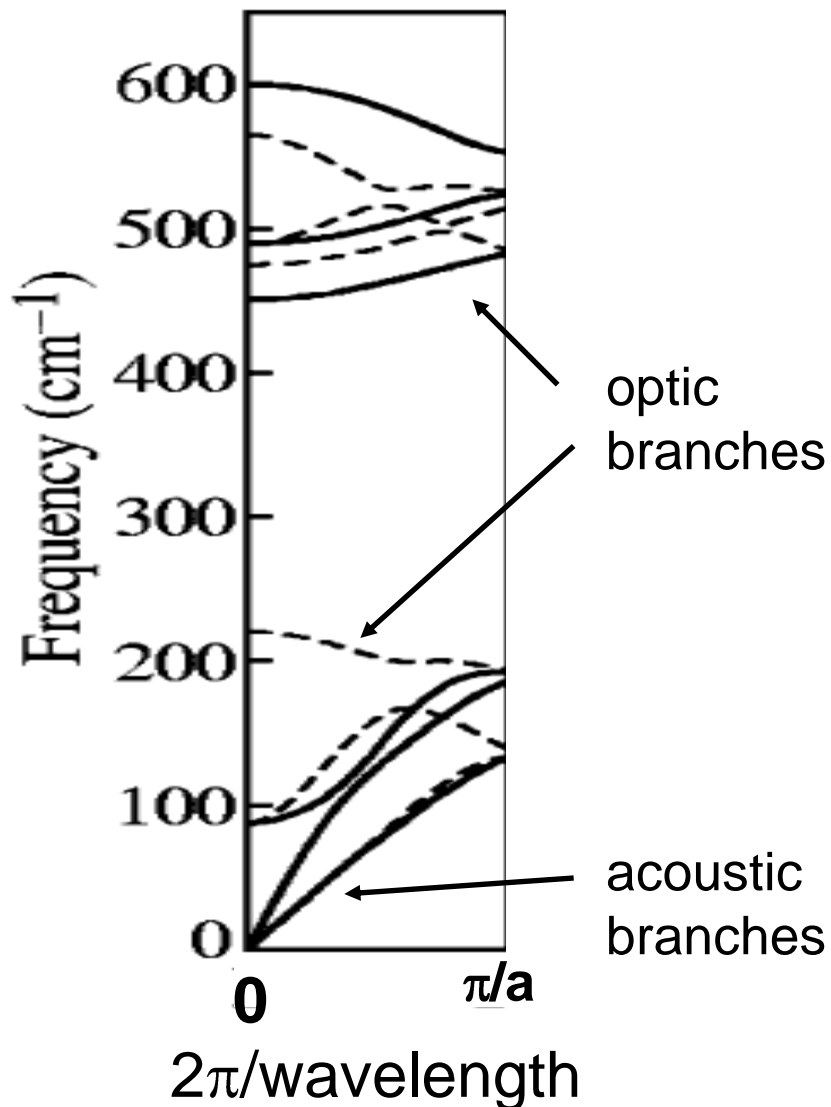


Raman spectroscopy for Materials Scientists

Lecture 2

- **Site group analysis; mode symmetries and Raman activity**
- **Raman tensor and polarisation-resolved measurements**
- ***ab initio* frequency computations; how reliable?**
- **Anharmonic and inhomogeneous line broadening**
- **Effects of point and extended disorder**

Dispersion for InN



The phonon “dispersion”, meaning the frequency as a function of wavelength, is usually plotted as frequency vs (wavelength)⁻¹, across the Brillouin zone. Then infinite wavelength is at zero, the zone centre, commonly labeled the Γ (gamma) point. It’s the frequencies along the left-hand edge that have infinite wavelength.

In a perfect crystal only the zone centre phonons can be Raman active, and usually not even all of those are.

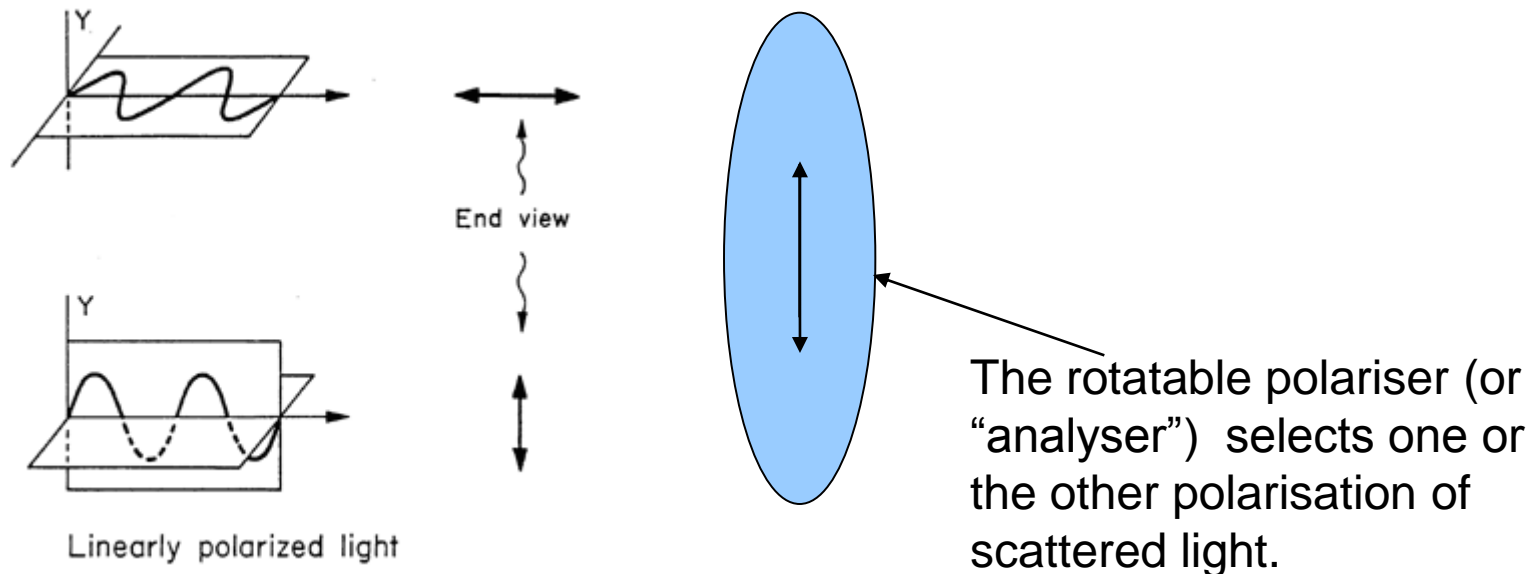
Symmetry analysis

- The ions displaced during the vibrations alter the symmetry, and the zone-centre vibrational “modes” are characterised by that lowered symmetry.
- Those modes in which all the symmetry elements of the crystal are retained are labeled A_1 .
- A_2 , B, E, F are used for modes that introduce a lowered symmetry, and
- E and F modes are doubly and triply degenerate, respectively. For example those modes that involve motion in the basal plane of a tetragonal crystal have the same character and frequency for displacements along either x or y; they are E modes.
- It is worthwhile knowing how to determine the zone-centre vibrational mode symmetries and their Raman activity, for which I suggest the paper by Rouseau et al. There is no need to sort out how their tables are determined, but you should learn to use them. That will be done in the tutorial.

