

Thermodynamic models to unravel superconducting physical properties and parameters

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Superconductivity
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EGQCA
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$\text{Al}_x\text{Mg}_{1-x}\text{B}_2$
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Nb–Ti alloys
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Nb–V alloys
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Conclusions
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Acknowledgements
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Outline

1 Superconductivity

2 EGQCA

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7 Acknowledgements

Superconductors and superconductivity (SC)

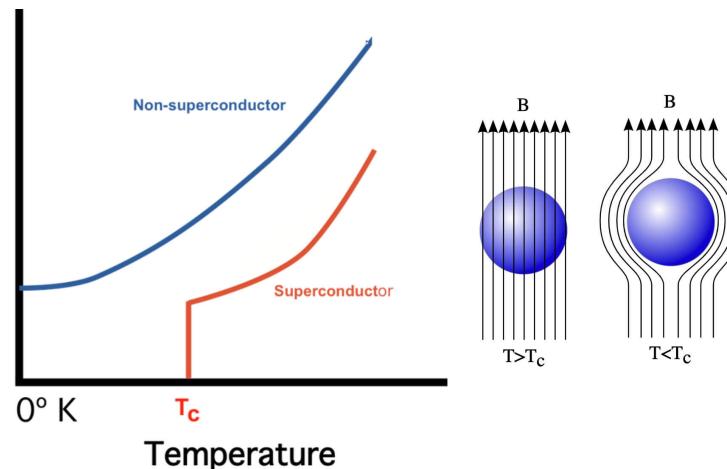


Figure 1: Main SC properties

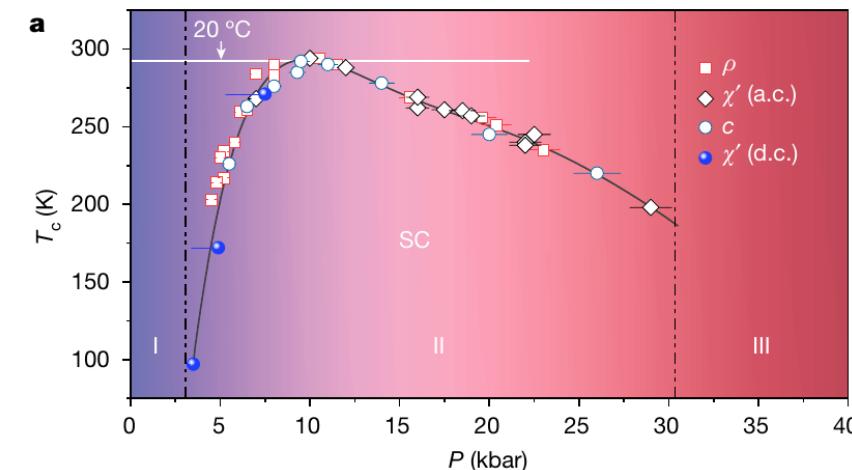


Figure 2: Ranga Dias et al. claim for near room condition SC in Lu-H-N (N. Dasenbrock-Gammon et al, Nature 615 2023 244)

Superconductors and superconductivity (SC)

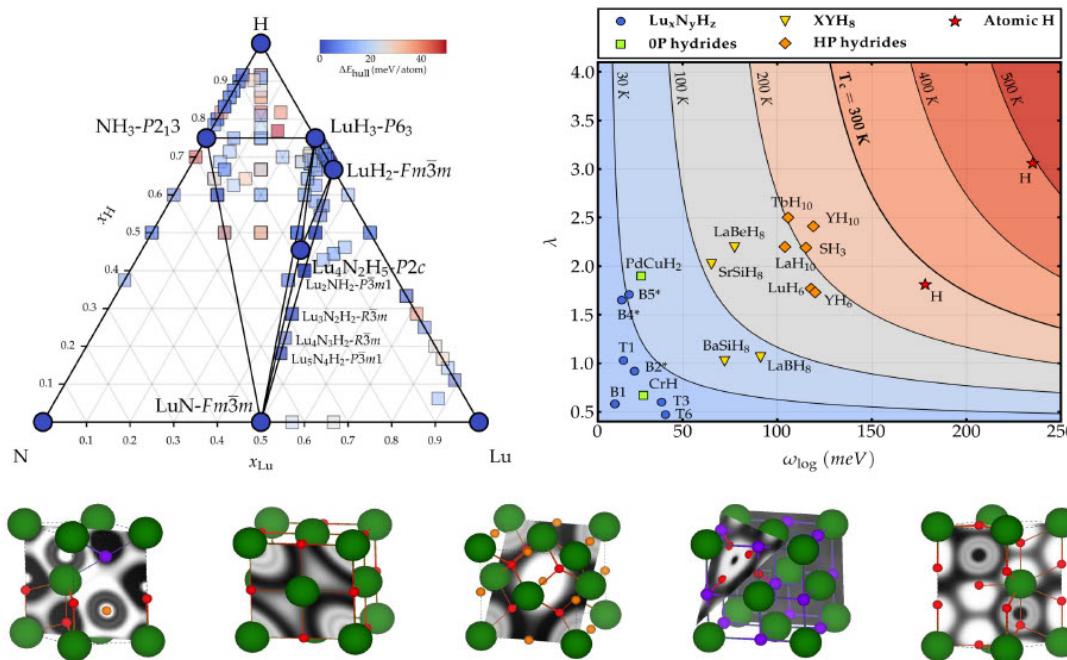


Figure 3: Ferreira, P.N., Conway, L.J., Cucciari, A. et al. *Search for ambient superconductivity in the Lu–N–H system*. **Nature Communications** 14, 5367 2023



