Impurity vibration modes in diluted semiconductor alloys

Andrei Postnikov and Olivier Pagès

Laboratoire de Physique des
Milieux Denses

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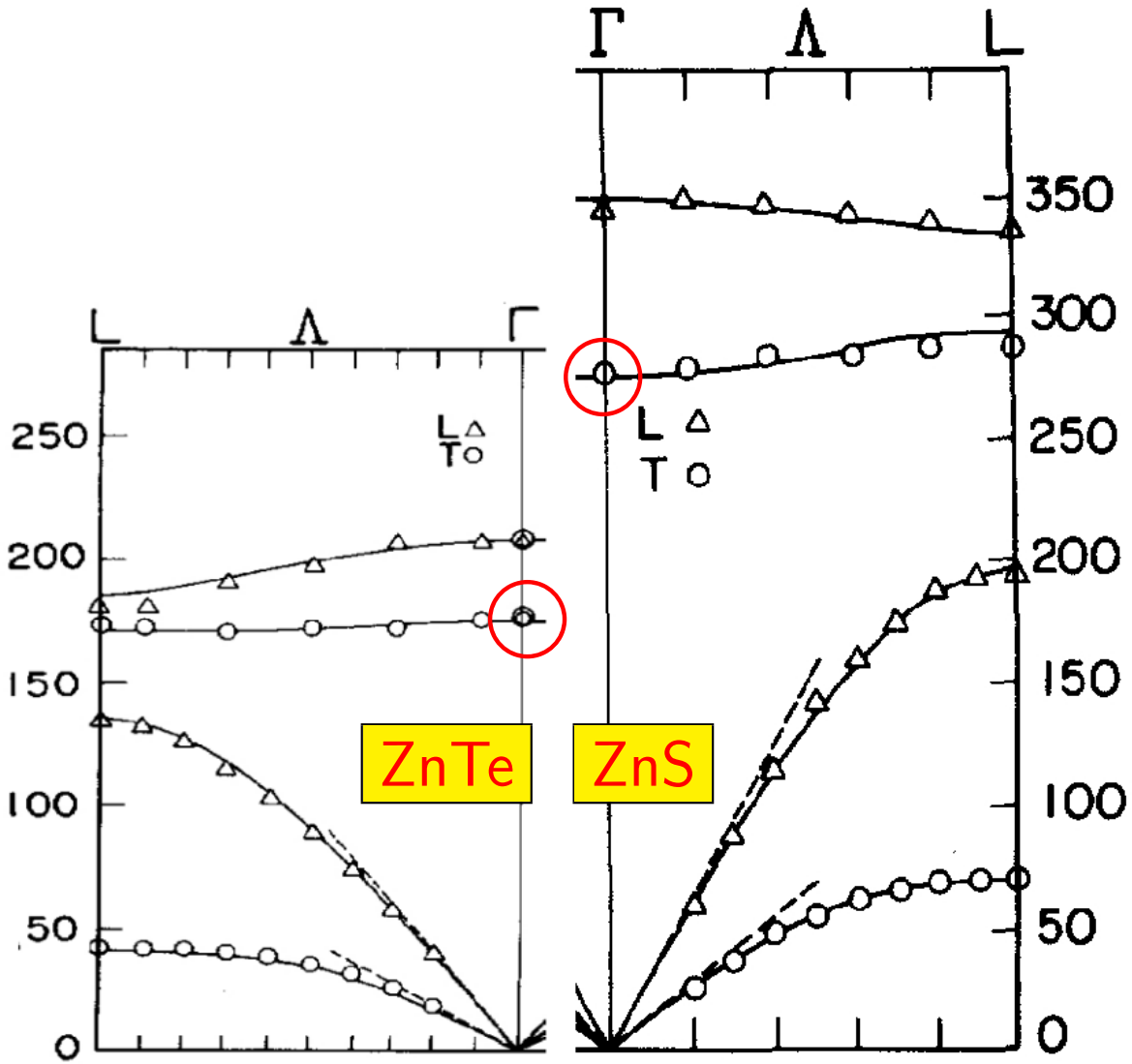
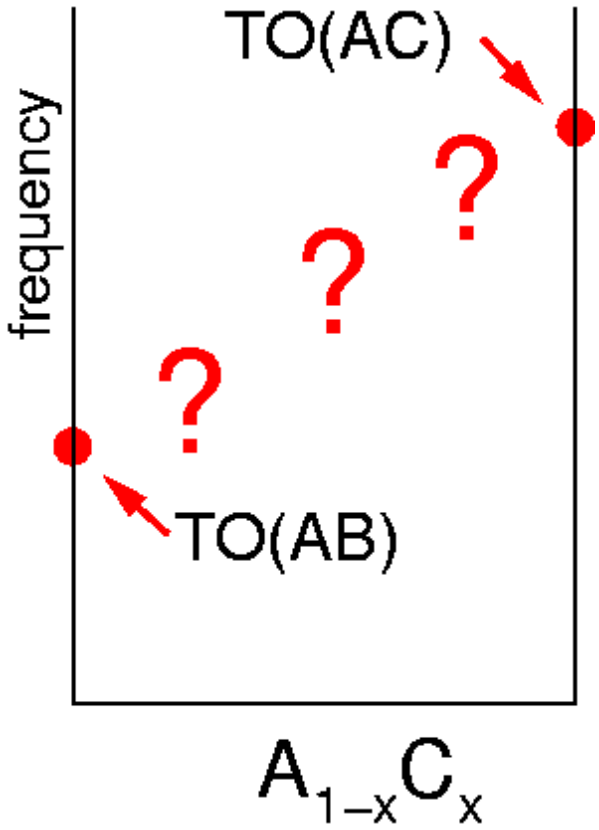
Introduction + Background

- Combined use of Raman spectroscopy (high resolution in the frequency domain) and *ab initio* phonon calculations (direct link between structure and vibrations spectrum) alloys to probe microstructure and ordering tendencies in semiconductor alloys.
- Impurity modes (to be compare with bulk modes) are important benchmarks in such studies.
- In the present contribution, we focus on single/double impurity modes only and leave away other problematic issues (concentrations fluctuations, ordering, ...).
- *Ab initio* calculations with the LDA, pseudopotentials, either finite-displacement [SIESTA: (Zn,Be)Se, (Ga,In)As, (Ga,In)P] or linear responce [PWSCF: Zn(Se,Te)]; 64-atom supercells

Γ-TO frequency on doping: how does it vary?





Modified-Random-Element-Isodisplacement

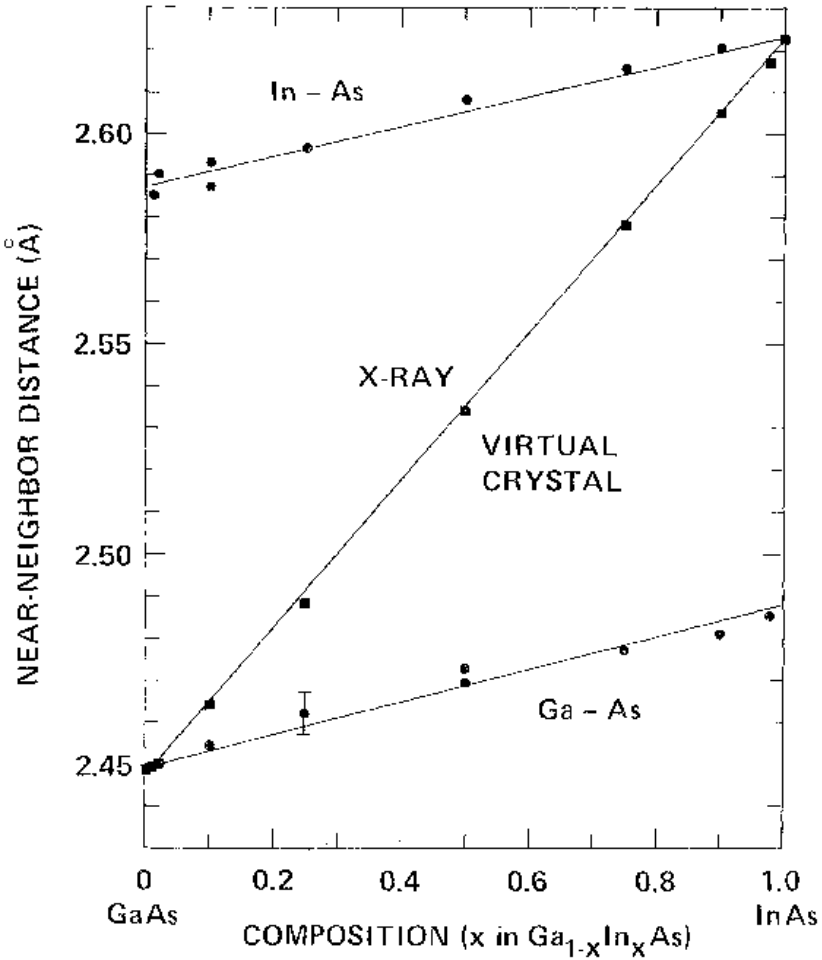


FIG. 2. Near-neighbor distances, Ga-As (lower curve) and In-As (upper curve), vs mole fraction InAs in the alloy $Ga_{1-x}In_xAs$. The average cation-anion spacing calculated from the measured lattice constant, namely, $3^{1/2}a_0/4$ (middle curve), is seen to accurately follow Vegard's Law.

J. C. Mikkelsen, Jr. and J. B. Boyce, EXAFS, PRL **49**, 1412 (1982):

"In random solid solutions of $Ga_{1-x}In_xAs$, the Ga–As and In–As near-neighbor distances change by only 0.04 Å as x varies from 0.01 to 0.99, despite the fact that the alloy accurately follows Vegard's law, with a change in average near-neighbor spacing of 0.17 Å. This result contradicts the underlying assumption of the virtual-crystal approximation."

Modified-Random-Element-Isodisplacement

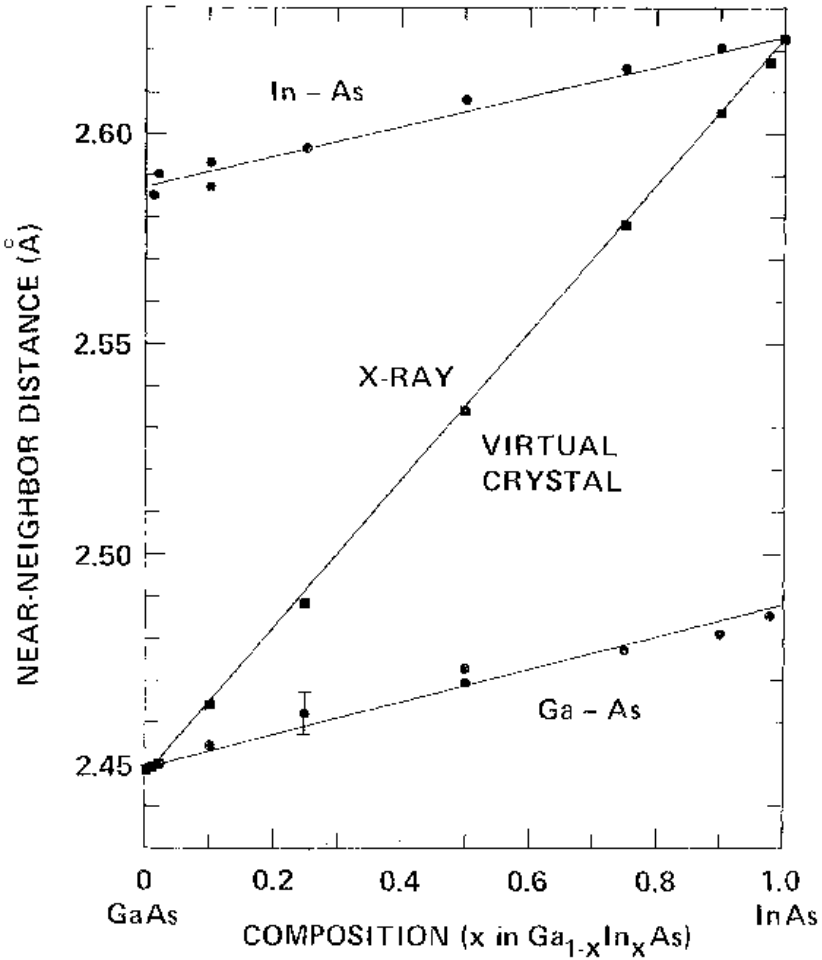
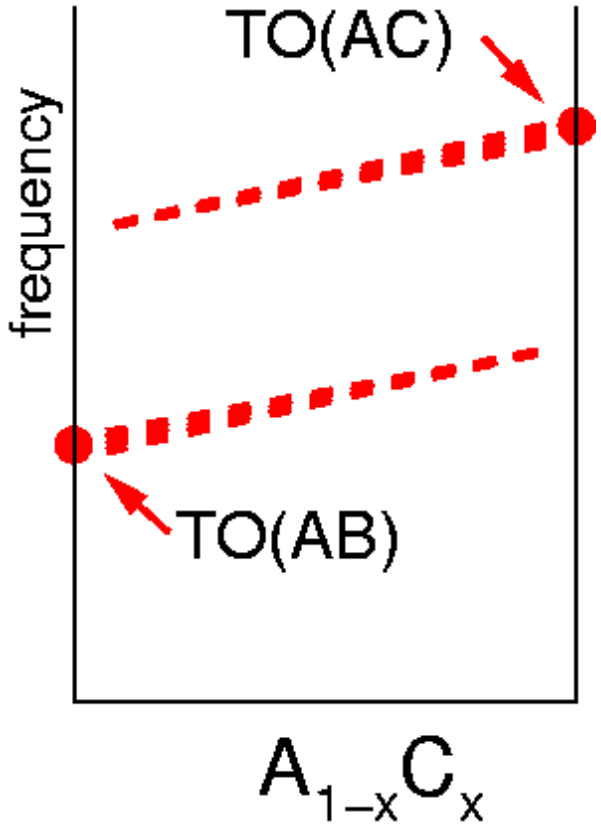


FIG. 2. Near-neighbor distances, Ga-As (lower

follow Vegard's Law.