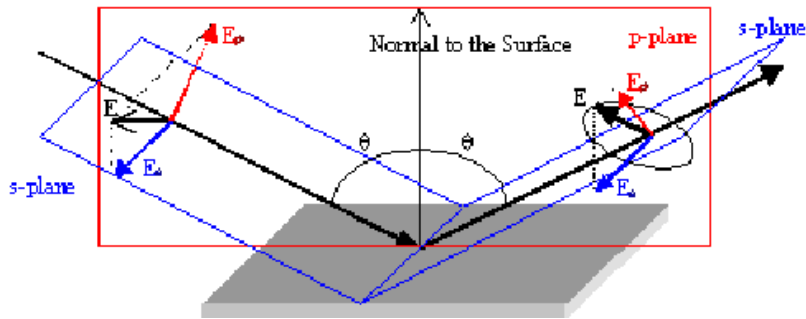
Polarisation-resolved measurements

There are two orthogonal polarisations in an EM wave, and the Raman signal expected depends on the polarisations of the incident and scattered light relative to the crystal axes.

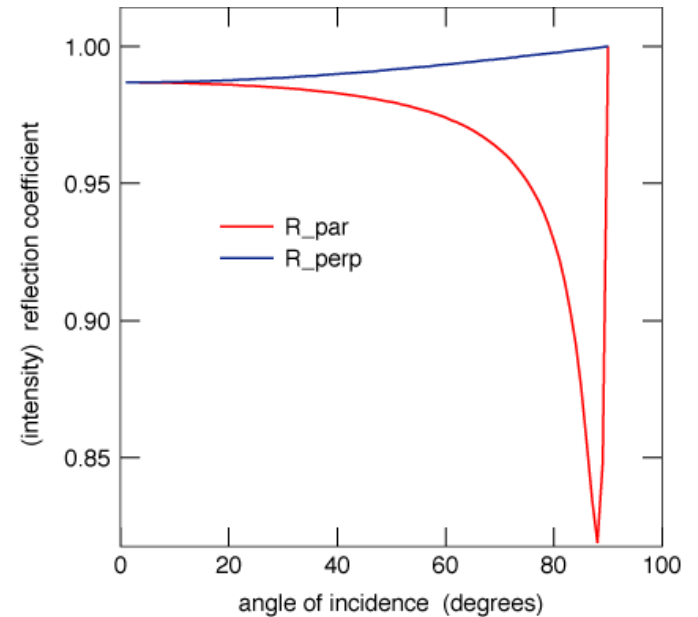
The incident polarisation is determined by the laser and guiding mirror configuration and the scattered light can be passed through a polariser, selecting one or the other polarisation, so the polarising character of any one observed mode can be determined.



Reflections OK for light linearly polarised along either S or P, but NOT for an arbitrary polarisation OR for the phase between them required for circular polarisation, but that's another story.



The plane defined by the incident and reflected beams is called the “plane of incidence”, shown in red. The reflectivity is different for light polarised in that plane or perpendicular to it.



All reflections in any polarisation-resolved experiment must have the beam polarisation either in the plane of incidence (P) or perpendicular to it (S).

Raman tensor

The “polarisation selection rules” for the various zone-centre symmetries are also available from Rouseau et al, there given in terms of the “Raman tensor”.

$$\text{Scattered amplitude} = [\mathbf{e}_s \cdot \mathbf{R} \cdot \mathbf{e}_i] |\mathbf{E}_0| ; \text{Scattered intensity} = [\mathbf{e}_s \cdot \mathbf{R} \cdot \mathbf{e}_i]^2 |\mathbf{E}_0|^2$$

\mathbf{e}_i = the incident polarisation vector

\mathbf{e}_s = the scattered polarisation vector

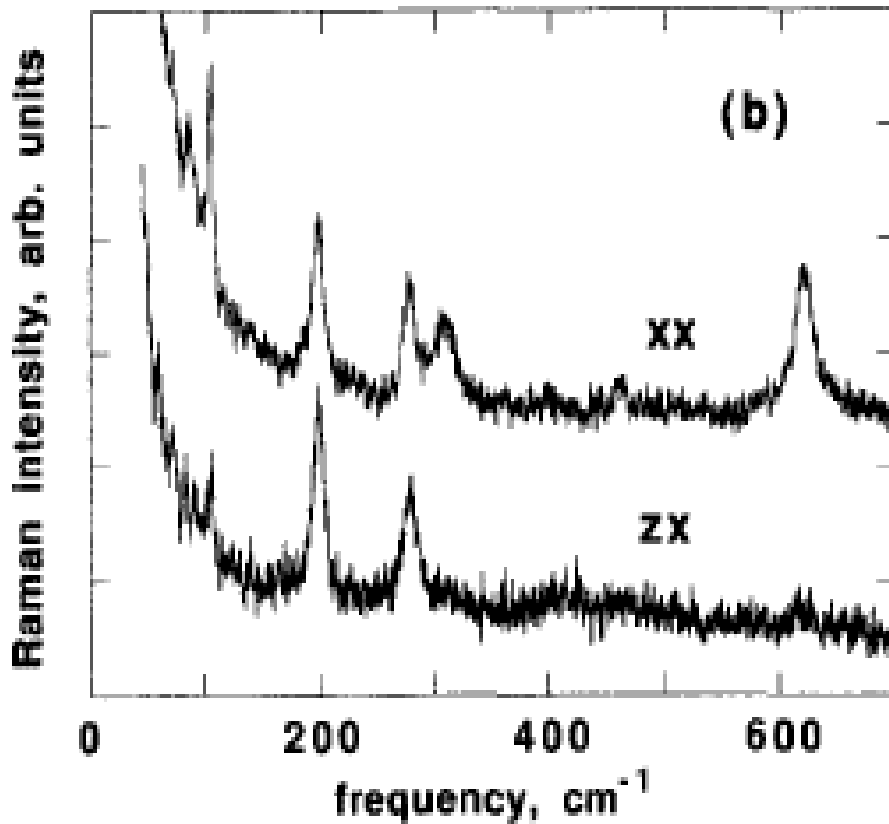
$|\mathbf{E}_0|$ = incident amplitude

\mathbf{R} = the Raman tensor

The elements of \mathbf{R} depend on the mode symmetry (A, B, ...) and are also given in the Rouseau paper. Tensor multiplication will be described in the tutorial, if you don't already know how to do it.

So now we can determine how many Raman features we should see and under what polarisation conditions.

Polarised Raman spectra from (010) face of barium ruthenate



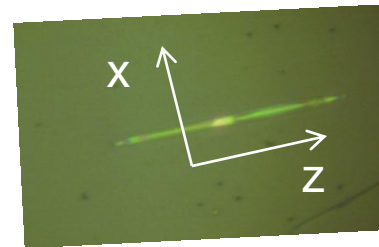
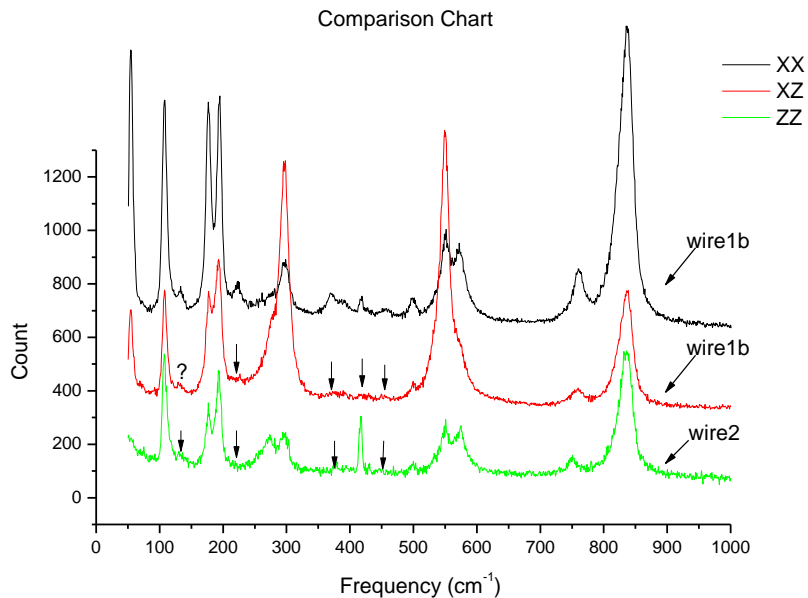
“XX”

incident polarisation along [100],
scattered-light polarisation selected
along [100]

“XZ”

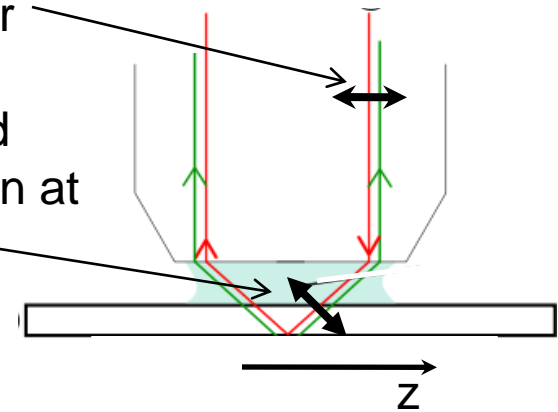
incident polarisation on [100],
scattered-light polarisation selected
along [001]

Raman of non-perovskite PbTiO_3 nanowires, polarisation-resolved data.



z polarisation
at analyser

is of mixed
polarisation at
the focus.



