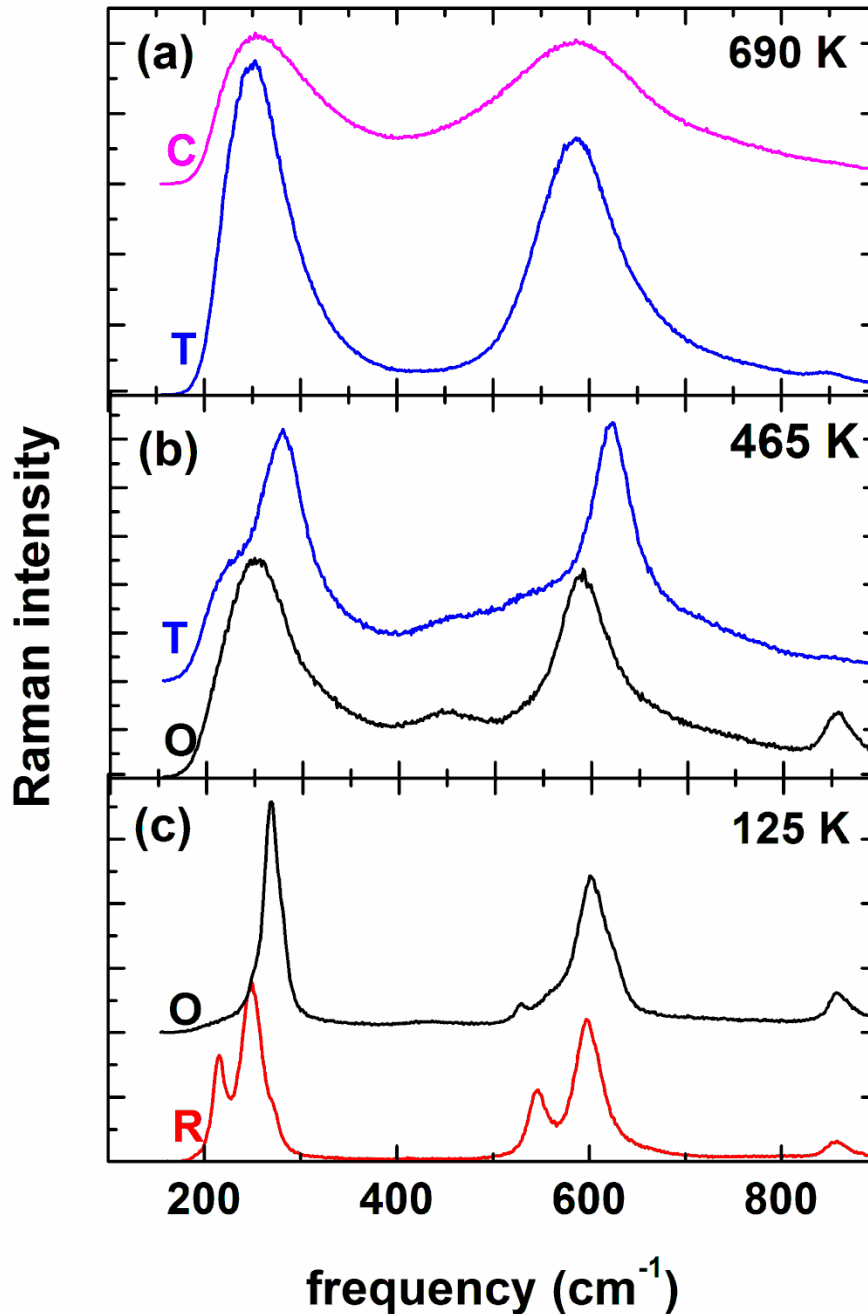


Raman Spectroscopy for Materials Science Lecture 3

- **Signatures of structural phase transitions**
- **Line doubling, Soft modes**
- **Size effects**
- **Sampled volume**
- **Ultrathin films**
- **Nanostructured materials**

Phase transitions

- **The Raman spectra depend on the lattice vibrations, and in turn on structure, as we have seen in lectures 1 and 2.**
- **They do not relate directly to the structure; there is no one-to-one relationship that permits the structure to be inferred from the spectra.**
- **But they can be used very effectively as a proxy for structural changes.**

