Vibrational Spectroscopy

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LO/TO Splitting
Two similar structures Zincblende and diamond dispersion
LO/TO splitting
DFPT with LO/TO splitting in NaCl
LO/TO splitting in non-cubic systems
The non-analytic term and Born Charges
Electric Field response in CASTEP
Ionic and Electronic Dielectric Permittivity
Example: NaHF2
Dynamical charges in NaHF2
Modelling of spectra

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Two similar structures

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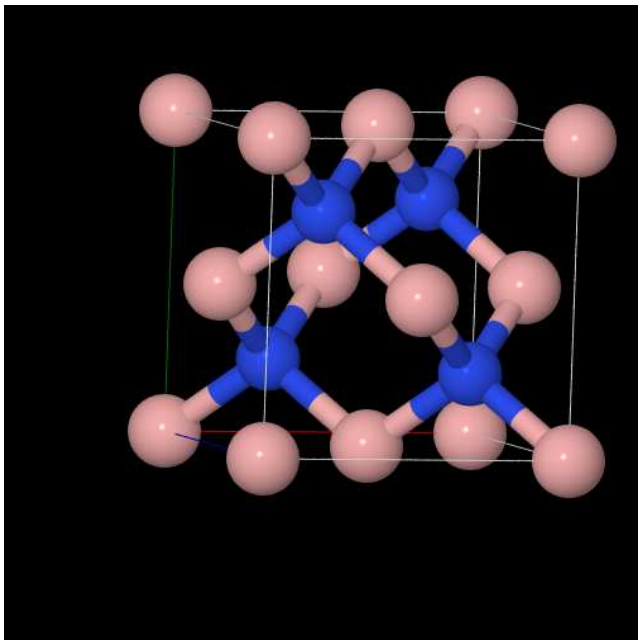
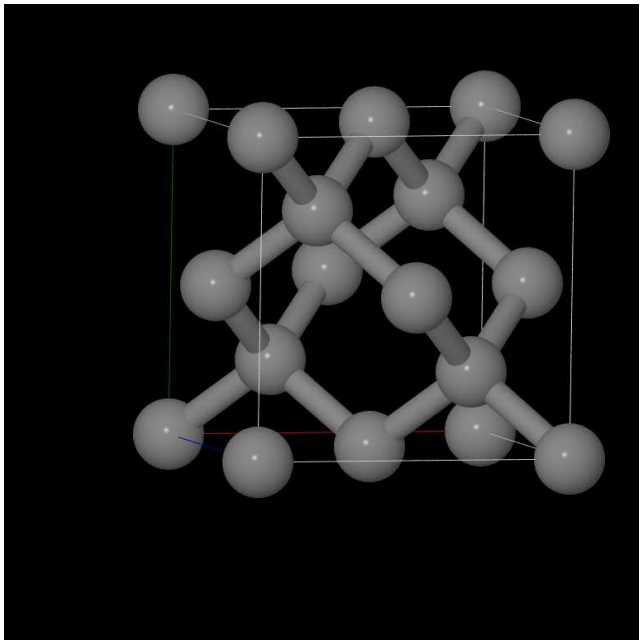


Zincblende BN



Diamond

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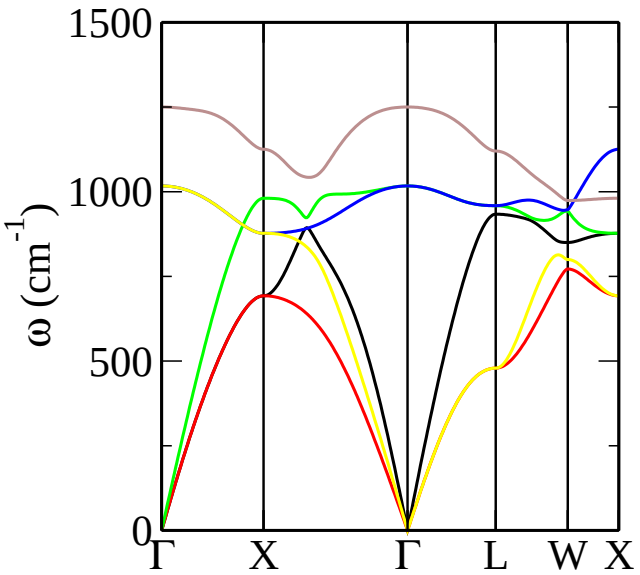
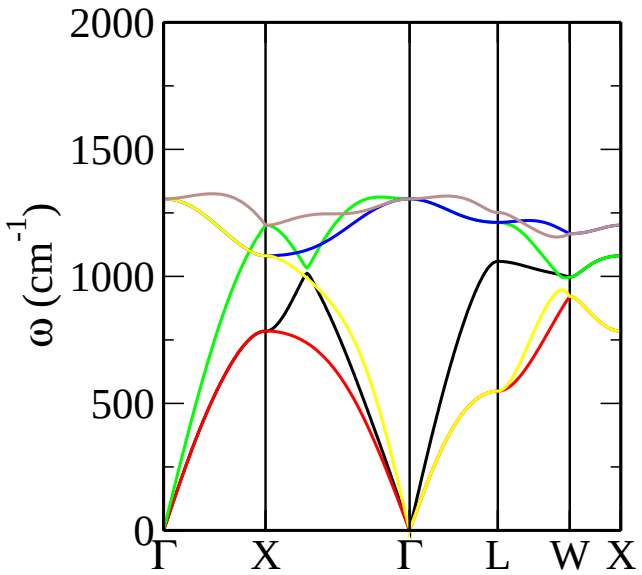
BN-zincblende



diamond



Cubic symmetry of Hamiltonian predicts *triply degenerate* optic mode at Γ in both cases.

2+1 optic mode structure of BN violates group theoretical prediction.

Phenomenon known as **LO/TO splitting**.

