DIFFRACTION STUDIES OF ICE

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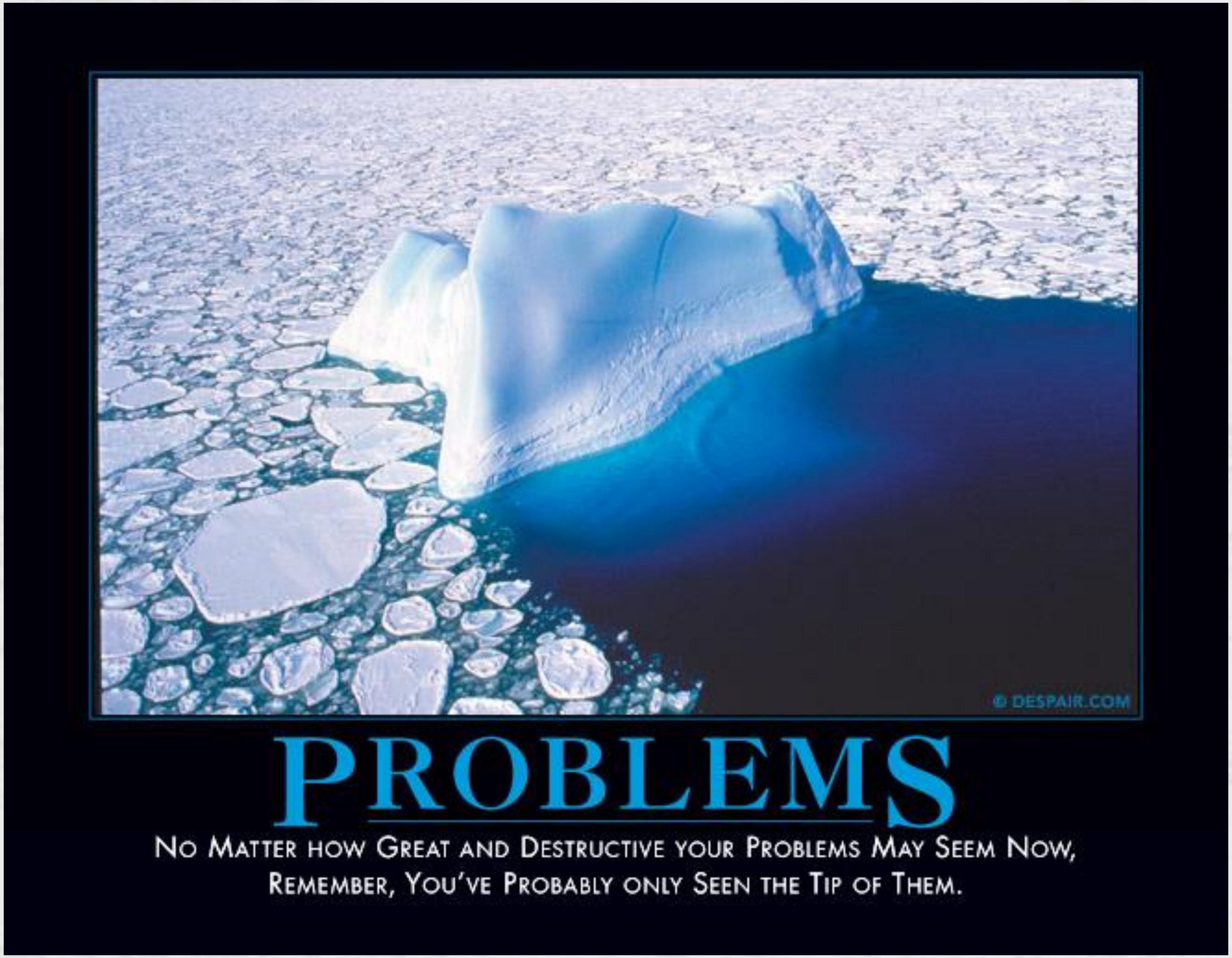
Ice as the mild threat



ice Ih
the only ice
in the crust

Ice as the absolute weapon

Ice IX : melting point 45.8°C at ambient pressure

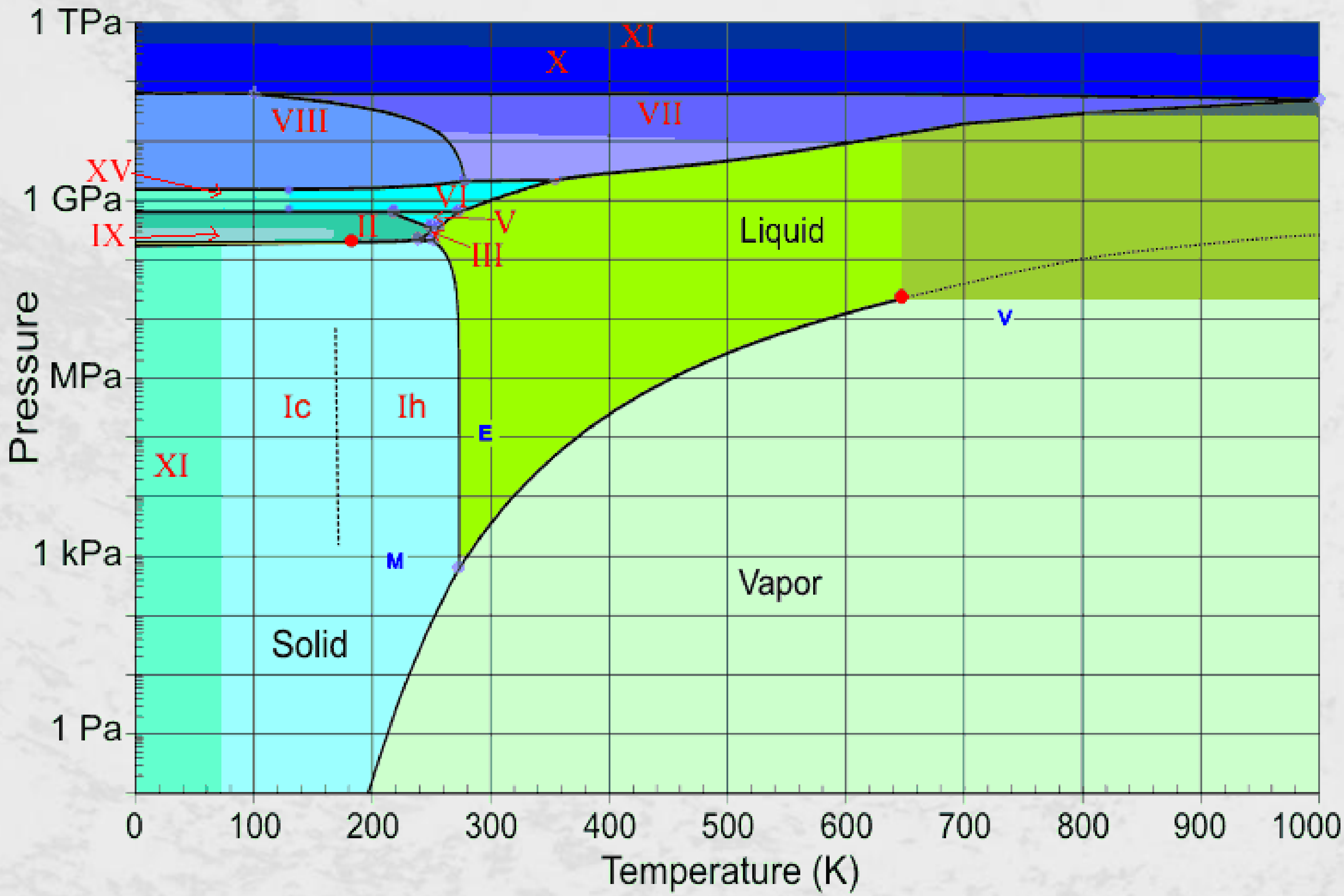
• more stable polymorph of water than common ice (Ice Ih), but with large activation barrier