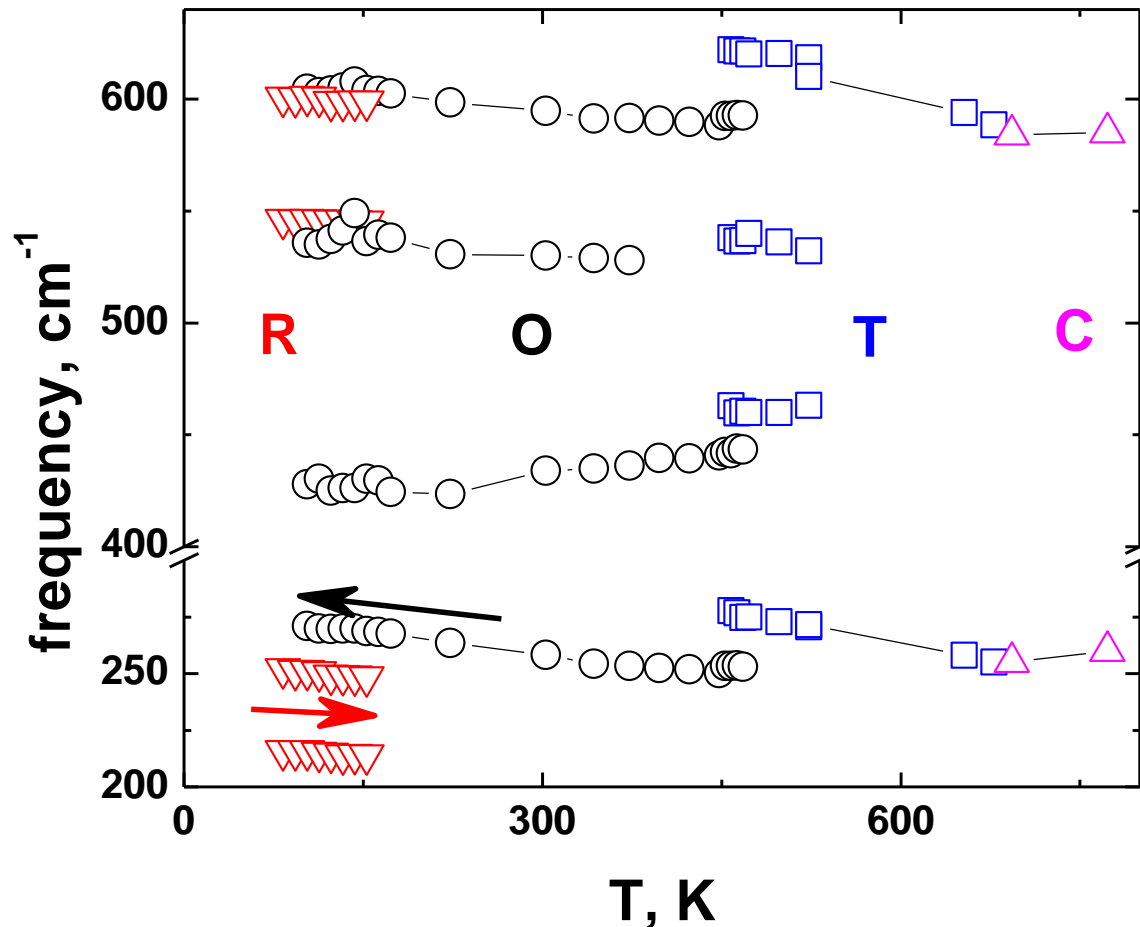


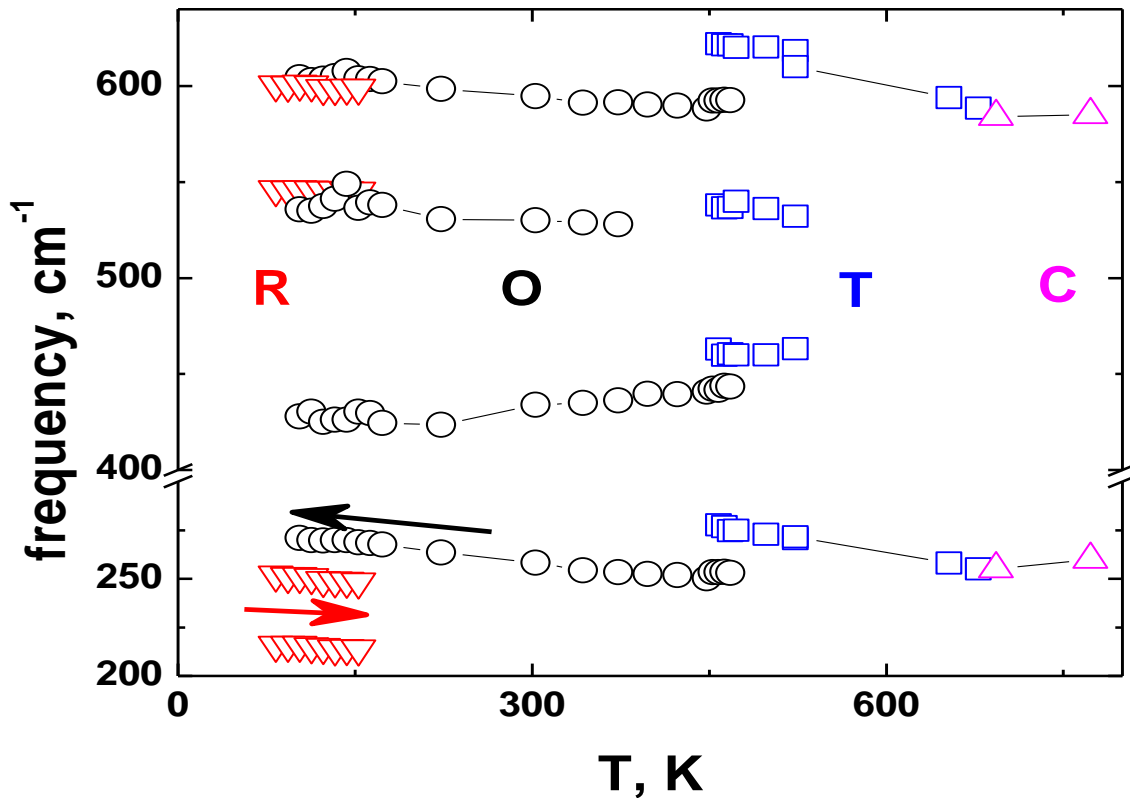
There is no one-to-one relationship between space group and Raman pattern, but the discontinuous changes can be used for a proxy for structural changes.

Within the hysteretic band the phase depends on whether the temperature is increasing or decreasing; eg at 465 K the phase is orthorhombic with increasing T and tetragonal with decreasing T.

Qualitative changes are clear here, but they can be emphasised by fitting the lines and plotting frequencies, widths, amplitudes vs T.

The frequency of the peaks (fitted to Lorentzians) plotted vs T show discontinuities at the phase transitions along the series **Rhomboidal-Orthorhombic-Tetragonal-Cubic**. Notice the hysteresis (supercooling/superheating) at the phase boundaries.

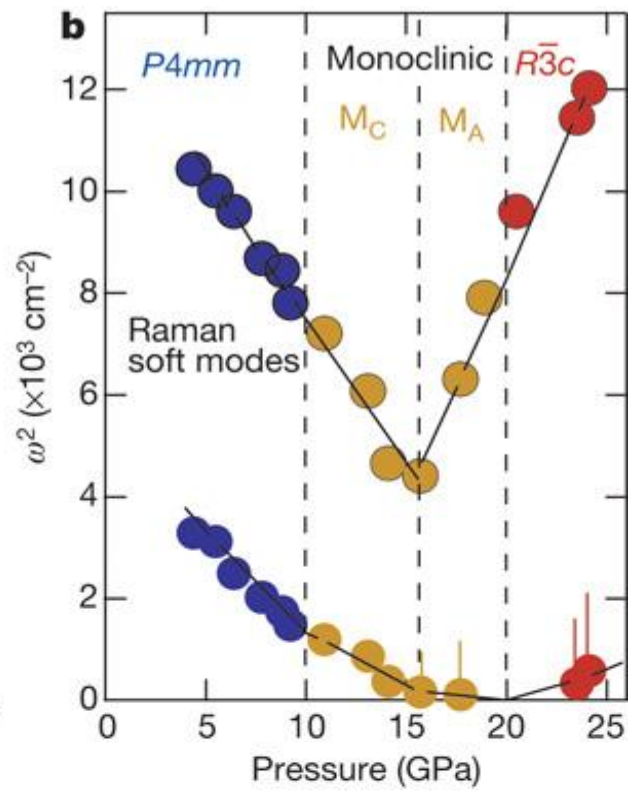
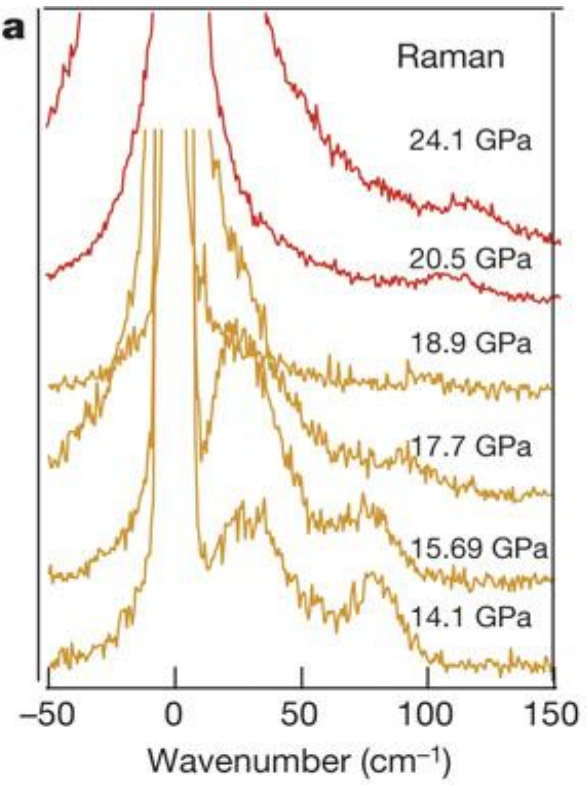




Symmetry classifications (A, B, E, F) change across the phases; they have specific definitions within different point groups.