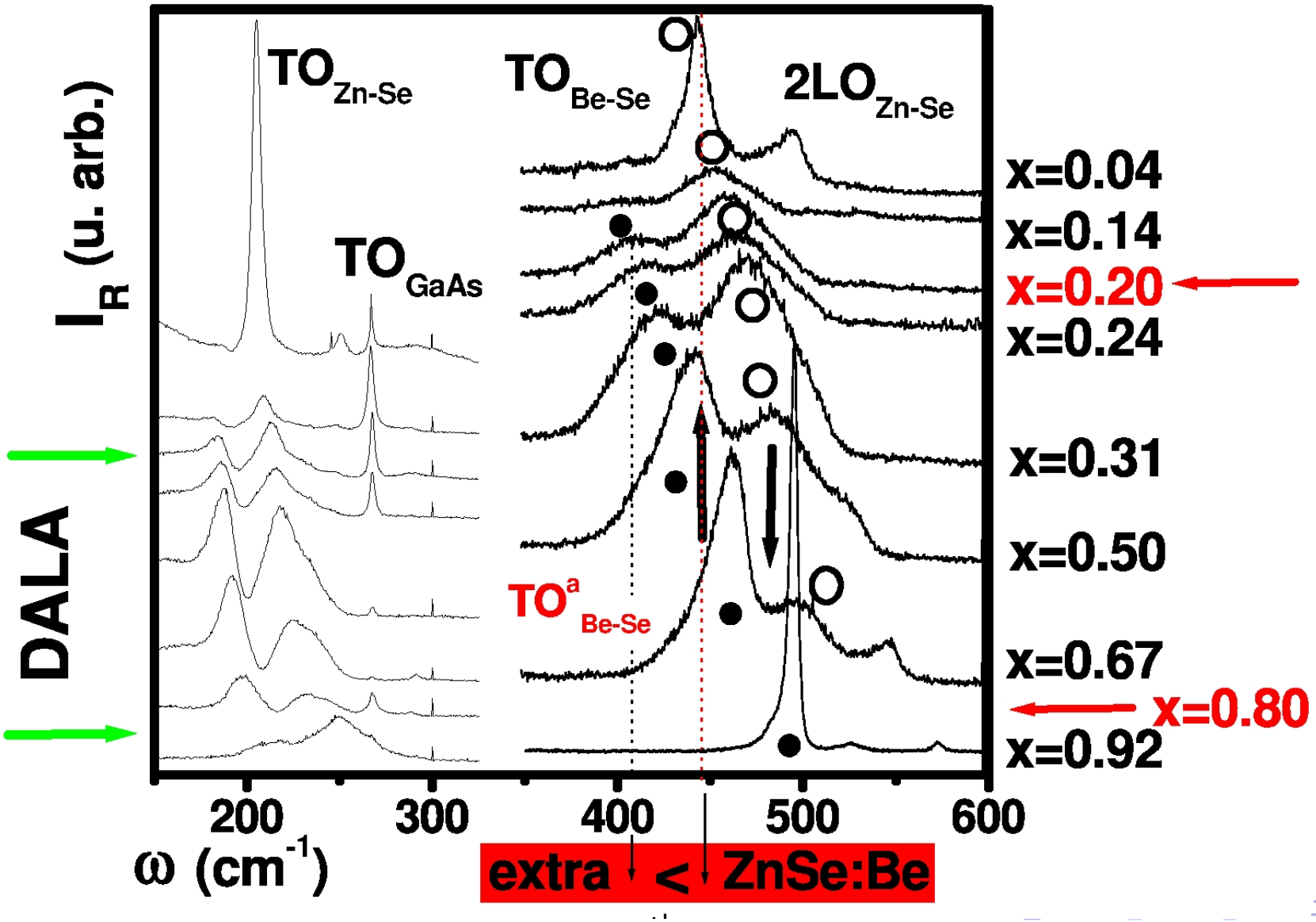
1-bond → 1-mode behaviour?



Individual cation-anion bonds tend to retain their lengths as in parent compounds. Average lattice constant changes linearily. On alloying, elastic contrast is reduced.

A realistic "one bond – two modes" situation in (Zn,Be)Se

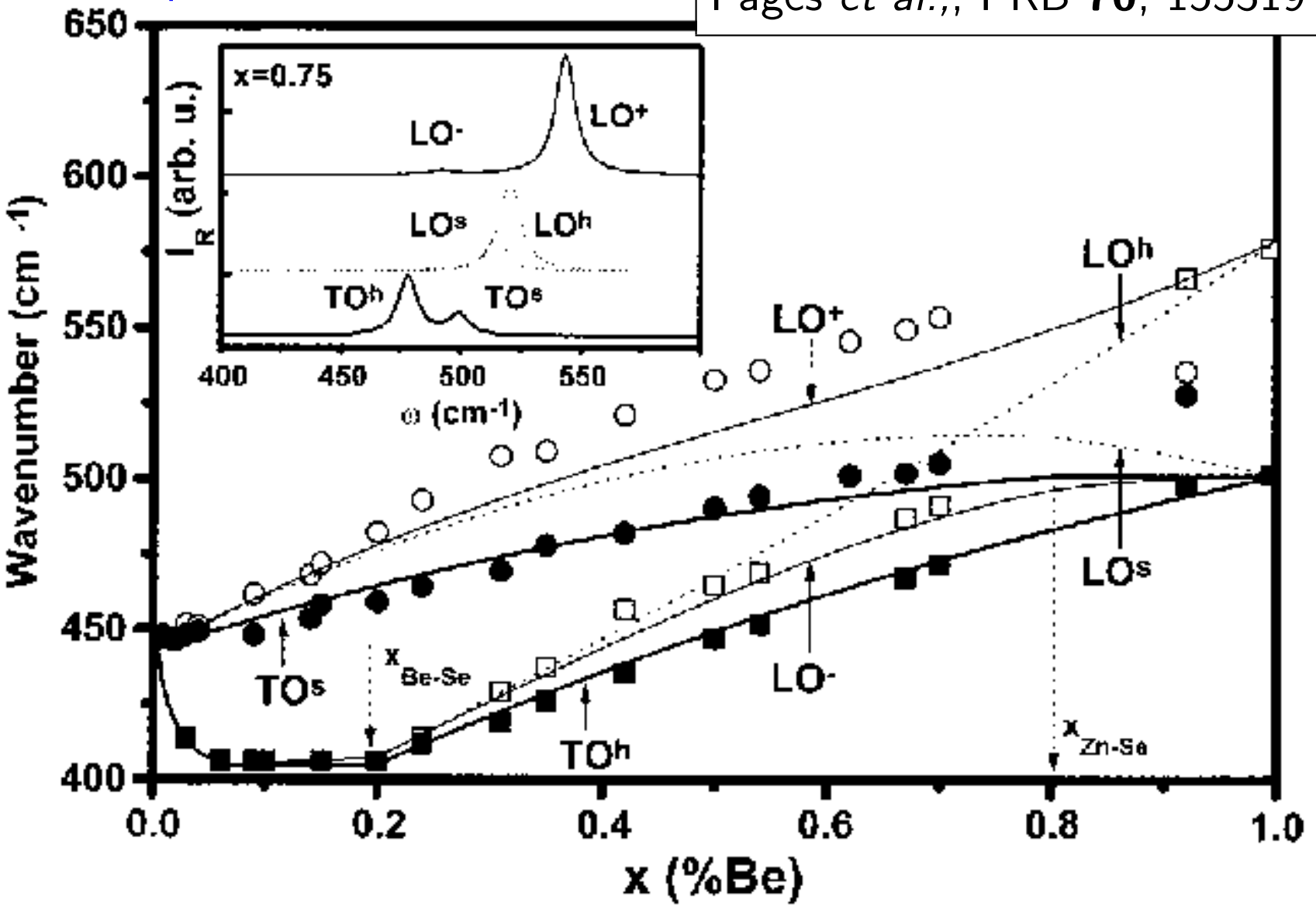
split modes in the TO_{Be-Se} branch



A realistic "one bond – two modes" situation in (Zn,Be)Se

position of peaks of the BeSe-branch

Pagès *et al.*,, PRB **70**, 155319 (2004)

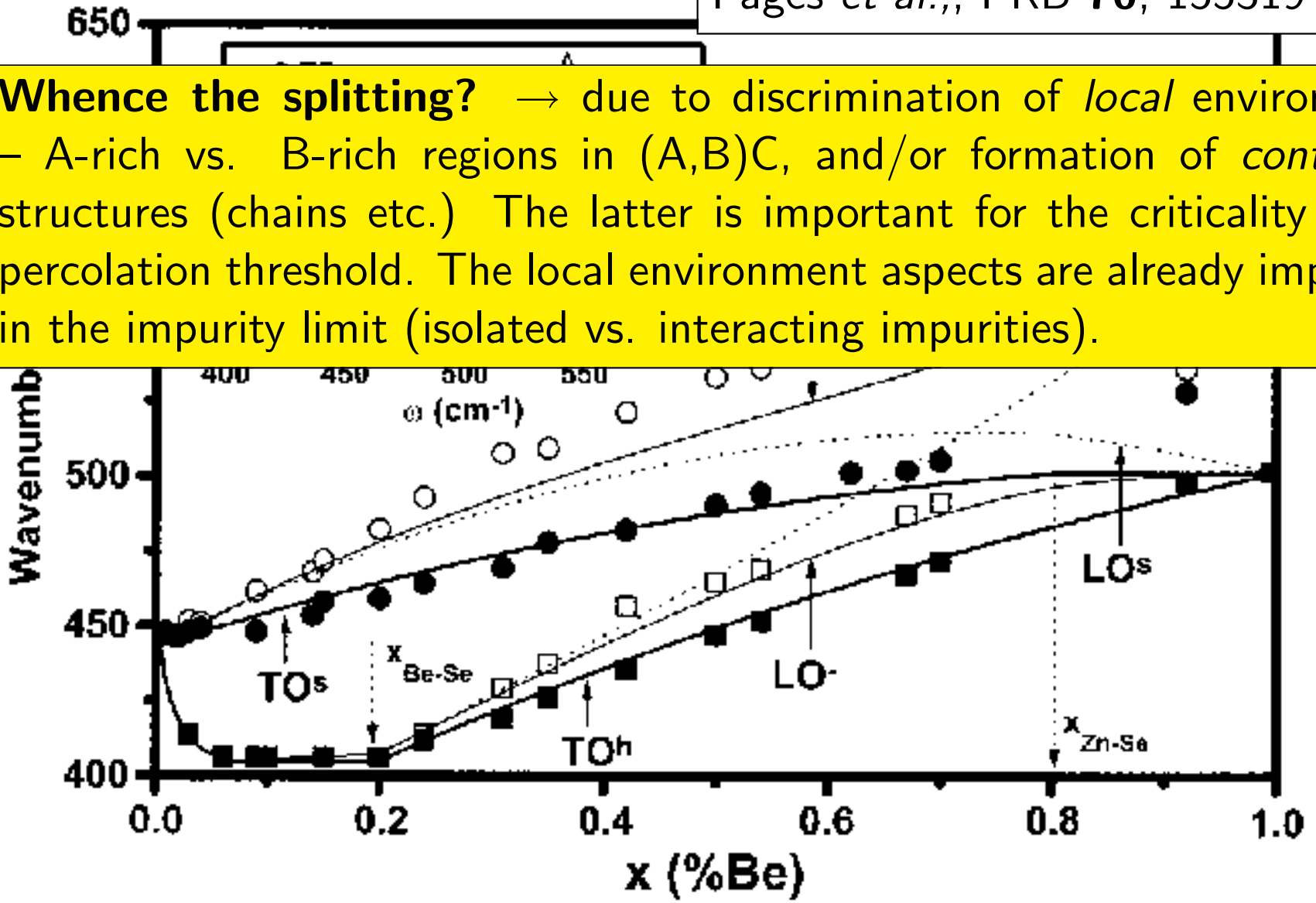


A realistic "one bond – two modes" situation in (Zn,Be)Se

position of peaks of the BeSe-branch

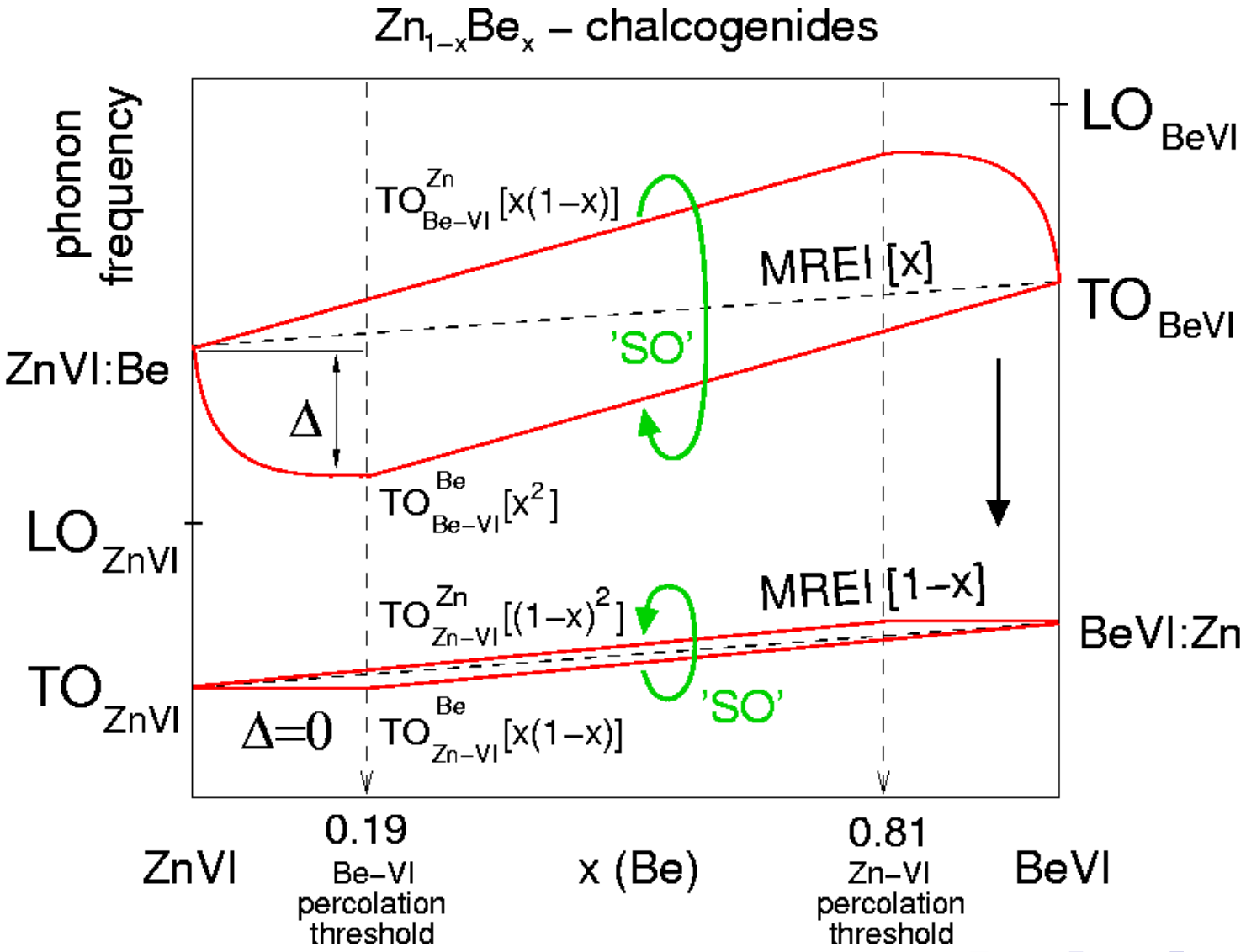
Pagès *et al.*,, PRB **70**, 155319 (2004)

Whence the splitting? → due to discrimination of *local* environments – A-rich vs. B-rich regions in (A,B)C, and/or formation of *continuous* structures (chains etc.) The latter is important for the criticality at the percolation threshold. The local environment aspects are already important in the impurity limit (isolated vs. interacting impurities).