• liquid water below 45.8°C is effectively supercooled

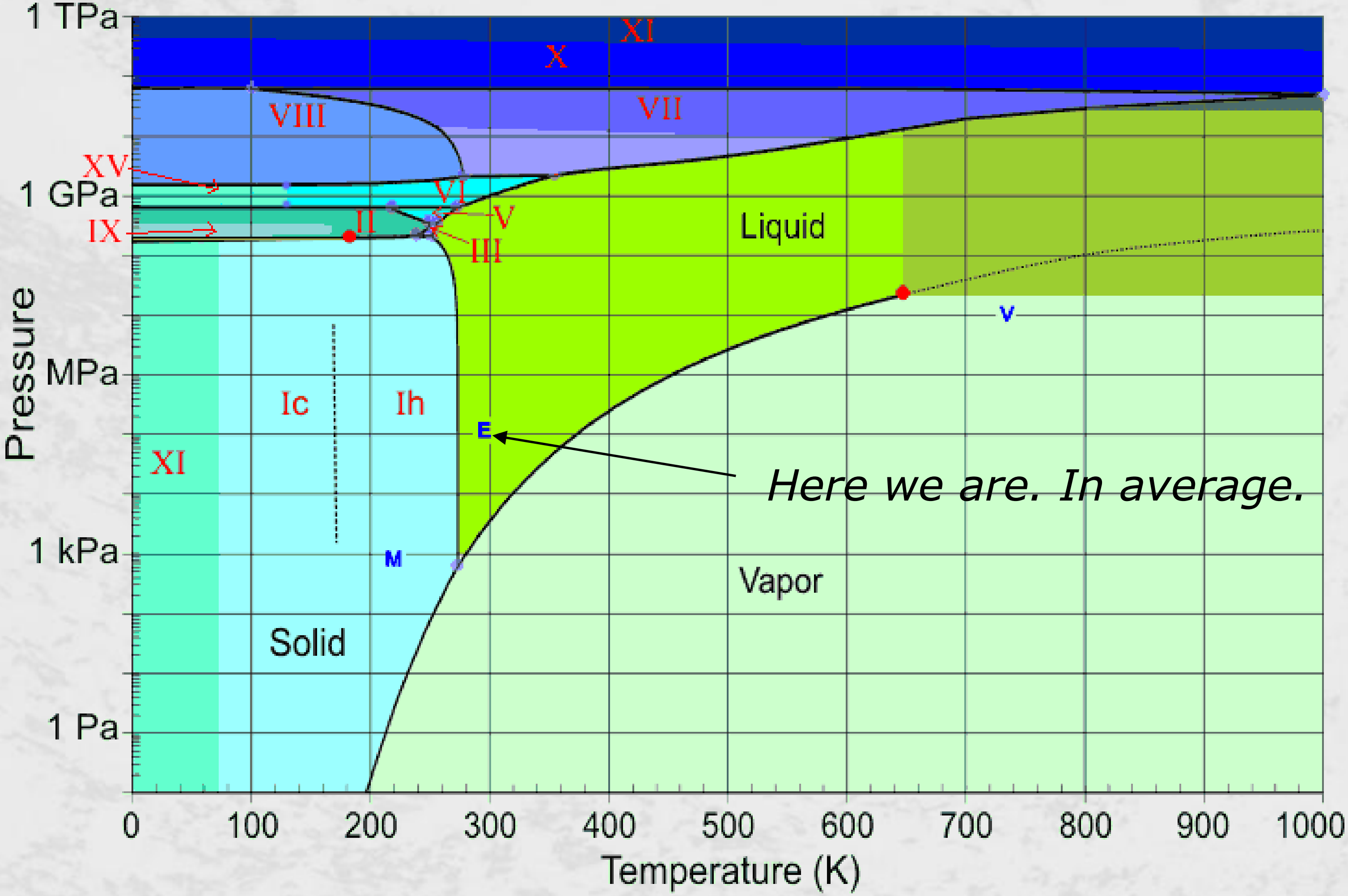
• in contact with liquid water Ice IX acts as a seed crystal, and causes the solidification of the entire body of water which quickly crystallizes as ice-nine

[K. Vonnegut, Cat's Cradle]

Phase diagram of water



Phase diagram of water

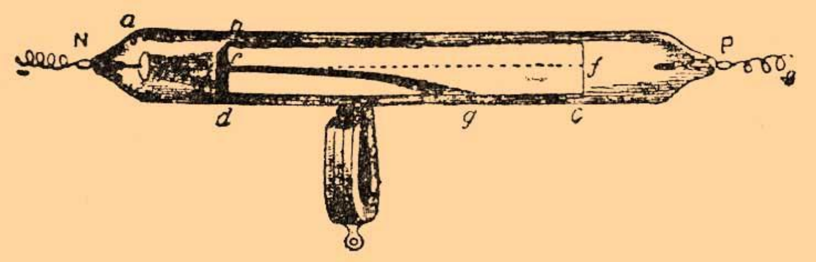


16 *crystalline phases*

3 *(?) amorphous solids*

Experiment: neutrons vs. X-rays

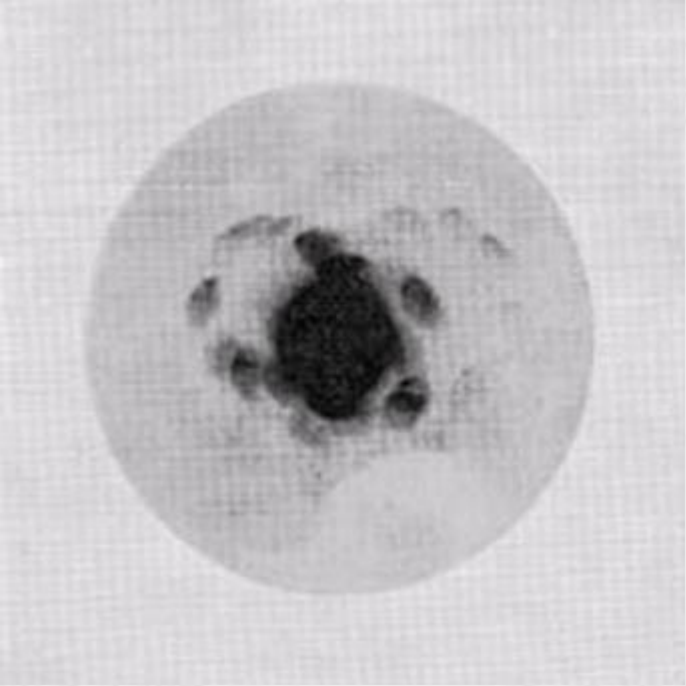
2012: 100 years of x-ray diffraction



Фиг. 1.

Относительно природы Рентгеновских лучей до сих пор ничего неизвестно. Было высказано предположение, что Рентгеновские лучи представляют собой продольные колебания эфира. Эту идею разделял сам Рентген. Однако, никаких данных, подтверждающих такую гипотезу, не имеется.

Энциклопедия Брокгауза Ф.А. и Ефрона И.А. (1899)

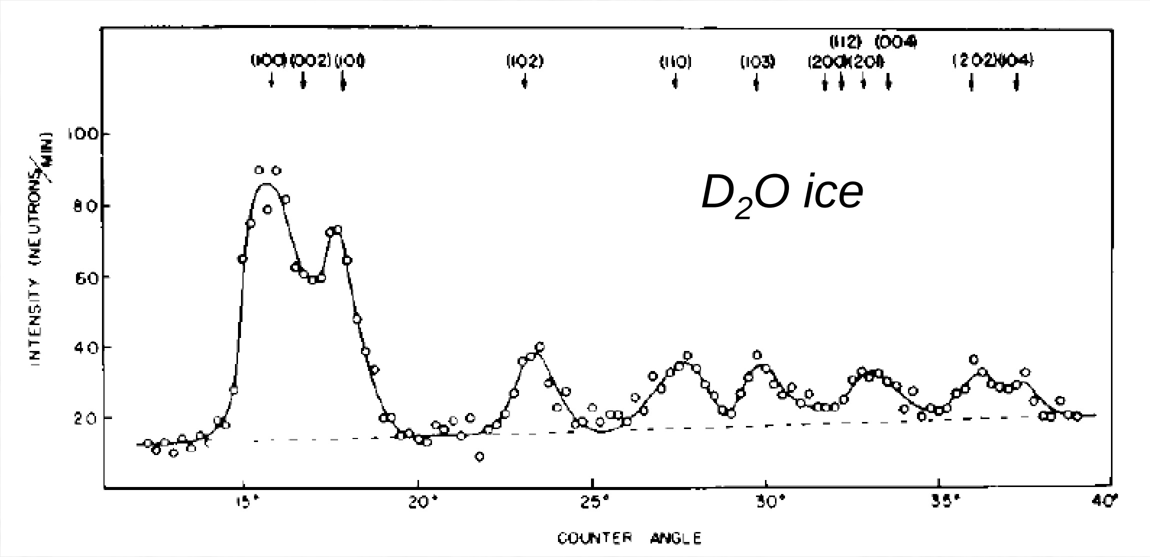


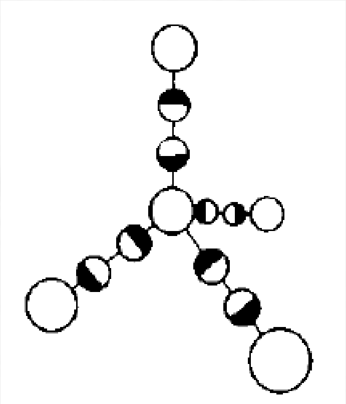
Friedrich & Knipping's first successful diffraction photograph (1912)