Soft-mode spectroscopy

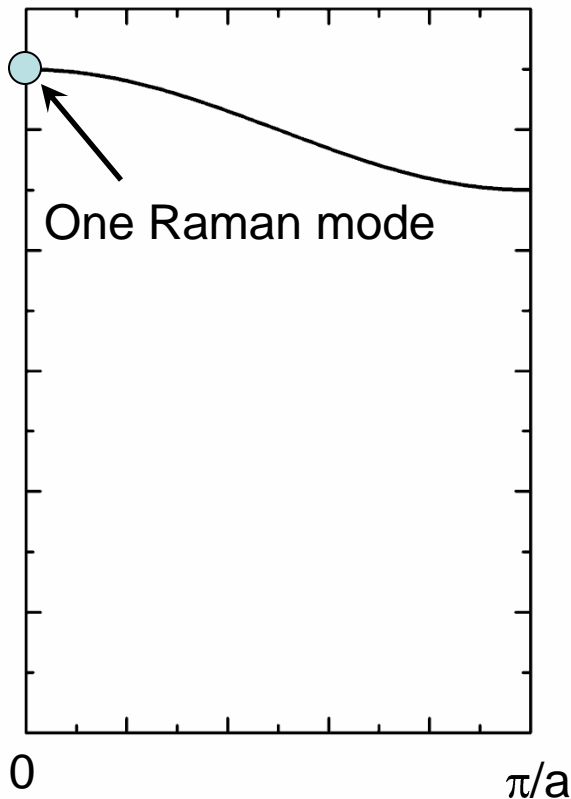
- Reveals the weakening restoring force on ions as a displacement transition is approached. The weaker forces lead to a reduced frequency (“softening”) of some vibrations.
- Probes of the *fundamental* mechanism driving those transitions.
- The soft modes are all at low frequencies, typically well below 100 cm^{-1} , requiring triple monochromators and great care. Mostly left to Raman/IR experts.



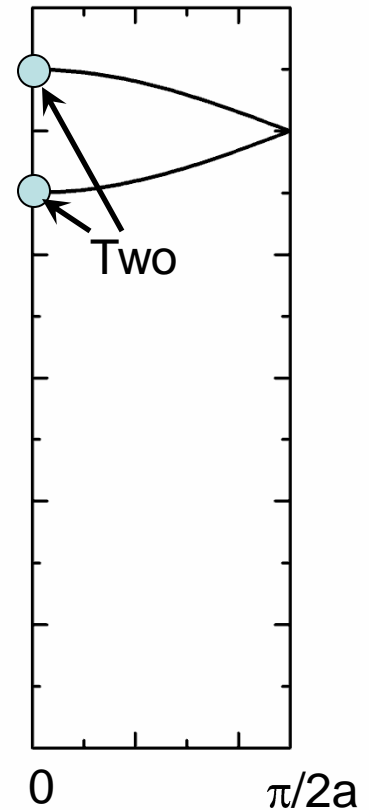
Soft modes in PbTiO_3 near the phase transition driven by pressure.

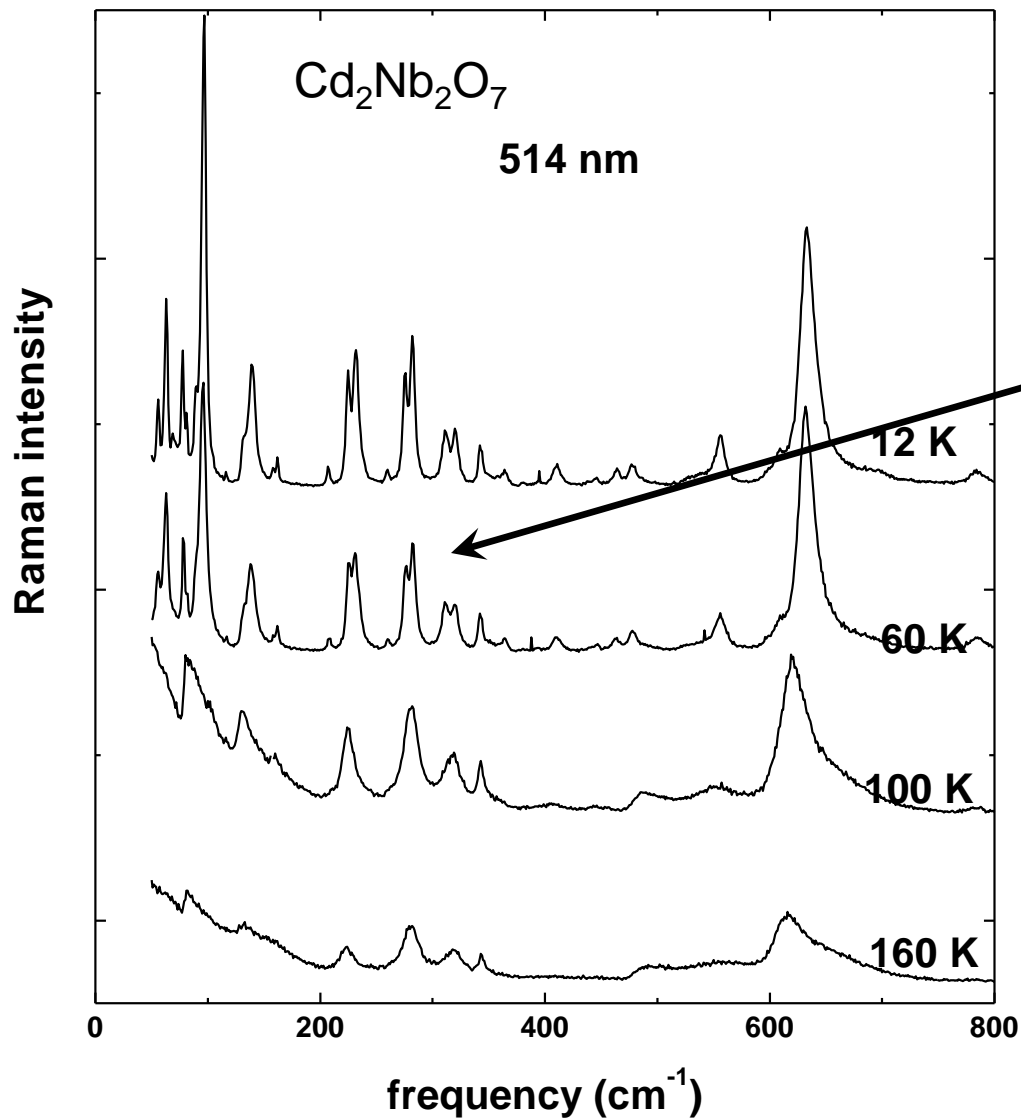
Ahert et al, Nature 451 545 (2008).

Some structural phase transitions (eg alternate O octahedra rotations, and all transitions to an antiferroelectric phase?) increase the unit cell size by some integer N, which then reduces the Brillouin Zone by a factor 1/N. That brings zone-boundary modes to the zone centre and often shows a pair of Raman lines where there was only one before.



Brillouin zone halved, the optic branch "folds", moving the zone-boundary mode to the zone centre.





Doubling of zone centre modes signals doubling (or more) of unit cell in the low-T phase.