LO/TO splitting

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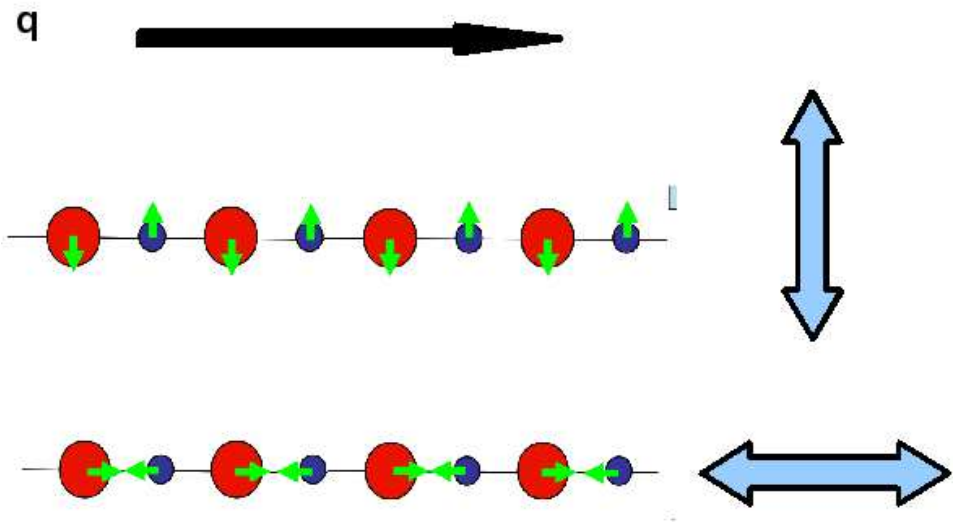

- Dipole created by displacement of charges of long-wavelength LO mode creates induced electric field.
- For TO motion $\boldsymbol{E} \perp \boldsymbol{q} \Rightarrow \boldsymbol{E}.\boldsymbol{q} = 0$
- For LO mode $\boldsymbol{E}.\boldsymbol{q} \neq 0$ and E-field adds additional restoring force.
- Frequency of LO mode is upshifted.
- Lyndane-Sachs-Teller relation for cubic case: $\frac{\omega_{LO}^2}{\omega_{TO}^2} = \frac{\epsilon_0}{\epsilon_\infty}$
- LO frequencies at $\boldsymbol{q} = 0$ depend on *dielectric permittivity*

DFPT with LO/TO splitting in NaCl

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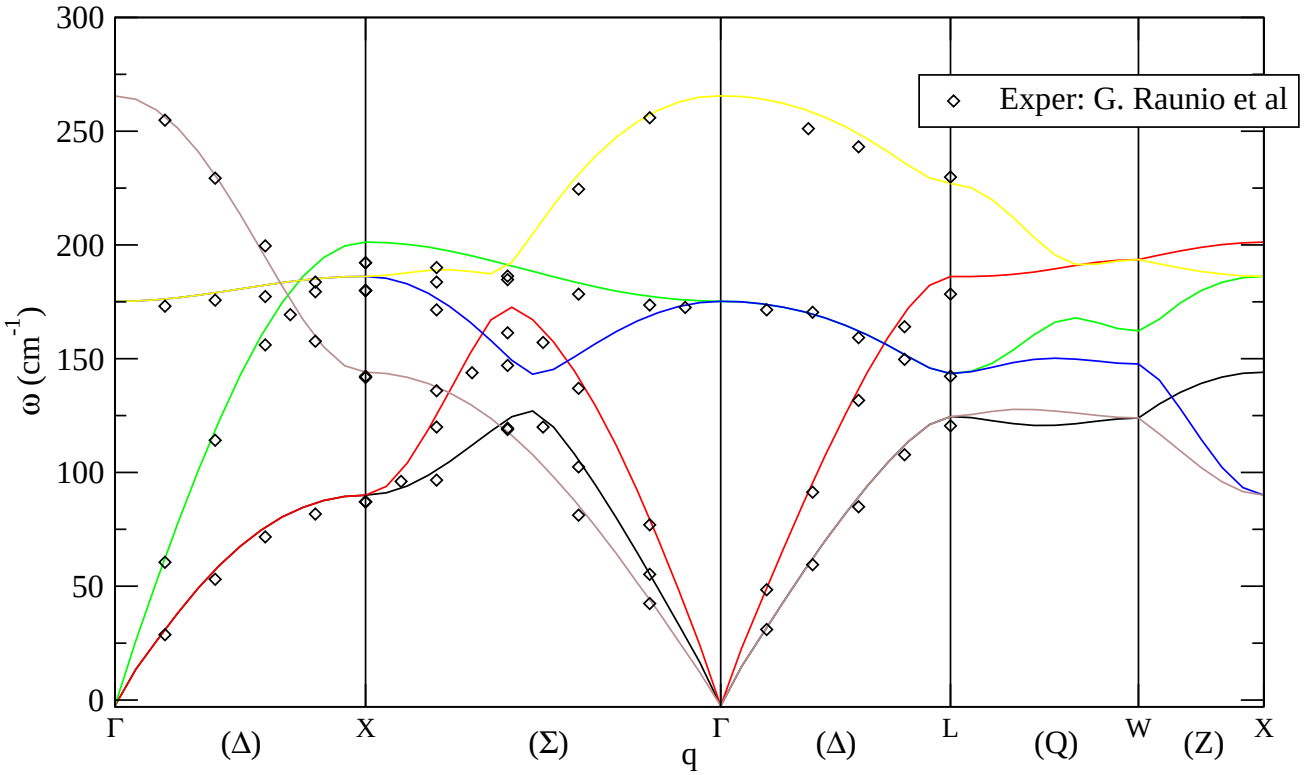
LO modes can be seen in infrared, INS, IXS experiments, but not raman.