The polarisation is not retained through a strongly focussing element, e.g. a microscope, so the “wrong” spectral lines do not disappear completely.

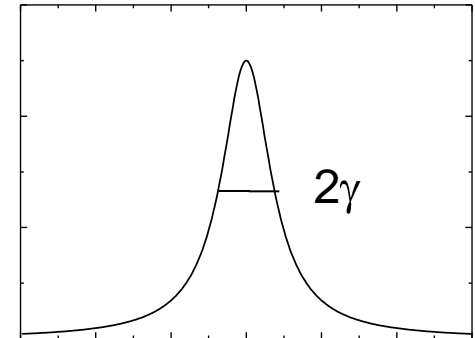
	calculated	experiment
60	831 Ag	837 Ag
57	748 Bg	761 Bg
56	684 Bg	
52	609 Ag	573 Ag
51	586 Eg1	550 Eg
50	586 Eg2	550 Eg
49	507 Ag	499 Ag
47	457 Bg	457 Bg
44	430 Bg	392 Bg
43	407 Ag	
42	388 Bg	370 Bg
35	299 Eg1	297 Eg
34	299 Eg2	297 Eg
33	289 Ag	
32	282 Bg	
31	281 Eg1	274 Eg
30	281 Eg2	274 Eg
29	276 Ag?	
25	235 Bg?	224 Bg
21	217 Ag	193 Ag
19	194 Bg?	
18	192 Eg1	
17	192 Eg2	
16	177 Ag	178 Ag
13	112 Ag	107 Ag
12	104 Bg	134 Bg
8	64 Bg	56 Bg
7	62 Ag	
6	43 Eg1	
5	43 Eg2	

Detailed comparison with expected vibrational frequencies is not so simple. These are the experimental lines for the nanowires of the previous slide, labelled with the symmetry characters determined from their polarisations, compared with an *ab initio* prediction. We see most of the predicted features, but shifted up to 10% or more.

The line width and shape carry information essential for their interpretation, even for basic understanding.

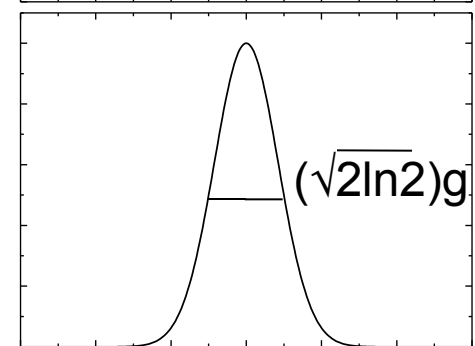
- For a weakly damped oscillator with displacement $\approx \exp[(-i\omega_0 + \gamma)t]$, scattered intensity $\approx 1/[(\omega - \omega_0)^2 + \gamma^2]$

Lorentzian lineshape

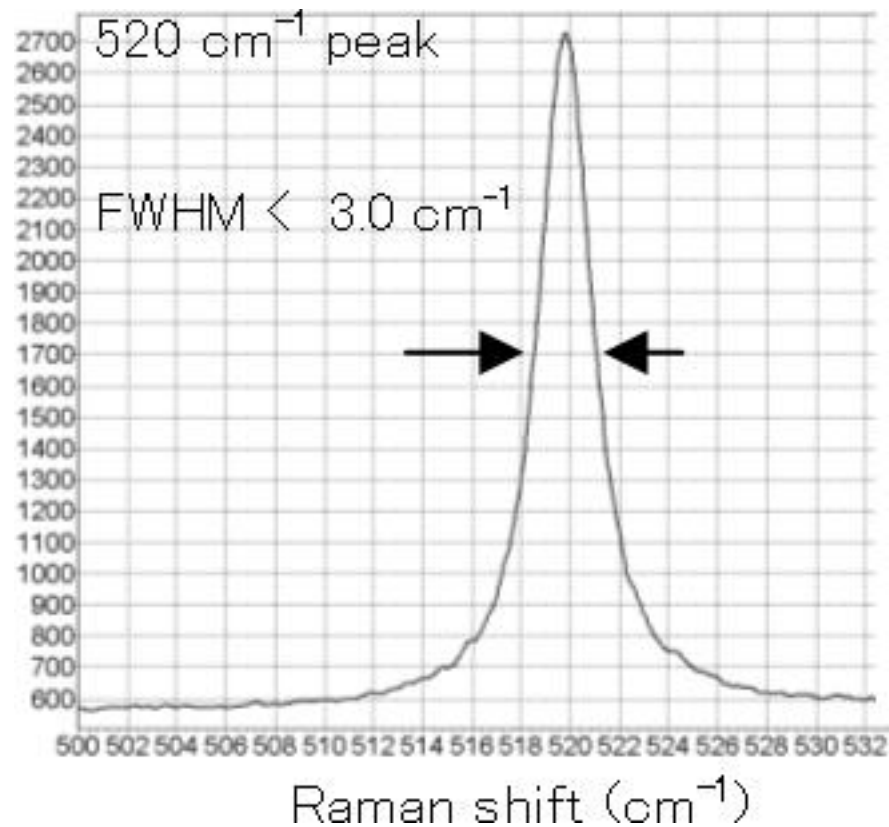


- For disorder (“inhomogeneous”) line broadening a Gaussian lineshape is often used: scattered intensity $\approx \exp[-(\omega - \omega_0)^2/2g^2]$

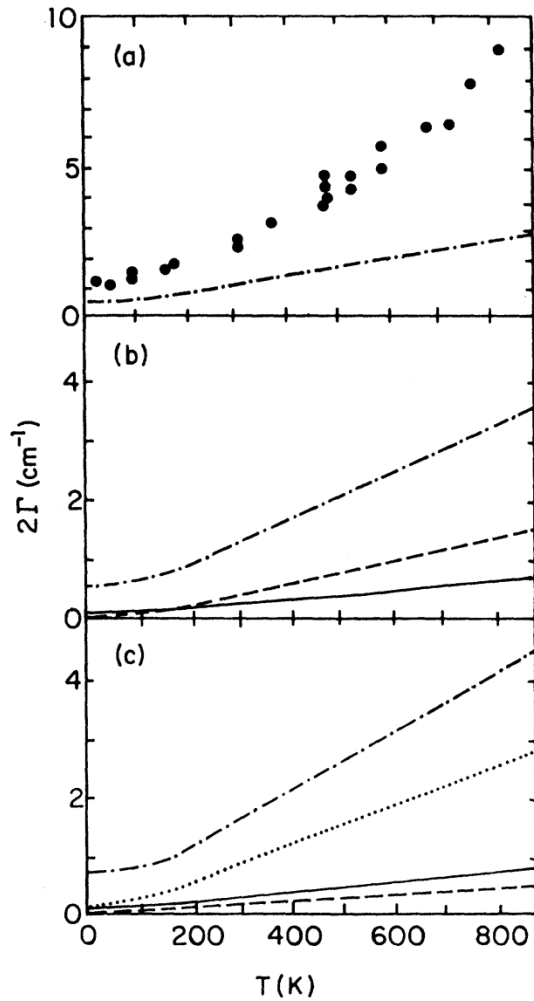
There is little rigorous justification; it is merely a convenience