Summary, structural phase transitions

- **Structural phase transitions alter the crystal's vibrational behaviour, so that**
- **Raman spectra show changes across those transitions; Raman spectroscopy provides a convenient proxy for structural phase changes.**
- **Raw spectra show their effects, though fitting the lines can give a clearer interpretation.**
- **Doubling of features, frequency shifts, line width changes,... are the typical signatures of structural transitions.**
- **Soft modes signal softening of restoring forces typical of many structural transitions.**

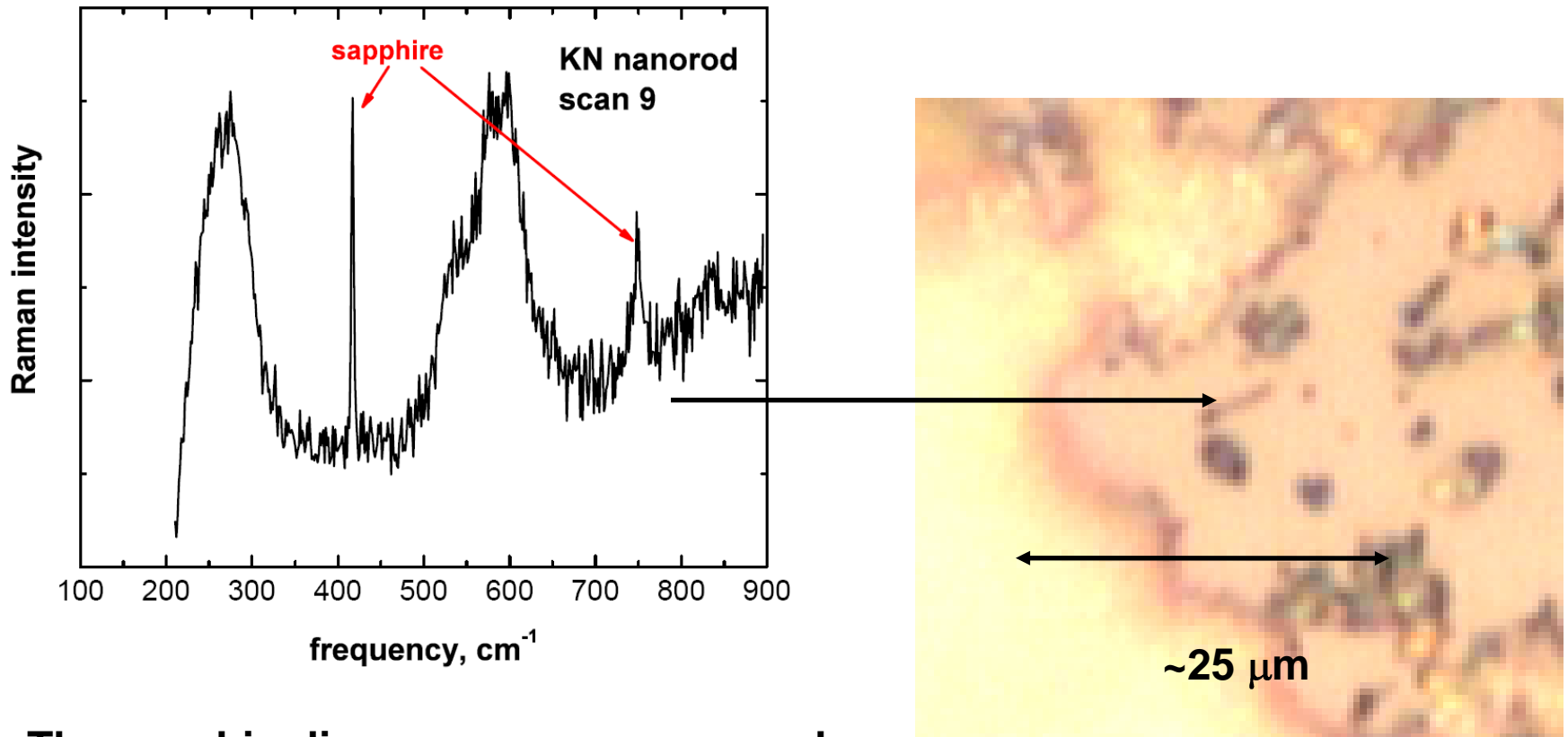
Size matters

- The focus of Raman spectroscopy is ~ 500 nm,
- some 1000 interatomic separations.
- The scale of size effects is determined by the scale of interactions, most often a few to tens of interatomic separations, \ll Raman focusability.
[Exceptions exist, eg superconducting interactions.]
- So detecting size effects on single nanostructured elements takes some special effort.

Individual nanoparticles

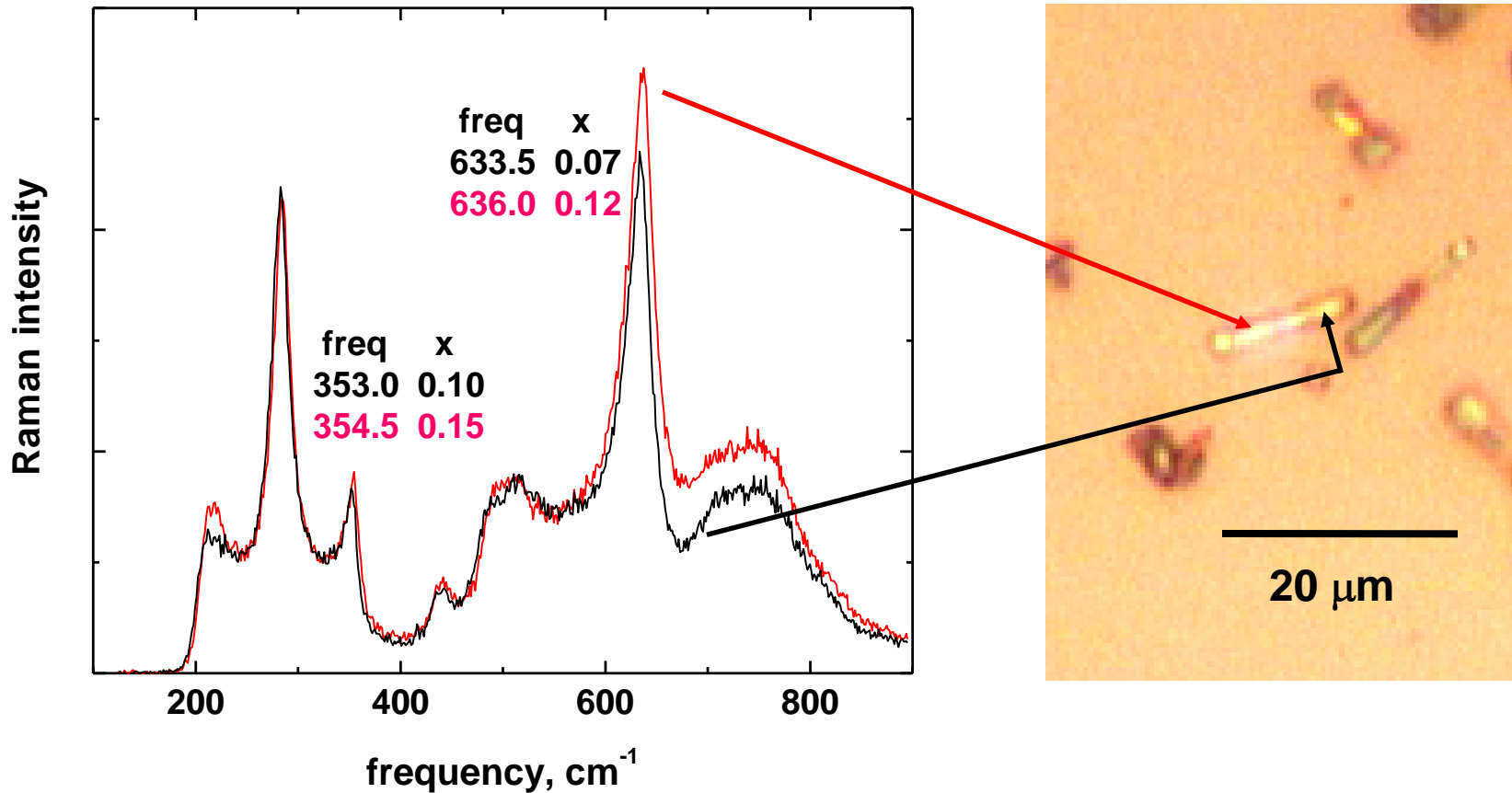
- The first challenge is to separate the nanoparticles and find them at the Raman microscope.
- The second is to collect their Raman signal and separate it from the signal of the supporting substrate.