NaCl phonon dispersion



LO/TO splitting in non-cubic systems

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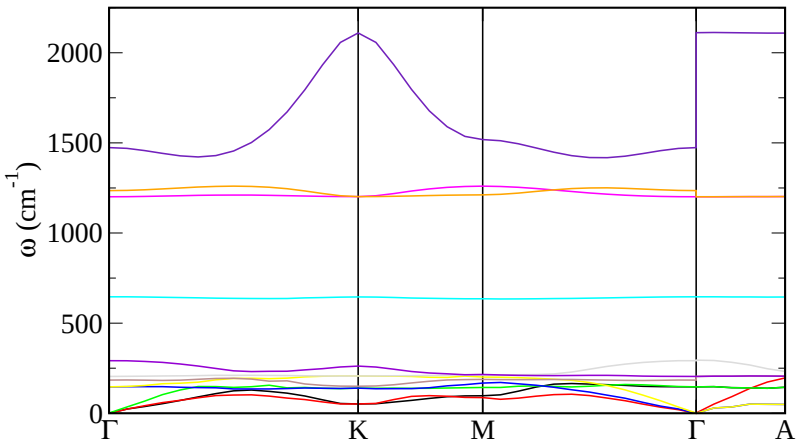
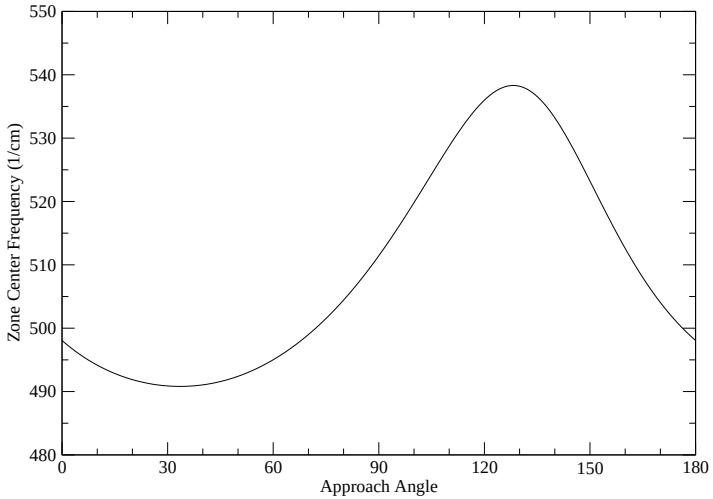


In systems with unique axis (trigonal, hexagonal, tetragonal) LO-TO splitting depends on *direction* of $\boldsymbol{q}$ even at $\boldsymbol{q} = 0$.

LO frequency varies with angle in α-quartz



The non-analytic term and Born Charges

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LO-TO splitting at $\boldsymbol{q} \rightarrow 0$ is automatically included in DFPT. At $\boldsymbol{q} = 0$ exactly, need to add additional *non-analytic* term to dynamical matrix

$$C^{\kappa,\kappa'}_{\alpha,\alpha'}(\boldsymbol{q}=0)(NA) = \frac{4\pi}{\Omega_0}\frac{\sum_\gamma q_\gamma Z^*_{\kappa,\gamma\alpha}\sum_{\gamma'} q_{\gamma'} Z^*_{\kappa',\gamma'\alpha'}}{\sum_{\gamma\gamma'} q_\gamma \epsilon^\infty_{\gamma\gamma'} q_{\gamma'}}$$

$\epsilon^\infty_{\gamma\gamma'}$ is the dielectric permittivity tensor
$Z^*_{\kappa,\beta\alpha}$ is the Born Effective Charge tensor

$$Z^*_{\kappa,\beta,alpha} = V\frac{\partial P_\beta}{\partial x_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial E_\beta}$$

Z^* is *polarization per unit cell* caused by displacement of atom κ in direction α or *force exerted on ion* by macroscopic electric field.
$Z^*_{\kappa,\beta\alpha}$ and $\epsilon^\infty_{\gamma\gamma'}$ can both be computed via DFPT response to *electric field* perturbation.
(Dipole-dipole model use for Coulombic tail correction in Fourier interpolation procedure also depends on Z^* and ϵ^∞. *Not* included in most supercell calculations $\Rightarrow$ be suspicious of convergence in case of polar systems).

Electric Field response in CASTEP

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- Can also apply DFPT to *electric field* perturbation.
- Need trick to evaluate position operator. Evaluate $\nabla_{\boldsymbol{k}}\phi$. See NMR lecture for details.
- set `task = efield` or `task = phonon+efield`
- Convergence controlled by `efield_energy_tol`
- Computes *dielectric permittivity* for crystals and *polarisability* (for molecules)
- Includes *lattice contribution* for $\omega \longrightarrow 0$ response.
- Writes additional file *seedname*`.efield` containing $\epsilon_{\gamma\gamma'}(\omega)$ in infrared region.

```
=============================================================================
       Optical Permittivity (f->infinity)              DC Permittivity (f=0)
       ----------------------------------              ---------------------
        3.52475     0.00000     0.00000        10.00569     0.00000     0.00000
        0.00000     3.52475     0.00000         0.00000    10.00569     0.00000
        0.00000     0.00000     3.52475         0.00000     0.00000    10.00569
=============================================================================

=============================================================================
                                  Polarisabilities (A**3)
              Optical (f->infinity)                          Static  (f=0)
              ---------------------                          ------------
        5.32709     0.00000     0.00000        19.00151     0.00000     0.00000
        0.00000     5.32709     0.00000         0.00000    19.00151     0.00000
        0.00000     0.00000     5.32709         0.00000     0.00000    19.00151
=============================================================================
```

Ionic and Electronic Dielectric Permittivity

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- Pure covalent system - Si $Z^* = -0.009$,
- Ionic system, NaCl. $\epsilon_0 = 6.95$, $\epsilon_\infty = 2.70$. $Z^*(\mathrm{Na}) = 1.060$, $Z^*(\mathrm{Cl}) = -1.058$
- α-quartz, SiO_2:

$$\epsilon_\infty = \begin{matrix} 2.44 & 0.00 & 0.00 \\ 0.00 & 2.44 & 0.00 \\ 0.00 & 0.00 & 2.49 \end{matrix} \qquad \epsilon_0 = \begin{matrix} 5.01 & 0.00 & 0.00 \\ 0.00 & 4.71 & 0.15 \\ 0.00 & 0.15 & 4.58 \end{matrix}$$

(exp: $\epsilon_0 = 4.64/4.43$)

$$Z^*(\mathrm{O}_1) = \begin{matrix} -2.16 & -0.03 & 0.81 \\ -0.08 & -1.04 & 0.14 \\ 0.00 & 0.00 & -1.71 \end{matrix} \qquad Z^*(\mathrm{Si}) = \begin{matrix} 2.98 & 0.00 & 0.00 \\ 0.00 & 3.67 & 0.26 \\ 0.00 & -0.30 & 3.45 \end{matrix}$$

- Note anisotropic tensor character of Z^*.