Si line, resolved with 3 cm^{-1} width, possible only with great single crystals and spectrometers. That width is from a finite vibrational lifetime (i.e vibration damping) and shows T dependence



Measured broadening/calculated anharmonic inverse lifetime of Si



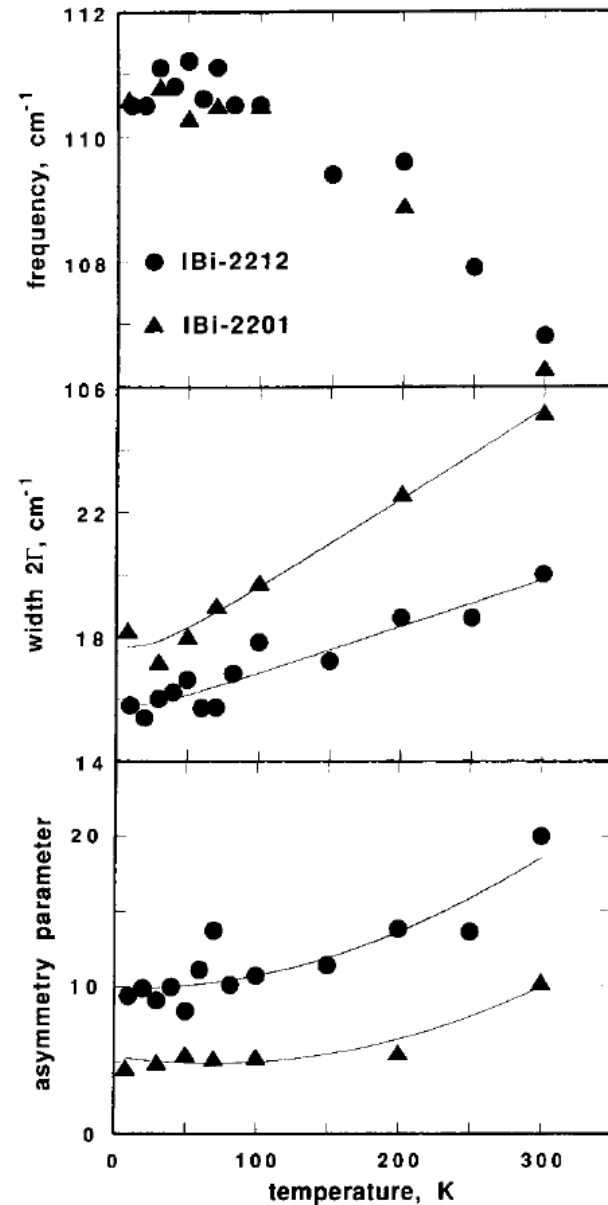
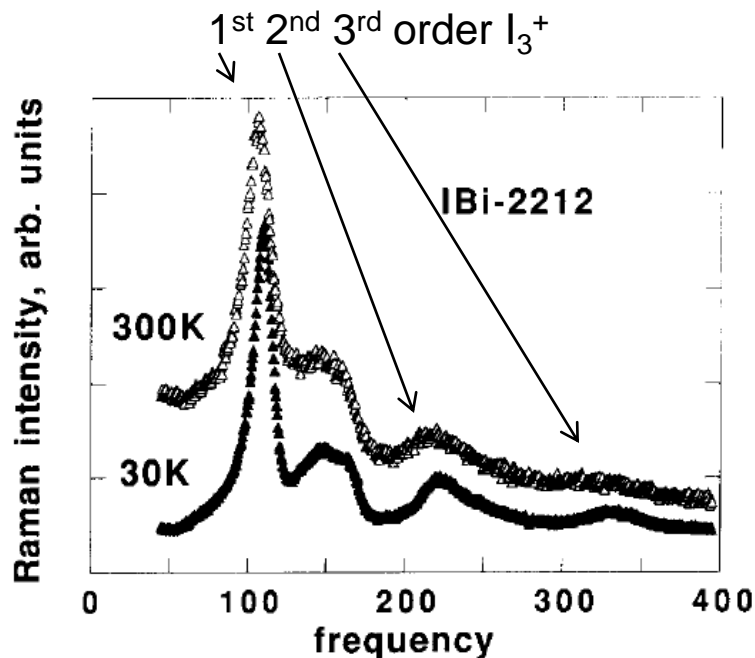
Raman line width/zone centre inverse lifetime

Non-zone centre calculations, so no Raman data

Iodine intercalated into $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$

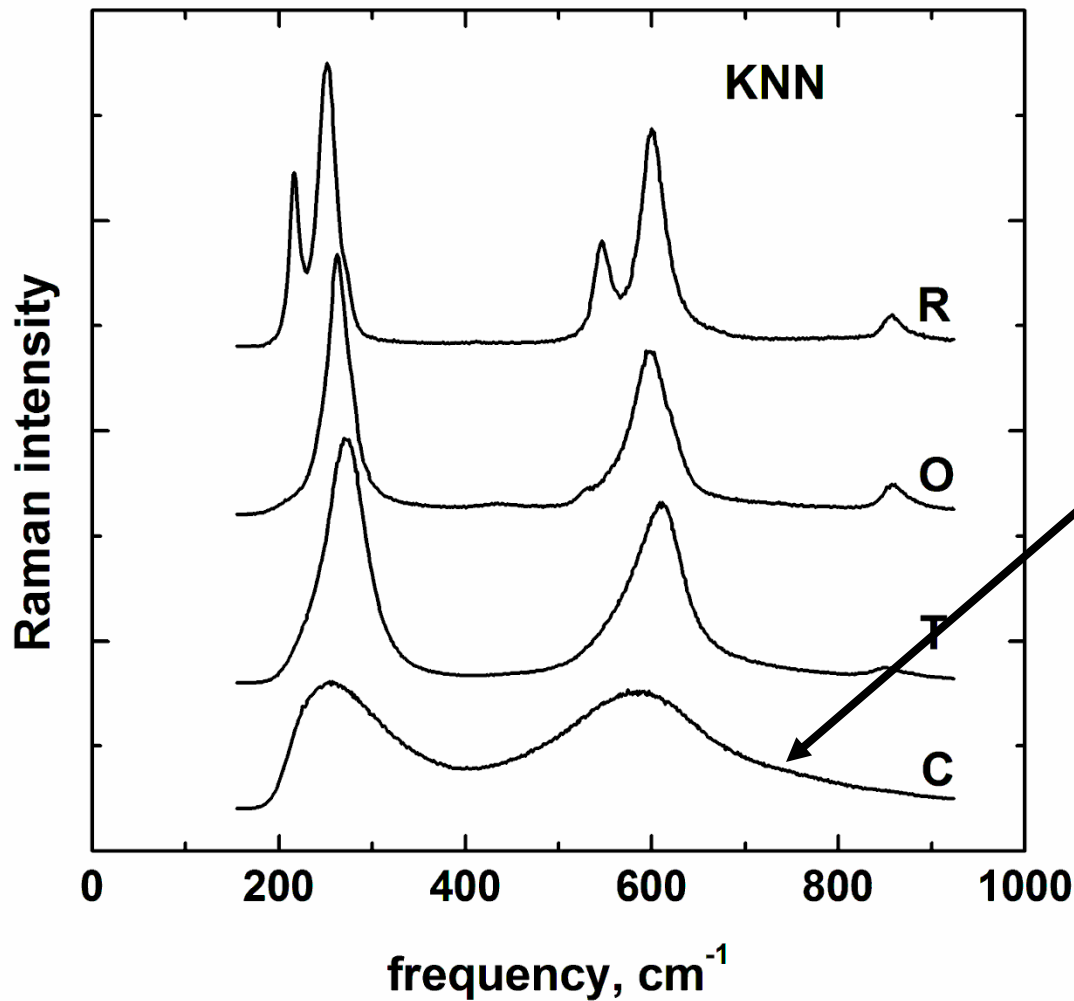
The frequency increases (“hardens”) as T is lowered, from thermal contraction.