The potential for moderate spatial resolution can be a major advantage as in this study of KNbO_3 nanowires dispersed on sapphire.



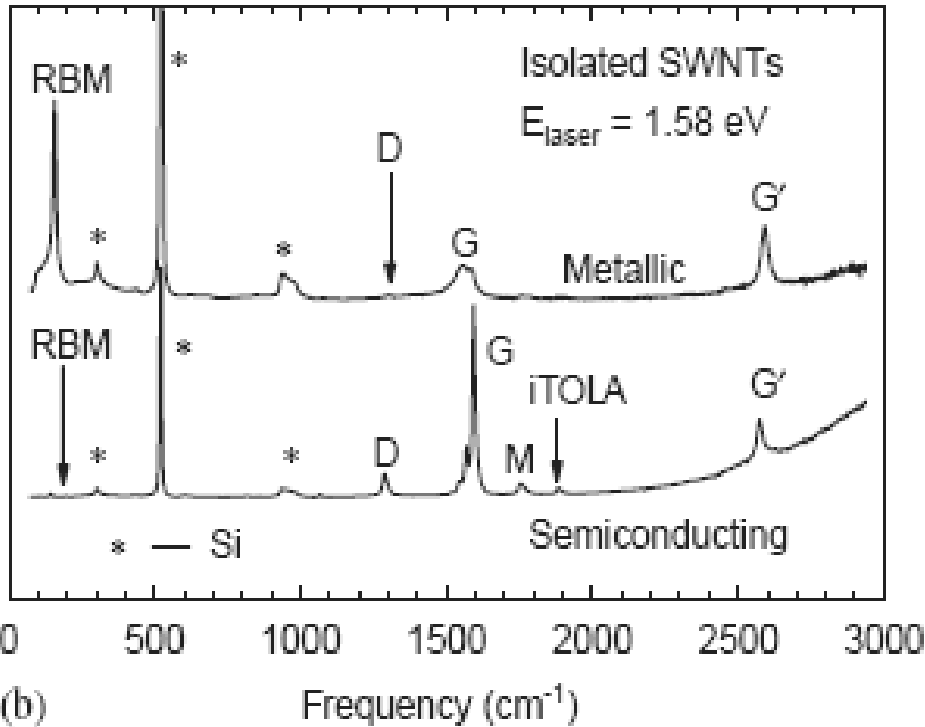
The sapphire lines are very narrow and weak, easily separated even though most of the illuminated area falls on the substrate.

Or to demonstrate that this PZT nanowire had a graded composition. Note that here the wire is so large that we see no sapphire signal.



Raman spectra from single carbon nanotubes on Si

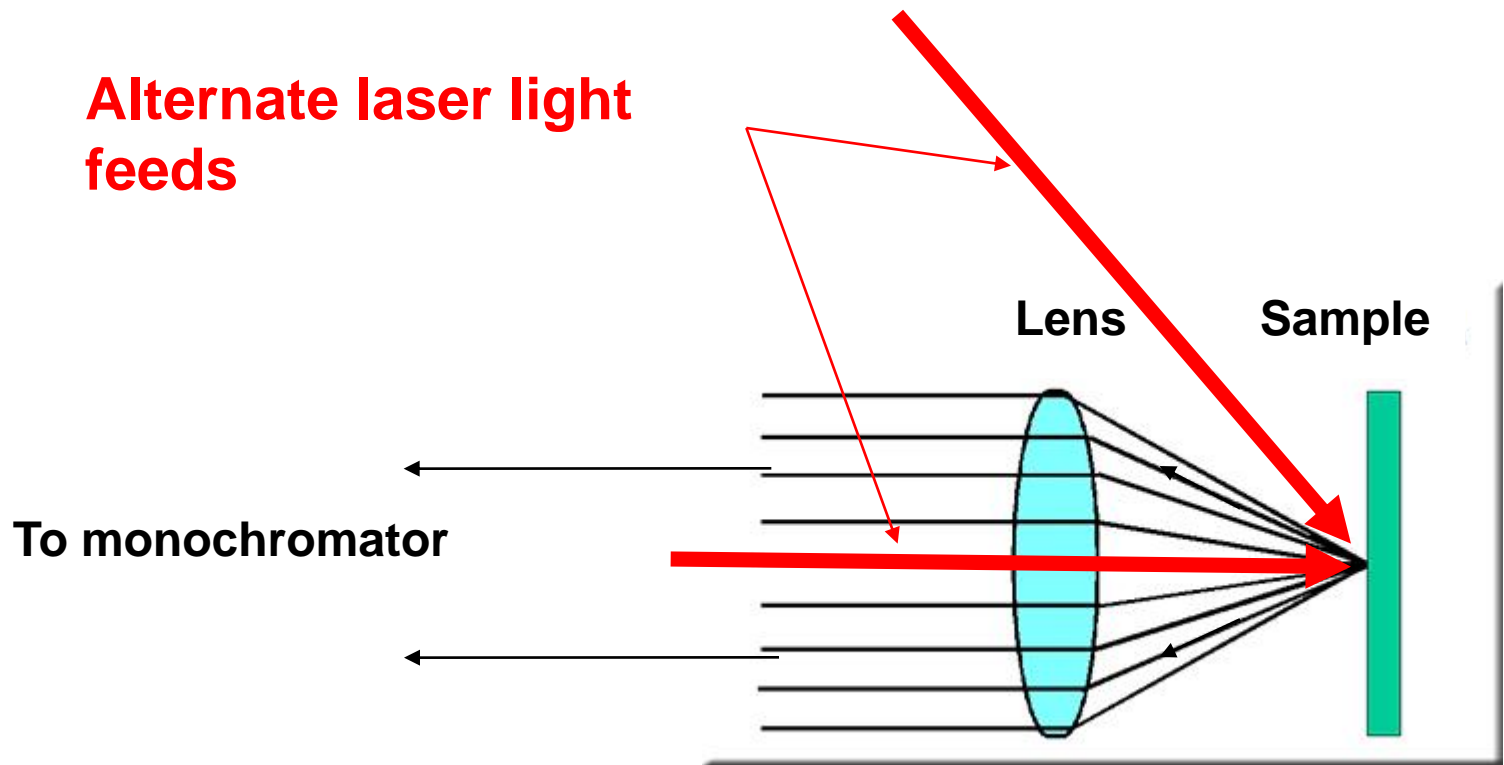
These data were collected on nanotubes that could not be seen in the microscope, but their Raman lines are well separated from the Si lines.



* - Silicon Raman lines

Most common backscattering geometry

The Raman scattered light is collected from the illuminated surface; this geometry required for any sample that is not transparent.



