{A}_{\boldsymbol{q}_1 j_1} \cdots \hat{A}_{\boldsymbol{q}_n j_n}$$

Self-consistent phonon theory

Hooton 1955, 1958, Werthamer 1970, Cochran et al. 1967
For review: Tadano-Tsuneyuki, JPSJ 87 041015(2018)

Mimic the free energy of an anharmonic system by an effective harmonic Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{U}_3 + \hat{U}_4 = \hat{\mathcal{H}} + (\hat{H} - \hat{\mathcal{H}})$$

$$\hat{\mathcal{H}} = \hat{T} + \hat{\mathcal{U}}_2 = \sum_q \boxed{\hbar\Omega_q} \left(\hat{a}_q^\dagger \hat{a}_q + \frac{1}{2}\right)$$

unknown

Gibbs-Bogoliubov inequality

$$F \leq \mathcal{F} + \langle H - \mathcal{H} \rangle_{\mathcal{H}}$$

Let us minimize

$$\begin{aligned} F' &= \mathcal{F} + \langle H - \mathcal{H} \rangle_{\mathcal{H}} = \mathcal{F} + \langle U_2 + U_3 + U_4 - \mathcal{U}_2 \rangle_{\mathcal{H}} \\ &= \mathcal{F} + \langle U_2 - \mathcal{U}_2 + U_4 \rangle_{\mathcal{H}} \end{aligned}$$

Self-consistent phonon theory

Hooton 1955, 1958, Werthamer 1970, Cochran et al. 1967
For review: Tadano-Tsuneyuki, JPSJ 87 041015(2018)

Let us minimize

$$
\begin{aligned}
F' &= \mathcal{F} + \langle H - \mathcal{H} \rangle_{\mathcal{H}} = \mathcal{F} + \langle U_2 + U_3 + U_4 - \mathcal{U}_2 \rangle_{\mathcal{H}} \\
&= \mathcal{F} + \langle U_2 - \mathcal{U}_2 + U_4 \rangle_{\mathcal{H}} \\
&= \sum_q \left[\frac{\hbar \Omega_q}{2} + \frac{1}{\beta} \log\left(1 - e^{-\beta \hbar \Omega_q}\right) \right] + \frac{1}{2} \sum_q \left(\frac{\hbar \omega_q^2}{\Omega_q} - \hbar \Omega_q \right) \left(n_q + \frac{1}{2} \right) \\
&\quad + \frac{1}{8} \sum_{q,q'} \frac{\hbar^2 \Phi(q; -q; q'; -q')}{\Omega_q \Omega_{q'}} \left(n_q + \frac{1}{2} \right) \left(n_{q'} + \frac{1}{2} \right).
\end{aligned}
$$

$$
\frac{\partial F'}{\partial \Omega_q} = 0
$$

$$
\boxed{
\begin{aligned}
\Omega_q^2 &= \omega_q^2 + \Omega_q I_q, \\
I_q &= \sum_{q'} \frac{\hbar \Phi(q; -q; q'; -q')}{4 \Omega_q \Omega_{q'}} \left[1 + 2n(\Omega_{q'}) \right].
\end{aligned}
}
$$

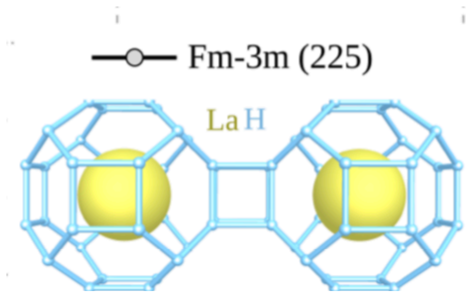
Self-consistent eq.