A realistic "one bond – two modes" situation in (Zn,Be)Se

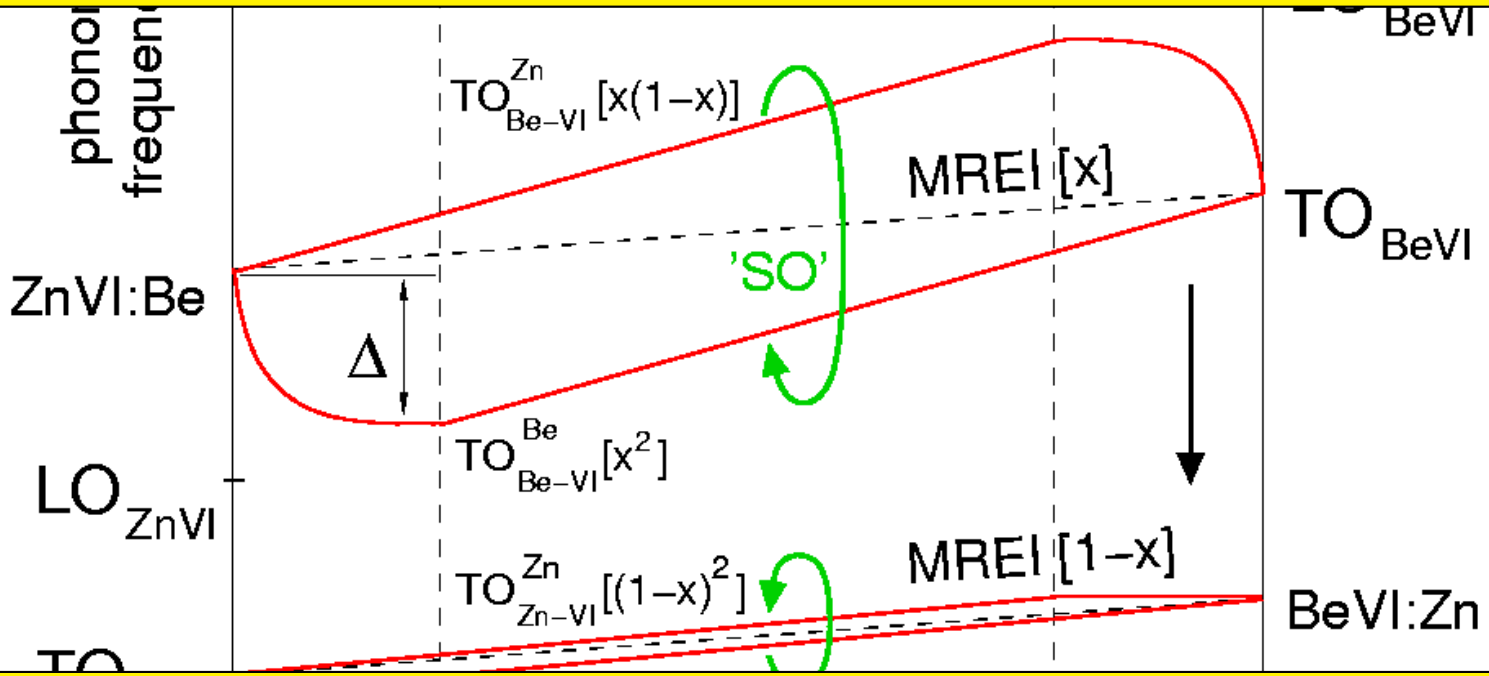
general scheme of mode coupling



A realistic "one bond – two modes" situation in (Zn,Be)Se

general scheme of mode coupling

Details of the "one bond – two modes" → percolation model and ordering tendencies will be addressed in the talk by Olivier Pagès.



For a phenomenological description of Raman spectra in alloys (superposition of multiple oscillators), one needs frequencies of the impurity modes and the Δ parameter, in both dilution limits. They can be obtained from *ab initio* calculation.

Immediate results of *ab initio* phonon calculations

In the following, we treat large supercells (64 atoms) and limit ourselves to $\mathbf{q}$=0 *of the supercell*. Vibrational density of states:

$$I_{\aleph}(\omega) = \sum_{\alpha \in \aleph} \sum_{i} |A_i^{\alpha}(\omega)|^2$$

with $A_i^{\alpha}(\omega)$: eigenvectors, $\aleph$: selected group of atoms α.
However, we'd like to keep trace on the $\mathbf{q}$-character of different vibrations, where $\mathbf{q}$ is wavevector *of the underlying cell*.

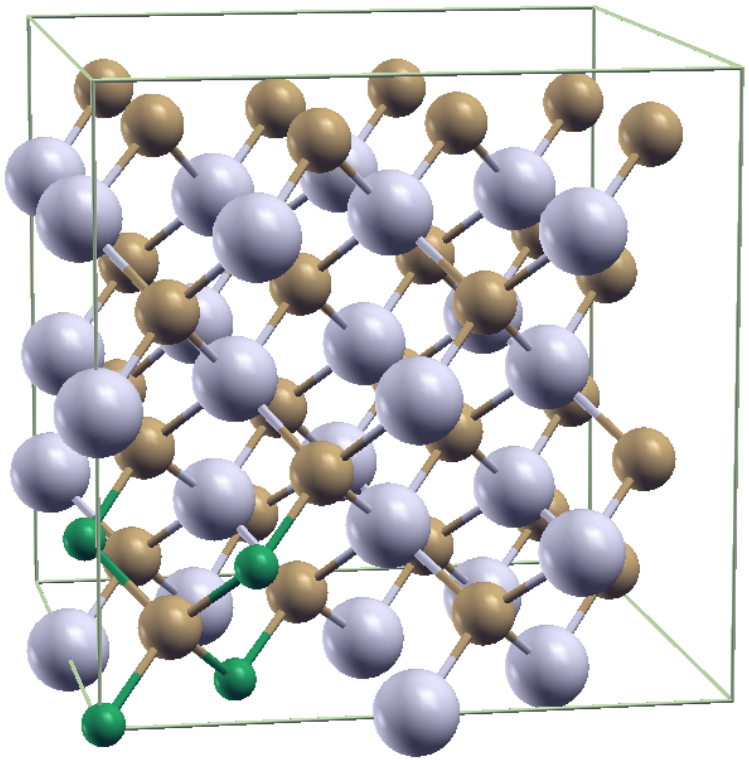
For an alloy, the neat dispersion relations $\omega(\mathbf{q})$ do not hold. Instead, we construct the *phonon spectral function*

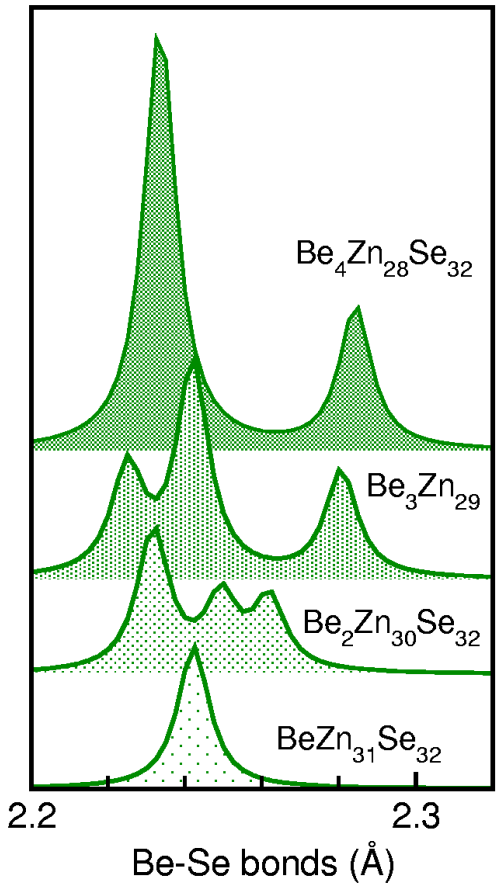
$$I_{\aleph}(\omega, \mathbf{q}) = \sum_{i} \left| \sum_{\alpha \in \aleph} A_i^{\alpha}(\omega) \exp(\mathbf{q}\mathbf{R}_{\alpha}) \right|^2$$

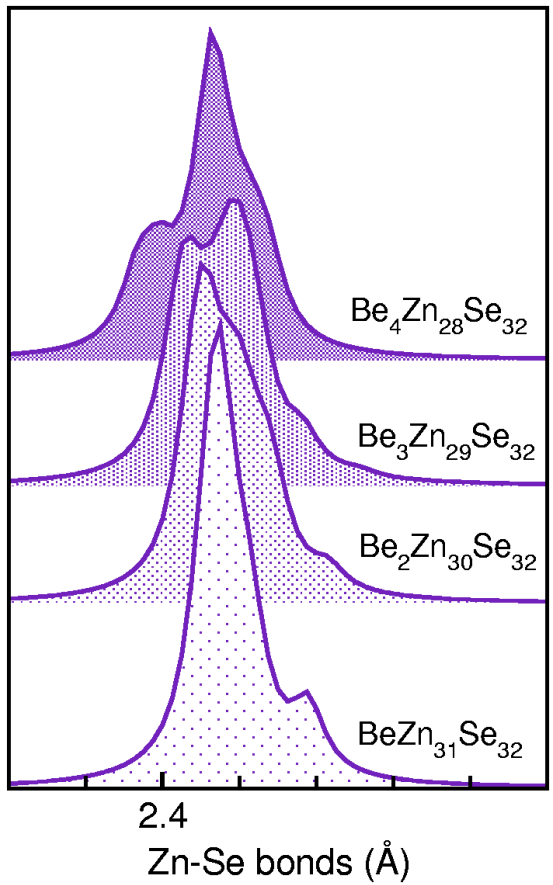
For comparison with Raman spectra, we look $I_{\aleph}(\omega, \mathbf{q} = 0)$.

$Be_xZn_{1-x}Se$: effect of Be clustering

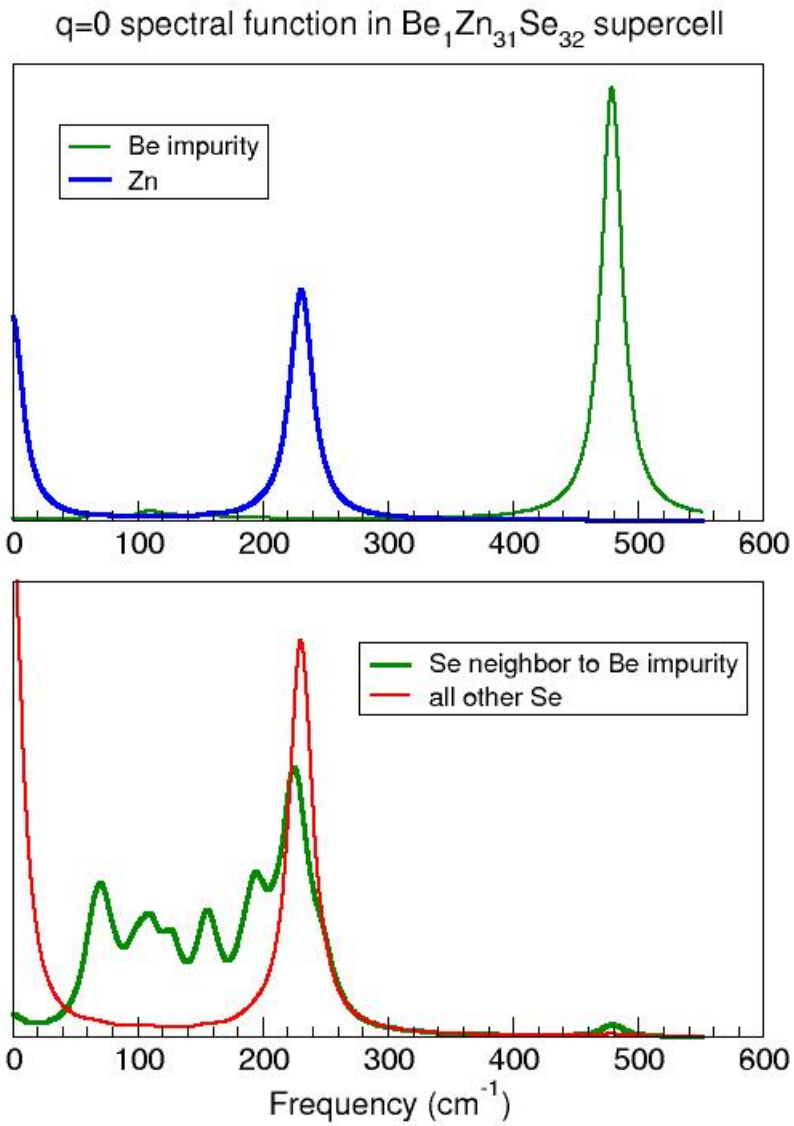
$Be_nZn_{32-n}Se_{32}$ supercells, n=1,2,3,4