Figure 4: Pedro “Mozão” Pires

Superconductivity and Superconductors (SC)

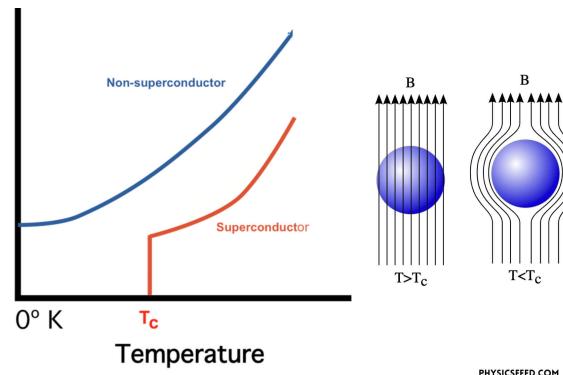


Figure 5: Main SC properties

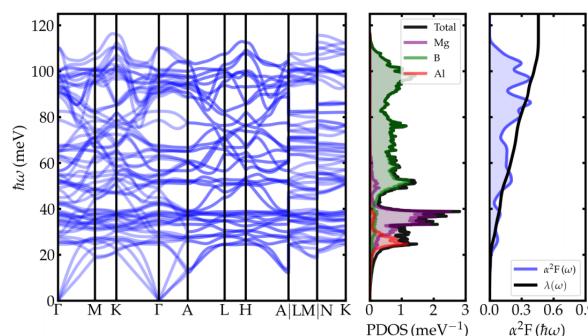


Figure 6: Phonon spectrum (example)

Phonon-mediated superconductors

- Eliashberg spectral function

$$\alpha^2 F(\omega) = \frac{1}{2\pi N_{EF}} \sum_{\vec{q}\nu} \delta(\omega - \omega_{\vec{q}\nu}) \frac{\gamma_{\vec{q}\nu}}{\hbar\omega_{\vec{q}\nu}}$$

- Electron-phonon mass enhancement parameter:

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

- Allen-Dynes formula for T_c :

$$T_c = \frac{f_1 f_2 \omega_{\log}}{1.20} \exp \left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right)$$

- f_1, f_2, ω_{\log} : simple functions of λ and μ^*
- μ^* : screened Coulomb pseudopotential (Morel–Anderson model) — very hard to calculate!
- What about disordered materials, such as SC alloys?

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Extended Generalized Quasi-Chemical Approximation (EGQCA)

- GQCA has been widely used in **semiconductors** for a long time to describe (e.g.) semiconducting gaps

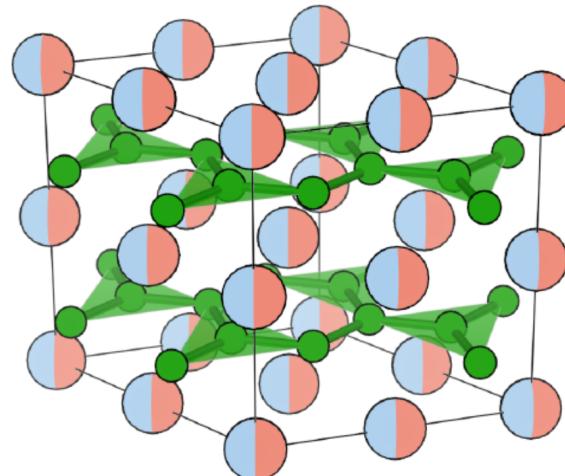


Figure 7: Cluster with substitution in one sublattice

- Enthalpy (static):

$$\Delta H = \sum_{j=1}^J p_j \Delta_j$$

- p_j : cluster (configuration) probabilities
- Δ_j : cluster excess enthalpies

- Entropy (configurational):

$$\Delta S(x, T, P) = k_B \ln W$$

$$W = \frac{N!}{N_A! N_B!} \frac{M!}{\prod_j M_j!} \prod_j (p_j^0)^{M_j}$$

- Free energy:

- GQCA:

$$\Delta G = \Delta H - T\Delta S$$

- EGQCA: a vibrational term is added:

$$\Delta G = \Delta H - T\Delta S + \Delta A$$

with ΔA the cluster phonon excess free energies

- Any property \mathcal{P} :

$$\mathcal{P}(x, T, p) = \sum_j p_j(x, T, p) \mathcal{P}_j$$

$$\Delta \mathcal{P}(x, T, p) = \sqrt{p_j(x, T, p) \mathcal{P}_j^2 - [\mathcal{P}(x, T, p)]^2}$$