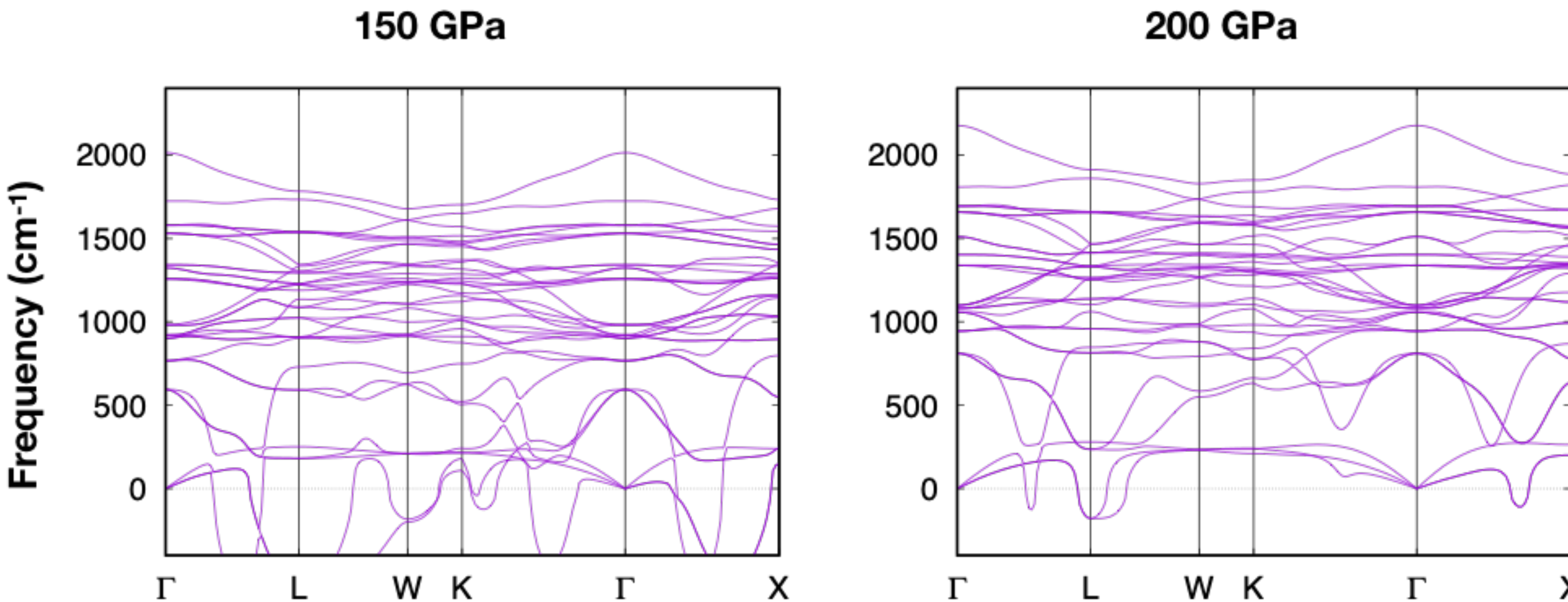
Stochastic implementation for self-consistent harmonic approximation (SSCHA) I. Errea et al., PRB 89 064302 (2014)