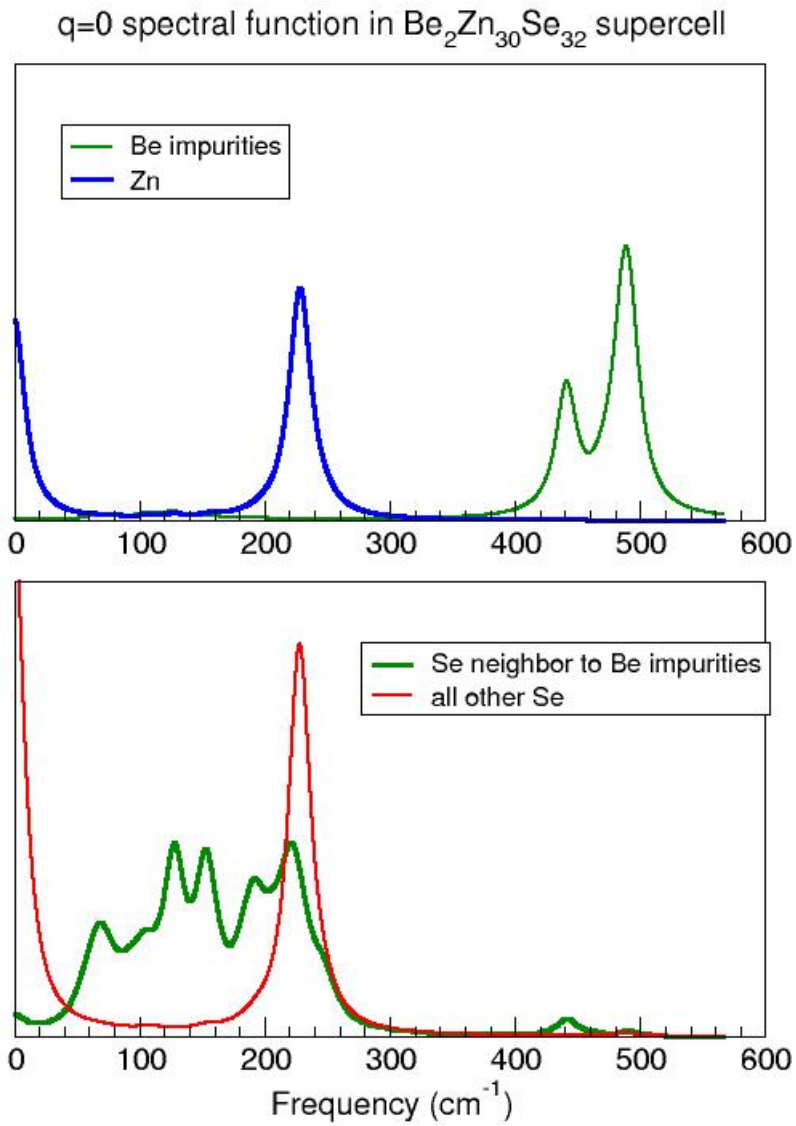




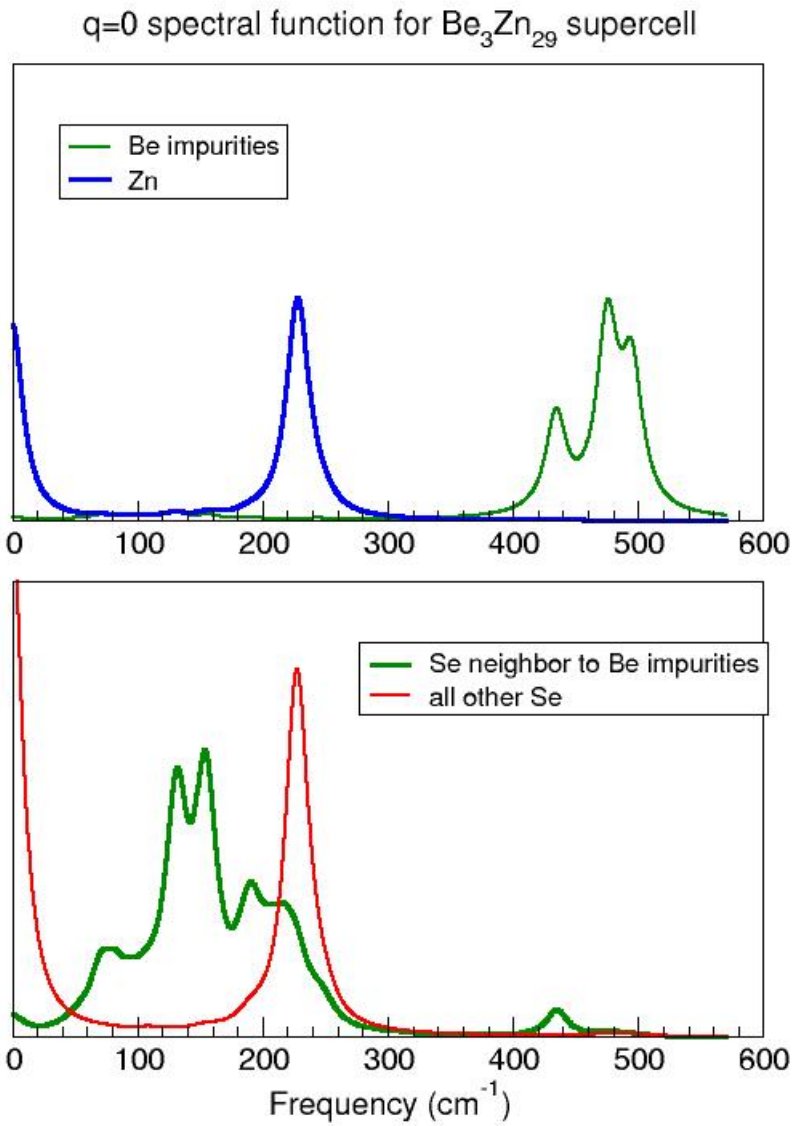


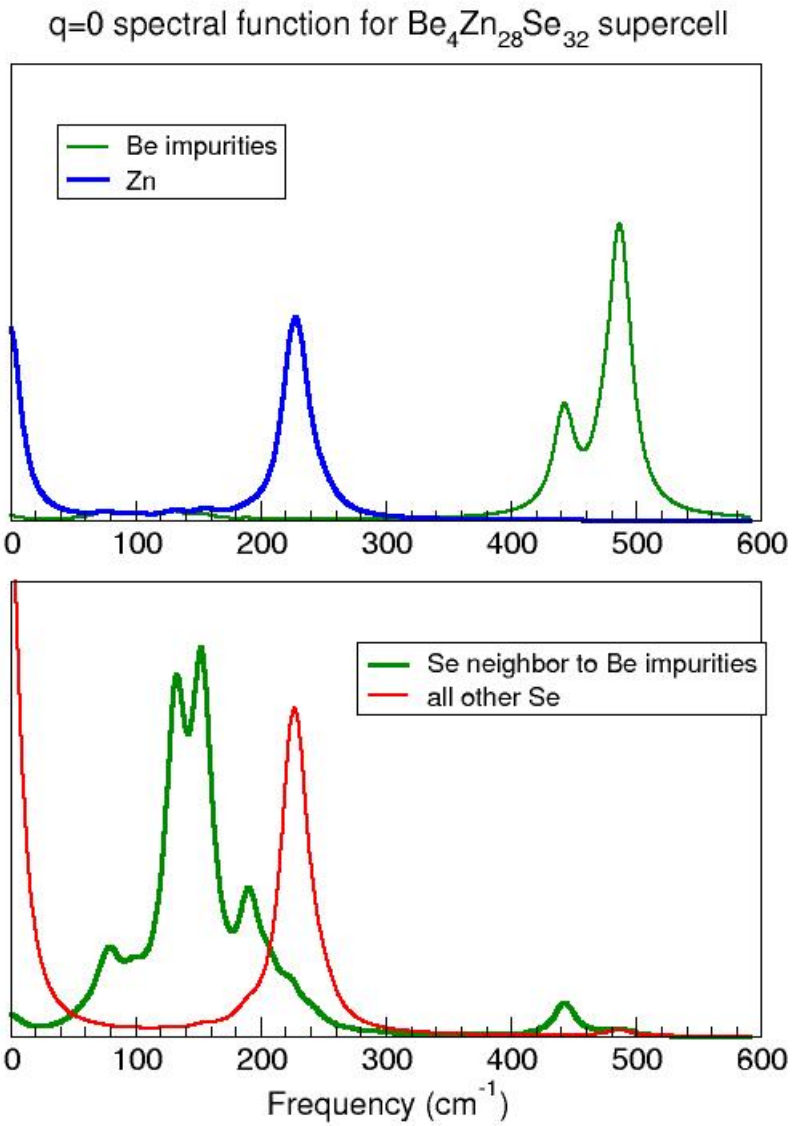
$Be_xZn_{1-x}Se$: effect of Be clustering



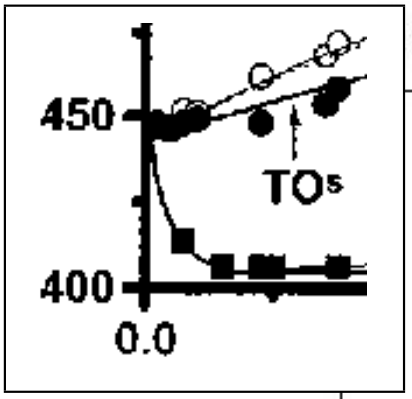


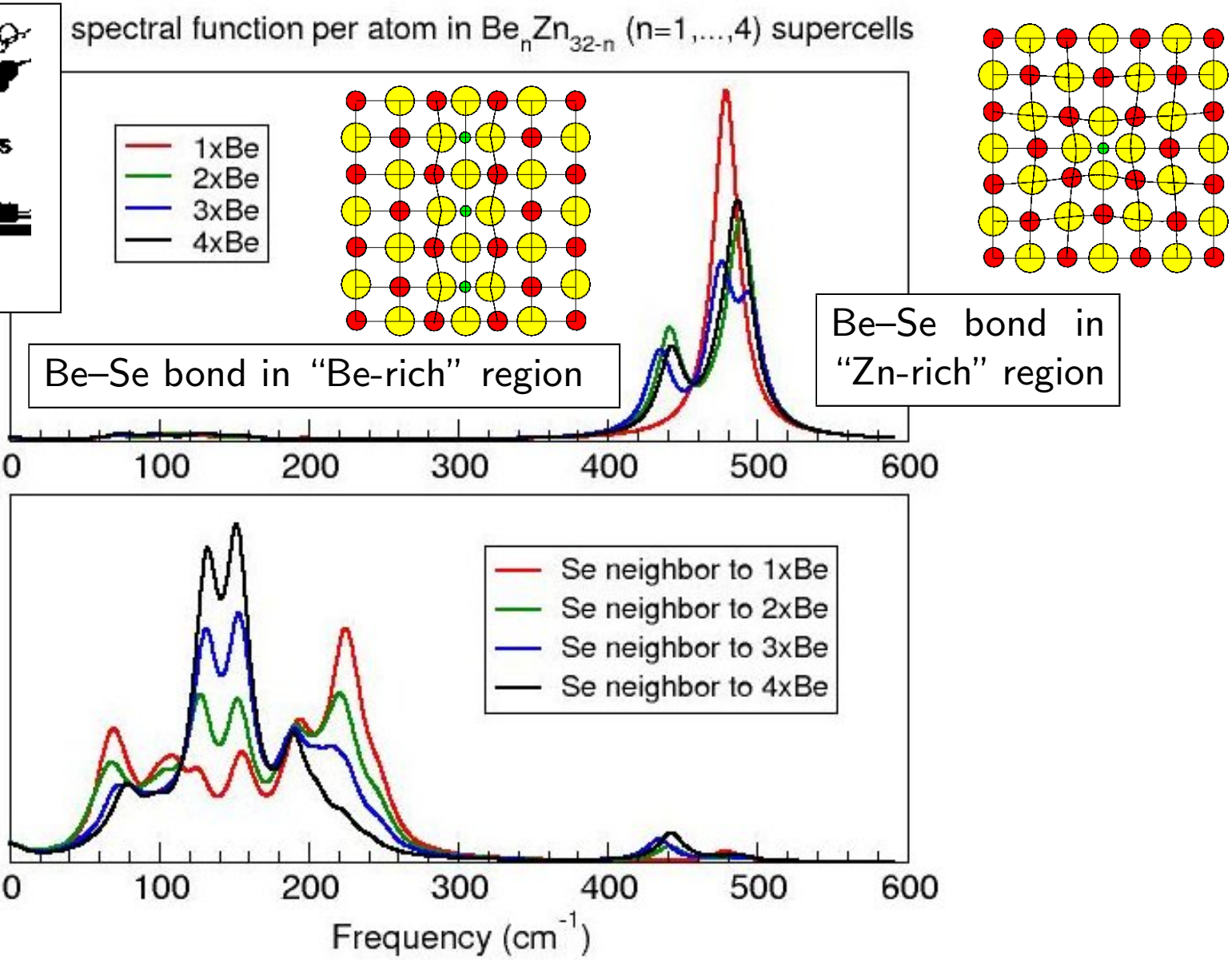
$Be_xZn_{1-x}Se$: effect of Be clustering