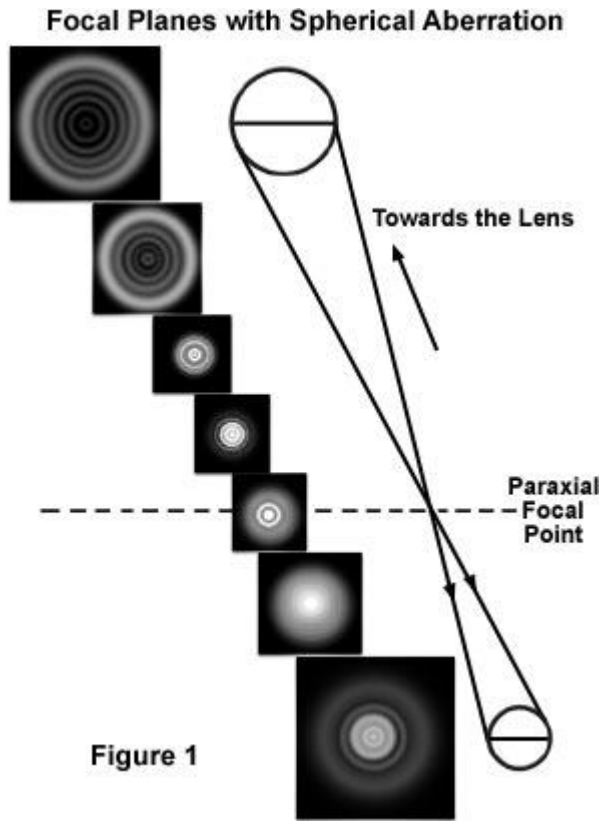
Raman sampling depth in opaque samples

- Incident light illuminates to a depth of about the attenuation length (δ), $I \sim \exp(-z/\delta)$
- and the scattered light escapes from about that depth.
- The combination gives scattered intensity $\sim \exp(-2z/\delta)$, so that the typical depth probed is $\delta/2$, $1/2$ of the attenuation length.
- In non-turbid samples (i.e. light is absorbed more strongly than scattered) δ is the optical skin depth, the inverse of the absorption coefficient at the laser wavelength.

Raman sampling depth in turbid samples

- Most ceramics will have optical properties dominated by scattering, signaled by a wide glowing halo about the focused laser spot.**
- Focusing is a challenge, but with care the Raman signal is from a layer of depth of about $\frac{1}{2}$ the distance between scattering centres.**

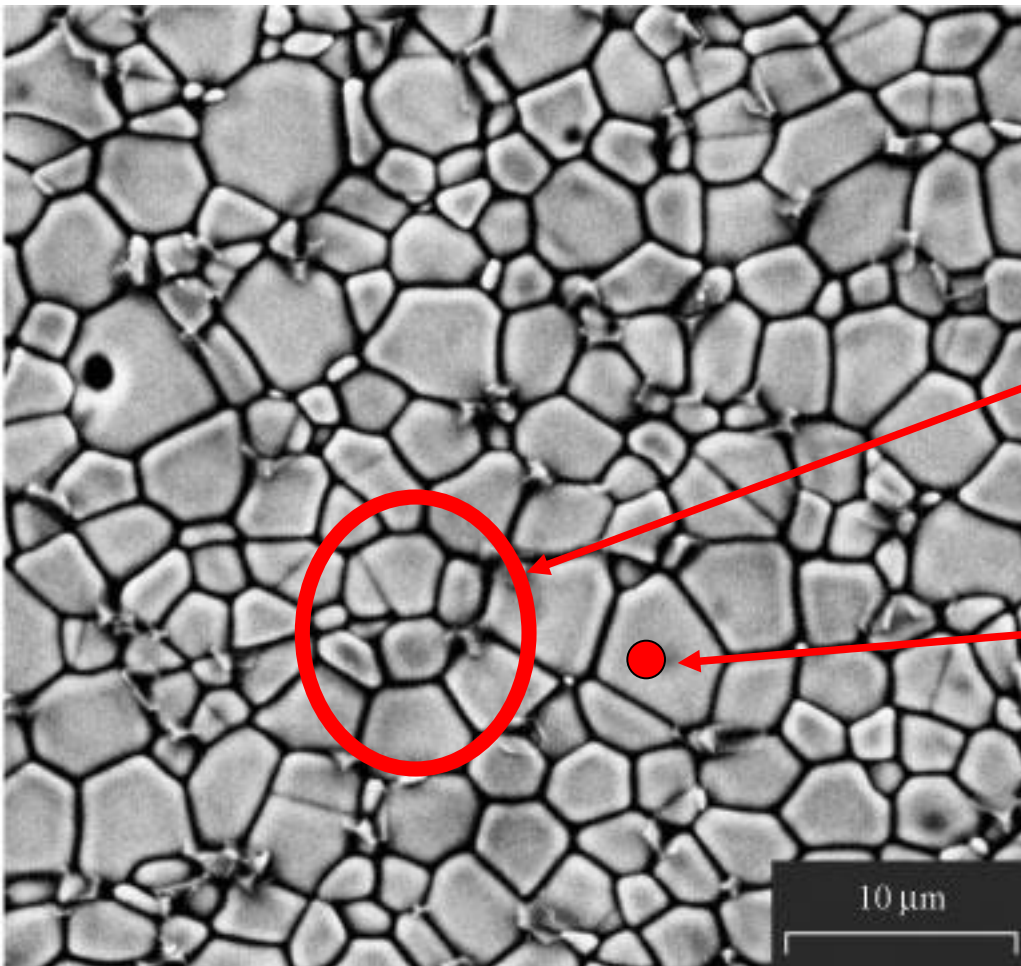
Can individual crystals be studied in polycrystalline or composites ceramics?



- The smallest spot, at focus, depends on the divergence of the laser beam and the optical (focusing) elements.
- The diffraction limit is the wavelength of light, $0.5 \mu\text{m}$.
- But that requires the best optics, in general achievable with microscopes, so-called micro Raman.
- More conventional, non-micro Raman, manages not much better than $5\text{-}10 \mu\text{m}$.

Focus diameter vs crystallite size is critically important; here the microscope might get spectra from one crystallite, but conventional Raman focusing catches at least several crystallites AND whatever fills the space between.

SnO_2/MnO



Typical conventional focus

Microscope focus

Are the Raman spectra typical of the bulk; when do size effects set in?

- We've seen broadening when the crystallites are < 10 nm, but that was merely a Raman coupling effect.**
- Surface-altered bonding configurations and lengths decay within about 0.5 nm, so in a particle of dimension scale D the fraction of ions affected is:**
$$4\pi(D/2)^2 \times 0.5\text{nm} / (4\pi/3)(D/2)^3 = 3\text{nm}/D;$$
- < 10% for particles 30 nm or larger.**
- But < 0.5% in crystallites that can be imaged in a Raman microscope.**