Phonon anharmonicity

I. Errea, RA et al., Nature2020

LaH_{10}

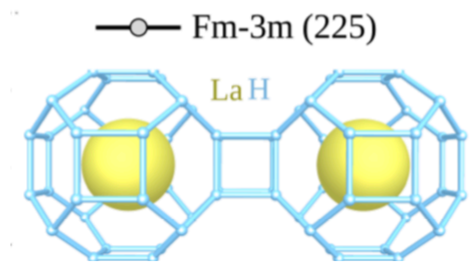


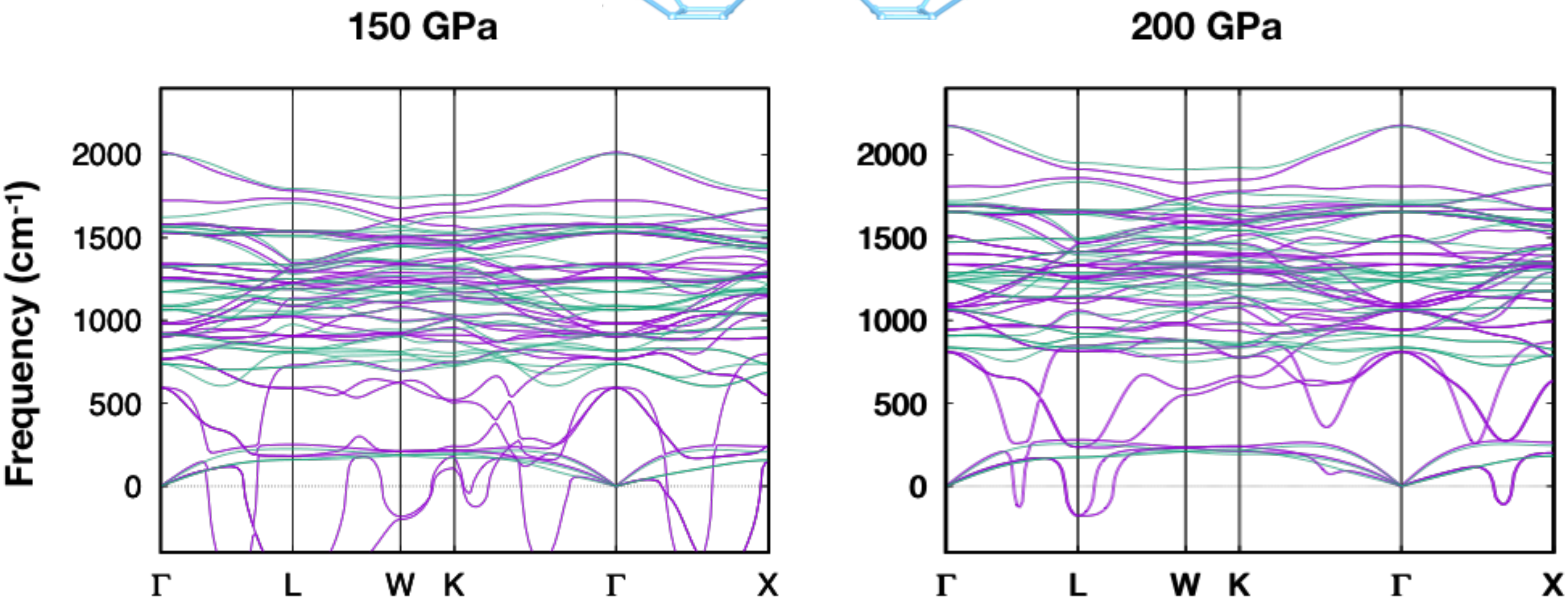