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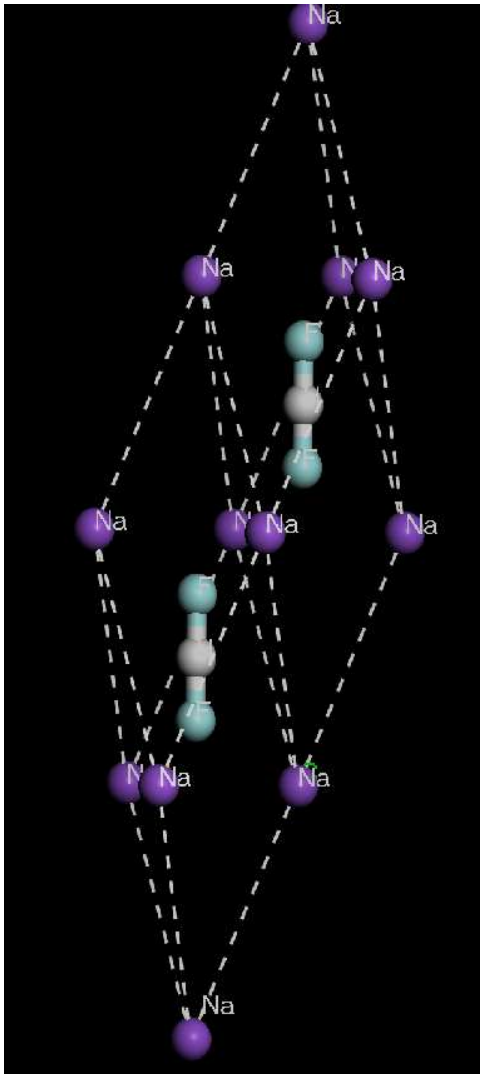
Modelling of spectra

- Unusual bonding, nominally ionic Na^+ FHF^-, with linear anion.
- Layer structure, $R\bar{3}$ space group.
- Phase transition to monoclinic form at ≈ 0.4 GPa.
- Phonon spectrum measured at ISIS on TOSCA
  - high-resolution neutron powder spectrometer.
  - No selection rule absences
  - Little or no anharmonic overtone contamination of spectra
  - No control over $(\boldsymbol{q}, \omega)$ path - excellent for molecular systems but spectra hard to interpret if dispersion present.



Dynamical charges in NaHF2

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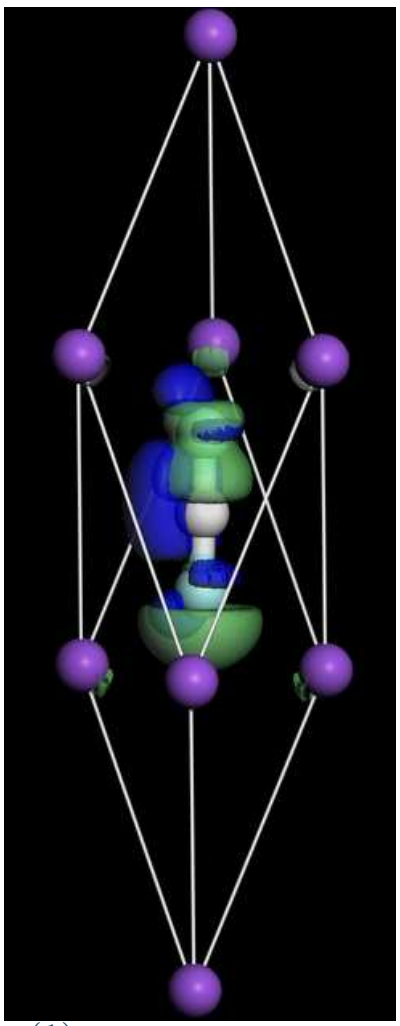
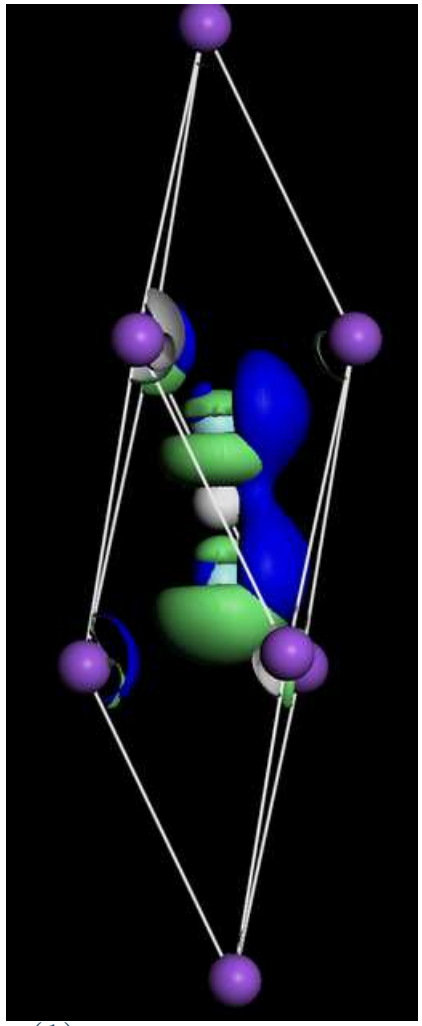
- highly anisotropic Z^*

xy	z	
0.34	2.02	(H)
−0.69	−1.52	(F)
1.06	1.04	(Na)

- charge density $n^{(1)}(\boldsymbol{r})$ from DFPT shows electronic response under perturbation
- Charge on F ions moves in response to H displacement in z direction.



$n^{(1)}(\boldsymbol{r})$ response to H_x (blue) and H_z (green)



$n^{(1)}(\boldsymbol{r})$ response to $\mathcal{E}_x$ (blue) and $\mathcal{E}_z$ (green)

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Modelling of powder IR
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Raman scattering of t-ZrO2
Inelastic X-Ray scattering
IXS of Diaspore

Modelling of spectra

Inelastic Neutron Scattering

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To model spectra need to treat scattering dynamics of incident and emergent radiation.
In case of INS interaction is between point neutron and nucleus - scalar quantity b depends only on nucleus – specific properties.

$$\frac{d^2\sigma}{dEd\Omega} = \frac{k_f}{k_i} b^2 S(\boldsymbol{Q}, \omega)$$

$\boldsymbol{Q}$ is scattering vector and ω is frequency - interact with phonons at same wavevector and frequency.
Full measured spectrum includes overtones and combinations and instrumental geometry and BZ sampling factors.
Need specific spectral modelling software to incorporate effects as postprocessing step following CASTEP phonon DOS calculation.
A-Climax : A. J. Ramirez-Cuesta Comput. Phys. Comm. **157** 226 (2004))