(E)GQCA model in action

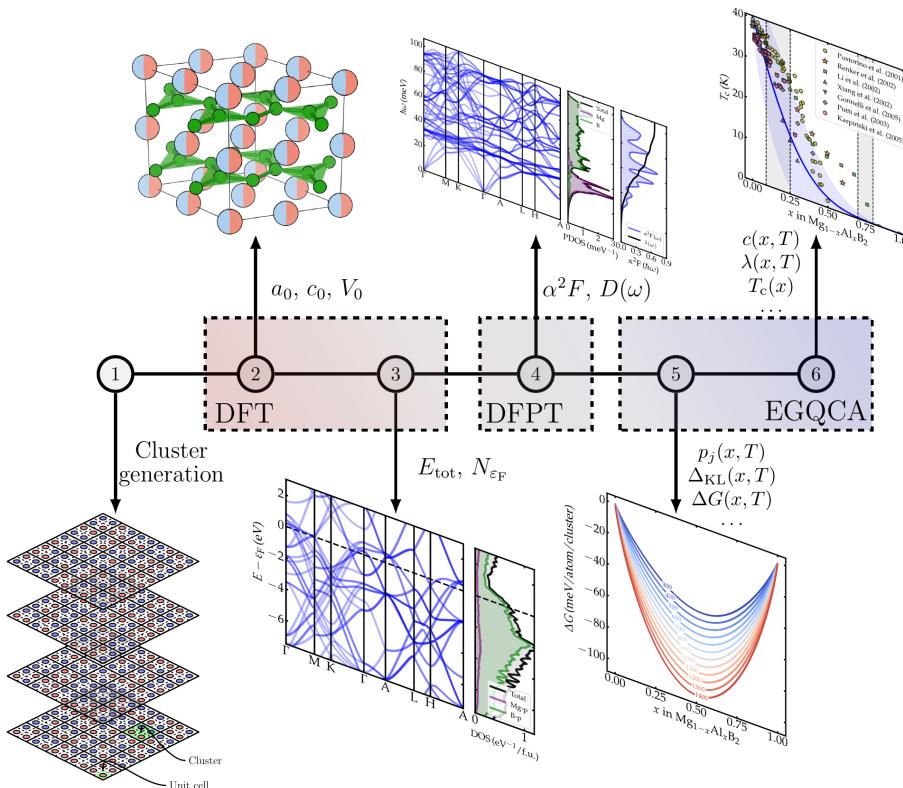


Figure 8: EGQCA workflow

Superconductivity
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MgB₂ parent structure and supercell

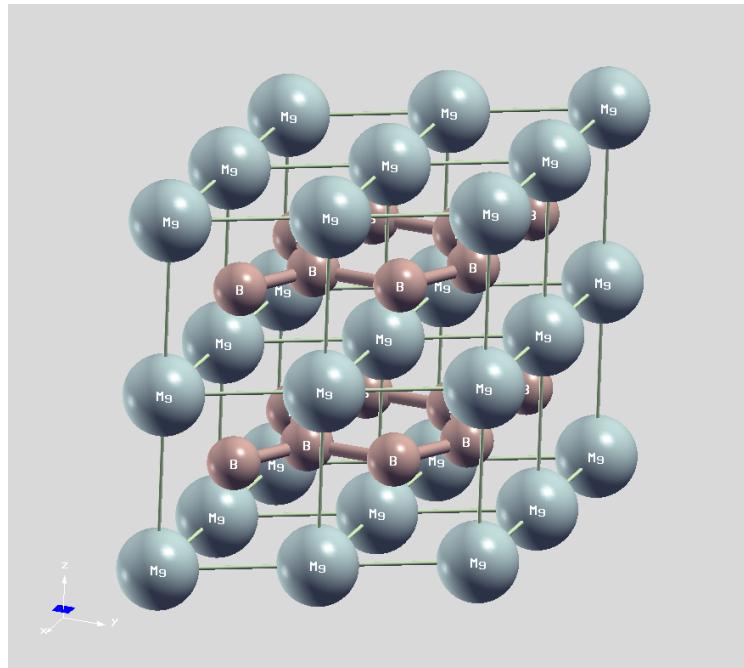


Figure 9: MgB₂ 2x2x2 supercell

- MgB₂: two-band gap superconductor, $T_c = 39$ K

- Narrow solubility range for most dopants
 - exception: Al (probably up to ≈ 75 at%); leads to loss of SC
- 2x2x2 supercell: 22 configurations for $\text{Al}_x\text{Mg}_{1-x}\text{B}_2$, $0 \leq x \leq 1$