Harmonic approximation: many negative modes

Phonon anharmonicity

I. Errea, RA et al., Nature2020

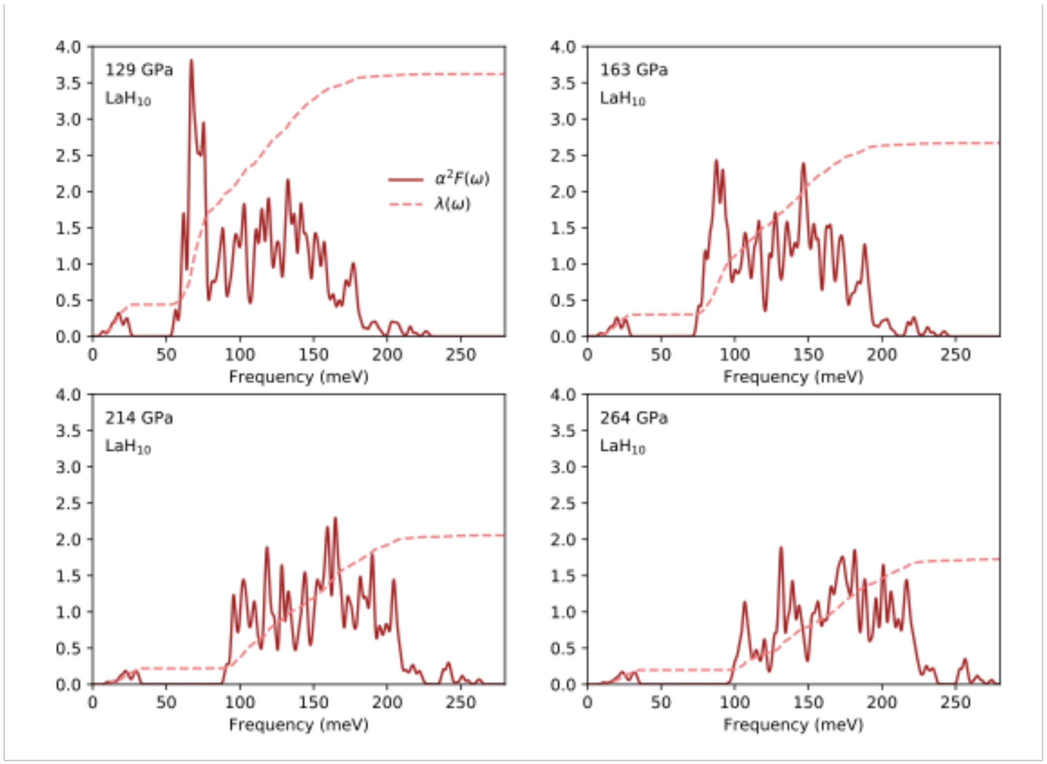


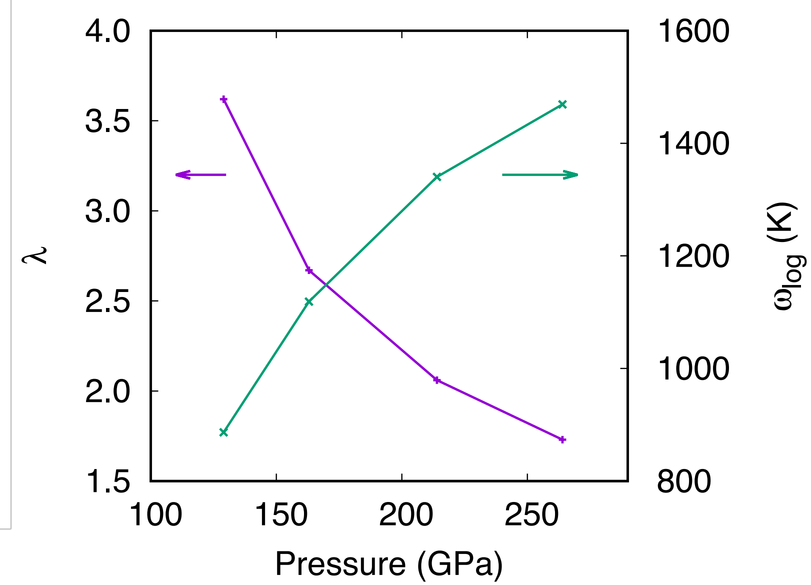