INS of Ammonium Fluoride

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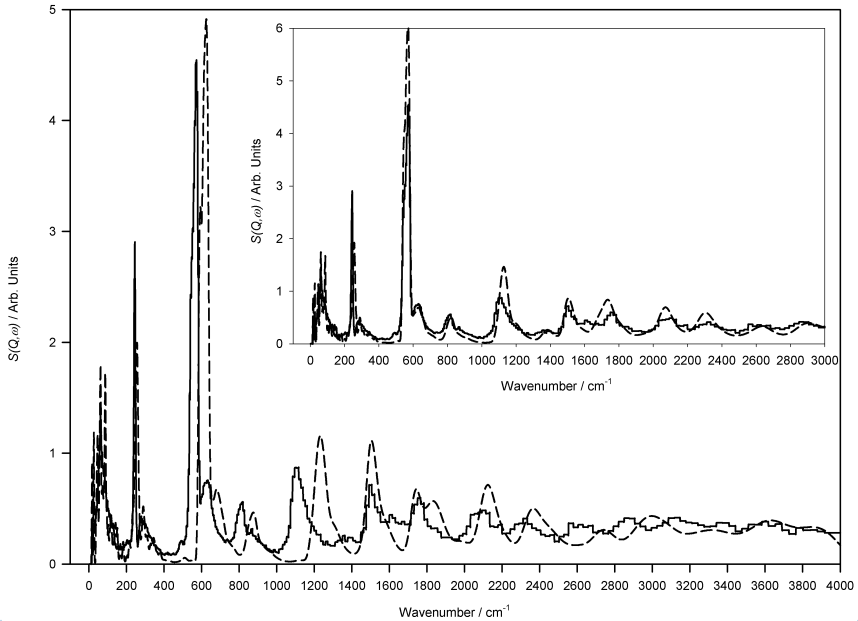
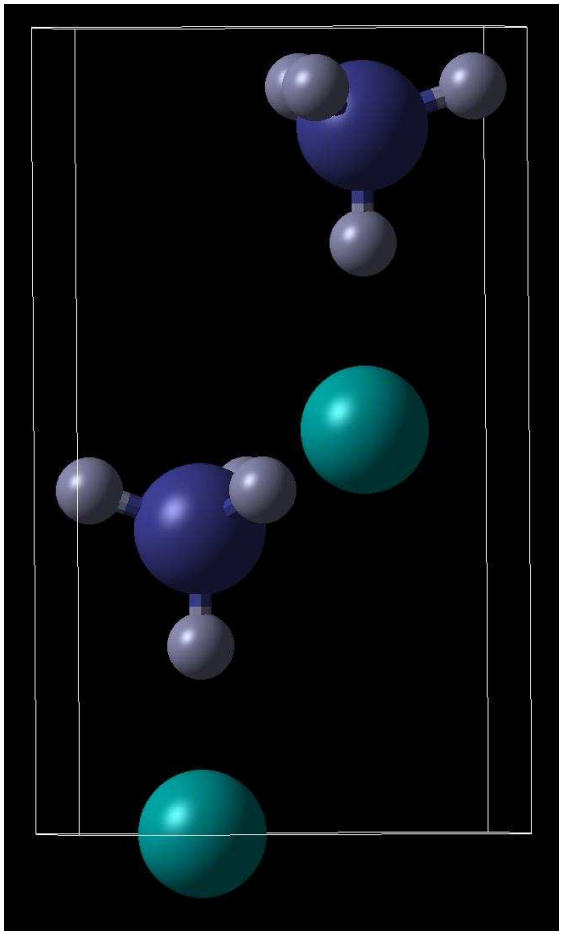
- NH_4F is one of a series of ammonium halides studied in the TOSCA spectrometer. Collab. Mark Adams (ISIS)
- Structurally isomorphic with ice ih
- INS spectrum modelled using A-CLIMAX software (A. J. Ramirez Cuesta, ISIS)
- Predicted INS spectrum in mostly excellent agreement with experiment
- NH_4 libration modes in error by $\approx 5\%$.
- Complete mode assignment achieved.





Single-crystal infrared

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Prediction of reflectivity of optically flat single crystal surface given as function of $\boldsymbol{q}$ - projected permittivity $\epsilon_{\boldsymbol{q}}(\omega)$

$$R(\omega) = \left| \frac{\epsilon_{\boldsymbol{q}}^{1/2}(\omega) - 1}{\epsilon_{\boldsymbol{q}}^{1/2}(\omega) + 1} \right|^2$$

with $\epsilon_{\boldsymbol{q}}$ defined in terms of ϵ^{∞} and mode oscillator strength $S_{m,\alpha\beta}$

$$\epsilon_{\boldsymbol{q}}(\omega) = \boldsymbol{q}.\boldsymbol{\epsilon}^{\boldsymbol{\infty}}.\boldsymbol{q} + \frac{4\pi}{\Omega_0} \sum_m \frac{\boldsymbol{q}.\boldsymbol{S}.\boldsymbol{q}}{\omega_m^2 - \omega^2} = \boldsymbol{q}.\boldsymbol{\epsilon}(\omega).\boldsymbol{q}$$

$\boldsymbol{\epsilon}(\omega)$ is tabulated in the *seend-name*`.efield` file written from a CASTEP efield response calculation.
Example BiFO3 (Hermet et al, Phys. Rev B 75, 220102 (2007)

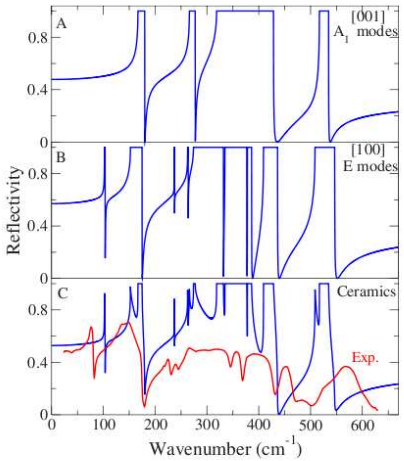

FIG. 1. (Color online) Calculated IR reflectivity spectra (blue) of a $BiFeO_3$ monocrystal (A), (B) and ceramics (C). Experimental data (20 K) from Ref. 12 (red).