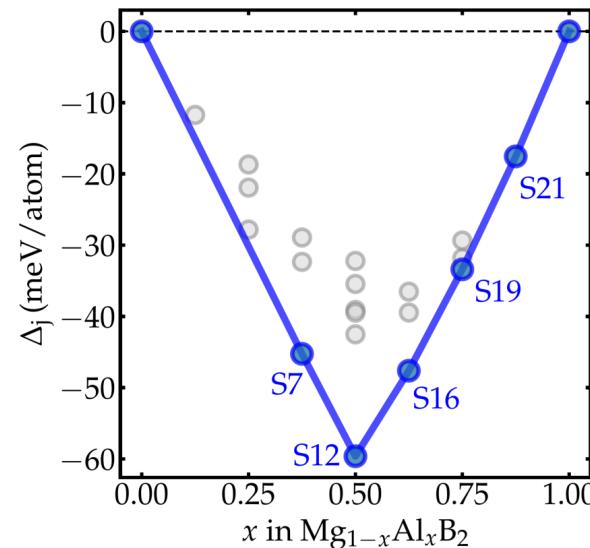


Figure 10: Excess enthalpy

Cluster probabilities

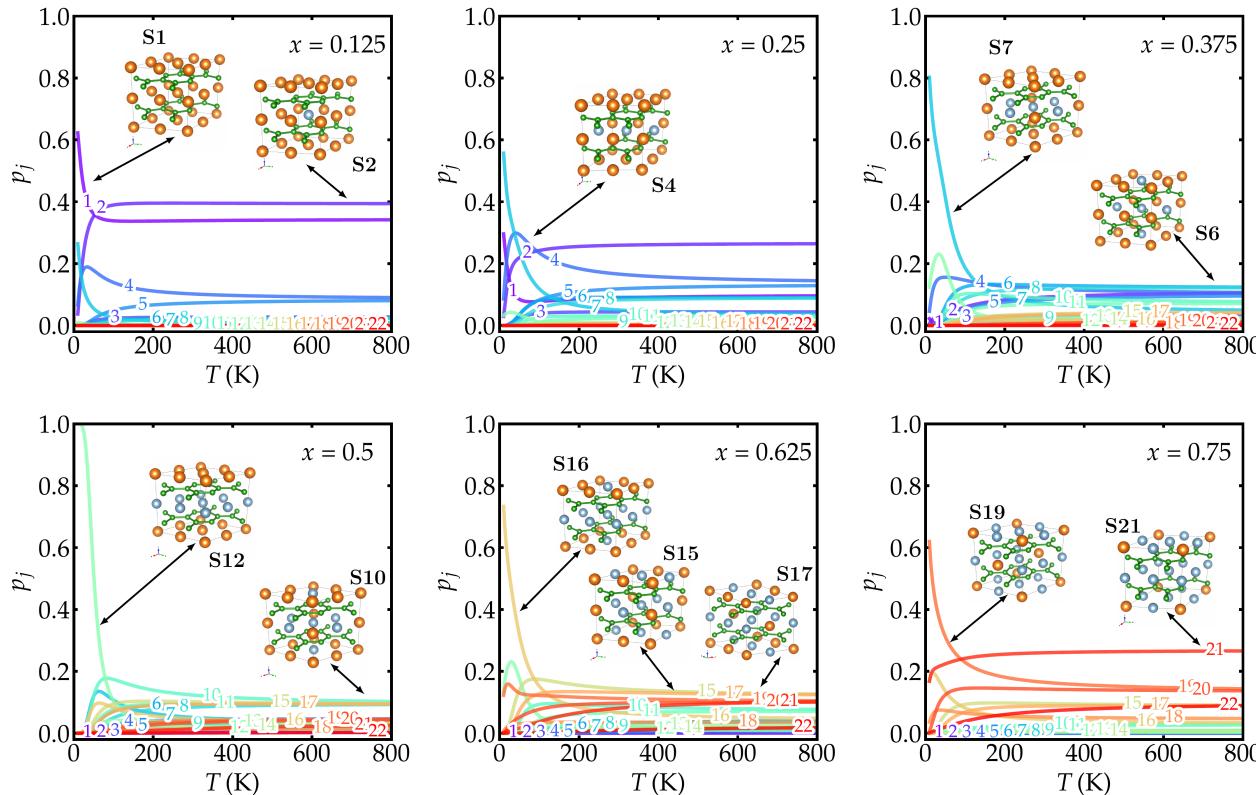


Figure 11: Cluster probabilities for selected compositions

Thermodynamic functions