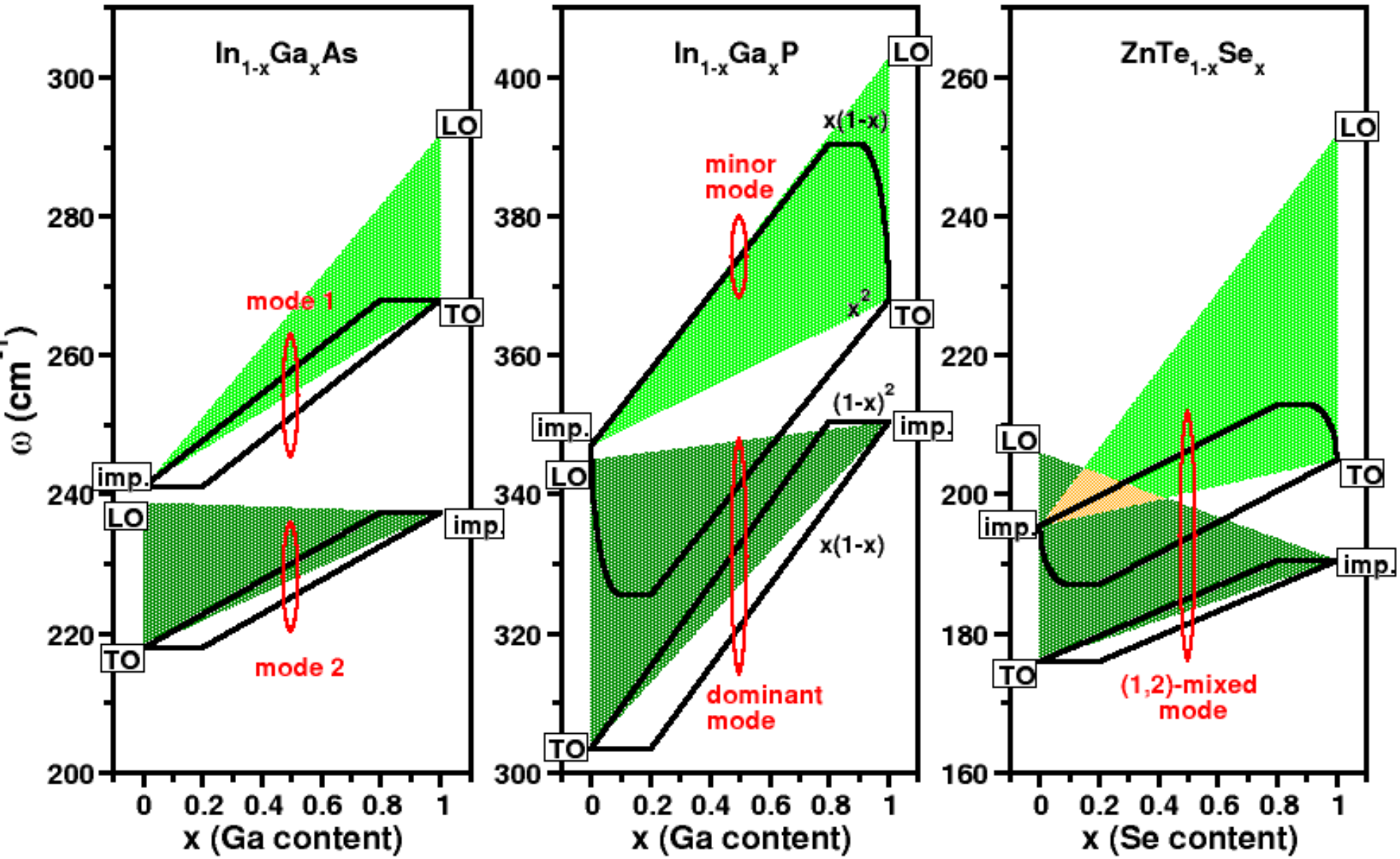


$Be_xZn_{1-x}Se$: effect of Be clustering

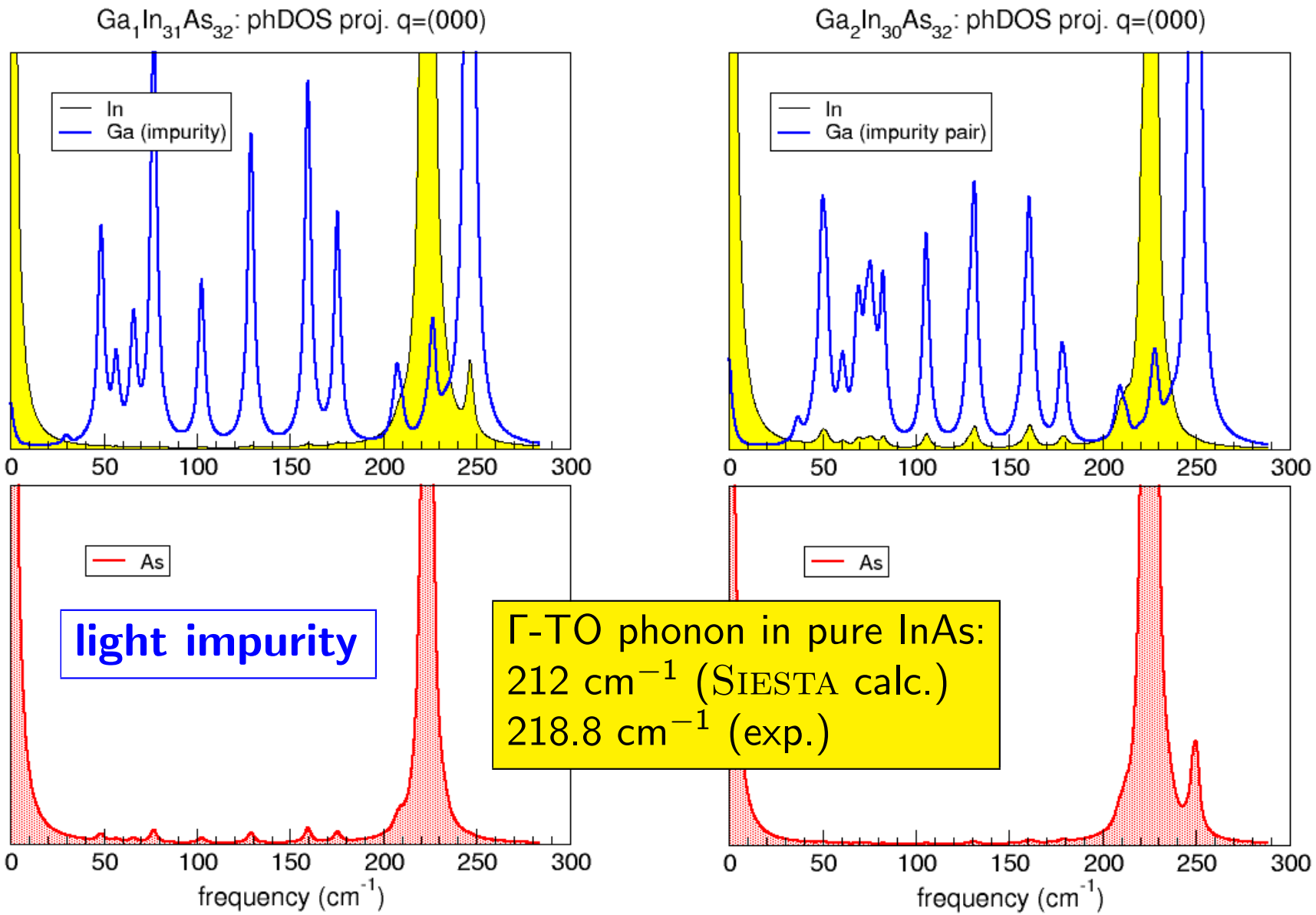




Unified description within the "percolation model"

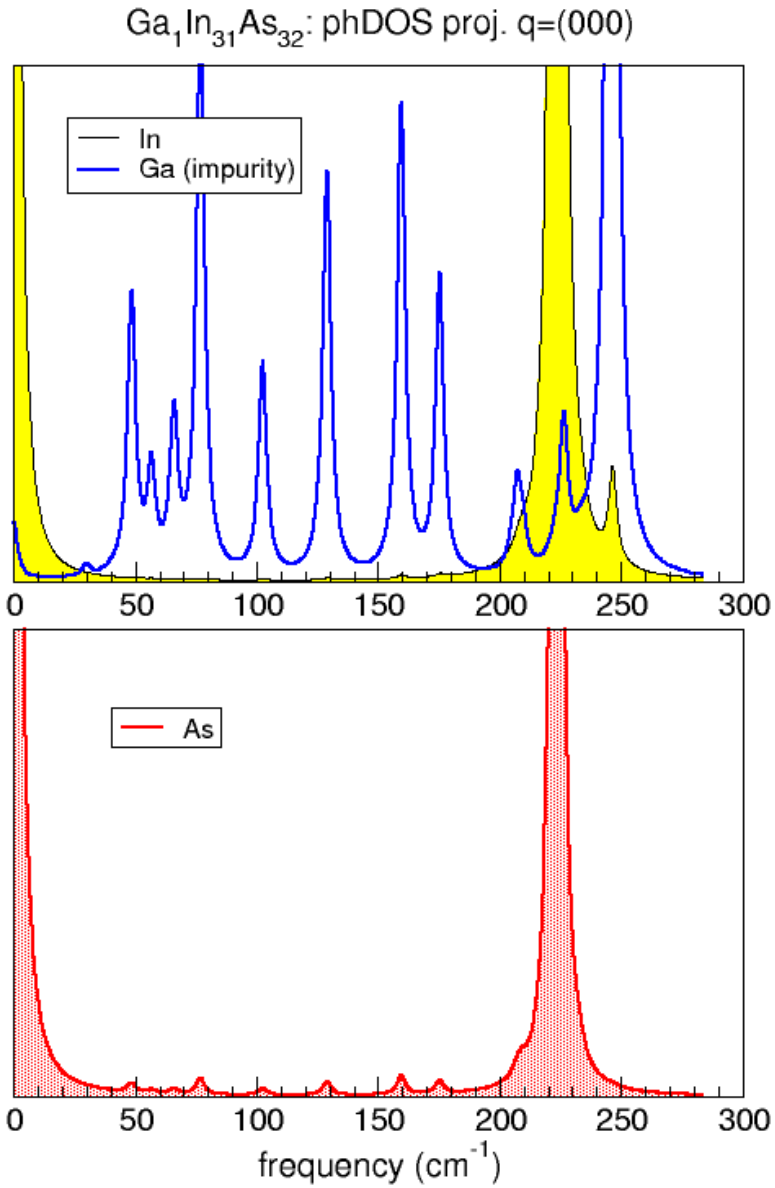


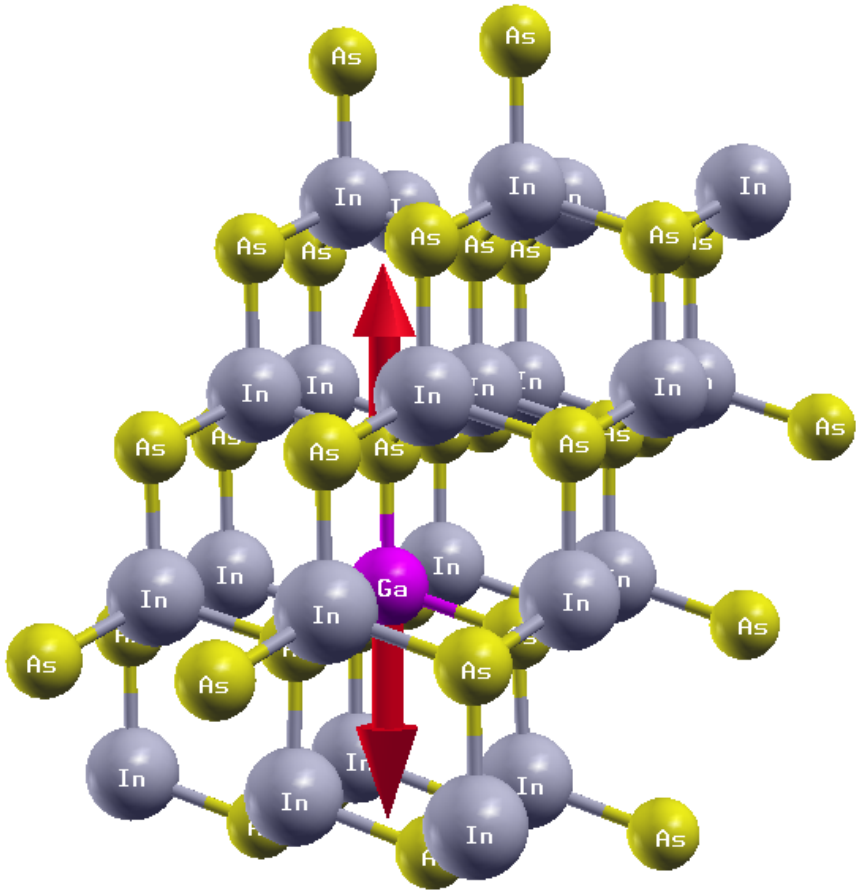
$Ga_xIn_{1-x}As$: $\mathbf{q}$=0 -projected phonon DOS



Γ-TO phonon in pure InAs:
212 cm^{-1} (SIESTA calc.)
218.8 cm^{-1} (exp.)

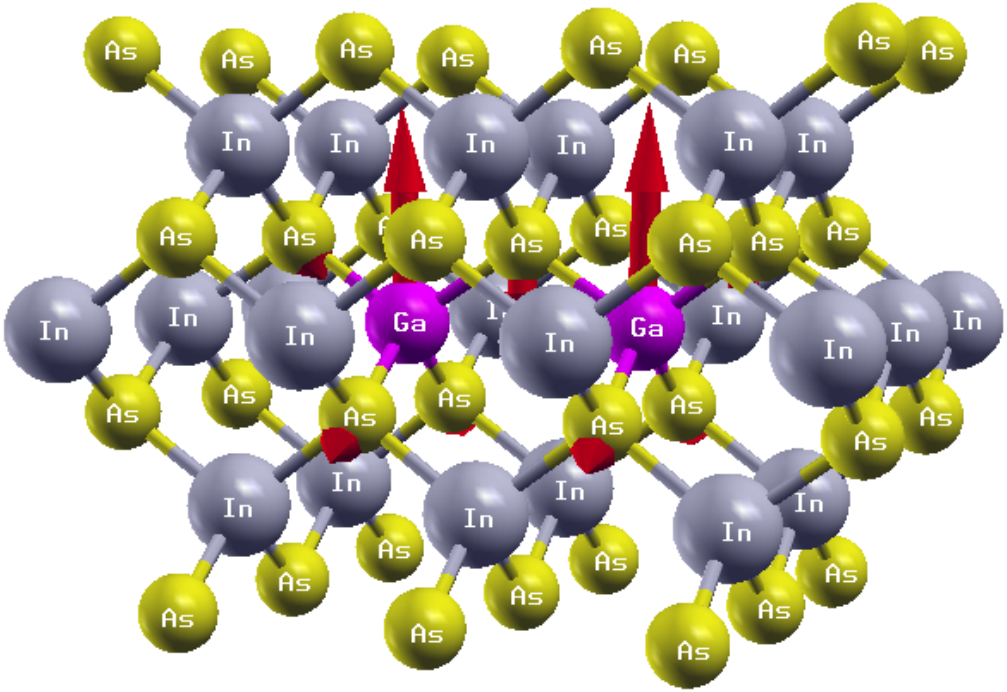
$Ga_xIn_{1-x}As$: **q**=0 impurity modes