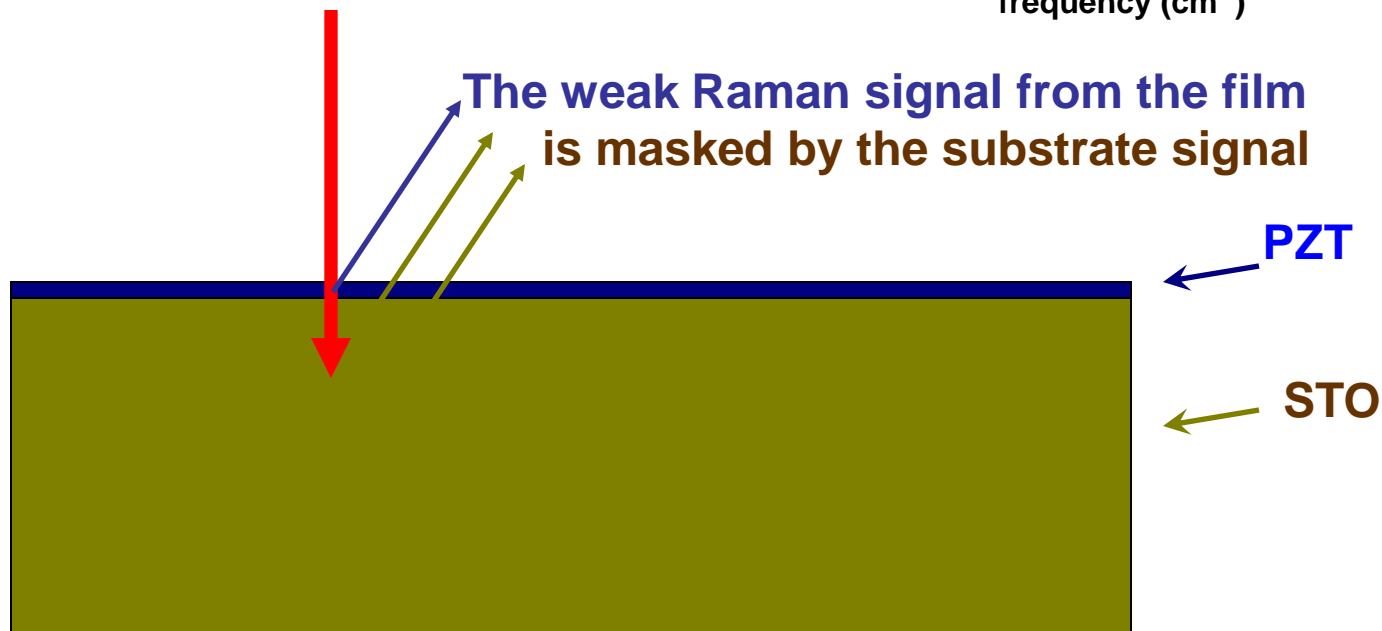
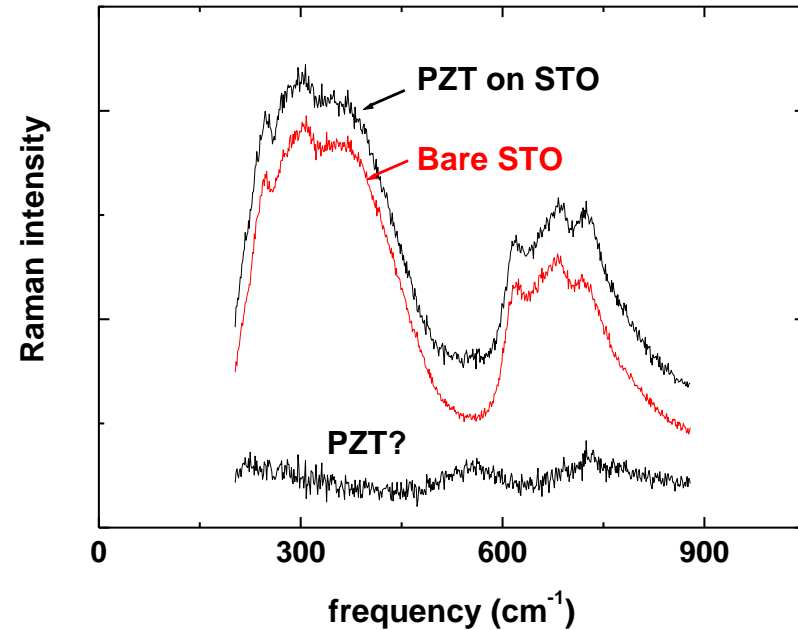
Can one determine the relative volume fractions of two components from Raman spectra?

- The Raman scattering strength of different chemical species can vary over orders of magnitude, so signal strength is unreliable without accurate cross section data.
- The very first Raman spectrum published for $\text{YBa}_2\text{Cu}_3\text{O}_7$ (YBCO) (the first high T_c superconductor) reported many lines, but not one was from YBCO, despite it being overwhelmingly the majority component in the ceramic sample!
- A sensible strategy is to establish one 50%/50% sample and use its spectrum as a standard.

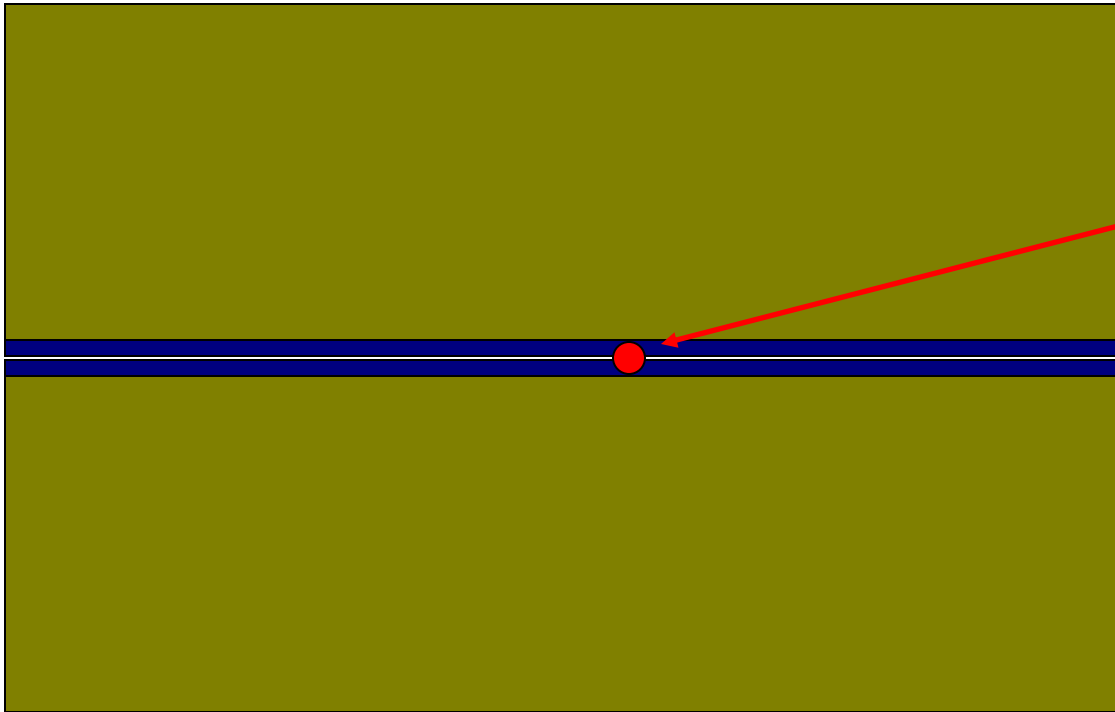
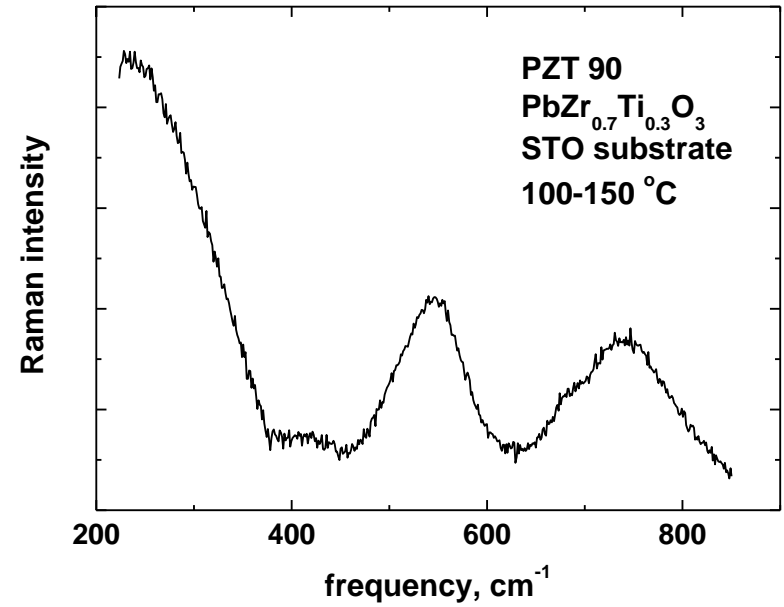
Ultrathin films

- **Since the development of molecular beam epitaxial techniques in the 1970s there has been a continuously advancing interest and exploitation of semiconductor, metal, ferroelectric, magnetic, ... thin films.**
- **Their structure and the effects of strain imposed by epitaxial growth are important, but not easily established.**
- **Raman has a role, but the thin-film signal is often masked by a much larger signal from the substrate.**
- **TERS can help, but there are easier strategies.**

Raman spectrum of a 300 nm thick PZT film on SrTiO₃



Two films could be imaged in profile, yielding a much clearer spectrum.