Powder infrared

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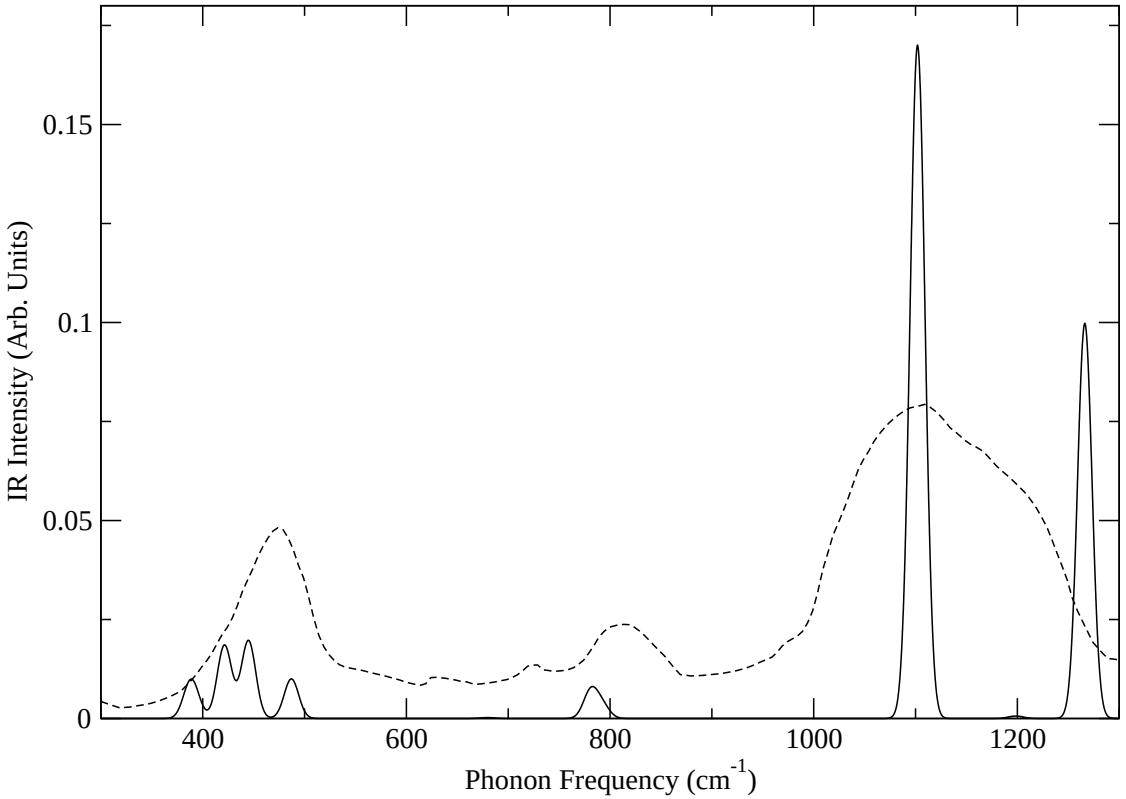
α-quartz



- Straightforward to compute peak *areas*.
- Peak shape modelling depends on sample and experimental variables.
- Multiphonon and overtone terms less straightforward.

Modelling of powder IR

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See E. Balan, A. M. Saitta, F. Mauri, G. Calas. *First-principles modeling of the infrared spectrum of kaolinite.* American Mineralogist, 2001, 86, 1321-1330. Spectral shape determined by optical effects and shifted LO modes in specific size/shape of crystallites.

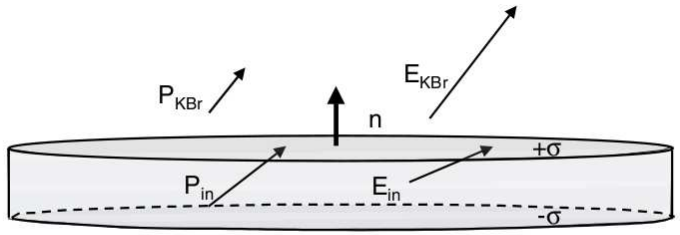

FIGURE 1. Schematic view of a dielectric plate showing the electric field and polarization vectors used to calculate the IR absorption spectrum. The surface charges +σ and −σ produce the depolarization field, $\mathbf{E}_{in}$-$\mathbf{E}_{KBr}$.

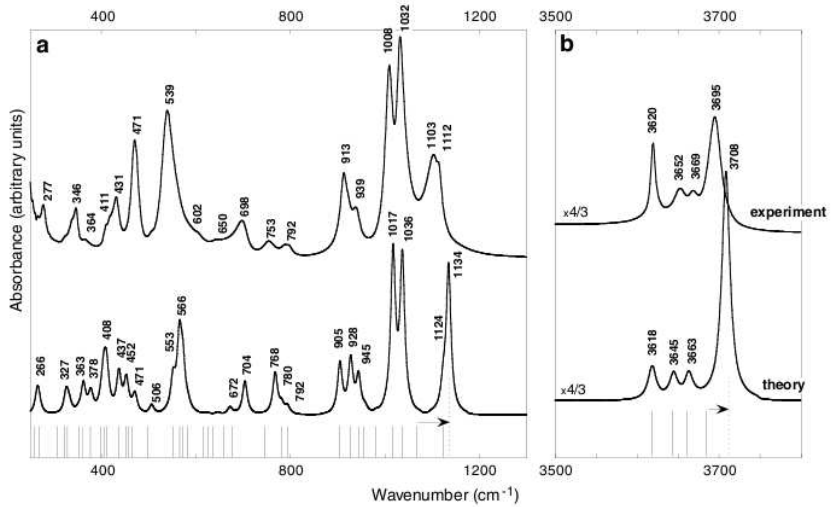

FIGURE 5. Experimental (top) and theoretical (bottom) IR absorption spectra of kaolinite: (a) mid-IR range, (b) OH-stretching region. Positions of the major features are indicated by their wavenumbers. The vertical bars at the bottom correspond to the theoretical TO phonon frequencies (see Table 4), i.e., to the resonances of the imaginary part of the dielectric function. Note the shift between the absorption bands (dotted vertical bars) and the corresponding TO frequencies observed for the Si-O and OH stretching modes polarized along **c**.