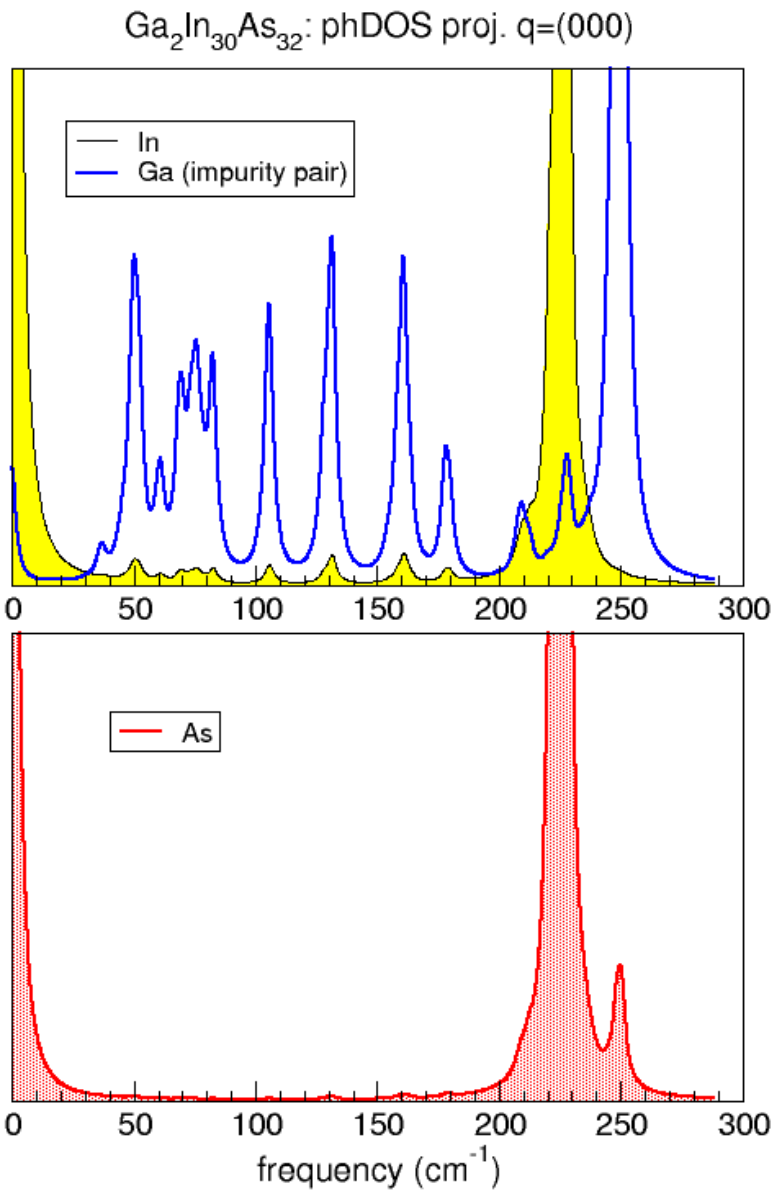




impurity modes #190–192,
ω=246 cm^{-1}

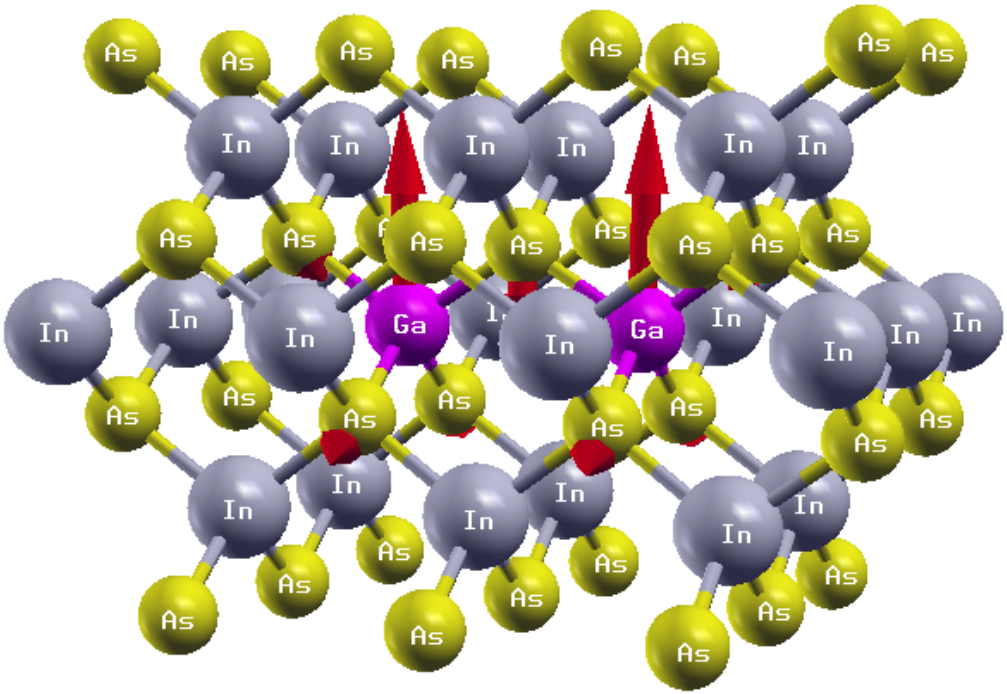
$Ga_xIn_{1-x}As$: **q**=0 impurity modes

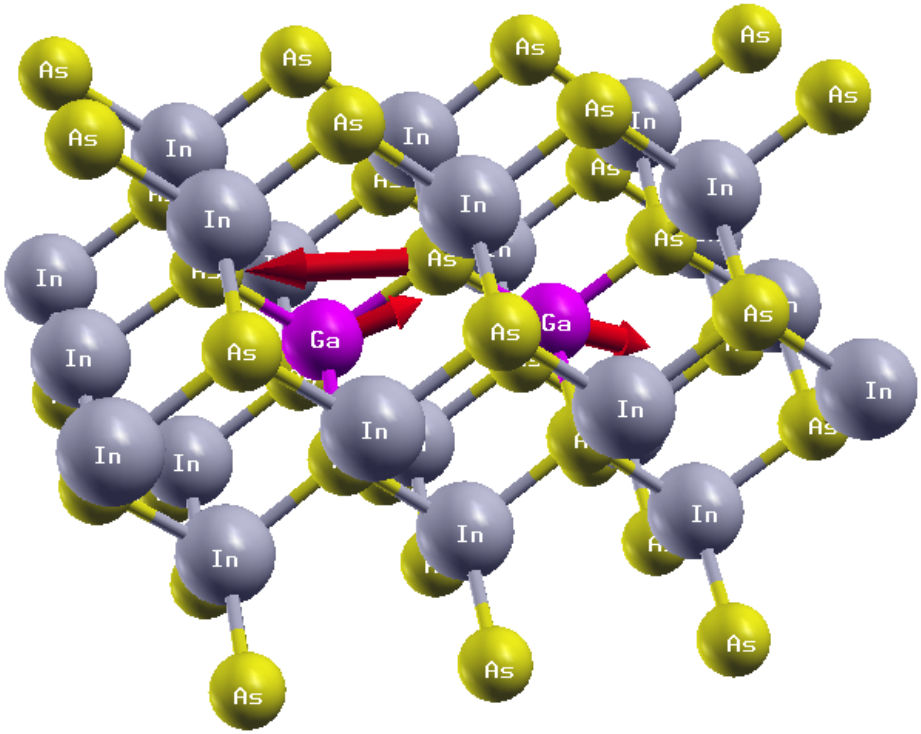




in-phase
two-impurity modes,
ω=248 – 251 cm^{-1}

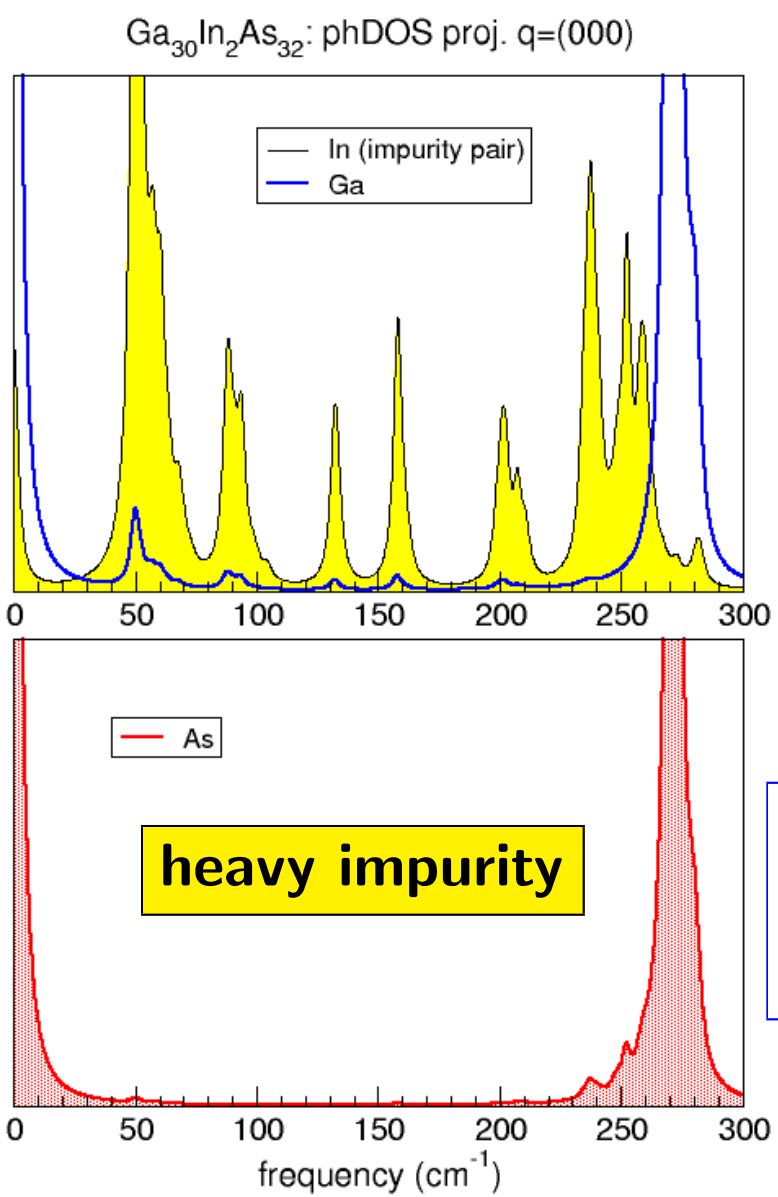
$Ga_xIn_{1-x}As$: $\mathbf{q}$=0 impurity modes