The line narrows with decreasing temperature from the reduction in anharmonic phonon decay.



For a perfect (>10 nm) crystal

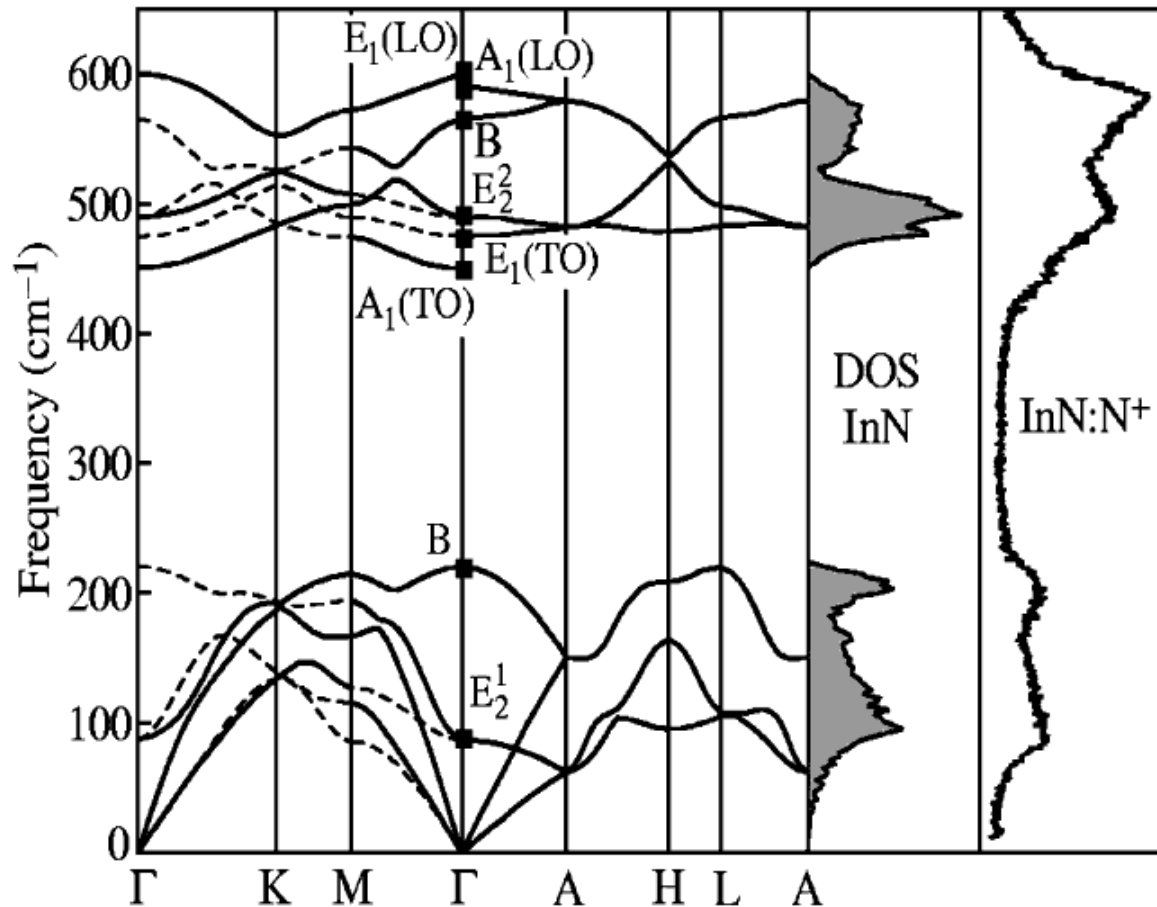
- Only vibrational waves (“phonons”) with nearly-infinite-wavelength are Raman active.
- And even many of those zone-centre modes are not Raman active; in particular
- No ion at a centre of inversion can be involved in a Raman-active phonon.



In the cubic perovskites ALL ions are at centres of inversion, so there should be NO Raman active phonons. The Raman signals seen in the cubic structure of most of them signal disorder.

Disorder effects 1

Point defects permit coupling to all modes, so one sees a spectrum that resembles the full density of vibrational modes.



Comparison of the vibrational mode density and the spectrum from charged N ions in InN.

Local modes

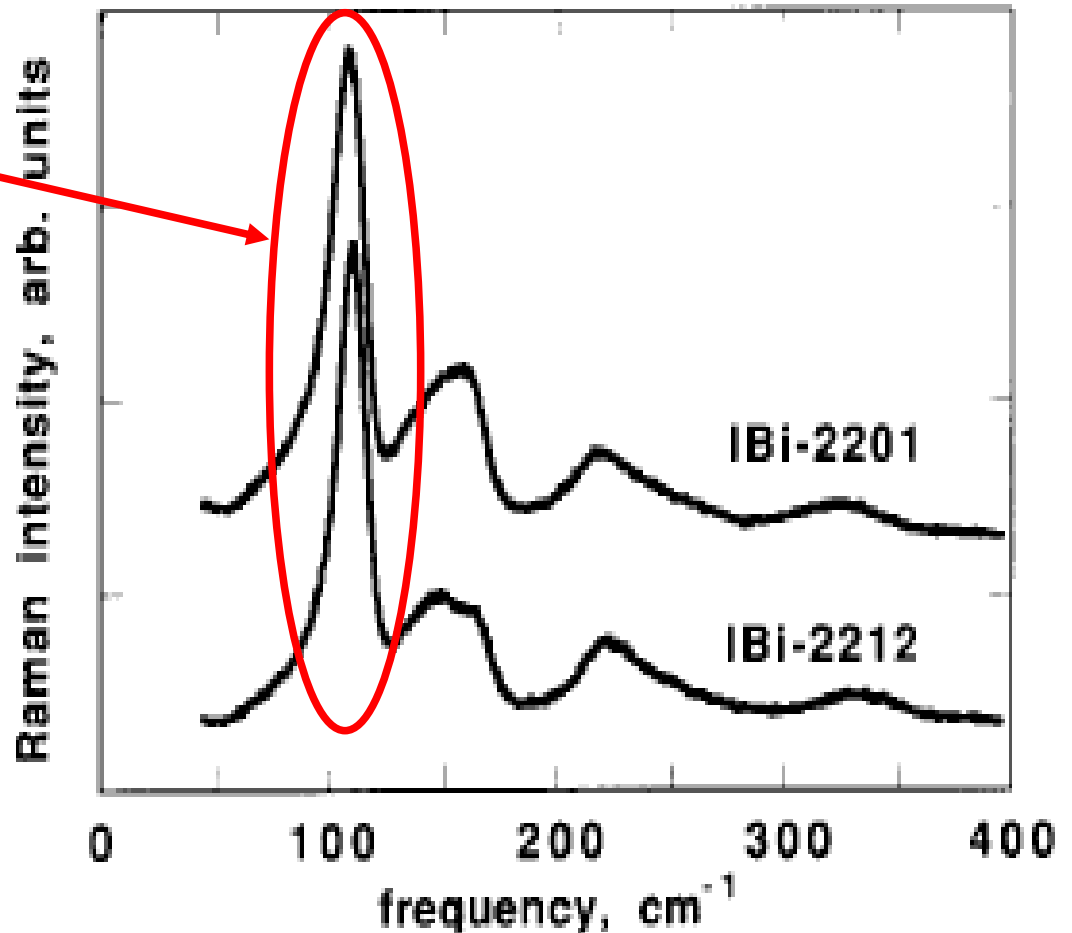
- Any point defect vibrates at its own frequency.
- That provides especially strong coupling to a phonon mode of the same frequency,
- but if the defect's natural frequency is above the optical phonon band then the vibrations are localised on the defect site, one sees a narrow local-mode feature.
- In either case their Raman signature is a moderately narrow feature, narrower for a fully decoupled local mode.