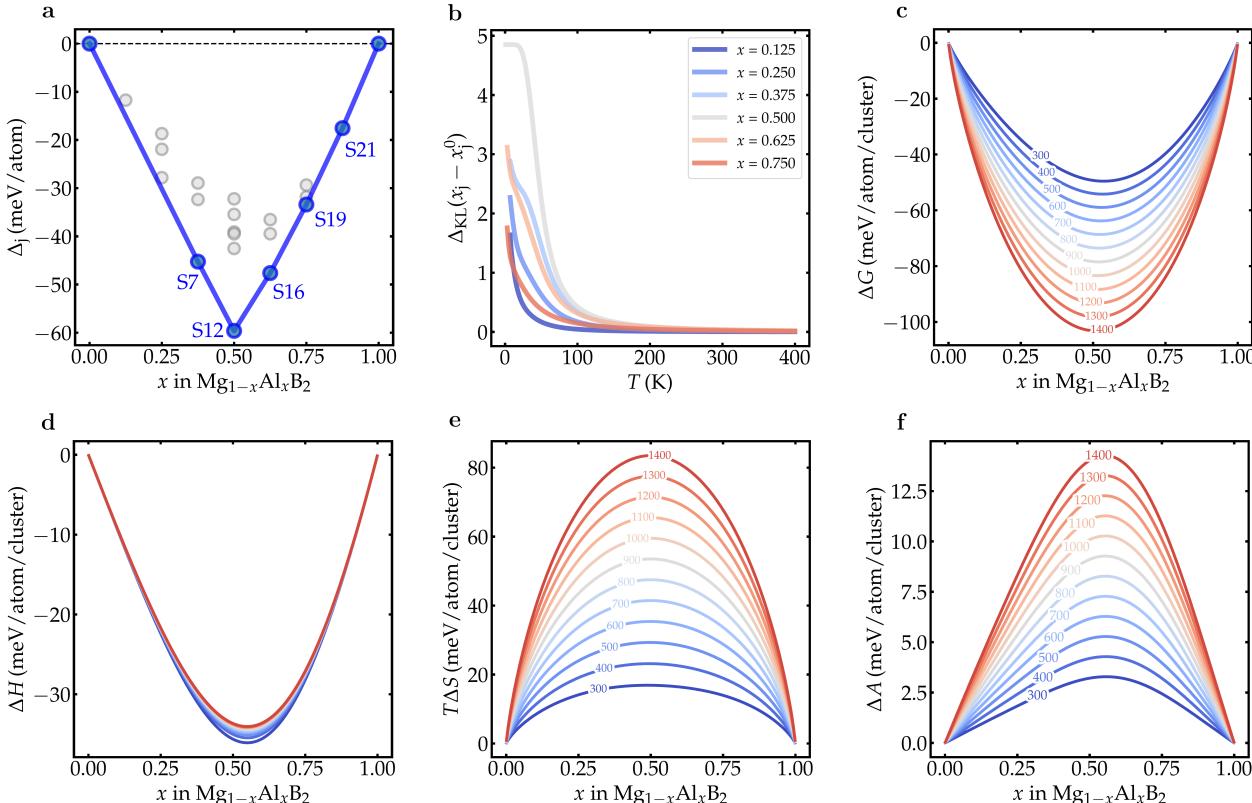


Figure 12: EGQCA Kullback-Leibler divergence and thermodynamic functions

Lattice parameters and T_c

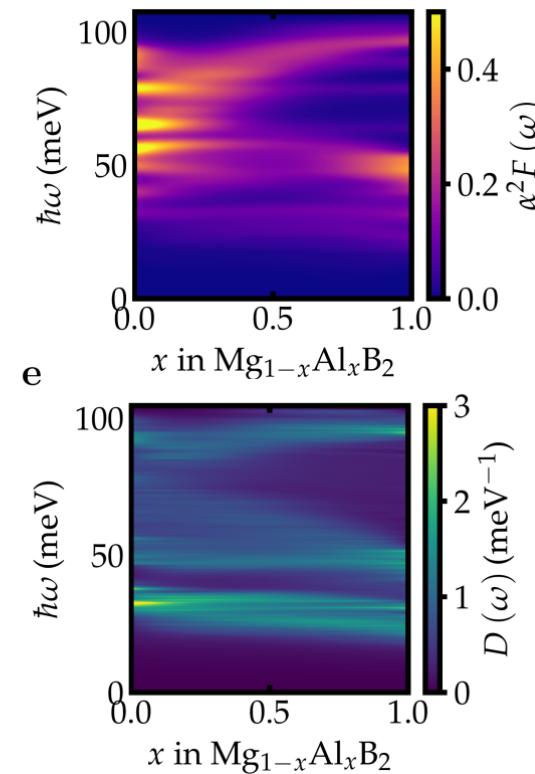
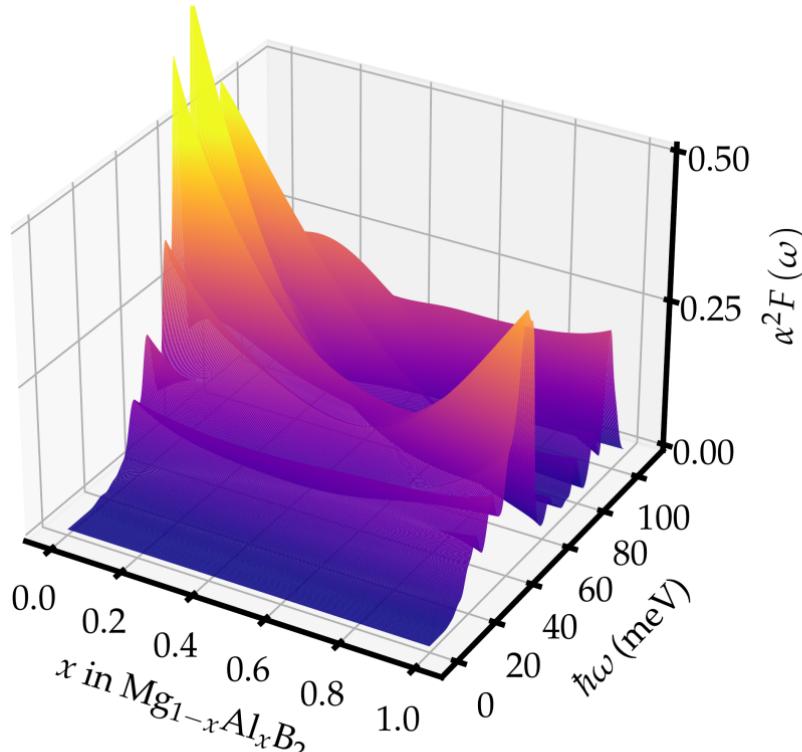