2012: 80 years since the discovery of neutrons

1932: discovery of neutrons (Chadwick)

1945/46: first diffraction patterns (Wollan, Sawyer, Shull)



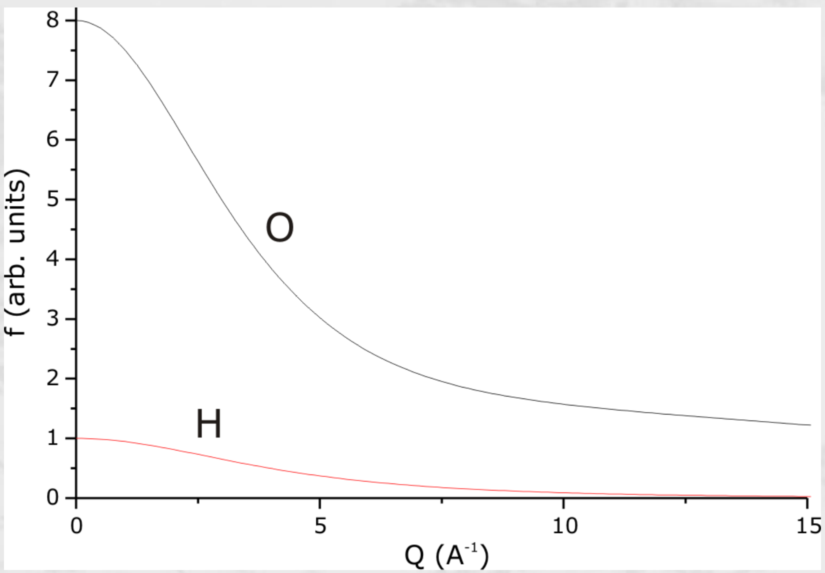


confirmation of half-hydrogen model of Pauling

Contrast in neutron and x-ray scattering

X-rays: f ~ Z

f(O)/f(H) ~ 8

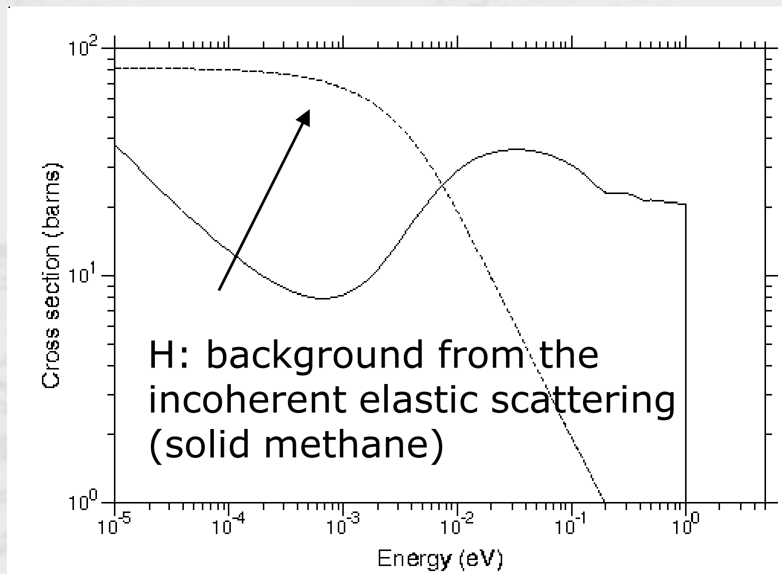


neutrons [barns]:

$\sigma_{coh}(H) = 1.76$ $\sigma_{inc}(H) = 79.9$

$\sigma_{coh}(D) = 5.59$ $\sigma_{inc}(D) = 2.04$

$\sigma_{coh}(O) = 4.23$ $\sigma_{inc}(O) \sim 0$



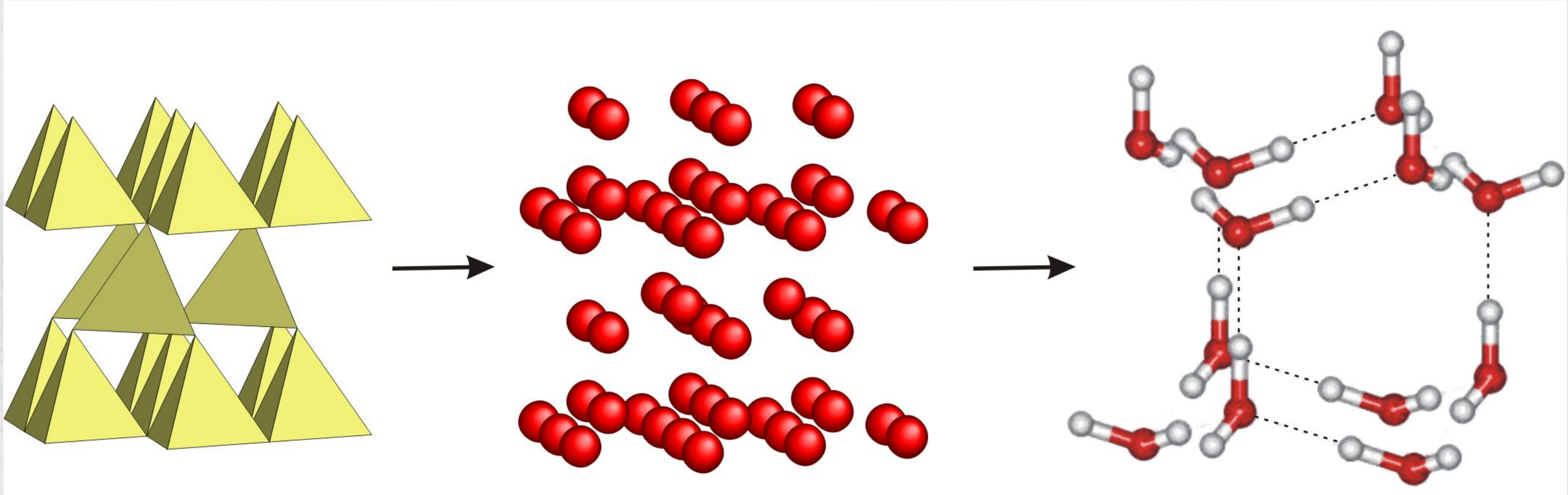
the most convenient: D_2O with neutrons?

High pressure studies

	X-rays	neutrons
ex situ quenched phases	+	+
in situ sapphire anvil cell	--	+
in situ diamond anvil cell	+	--

Ambient pressure polymorphs

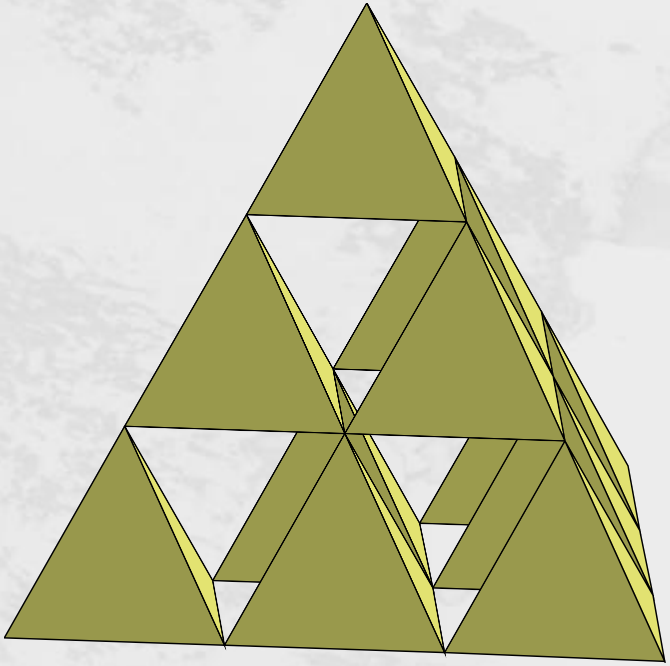
Building the ice Ih crystal



take the wurtzite — *replace all the atoms by oxygen* — *put in the hydrogen atoms randomly but according to the rules*

Bernal-Fowler rules:
1. four hydrogen-bonded neighbors for each water molecyle
2. two hydrogen atoms near each oxygen
3. one hydrogen atom on each O...O bond

Building the ice Ic crystal



take the sphalerite...