Local mode example 1

I_3^- in Bi-based high- T_C superconductors
(We've seen this before)

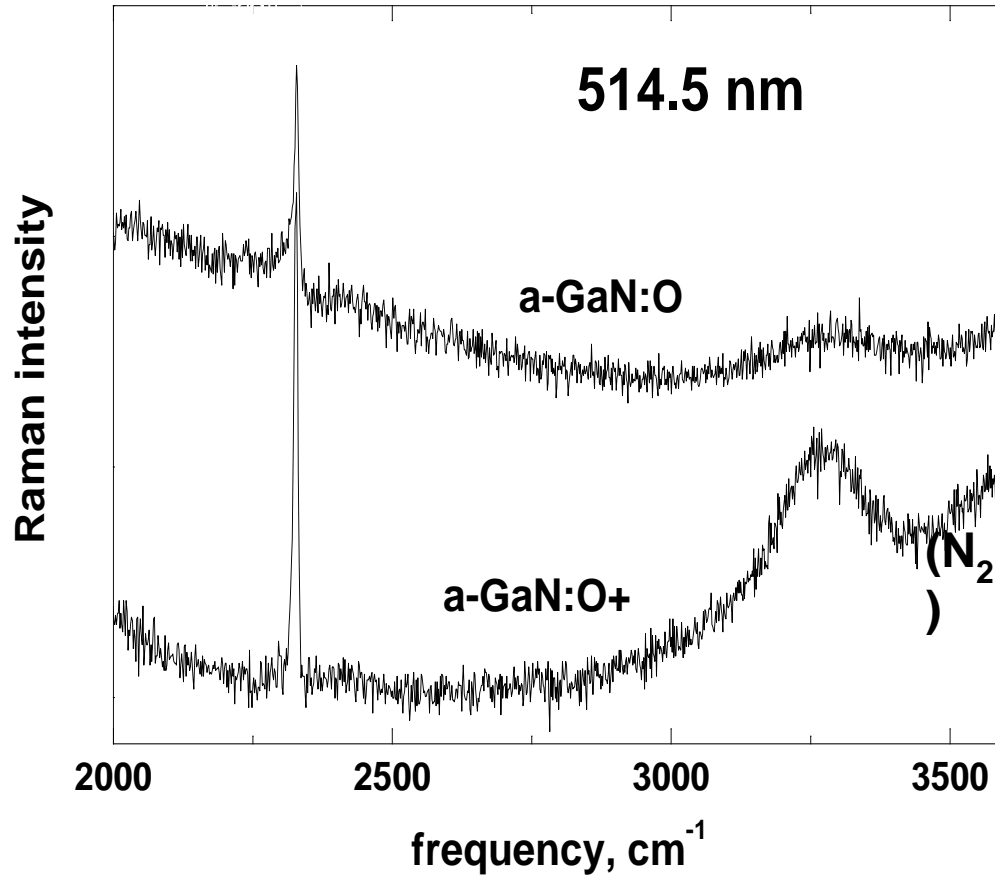
An I_3^- line at 110 cm^{-1}

$\Delta f/f \approx 0.15$, broadened by interaction with extended phonon modes because its frequency lies in the optic-branch band.



Local mode example 2

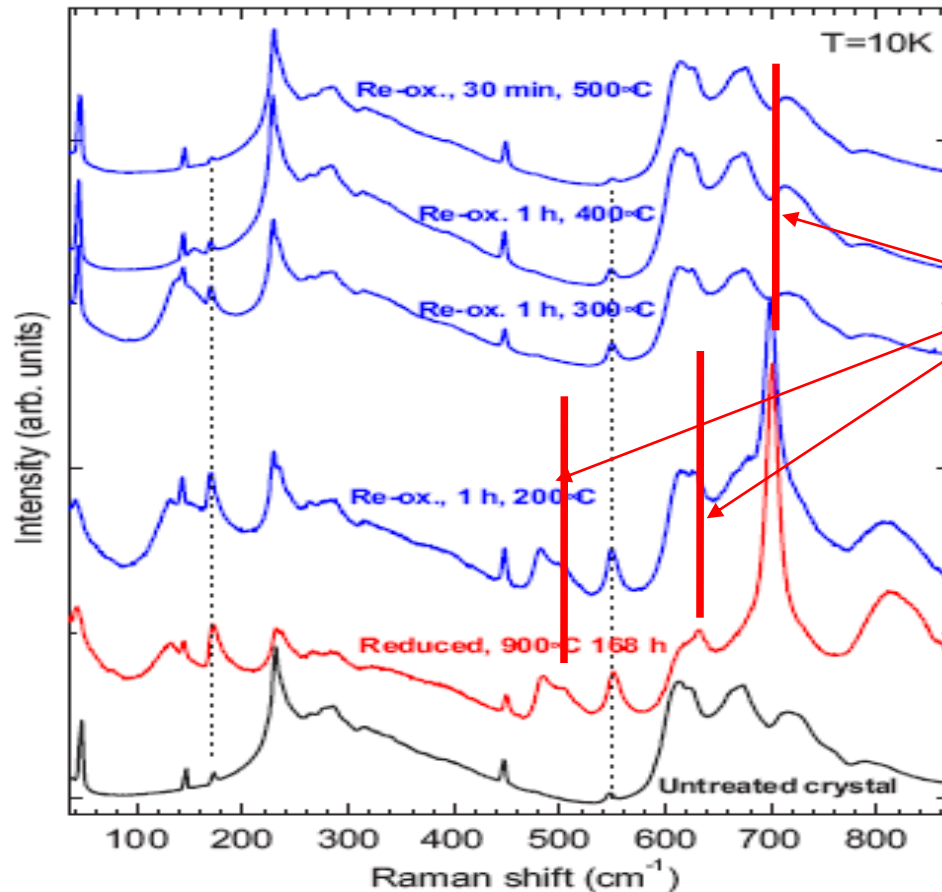
N_2 (2600 cm^{-1}) and -H (3250 cm^{-1}) in GaN



Both of these features are far above the optic vibrational band of GaN, so they are not coupled to lattice wave (phonons) and are very narrow:
 $\Delta f/f (\text{N}_2) \approx 0.01$
 $\Delta f/f (\text{-H}) \approx 0.03$