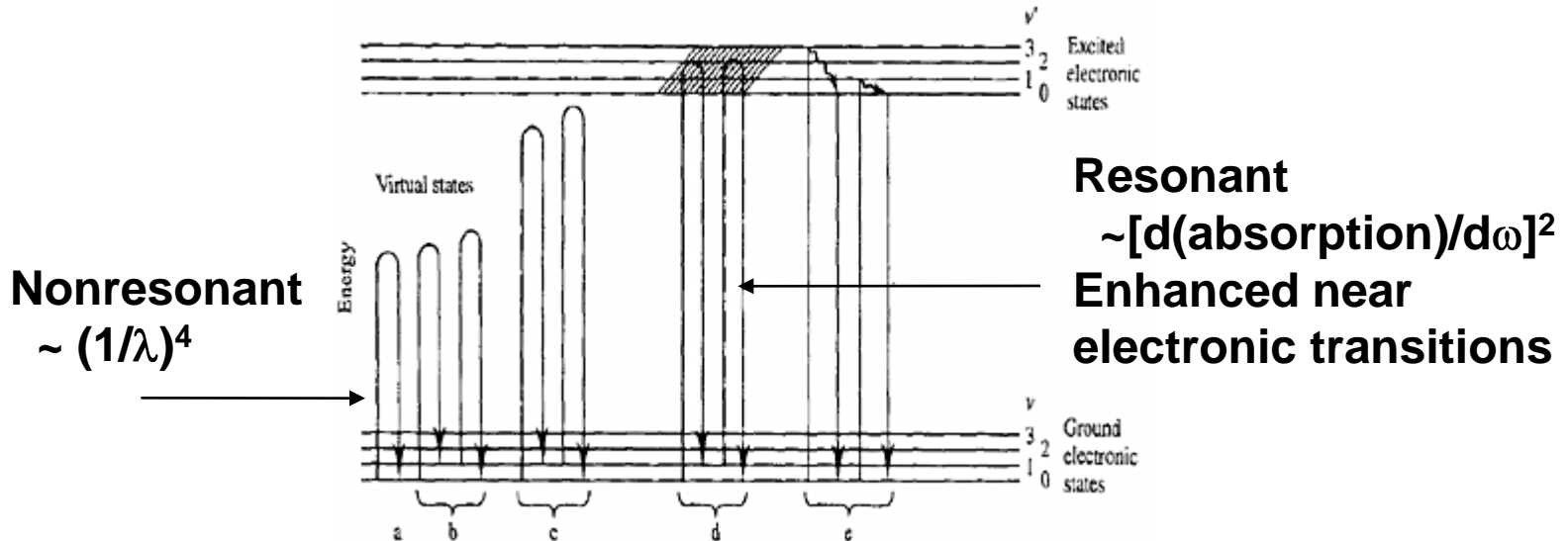
Focused spot size

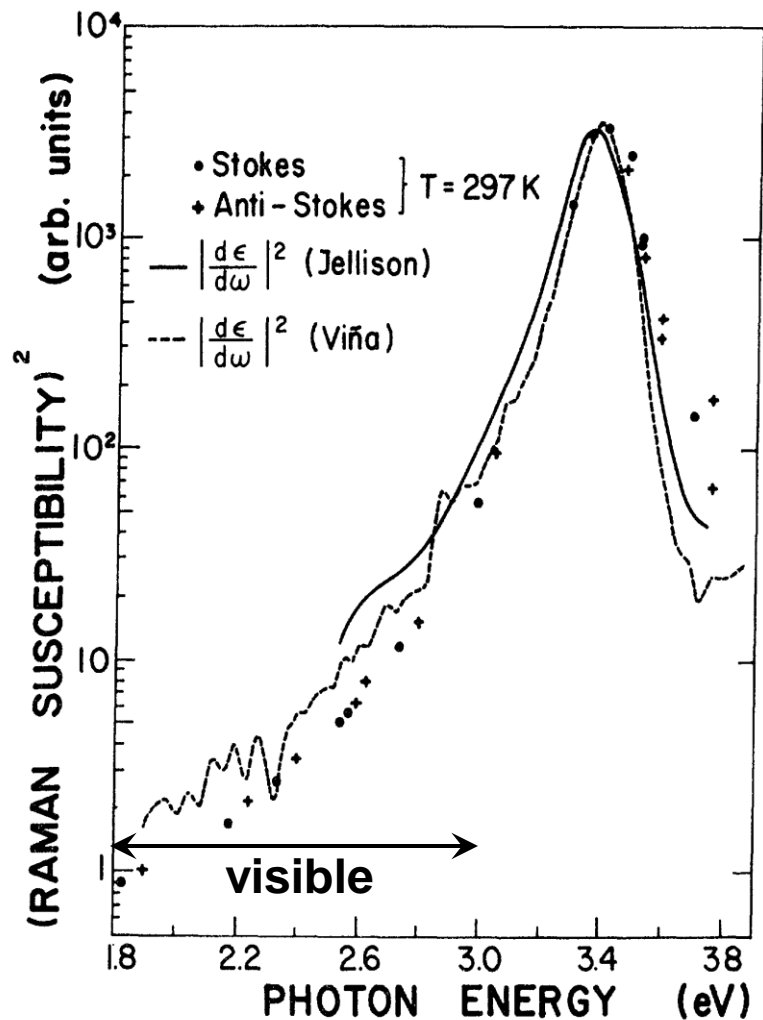
Resonance Raman spectroscopy

•The Raman “cross section”, effectively the scattering efficiency, depends crudely on the incident wavelength λ as

cross section $\sim (1/\lambda)^4$.

•But for photon energies near an electronic transition there can be an enormous enhancement.





Room temperature resonance Raman profile of Si

A factor of 30 variation across the visible, and Si has a relatively weak resonance profile.

Laser-line choice, IR, red, green, UV?

Different components in a multiphase sample are likely to show resonance at different frequencies.

One should try different excitation (laser) frequencies to enhance the signal from the component of interest.

Comparison with XRD

Very glib, approximate comparison only

Property	Raman	XRD
Sampled volume	< 1 μm^3	> 1 mm^3
Range of order probed	< 5 nm	> 10 nm
Relation to structure	indirect	direct
Speed	Faster	Slower

Summary, nanostructured and composite materials

- **Backscattering geometry for opaque samples**
- **Sampled depth; absorption or scattering length**
- **Single crystallite vs orientational average**
- **Resonant scattering**
 - signals from different components
 - importance of excitation choice