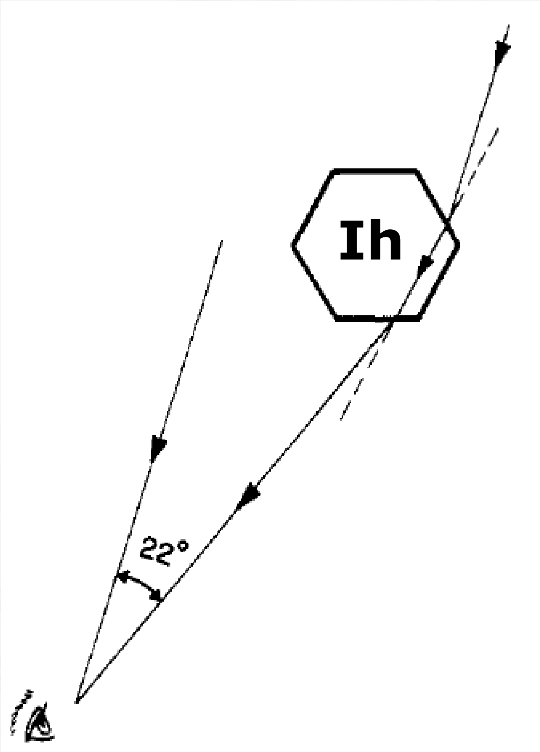
condensation of vapor below -80^{o}C

freezing small droplets (~6 mkm)

transformation of HP ices

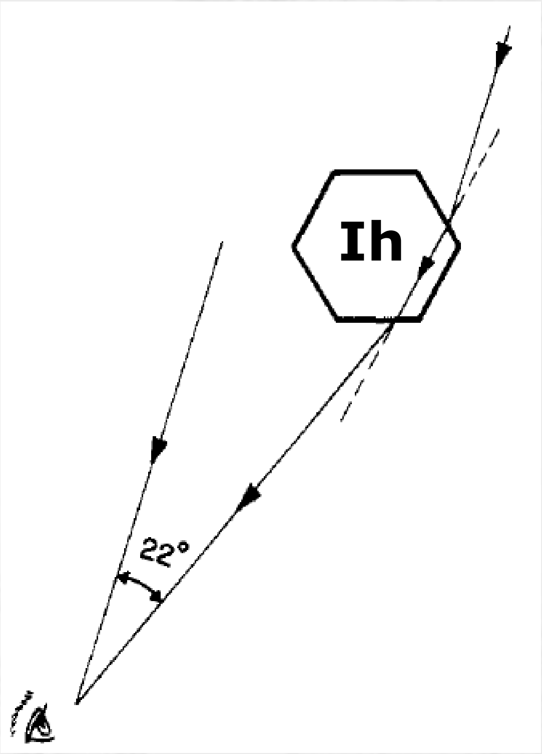
always metastable

Ice Ic in nature?



22^{o} - the commonest of the halos

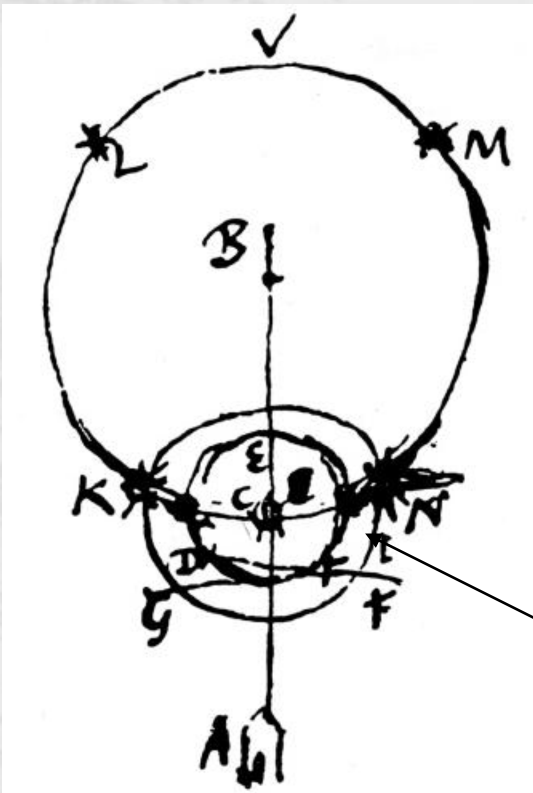
Ice Ic in nature?



22° - the commonest of the halos

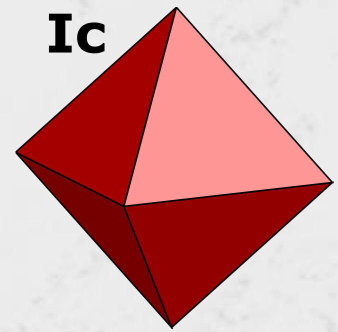
Ice Ic in nature?

28° halo observed at least
7 times since 1629



28° halo

Scheiner's sketch of his
observation made on
20.03.1629 at Rome

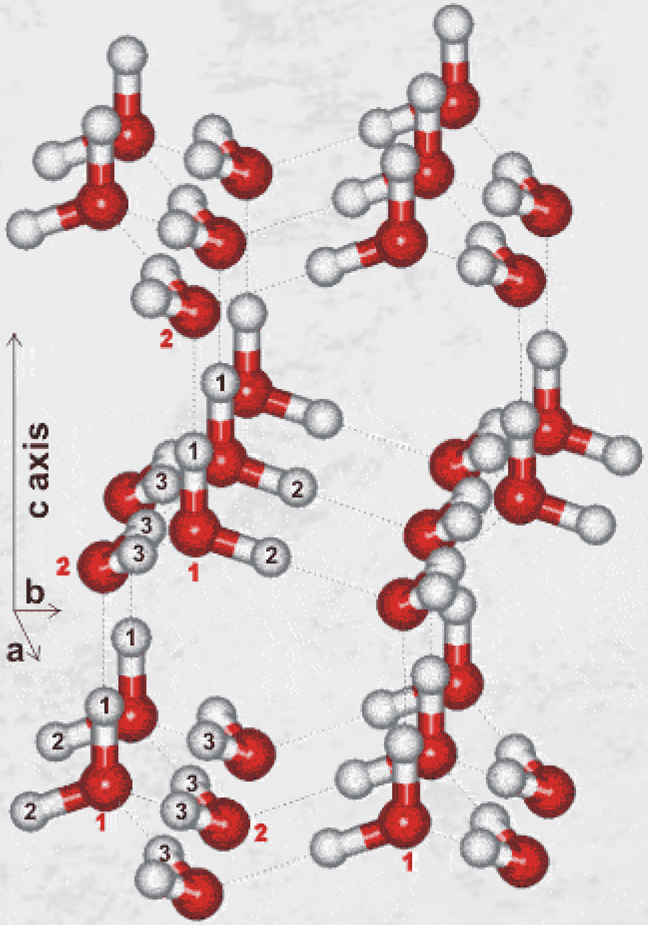


octahedral particles of ice Ic!

Cooling down to order the hydrogen?

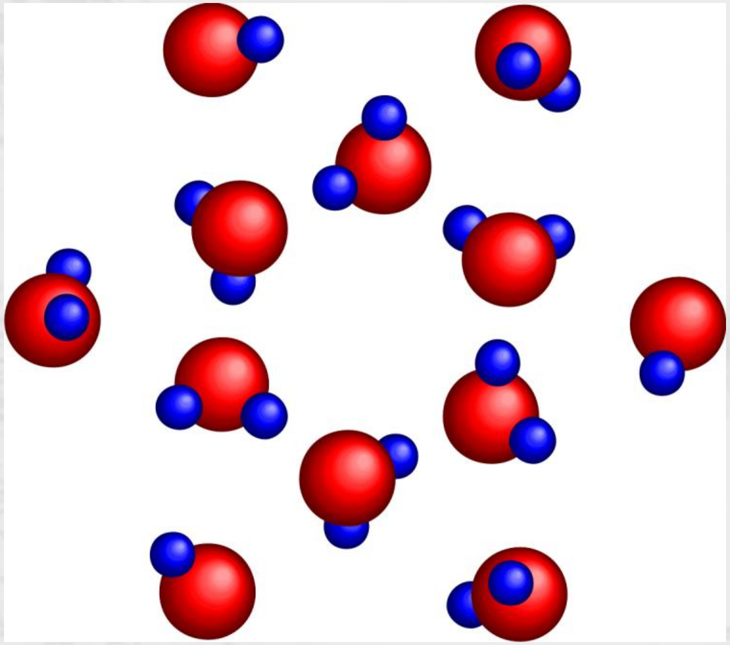
for the transition temperature
the activation barrier is too high
geological samples for that temperature
cannot be found on the Earth