Local mode example 3

O vacancy in SrTiO₃

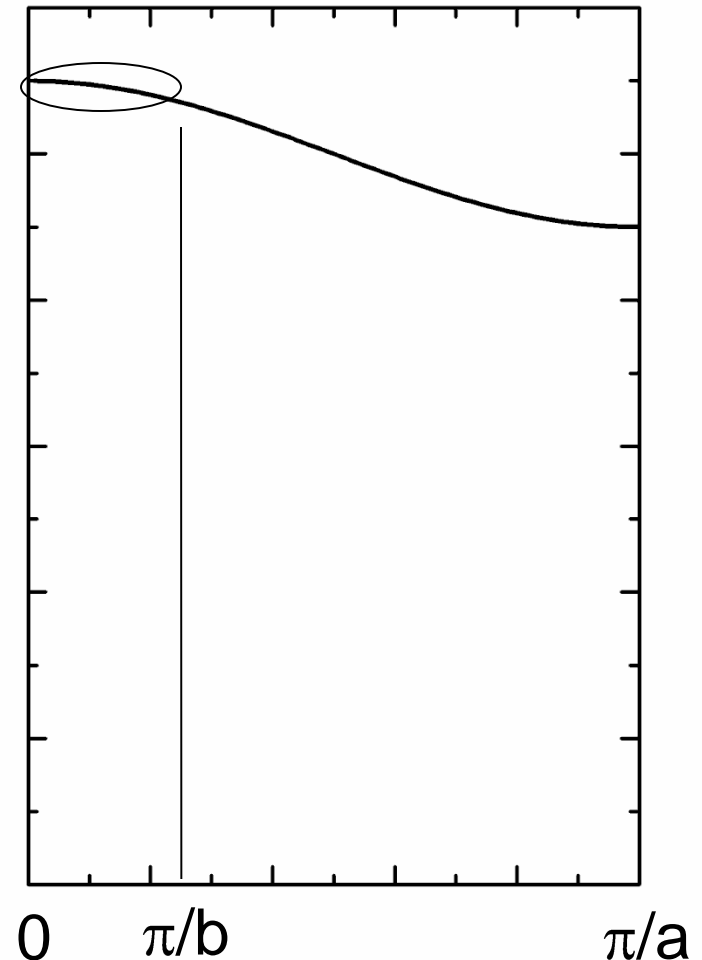


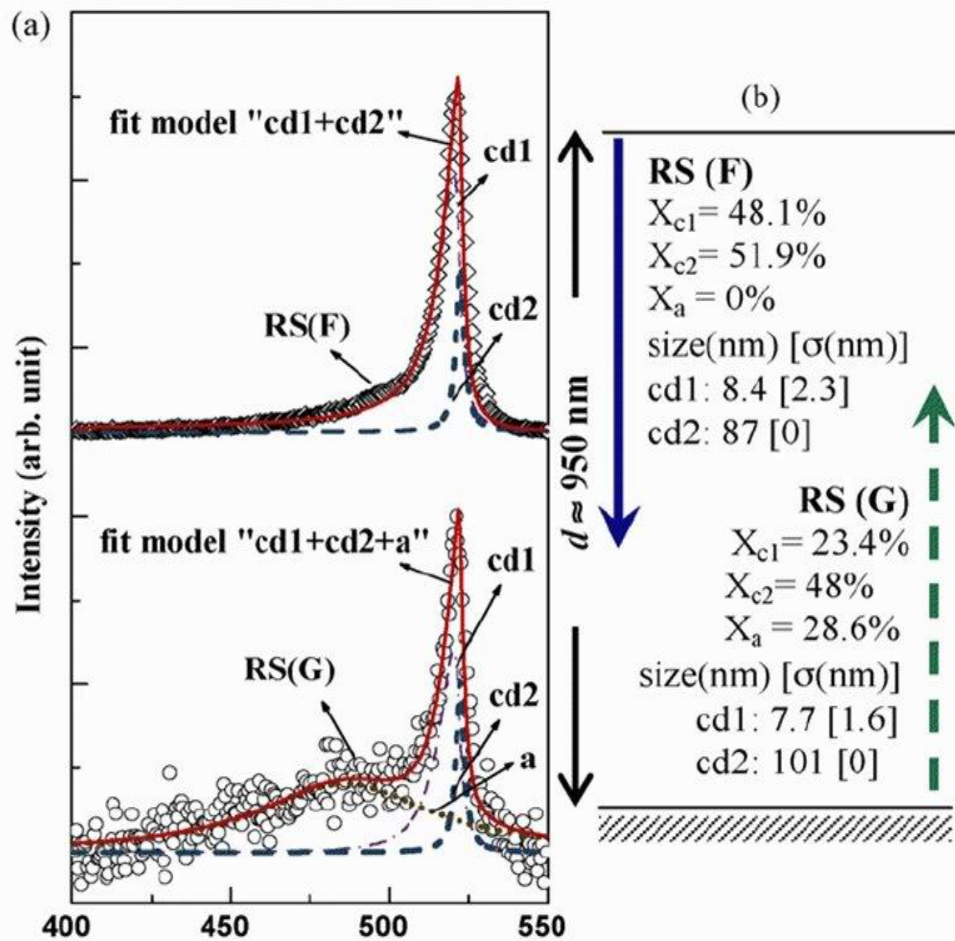
The three lines at 503, 630 and 700 cm⁻¹ are localised vibrations around O vacancies.

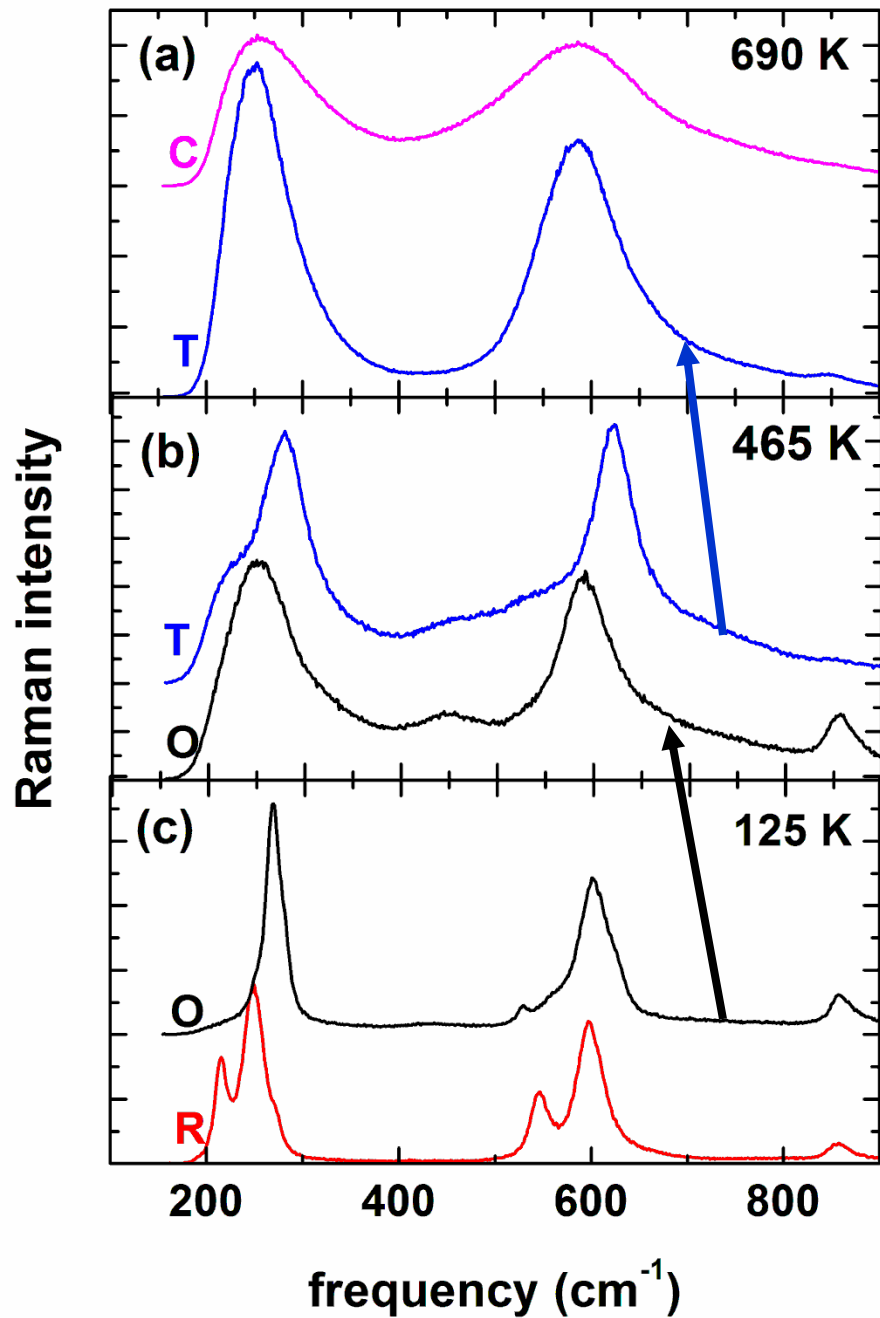
Disorder effects 2

Extended disorder, e.g. structural coherence on a scale of length b , renders modes within about π/b of the zone centre Raman active.