Figure 13: Eliashberg function and phonon spectra

Lattice parameters and T_c

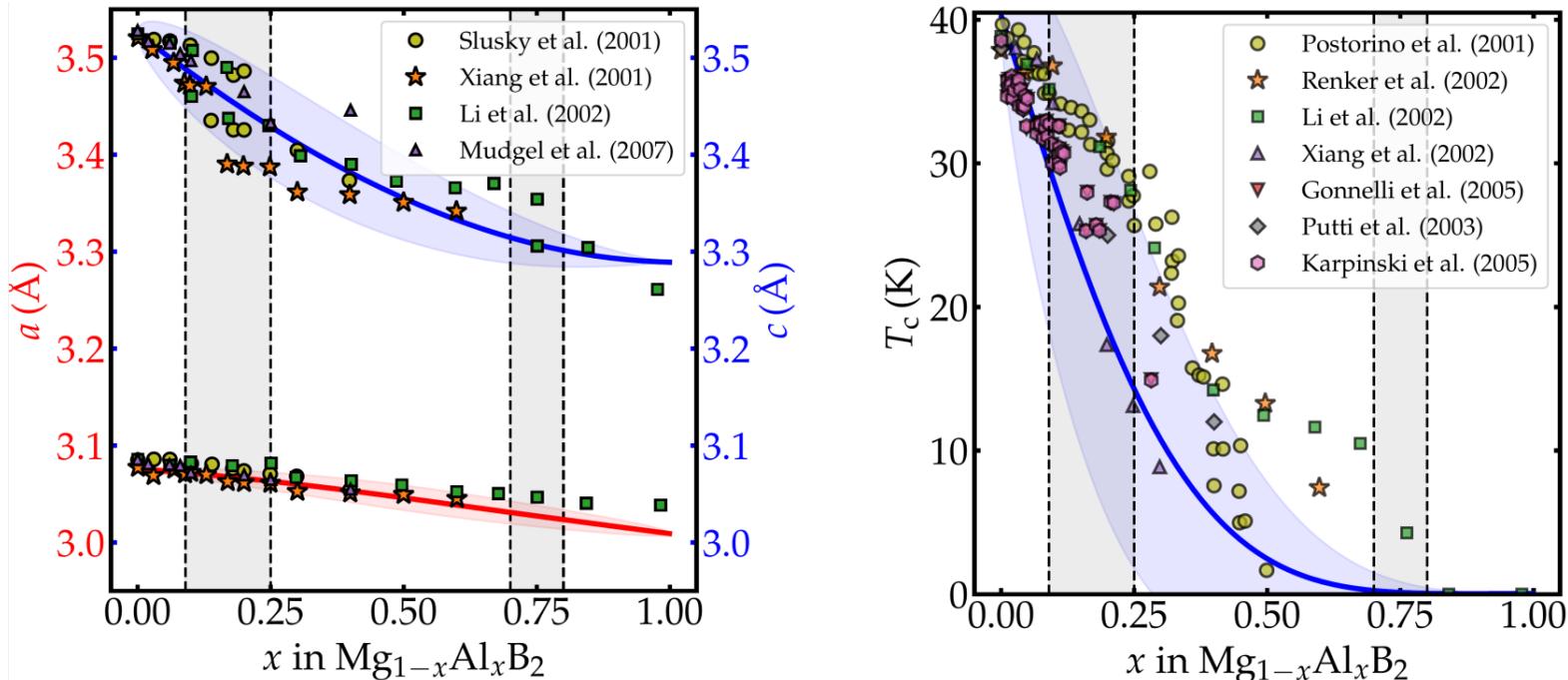


Figure 14: Lattice parameters and critical temperature for $\text{Al}_{1-x}\text{Mg}_x\text{B}_2$

- For T_c , a linear dependence on μ^* was adopted, based on the end-member values
- Gray regions are experimentally-found two-phase regions