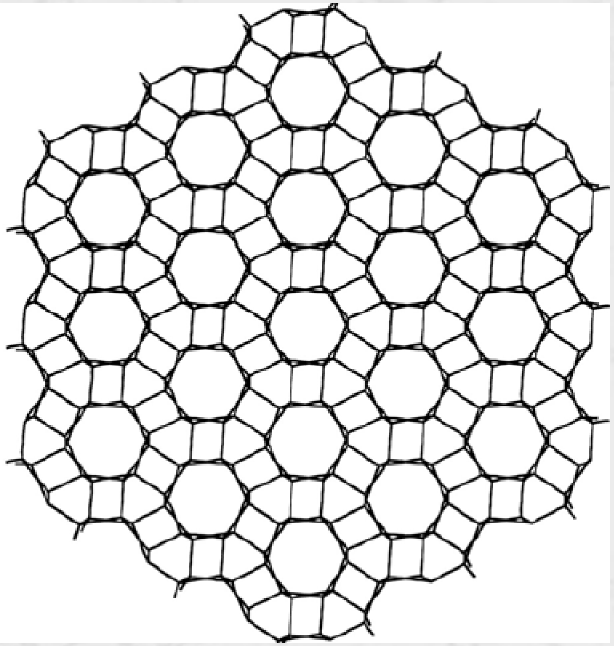
introduce the defects to increase the mobility!
KOH doping induces the ordering below 72 K:
polar structure with $Cmc2_1$ space group



High pressure polymorphs

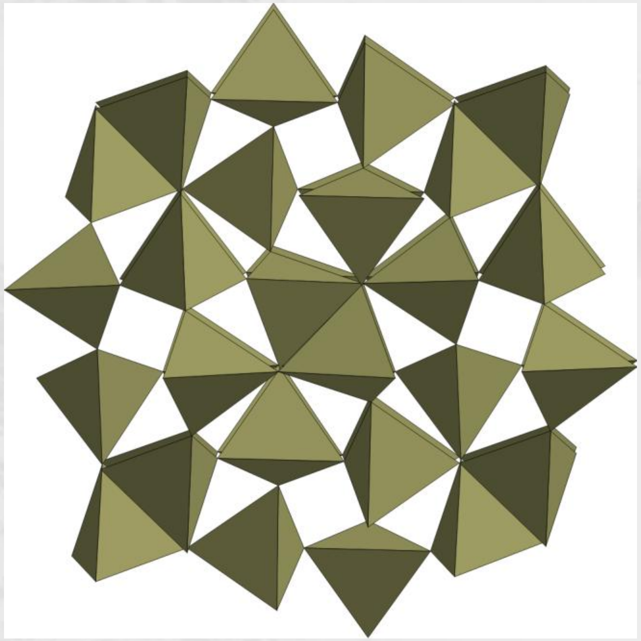
Ice II: clathrate-like





- 25% denser that ice Ih, but with larger cavities
- same H_2O framework as for helium hydrate - stabilized by He
- the only proton-ordered ice forming from the liquid
- 6,8,10-rings

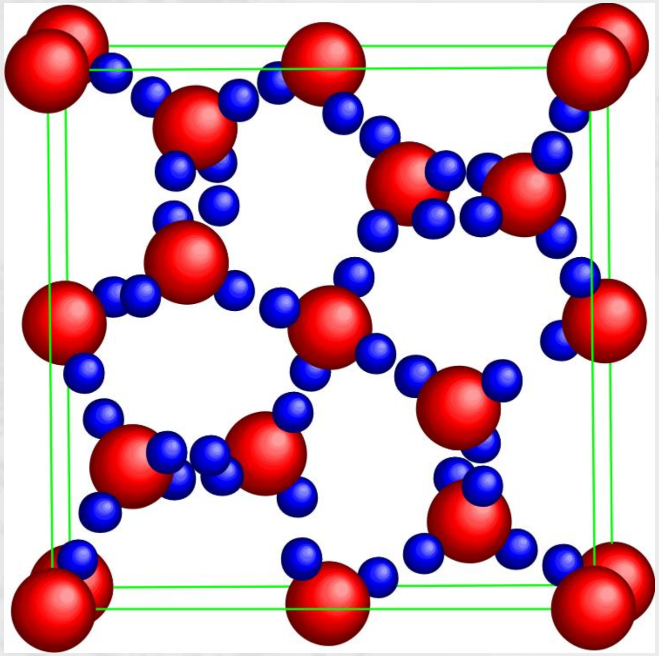
Ices III and IX: chiral



- *take the keatite (SiO_2) or Ge-III*
- *replace all the atoms by oxygen*
- *add hydrogen respecting the rules*
  - *random -> ice III*
  - *ordered -> ice IX (harmless)*

- the only ices with chiral structure - can be left or right
- 5,7,8-rings

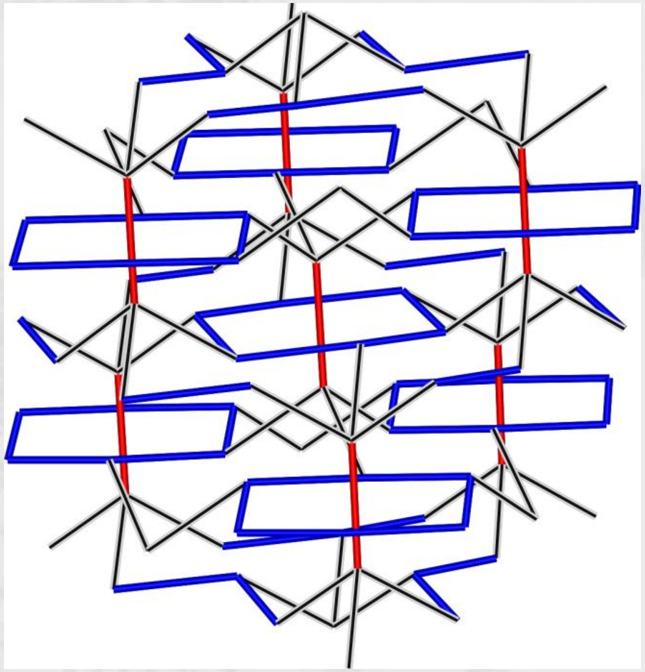
Ices XII and XIV: dense but simple



- *random -> ice XII*
- *ordered -> ice XIV*

- protons are quite far from O...O line
- 7,8-rings

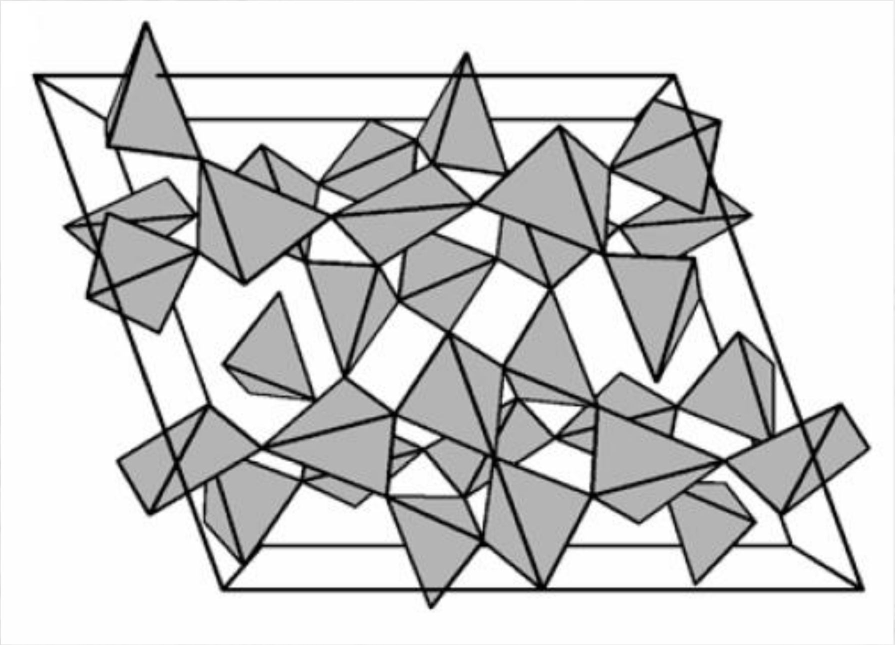
Ice IV: self-entangled/knot



- *ordered form is not known yet*

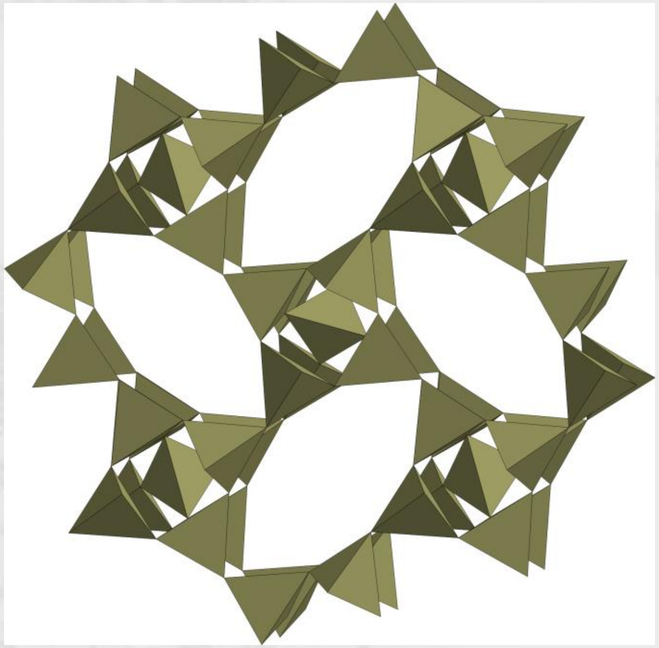
- much easier to obtain from D_2O
- 6,8,10-rings