No negative modes

Eliashberg function

I. Errea, RA et al., Nature2020





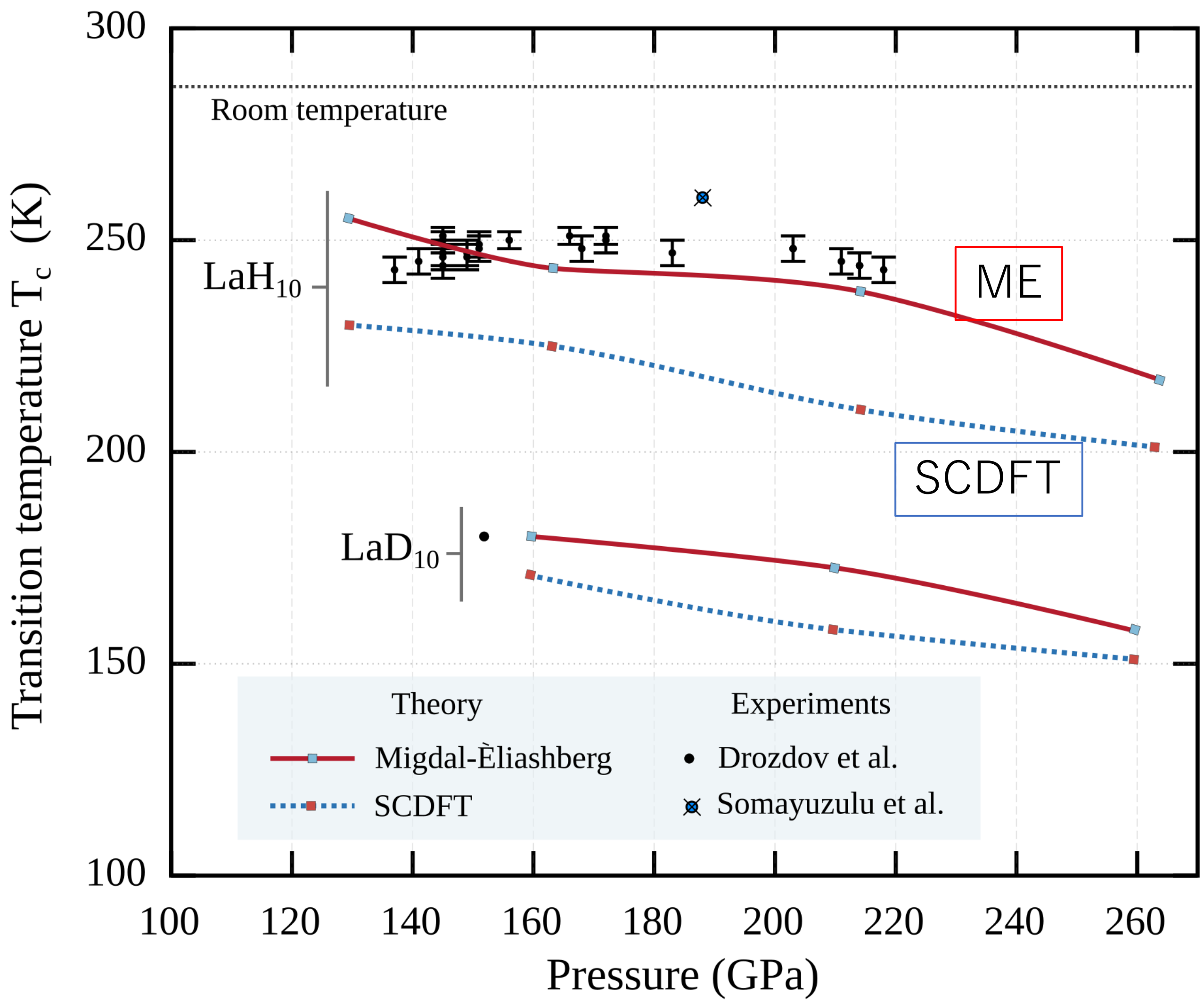
$$\lambda = 2\int d\omega \frac{\alpha^2F(\omega)}{\omega}$$