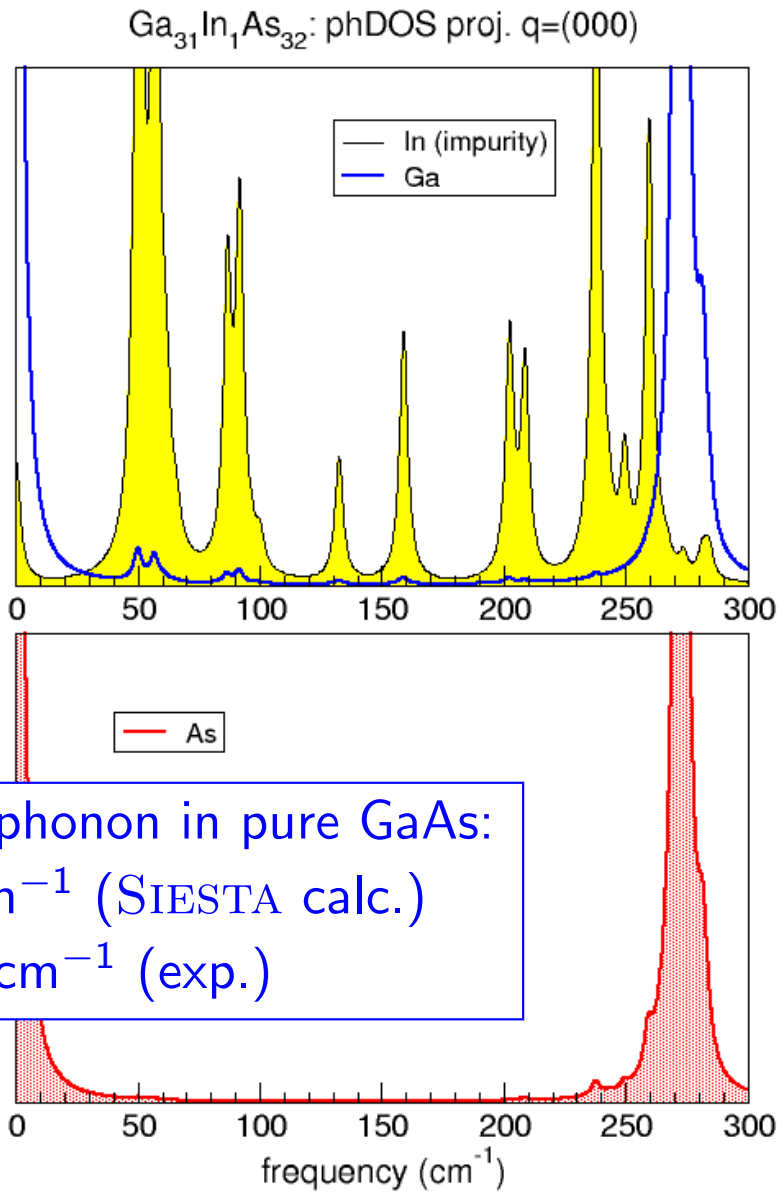




in-phase
two-impurity modes,
ω=248 – 251 cm^{-1}

$In_xGa_{1-x}As$: **q**=0 -projected phonon DOS

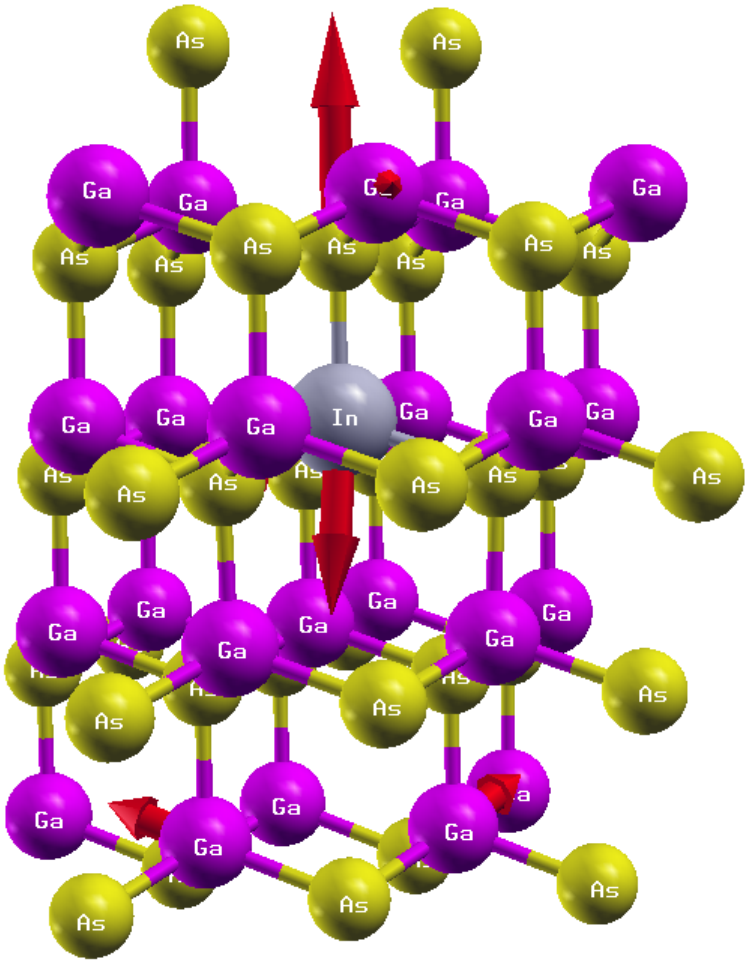




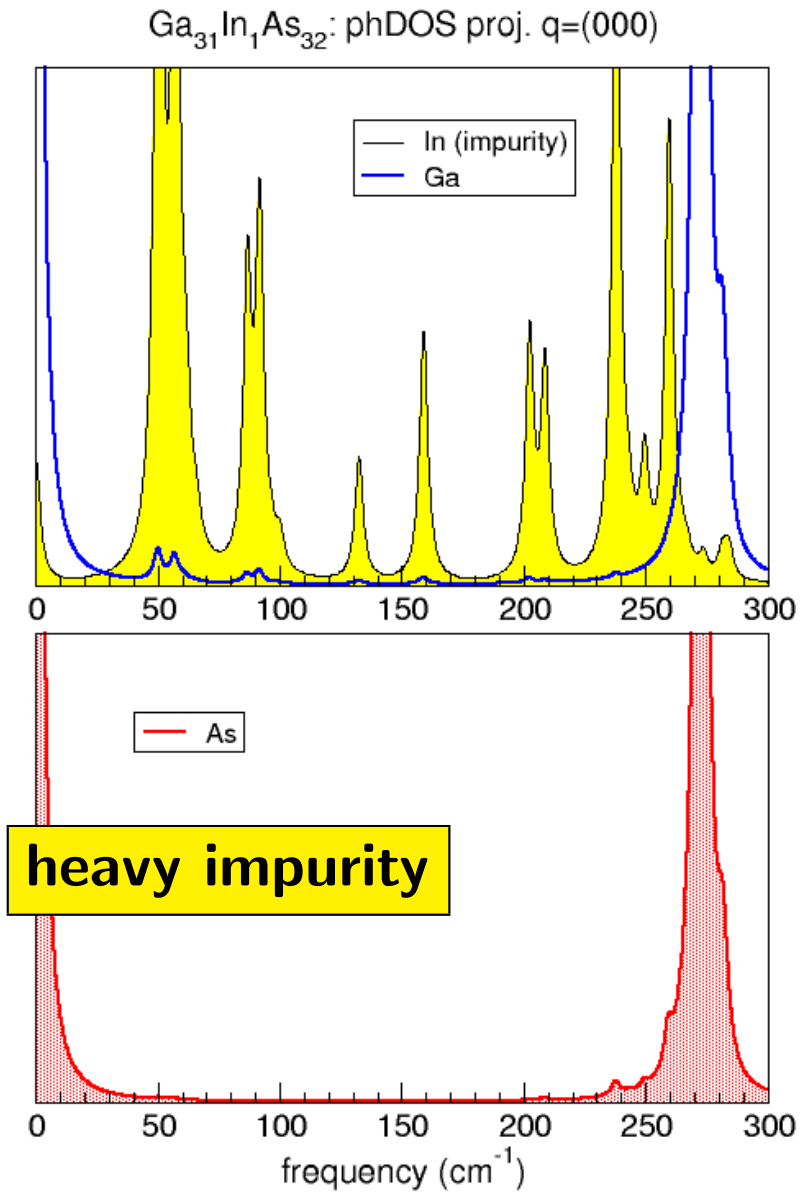
heavy impurity

Γ-TO phonon in pure GaAs:
264 cm^{-1} (SIESTA calc.)
268.6 cm^{-1} (exp.)

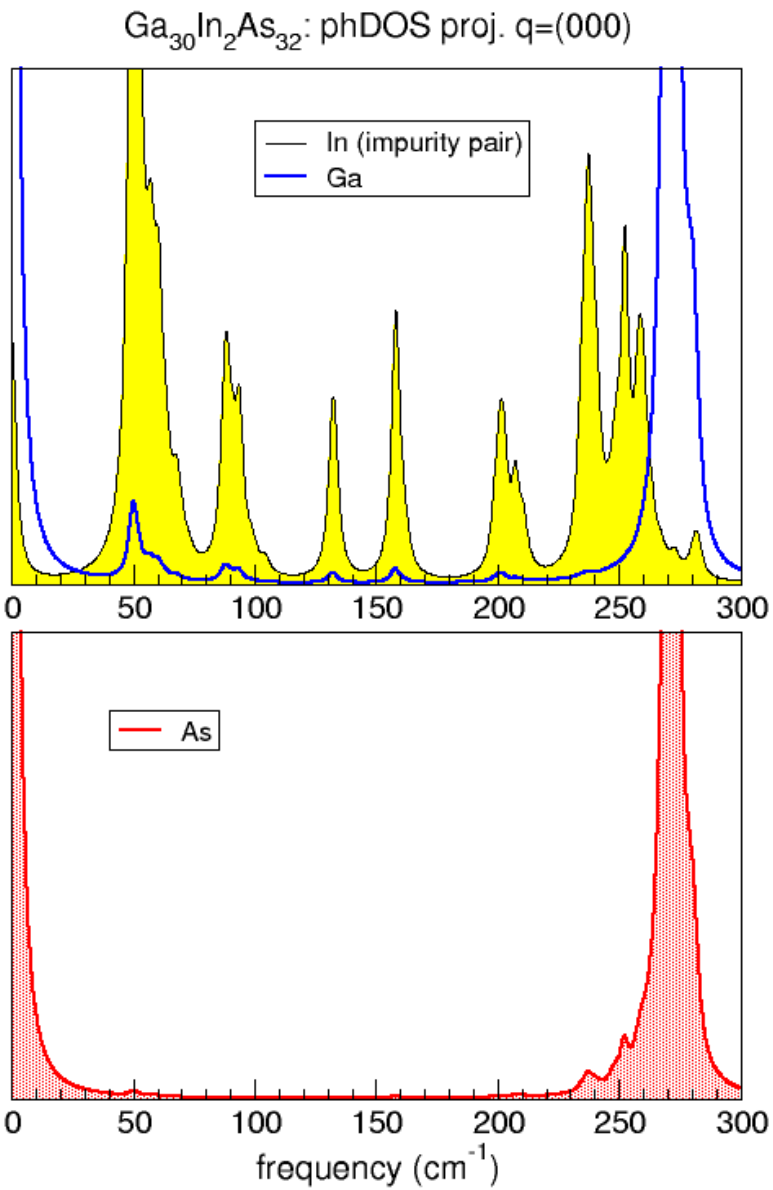
$In_xGa_{1-x}As$: **q**=0 impurity modes

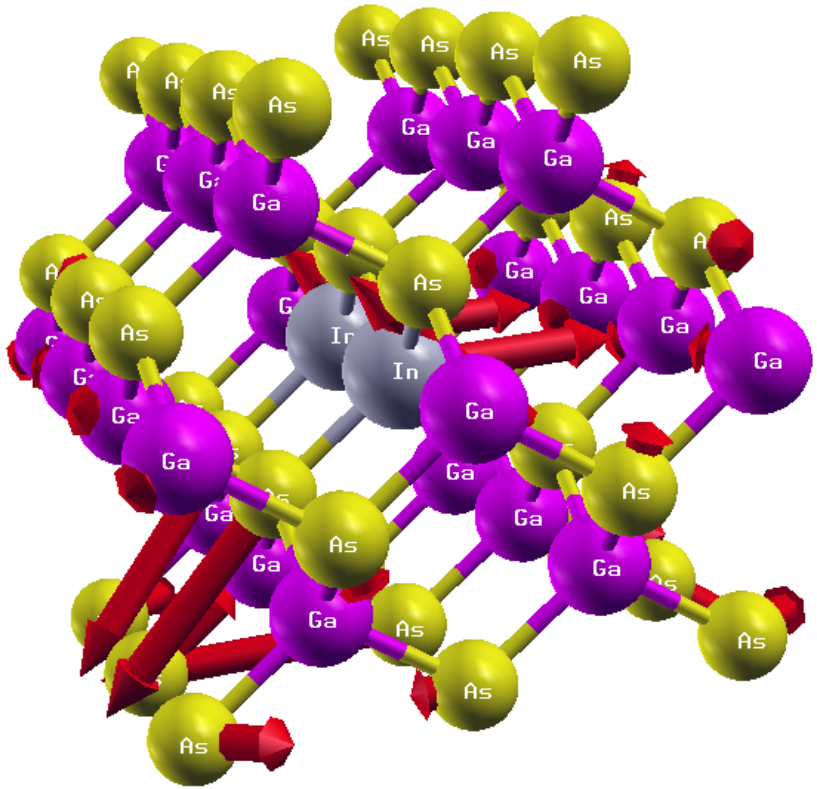


impurity modes #103–105,
ω=238 cm^{-1}



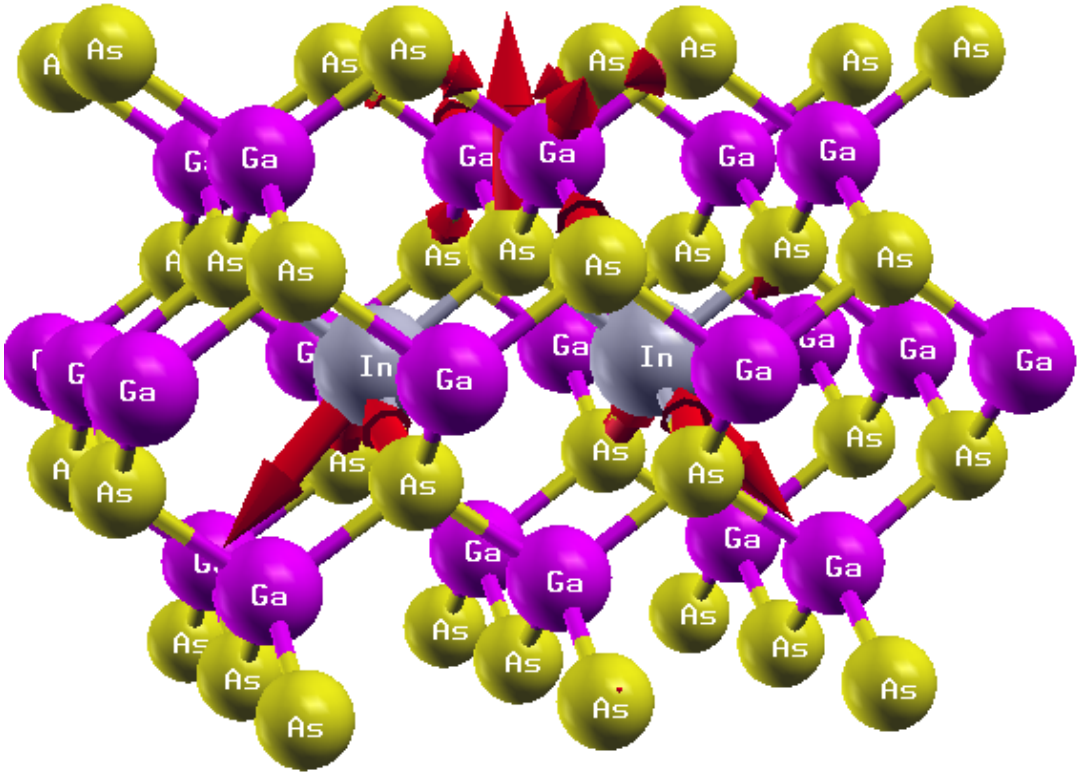
$In_xGa_{1-x}As$: **q**=0 impurity modes