Ices V and XIII: self-entangled/knot



- ice V (disordered) and XIII (ordered) contain 28 water molecules
- 4,5,6,8,9,10,12-rings

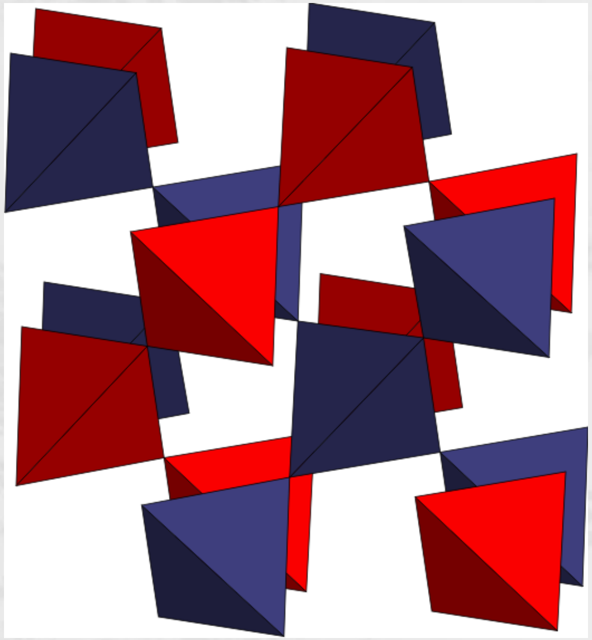
Ices VI and XV: self-clathrate



- *take the edingtonite mineral*
- *replace Si and Al the atoms by oxygen*
- *take the second network and entangle both*
- *add hydrogen respecting the rules*
    - *random -> ice VI*
    - *ordered -> ice XV*

- two subnetworks are not H-bonded
- 4,8-rings

Ices VII, VIII and X: self-clathrate



- *take Cu_2O structure*
- *replace Cu by hydrogen*
  - *ice X*
- *shift hydrogen respecting the rules*
  - *random -> ice VII (cubic)*
  - *ordered -> ice VIII (tetragonal)*

- two subnetworks are not H-bonded
- 6-rings

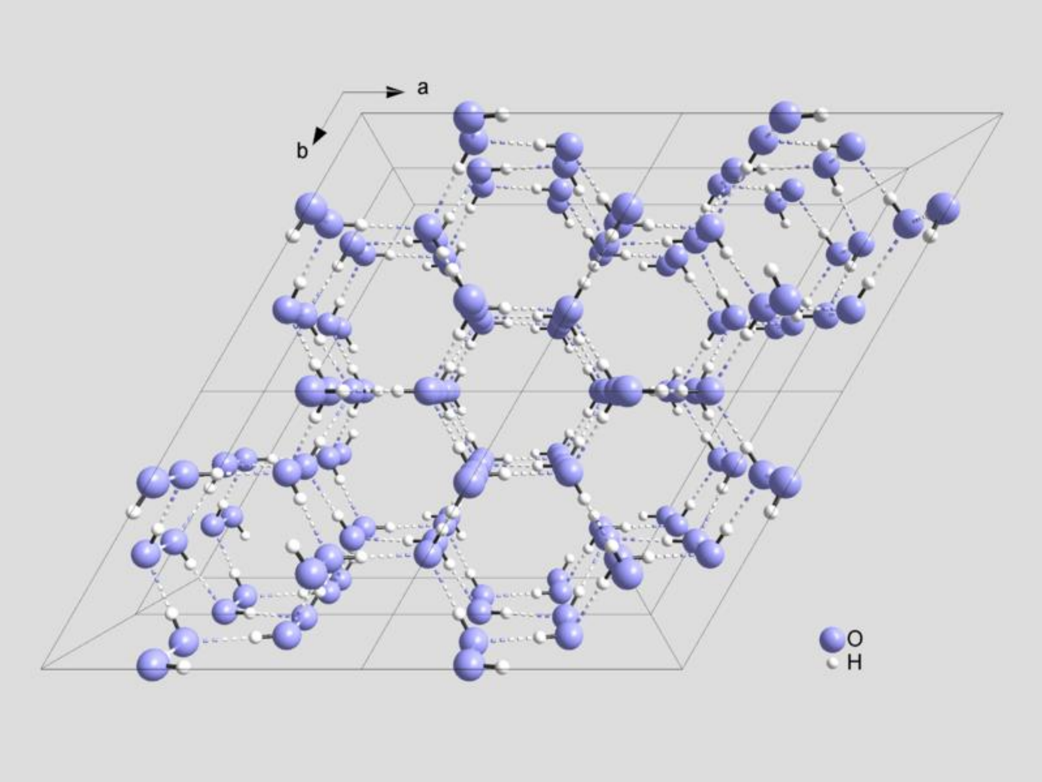
Proton ordering in ice polymorphs

Proton-disordered modifications	Corresponding proton-ordered modifications
Ice Ih	Ice XI
Ice Ic	—
—	Ice II
Ice III	Ice IX
Ice IV	—
Ice V	Ice XIII
Ice VI	Ice XV
Ice VII	Ice VIII
Ice XII	Ice XIV

H^+ or OH^- doping can be indispensible to produce the ordered phase

Diffuse scattering on ice

Moderate experimental matherial



diffuse x-ray scattering: the first and the last experiment in 1949 [*P. G. Owston, Acta Cryst. 2, 222-228 (1949)*]

diffuse neutron scattering: [J.-C. Li et al., Phil. Mag. B 69 1173 (1994)] interpretation is questionable