In this example all the modes inside the ellipse will be Raman active. The measured line would be broader than in a defect-free crystal but not as broad as from point defects.

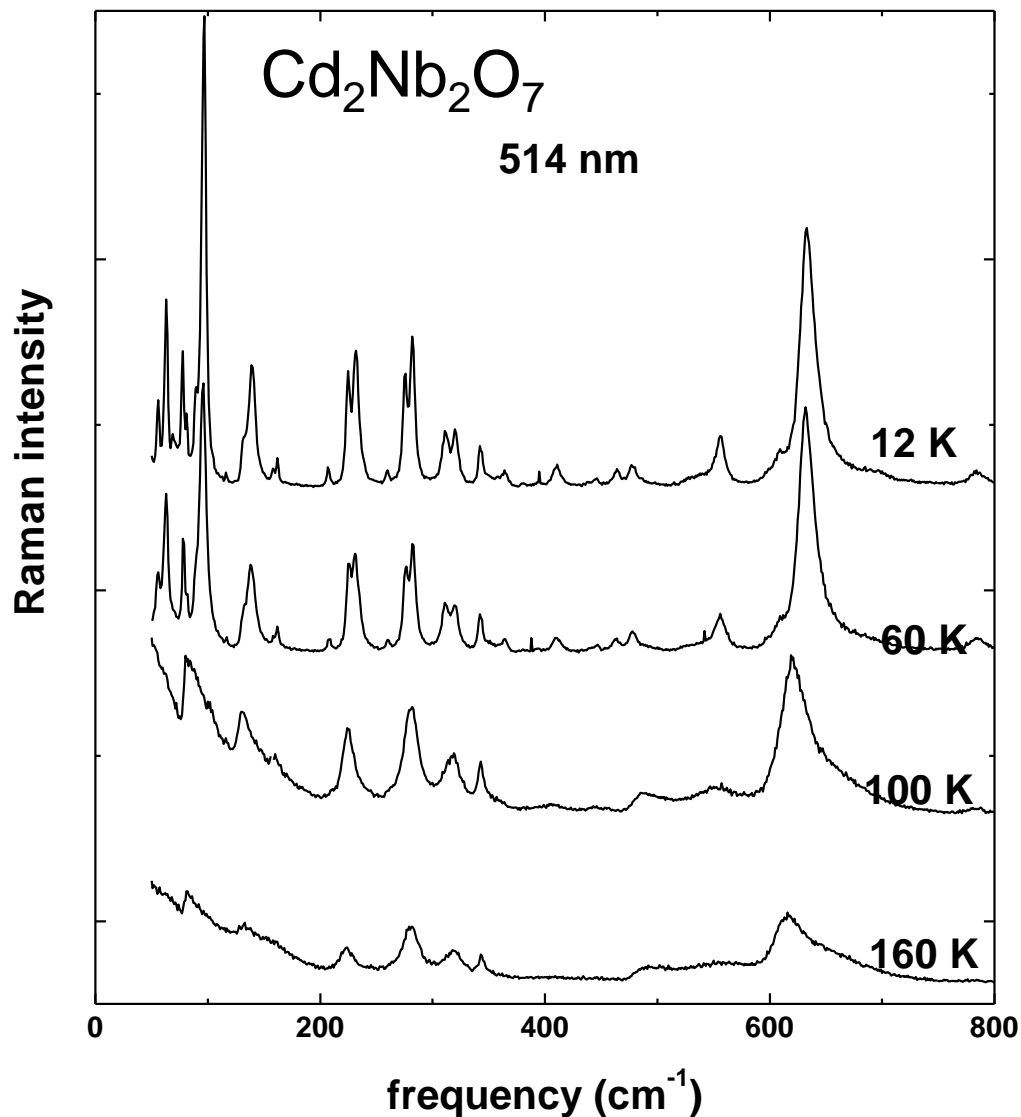






The broad bands in the C spectrum is almost certainly due to very short-range positional disorder, displacements uncorrelated in any but nearest-neighbour cells. The broadening of the highest-temperature T-phase data signal a similar disorder, perhaps the amplitude or direction of the displacements has a somewhat longer correlation length.

Disorder effects 2+3



Broadening of the lines above 80 K signals disorder on an intermediate scale, larger than point defects but smaller than 5 nm.

In addition to disorder-broadened phonons there is a “central mode”, rising toward 0 cm^{-1} , that signals dynamic (fluctuating) disorder.

Amorphous materials

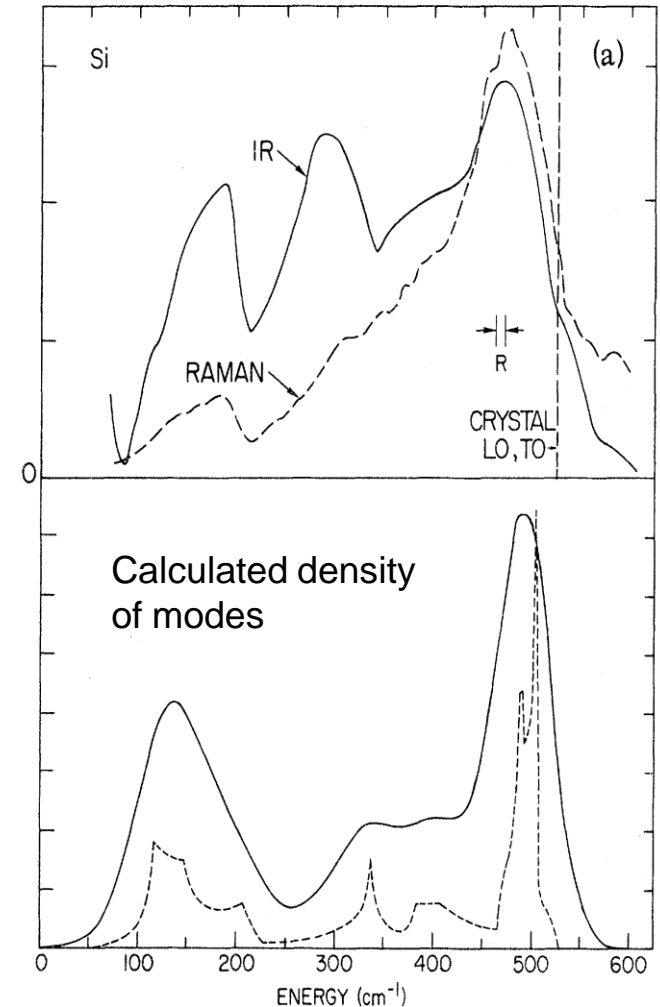
The most extreme disorder

Raman and IR spectra of a-Si compared with the broadened density of vibrational modes in a crystal.

Qualitative agreement based on similar local tetragonal nearest-neighbour coordination.

Disagreement in detail because the vibrational frequencies are dependent, though weakly, on the configurations at second and higher neighbour ionic shells.

Alben et al, Phys. Rev. B 11, 2271 (1975).



Summary

- **Site group analysis gives the number and symmetry of expected Raman lines**
- **and polarisation selection rules that permit assigning the symmetry of observed modes.**
- **calculated mode frequencies, a specialist activity, good to maybe 5%.**
- **Intrinsic line broadening from finite phonon lifetimes shows T dependence.**
- **Point defects make most phonon modes Raman active, lead to an approximate full density-of-modes signal.**
- **Extended defects (eg crystallites < 10 nm) broaden homogeneous lines.**
- **Static structural fluctuations near phase boundaries lead to broad lines.**
- **Dynamic fluctuations lead to a “central peak”.**