$$\alpha^2F(\omega) = \frac{1}{D(E_F)} \sum_{n\mathbf{k},m\mathbf{q},\nu} |g^{\nu}_{n\mathbf{k},m\mathbf{k}+\mathbf{q}}|^2 \delta(\xi_{n\mathbf{k}})\delta(\xi_{m\mathbf{k}+\mathbf{q}})\delta(\omega - \omega_{\nu\mathbf{q}}) .$$

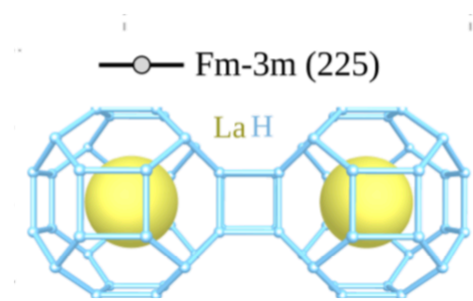
Large λ and ω coexist

Calculation of T_C

I. Errea, RA et al., Nature2020

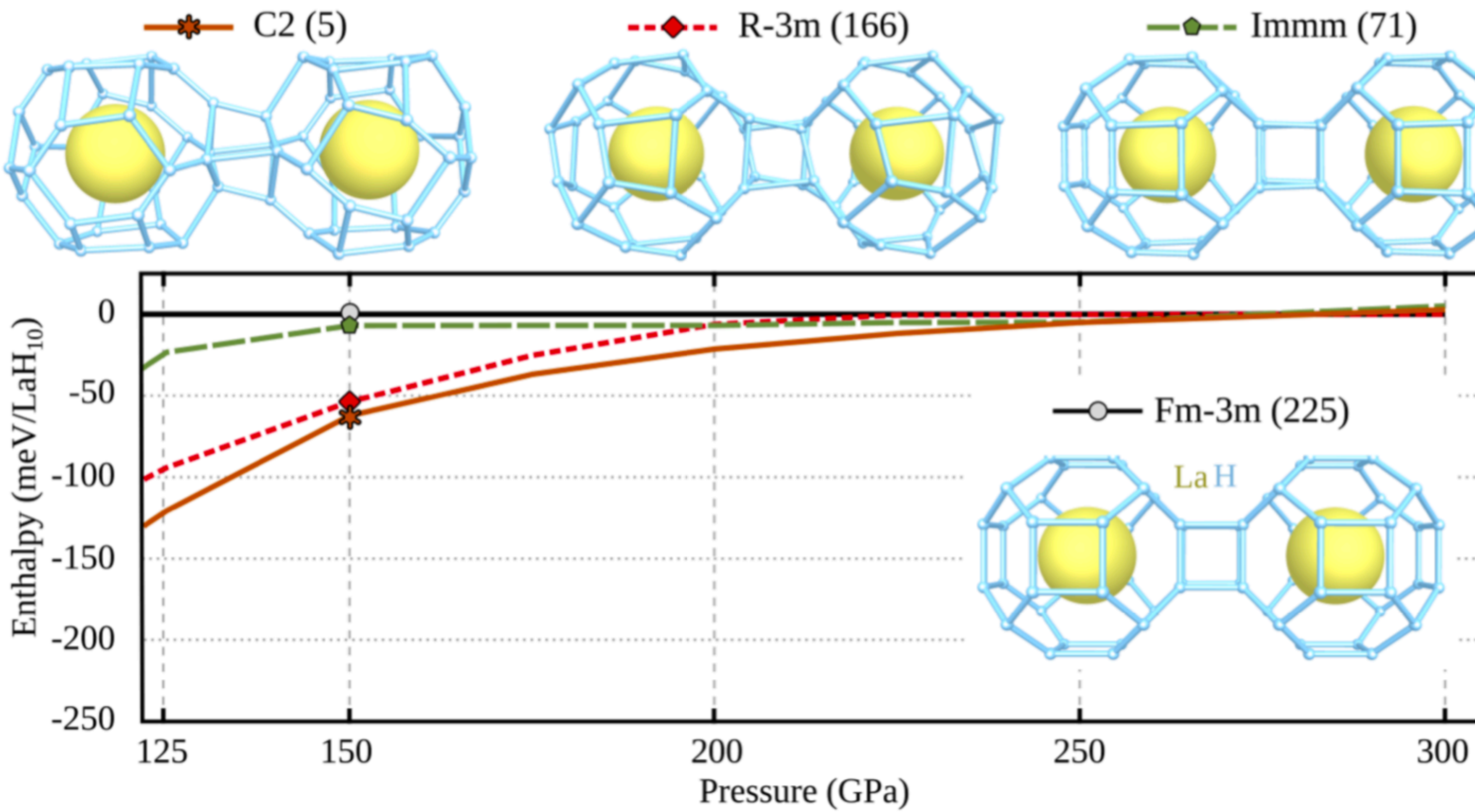