Exotic samples of common substance

natural single crystals
from Vostok station
depth: 3650 m
typical size: 1 m

Data collection

ESRF

SNBL at ESRF and follow-up
ID29 at ESRF

3600 images / angular step 0.1°

80 Gb of raw data (20 Gb compressed)

15 min of data collection

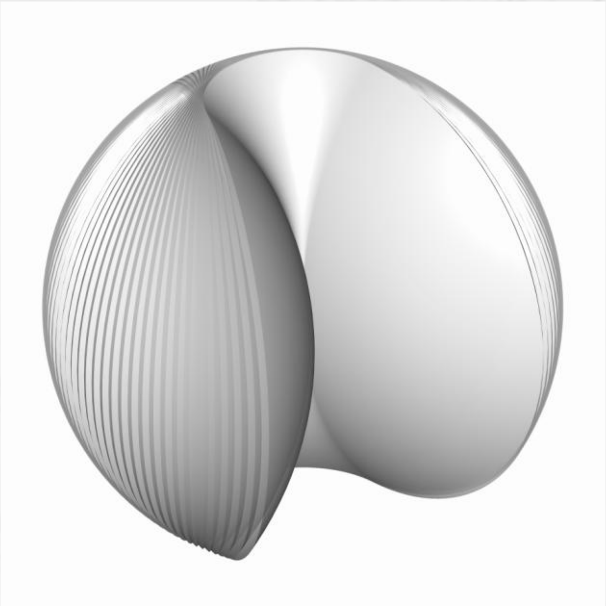
PILATUS 6M / Dectris

2D patterns → 3D

flat image
MAR
EDF
BSL
CBF
…

sphere

space filling

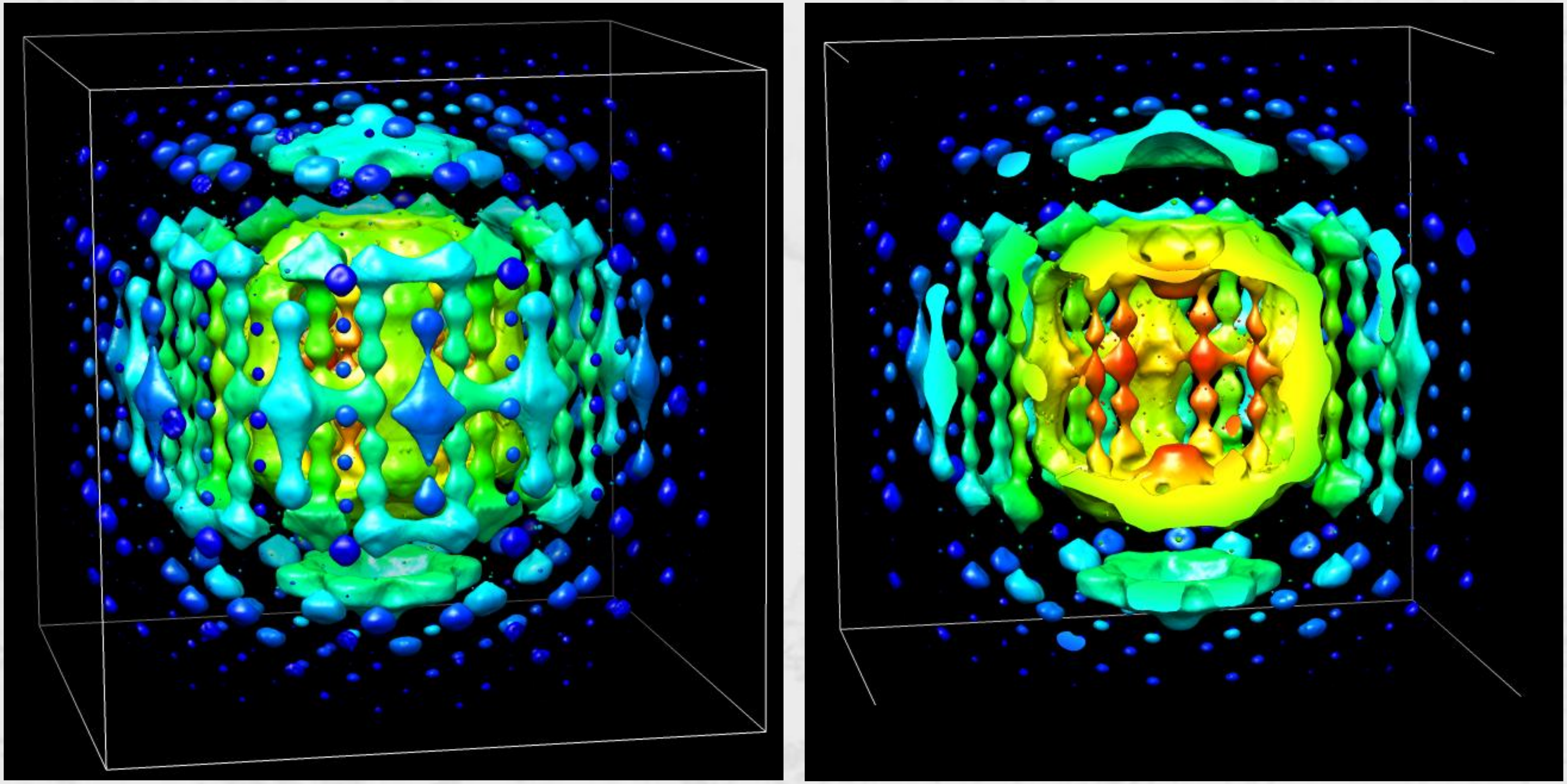


CCP4 map format

UCSF Chimera

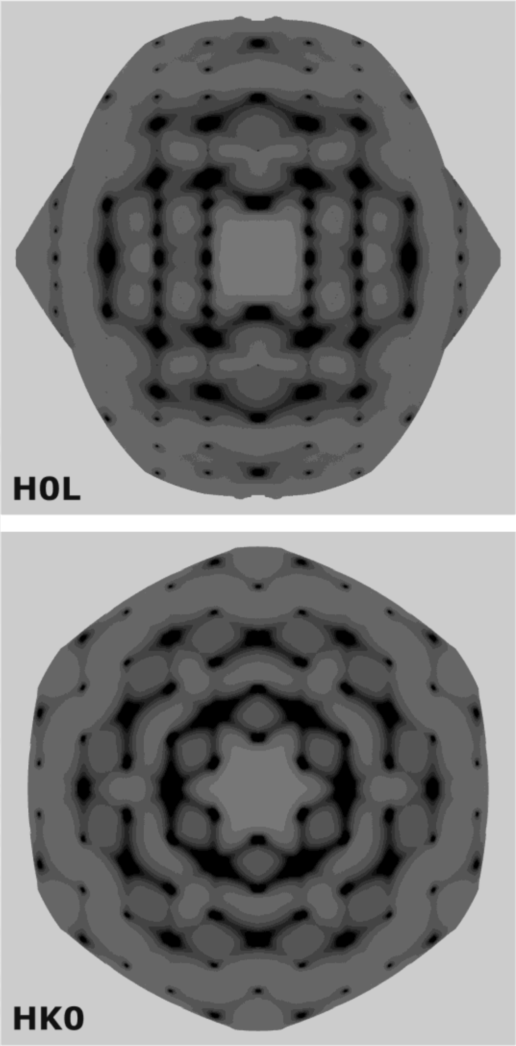
VRML
X3D
POV-Ray
…

Diffuse x-ray scattering in Ih ice



Diffuse x-ray scattering in Ih ice

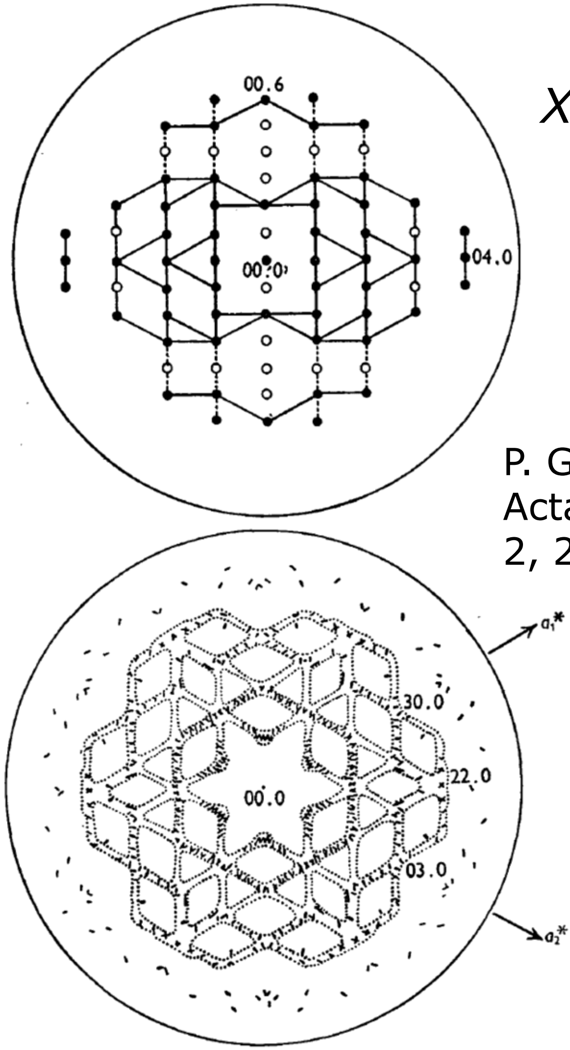
ID29@ESRF



2011

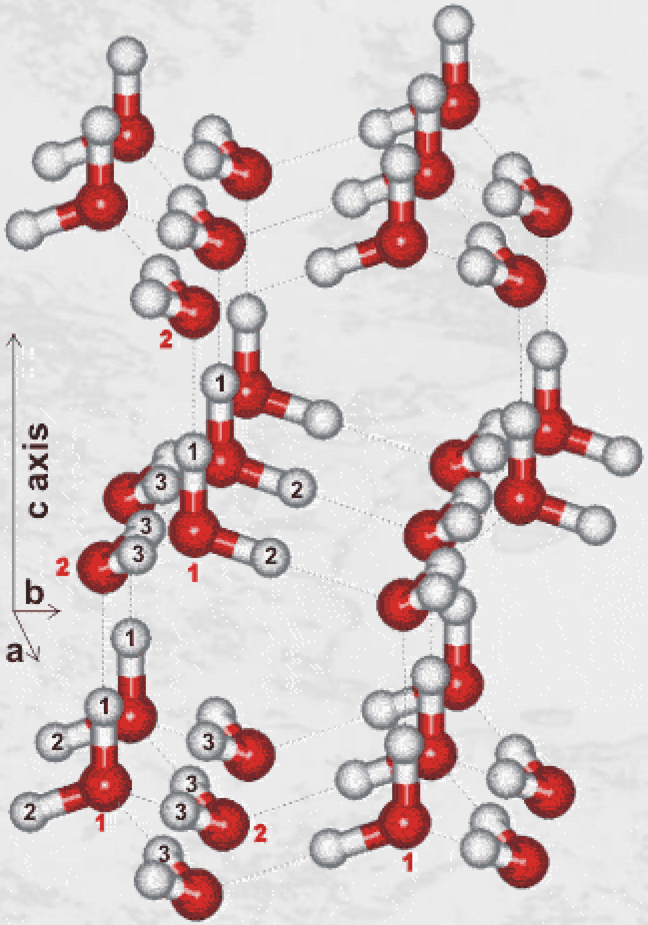
ice Ih 175 K

X-ray tube



P. G. Owston,
Acta Cryst.
2, 222 (1949)

Lattice dynamics: ice XI ab initio



$Cmc2_1$

orthorhombic but metrically close to the hexagonal

CASTEP package

DFT calculation (B. Wehinger)