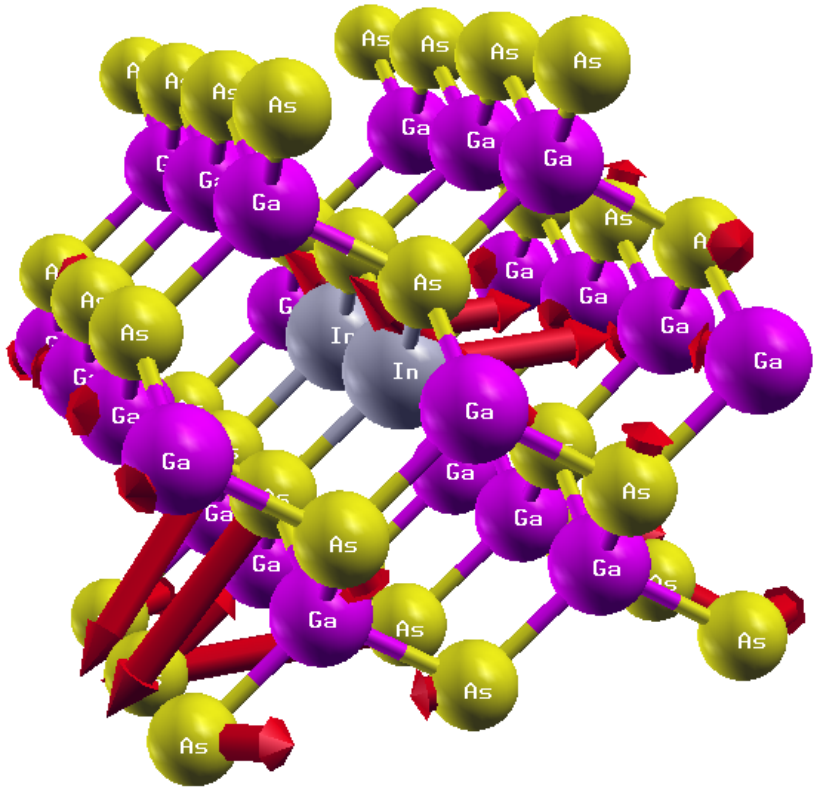




in-phase
two-impurity modes,
ω=235 – 241 cm^{-1}

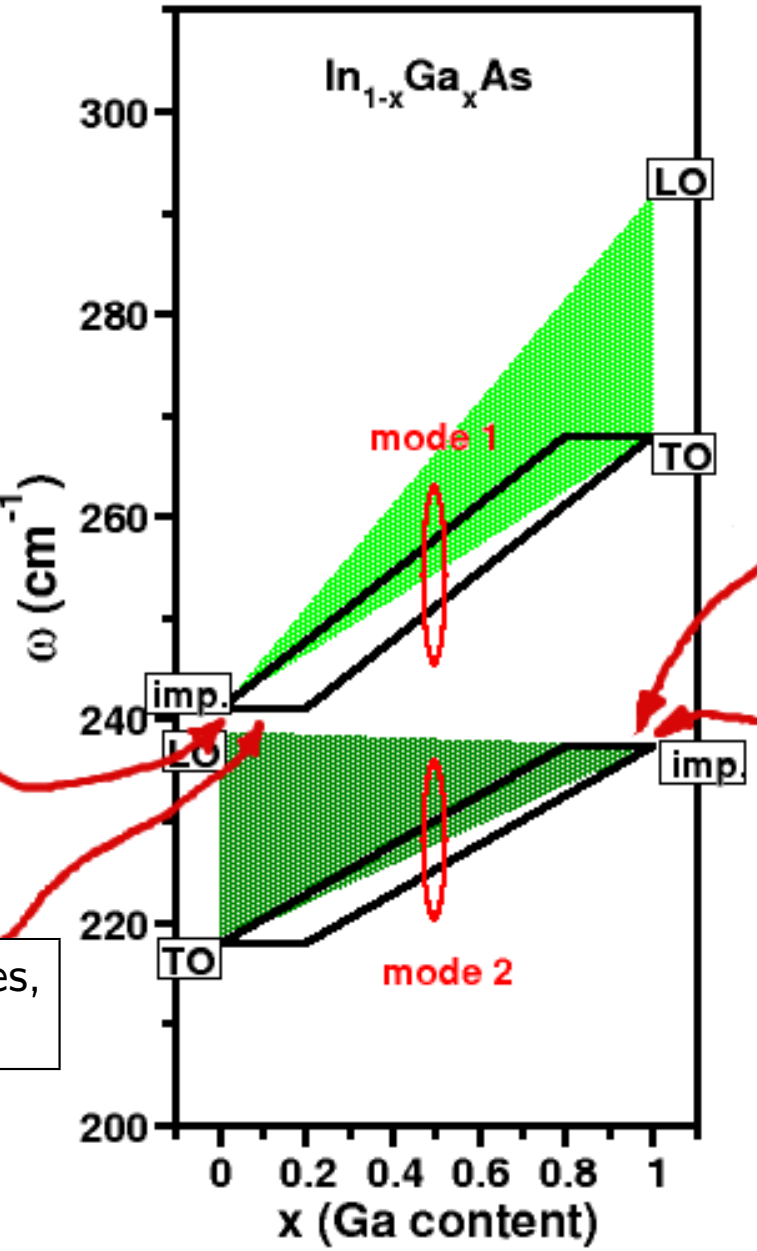
$In_xGa_{1-x}As$: $\mathbf{q}$=0 impurity modes





in-phase
two-impurity modes,
ω=235 – 241 cm^{-1}

(In,Ga)As: theory vs. experiment



No frequency shift
on doping
on both Ga-impurity
and In-impurity ends

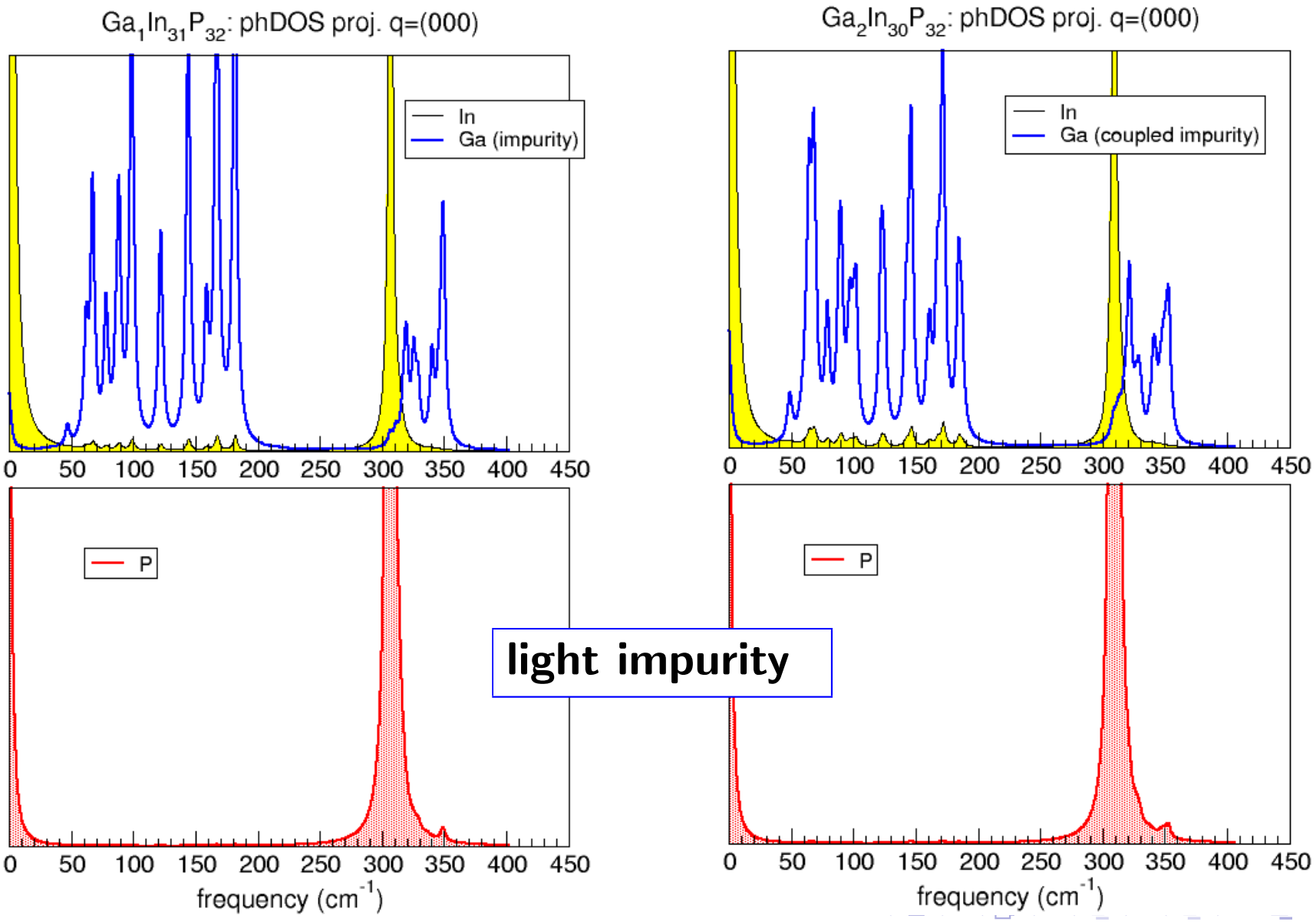
Ga impurity modes,
$\approx$246 cm^{-1}

two-In impurity modes,
ω=235 – 241 cm^{-1}

two-Ga impurity modes,
$\approx$245–251 cm^{-1}

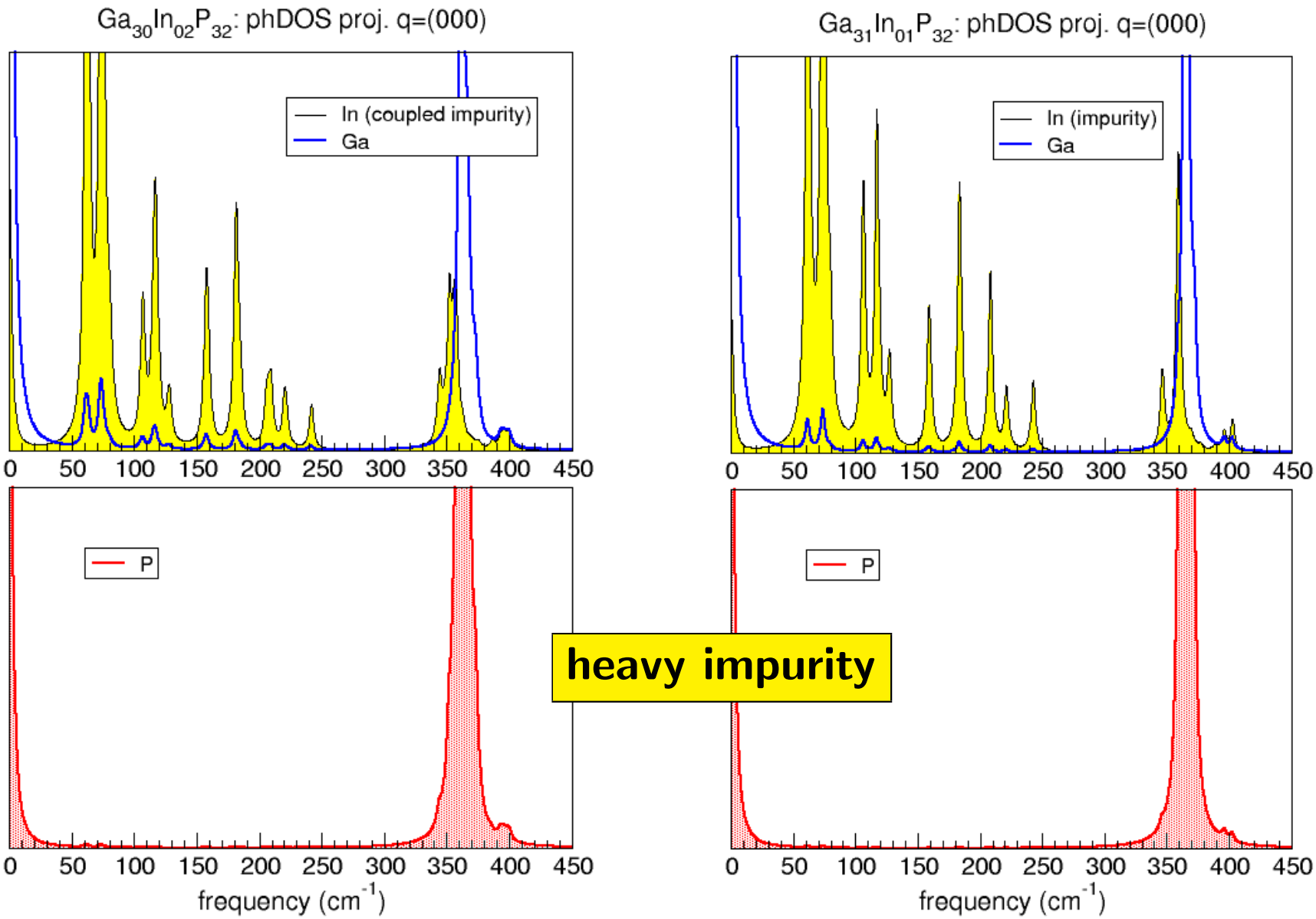
In impurity modes,
ω=238 cm^{-1}

$Ga_xIn_{1-x}P$: **q**=0 -projected phonon DOS



light impurity

$In_xGa_{1-x}P$: **q**=0 -projected phonon DOS



(In,Ga)P: theory vs. experiment

No frequency shift on In-doping side

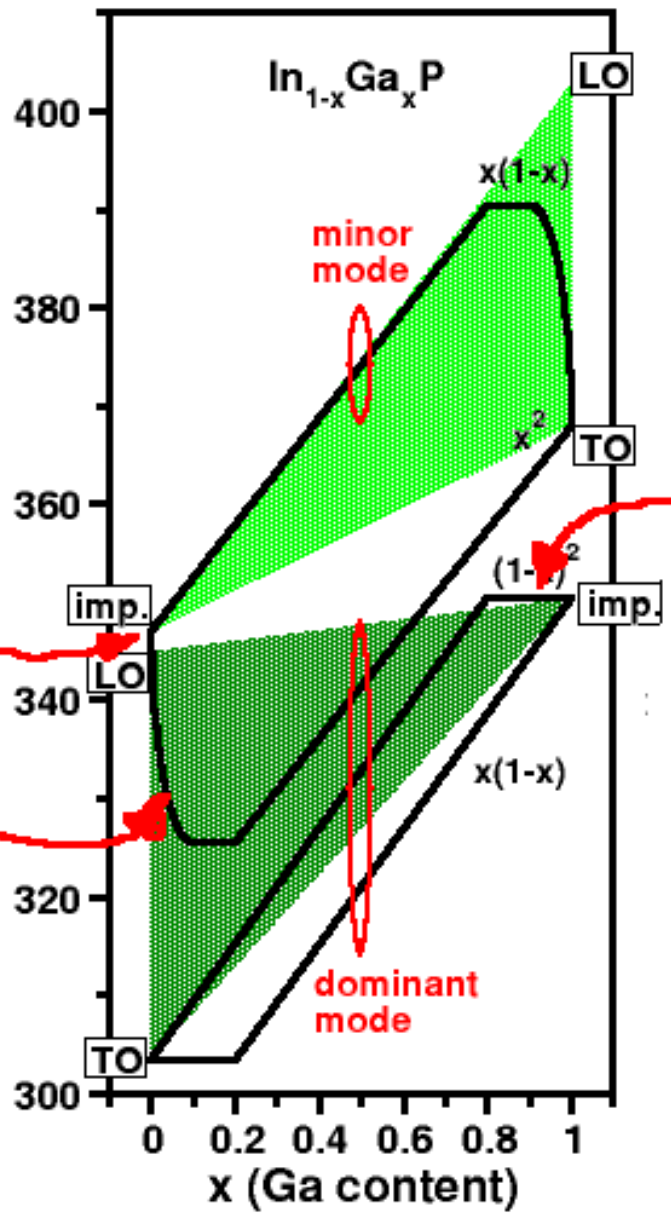
Ga impurity modes, $\approx$350 cm^{-1}

two-In impurity modes, ω=357 – 362 cm^{-1}

Large frequency shift on Ga-doping!

two-Ga impurity modes, $\approx$321–349 cm^{-1}

In impurity modes, ω=360 cm^{-1}



Conclusions

- Within each group (short, or long) of cation–anion bond lengths, a further discrimination occirs, depending on nearest environment.
  E.g in (Be,Zn)Se.: Be–Se in Be-rich region (longer) vs. Be–Se in Zn-rich region (shorter); Zn–Se in Zn-rich region (shorter) vs. Zn–Se in Be-rich region (longer).
- Force constants, in general, vary systematically with respective bond length, yielding the relation shorter bond length $\rightarrow$ harder vibration mode.
- The onset of 1 bond $\rightarrow$ 2 mode behaviour occurs already at several % concentration – just beyond the impurity limit.
- The "stabilization" of 1 bond $\rightarrow$ 2 mode behaviour ("percolation" regime) occurs between two percolation limits, $\approx$20% ... $\approx$80%.
- To read more: PRB **71**, 115206 (2005); PRB **65**, 35213 (2002); cond-mat/0610682; arXiv:0709.0930