T_c reproduced accurately without introducing any empirical parameter



Born Oppenheimer

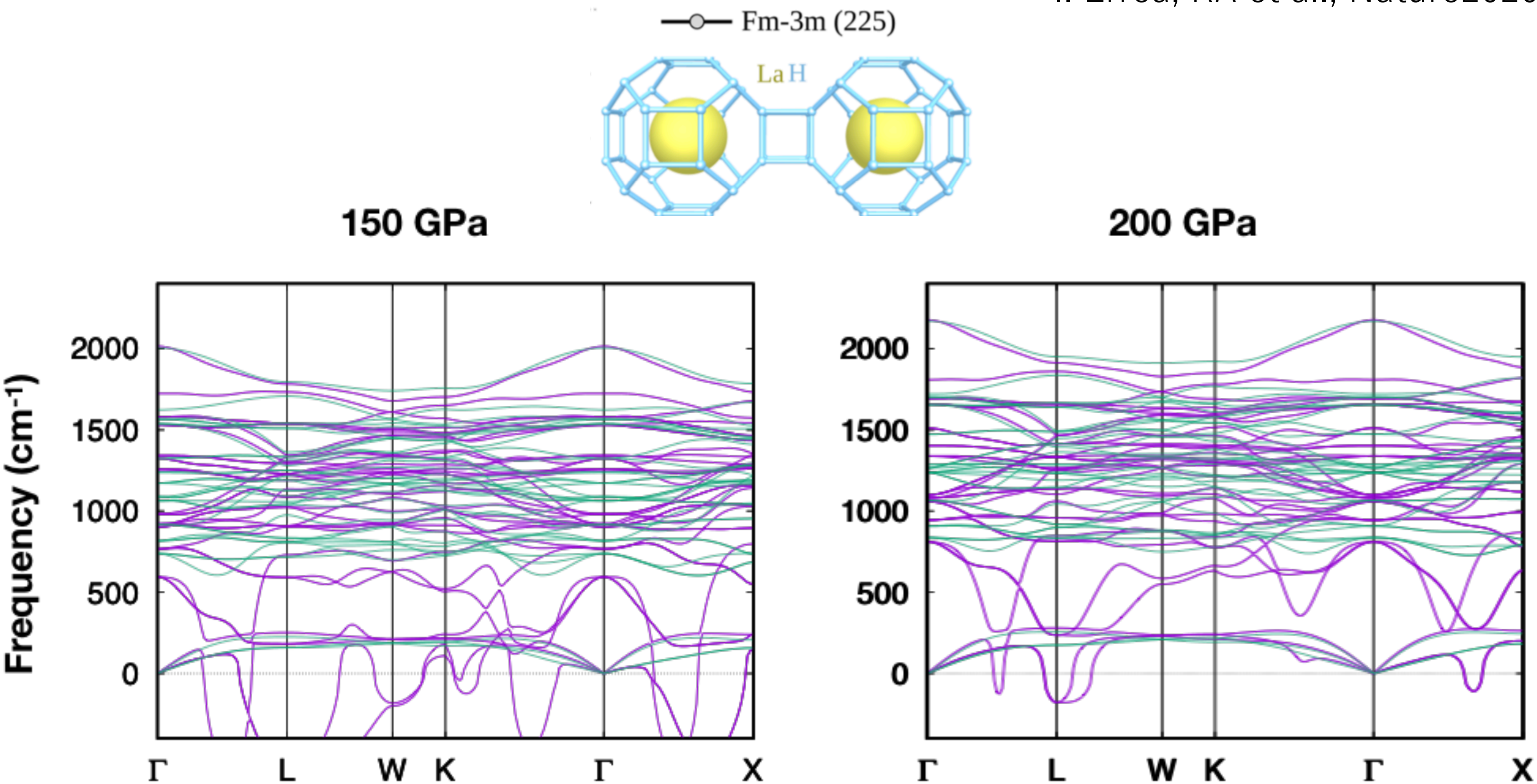
I. Errea, RA et al., Nature2020



Symmetric structure is not stable at P~150GPa

Phonon anharmonicity

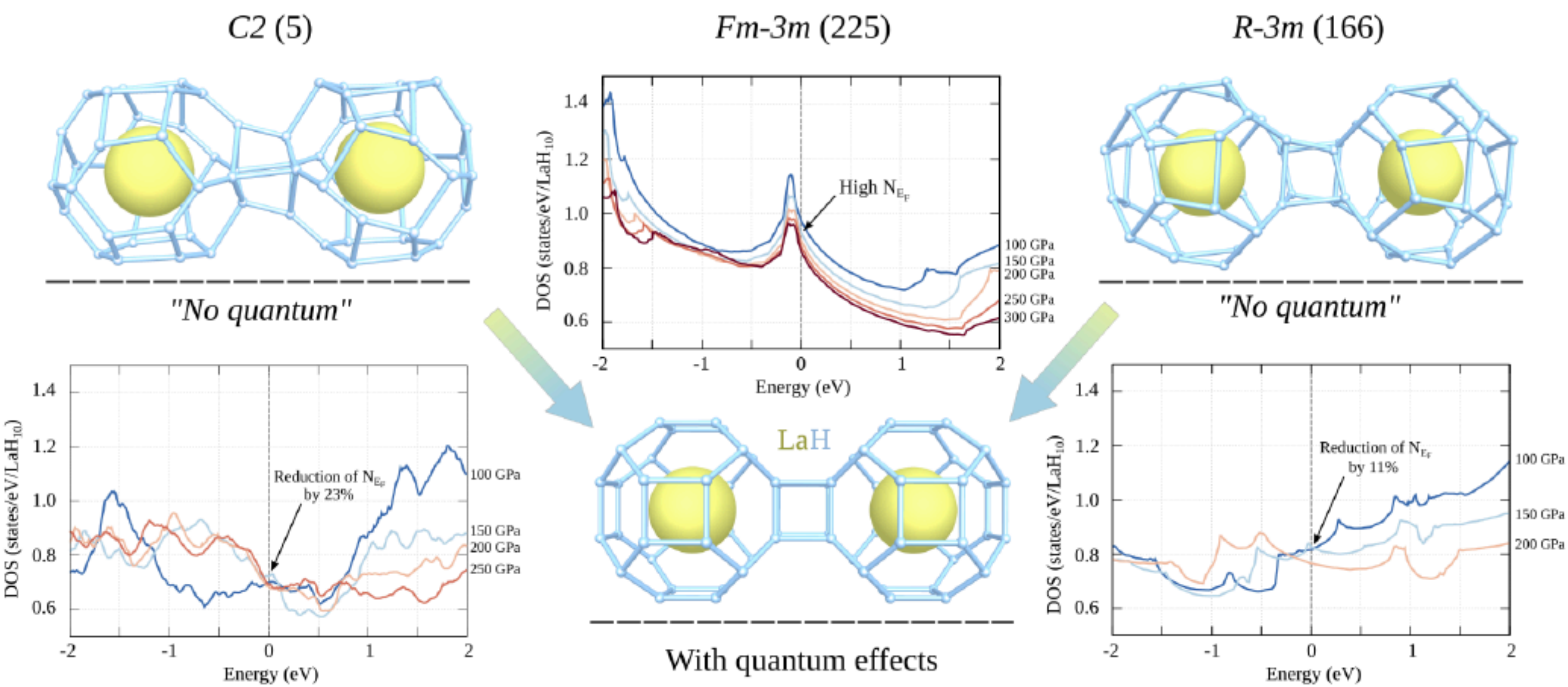
I. Errea, RA et al., Nature2020



No negative modes

Quantum effect

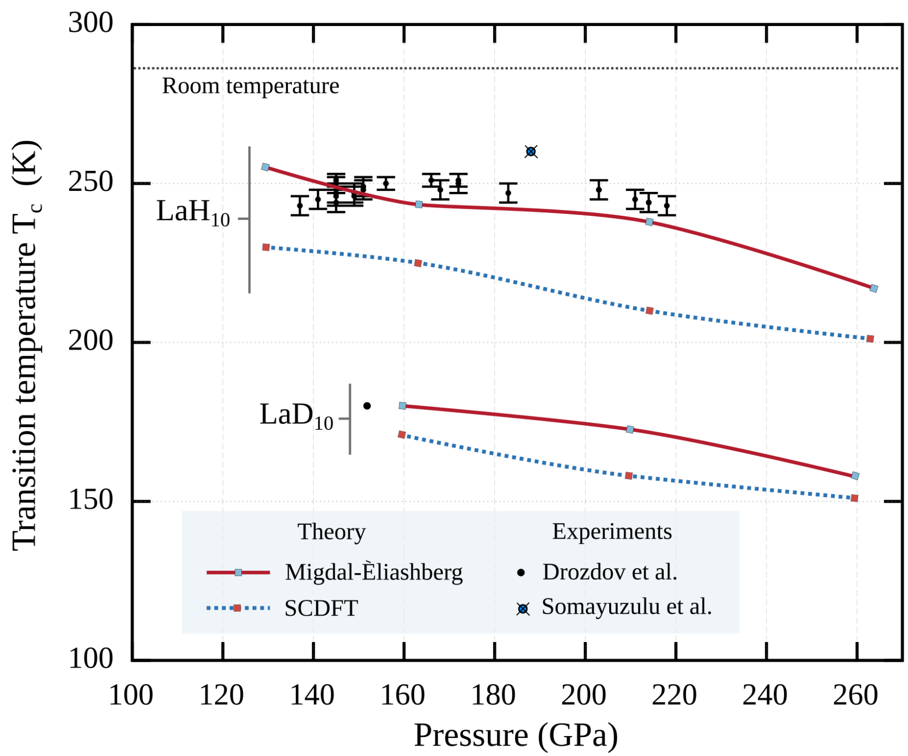
I. Errea, RA et al., Nature2020



LaH_{10} is a *quantum crystal*, which is hold via quantum effects.
Otherwise the colossal electron-phonon coupling destroy it.

Conclusion

Ab initio Eliashberg Calculation for superhydrides



1) Retardation effect

Efficient method with the IR basis

2) Phonon anharmonicity

Self-consistent phonon theory

3) Zero point motion