Non-resonant raman

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Raman scattering depends on raman activity tensor

$$I_{\alpha\beta}^{\text{raman}} = \frac{d^3E}{d\varepsilon_\alpha d\varepsilon_\beta dQ_m} = \frac{d\epsilon_{\alpha\beta}}{dQ_m}$$

i.e. the activity of a mode is the derivative of the dielectric permittivity with respect to the displacement along the mode eigenvector.
CASTEP evaluates the raman tensors using hybrid DFPT/finite displacement approach.
Raman calculation is fairly expensive $\Rightarrow$ and is not activated by default (though group theory prediction of active modes is still performed)
Parameter `calculate_raman = true` in a `task=phonon` calculation.
Spectral modelling of IR spectrum is relatively simple function of activity.

$$\frac{d\sigma}{d\Omega} = \frac{(2\pi\nu)^4}{c^4} \left|\boldsymbol{e}_S.I.\boldsymbol{e}_L\right|^2 \frac{h(n_m+1)}{4\pi\omega_m}$$

with the thermal population factor

$$n_m = \left[exp\left(\frac{\hbar\omega_m}{k_BT}\right) - 1\right]^{-1}$$

which is implemented in `dos.pl` using the `-raman` flag.

Raman scattering of t-ZrO2

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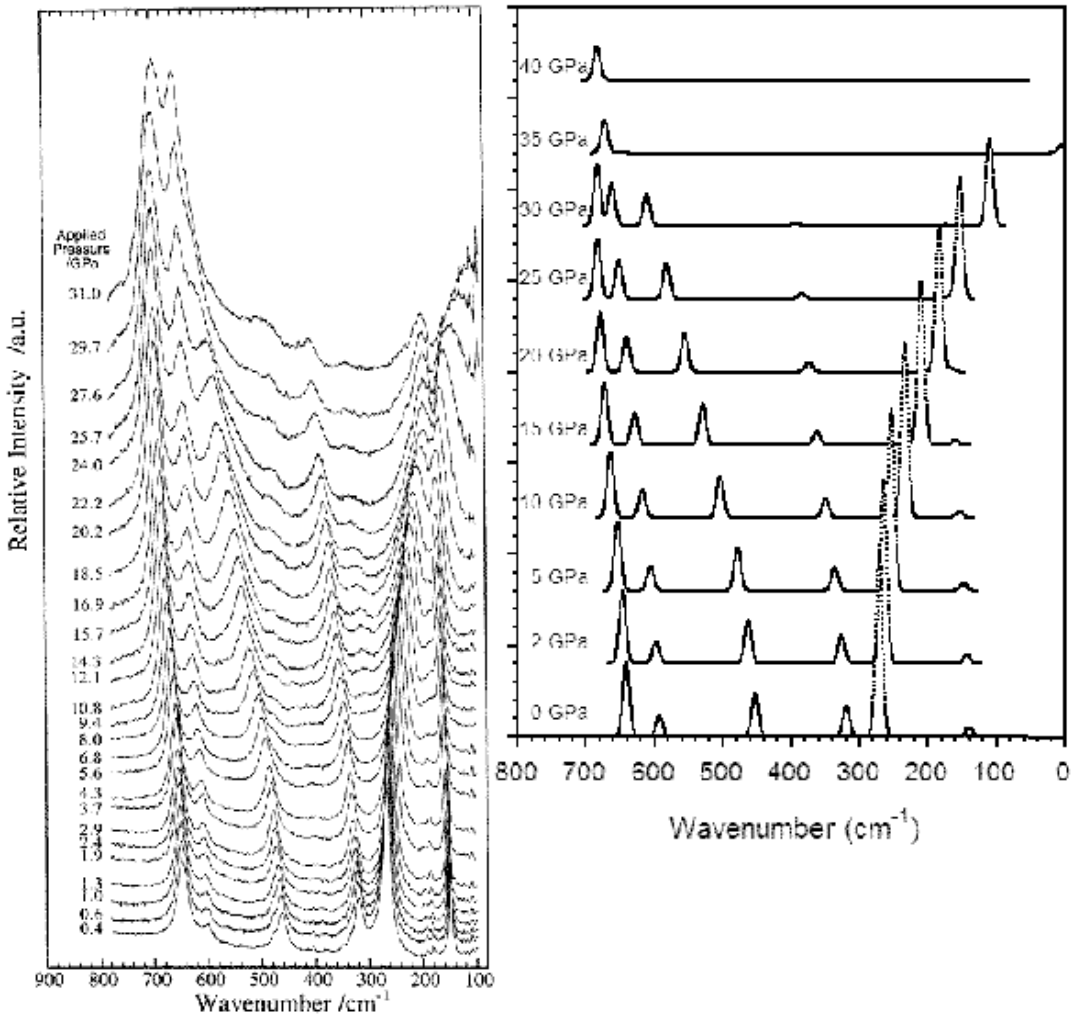

Inelastic X-Ray scattering

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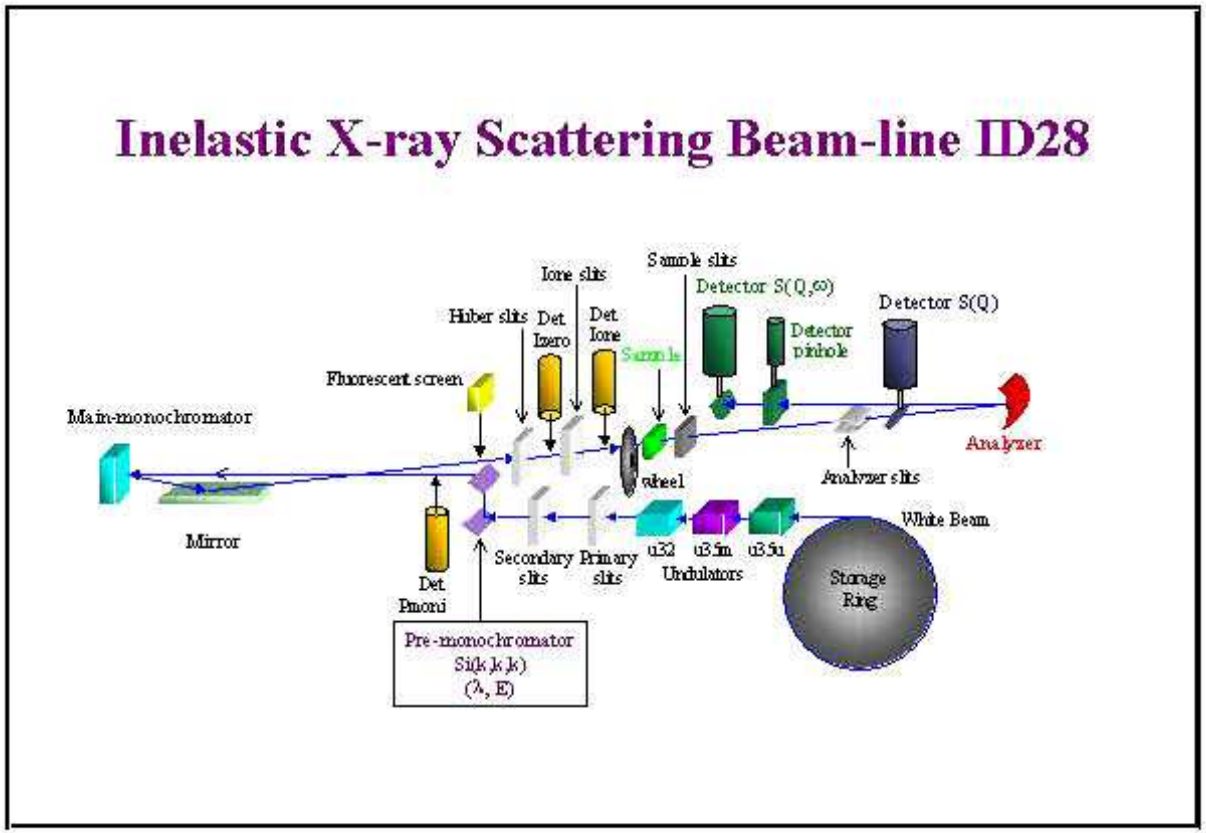
IXS spectrometers at ESRF, Spring-8, APS synchrotrons.