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Nb-Ti bcc solid solution

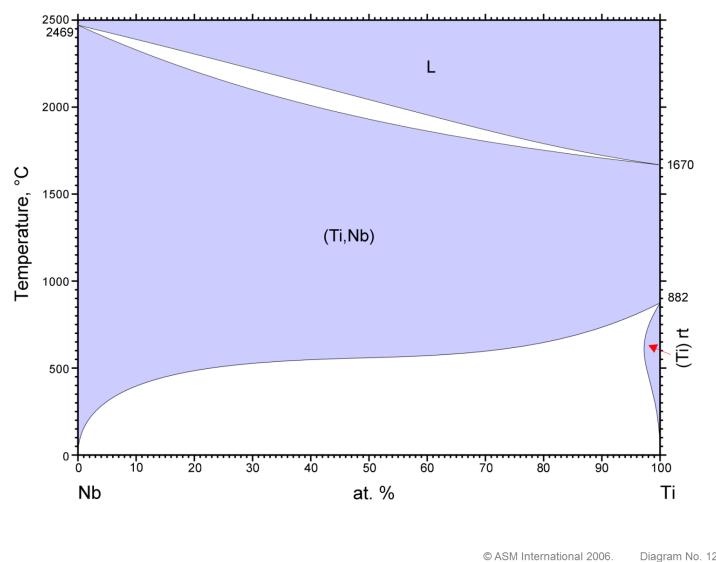


Figure 15: Nb-Ti equilibrium phase diagram

- EQQCA requires phonon calculations of mechanically unstable structures
- For instance, β -Ti, one of the end-members, is highly unstable at 0 K
- \Rightarrow GQCA used for bcc Nb-Ti alloys

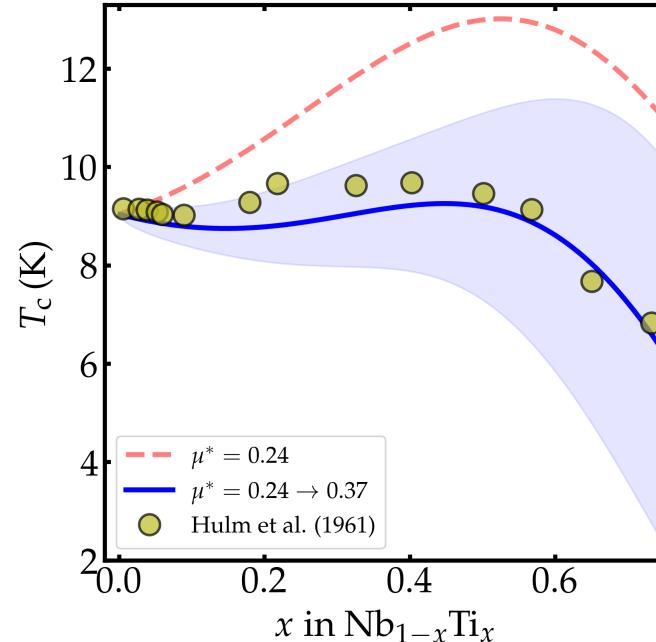


Figure 16: T_c for Nb-Ti alloys

- μ^* values either constant or linearly interpolated among stable clusters

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Nb-V solid solution

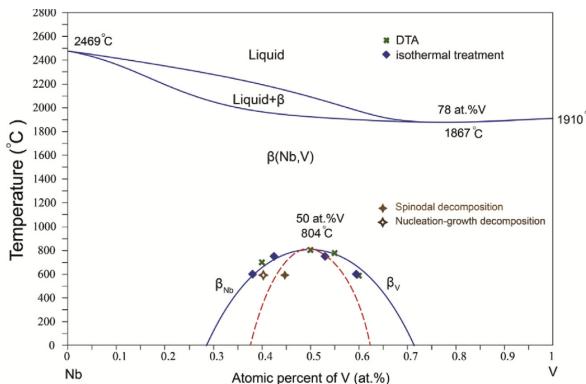


Figure 17: Experimental (J. Gao et al. J. Alloys Compd. 768 316 2018)

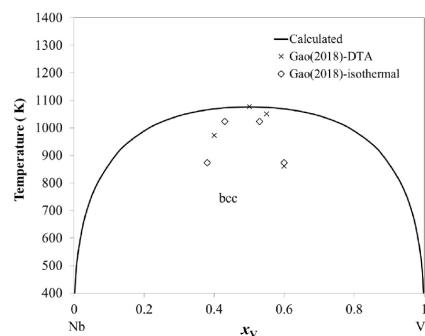


Figure 18: CE-CVM (S. Kumar et al. Calphad 78 102439 2022)

■ EGQCA:

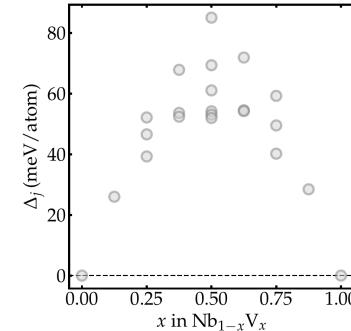


Figure 19: Excess enthalpies

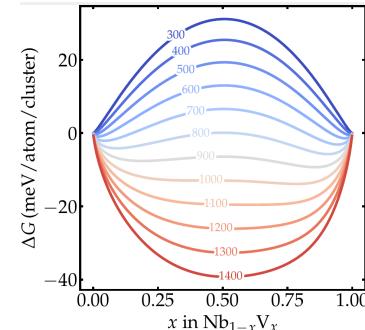


Figure 20: Free energy

Nb-V results

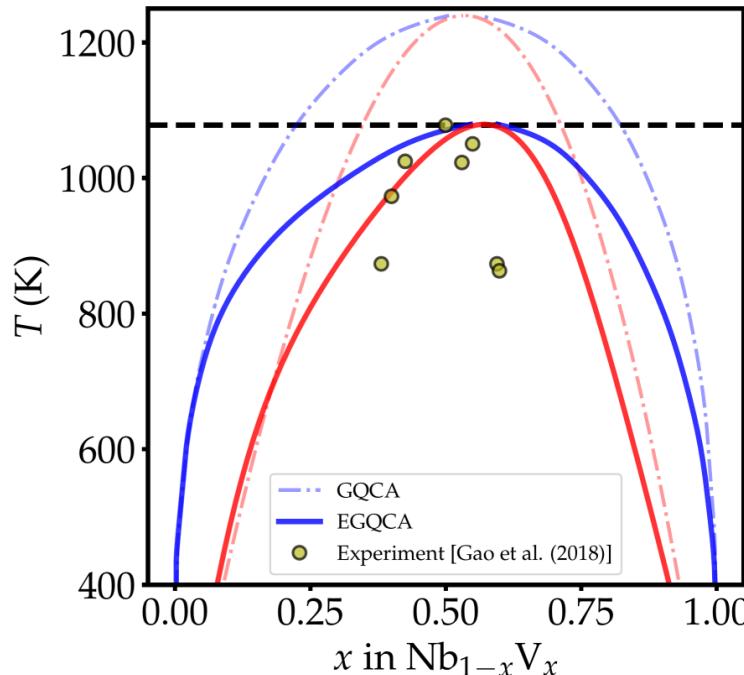


Figure 21: Influence of phonon free energy on phase diagram

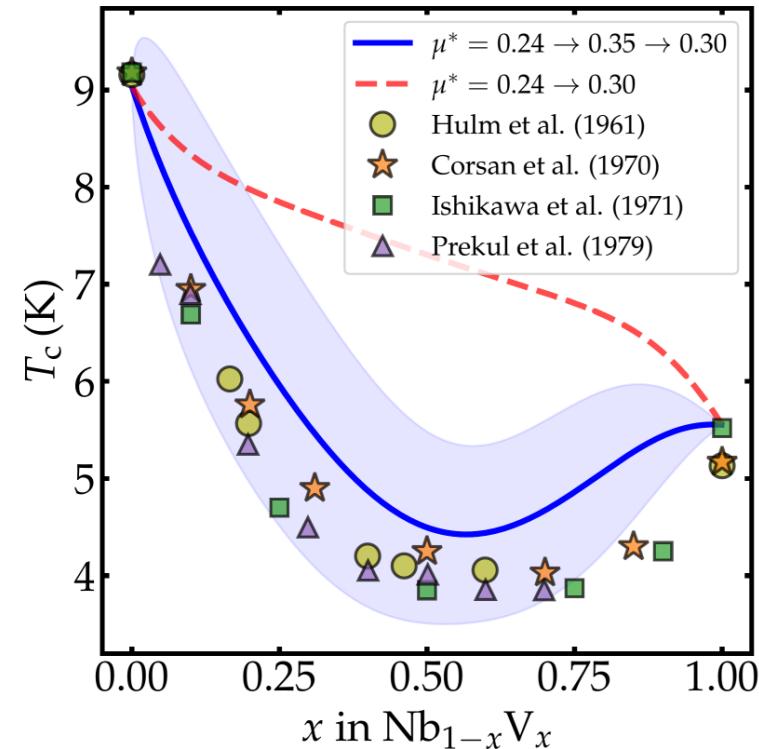


Figure 22: Possibility of thermodynamically model $\mu^*(x)$, instead of highly difficult calculations for disordered alloys

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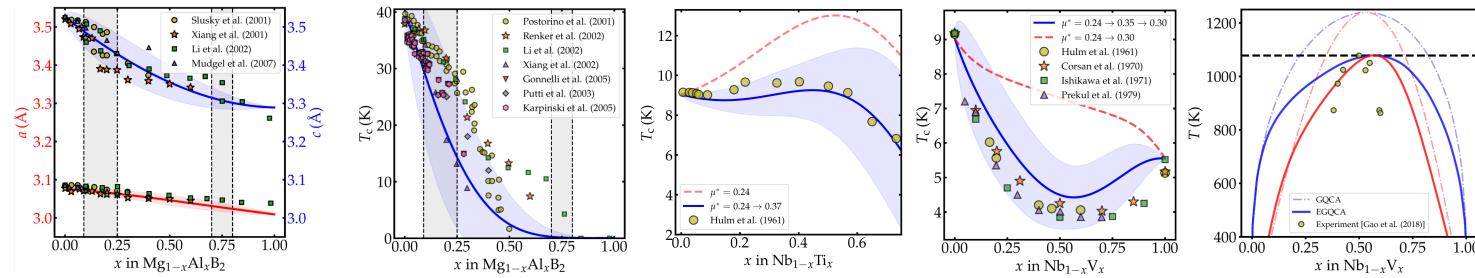
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Conclusions



- P. N. Ferreira et al, “*Ab initio modeling of superconducting alloys*” **Materials Today Physics** 48 101547 2024
<https://doi.org/10.1016/j.mtphys.2024.101547>
- Maybe in the near (or not-so-near?) future: SC thermodynamic databases

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<https://computeel.org>