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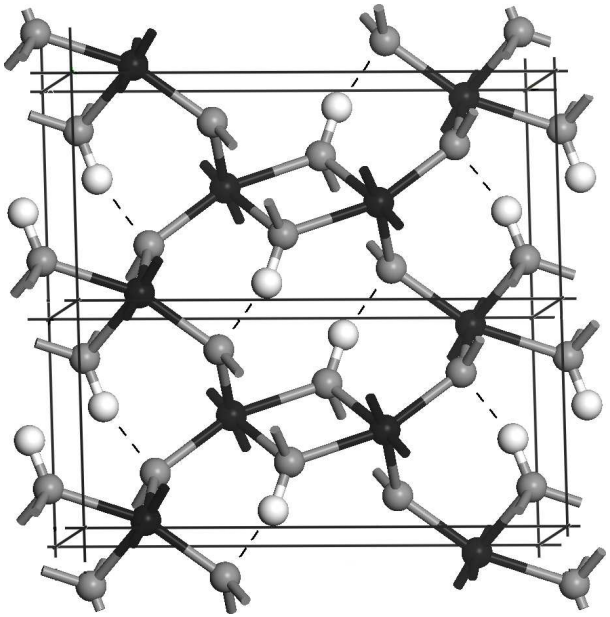
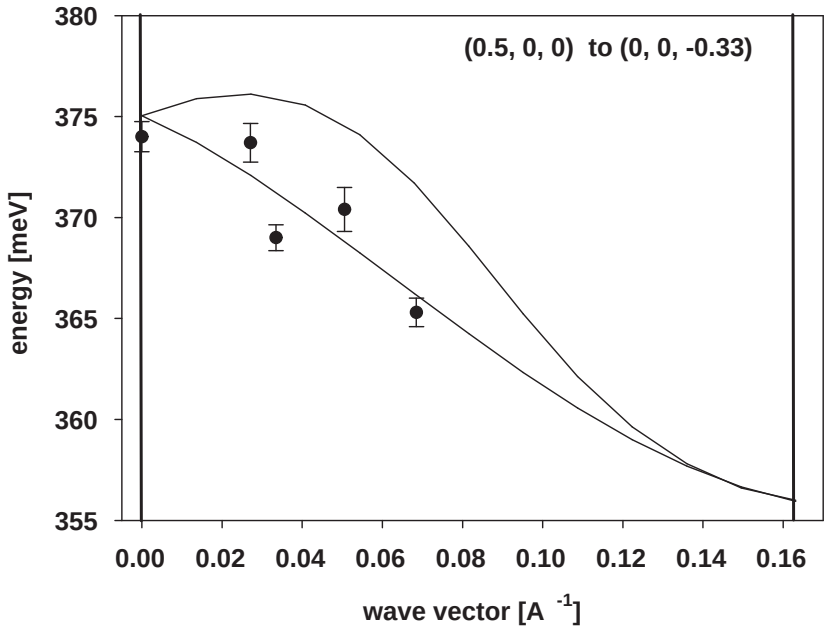
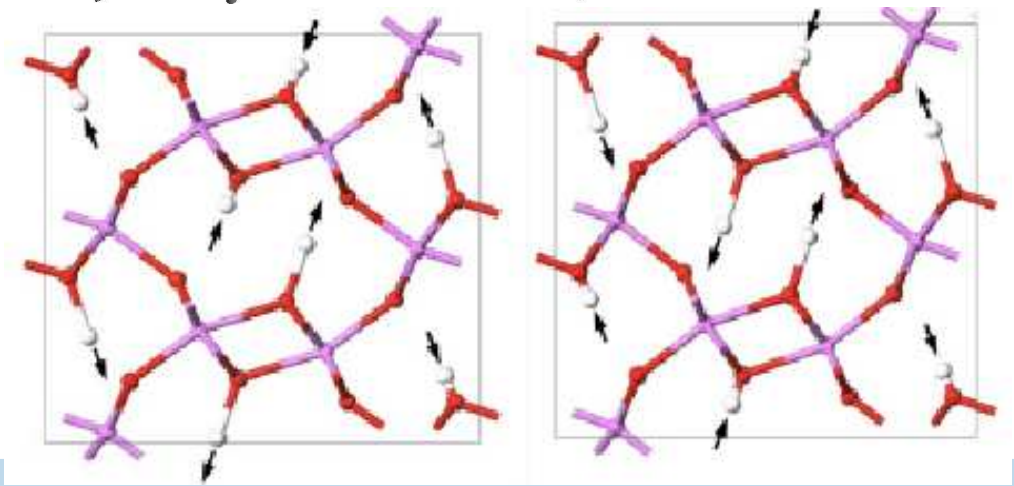
Inelastic X-Ray scattering
IXS of Diaspore

B. Winkler et al., Phys. Rev. Lett **101** 065501 (2008)