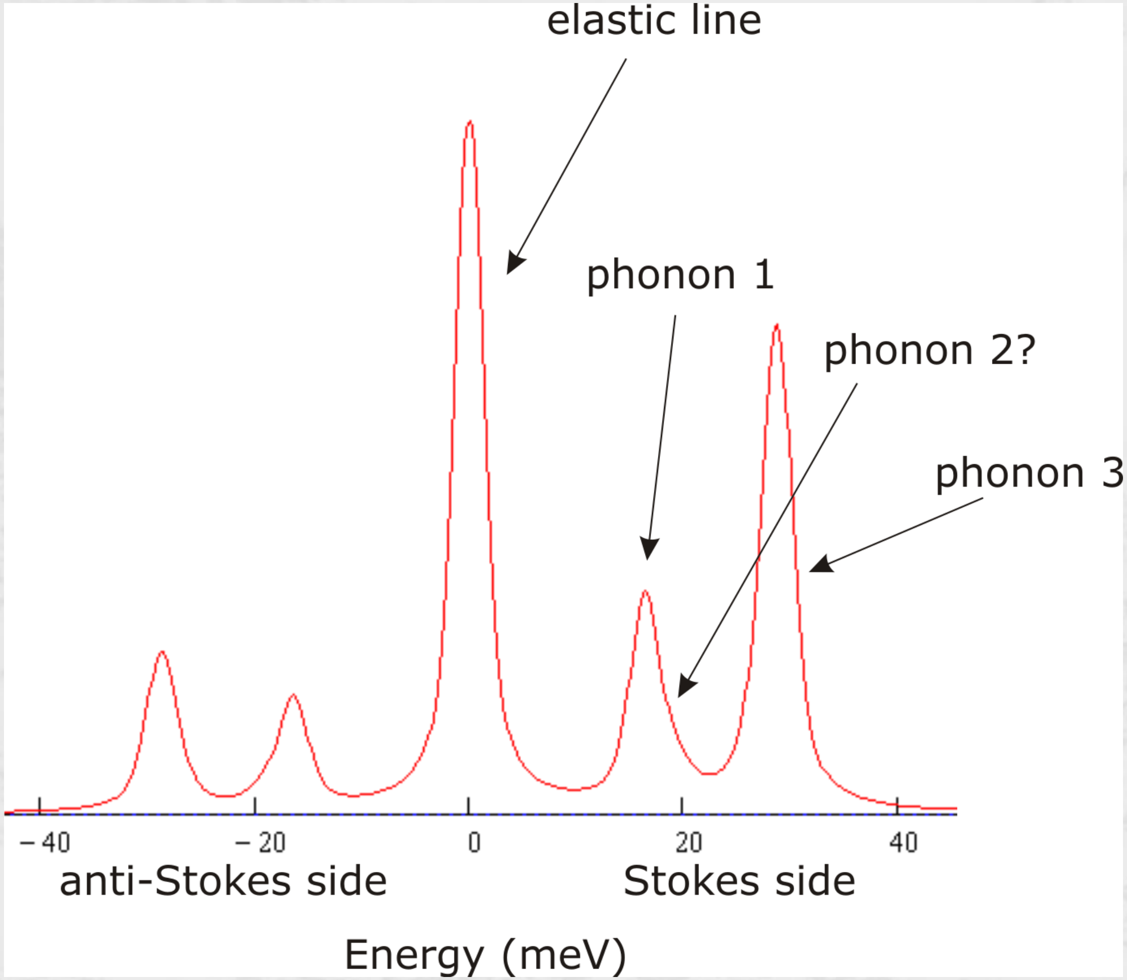
output:

eigenvalues and eigenfrequencies for all the phonons at any **q**

->

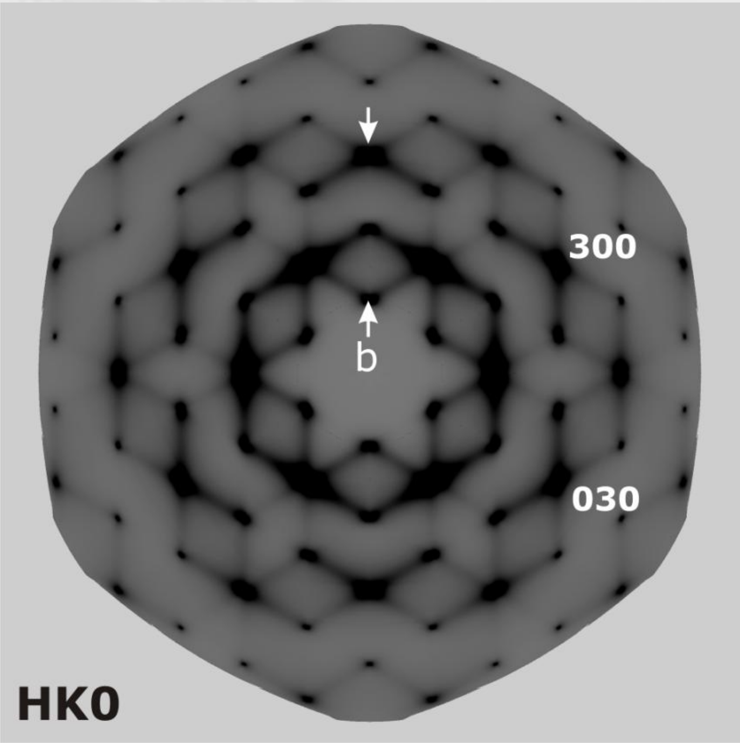
dynamical structure factor

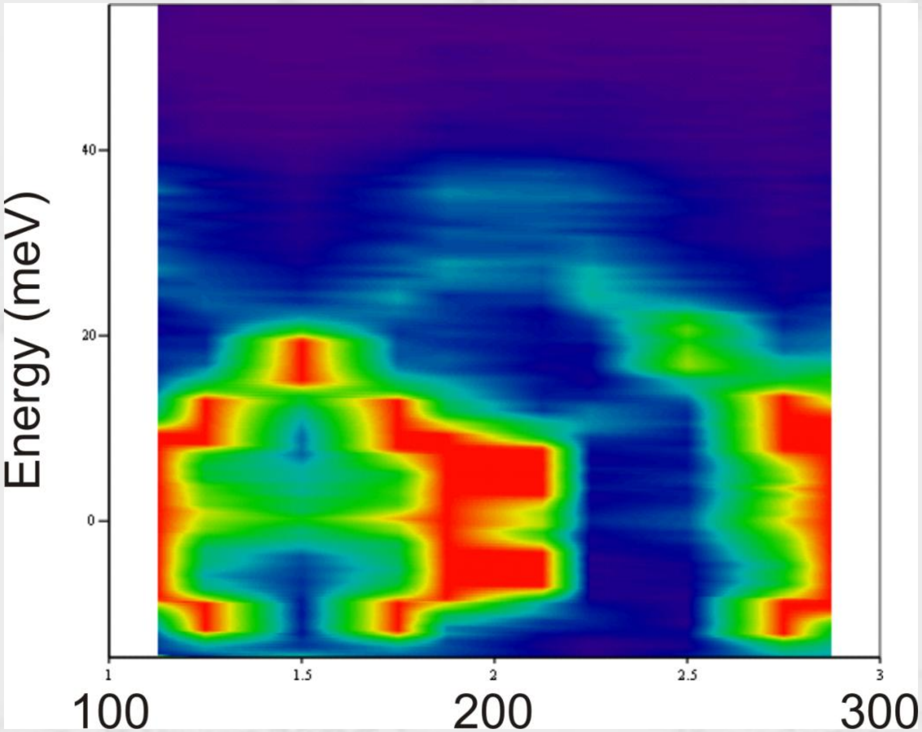
Inelastic spectra: appearence and interpretation



about the same formalism for neutron and x-ray inelastic scattering

First data on phonon dispersion / ID28

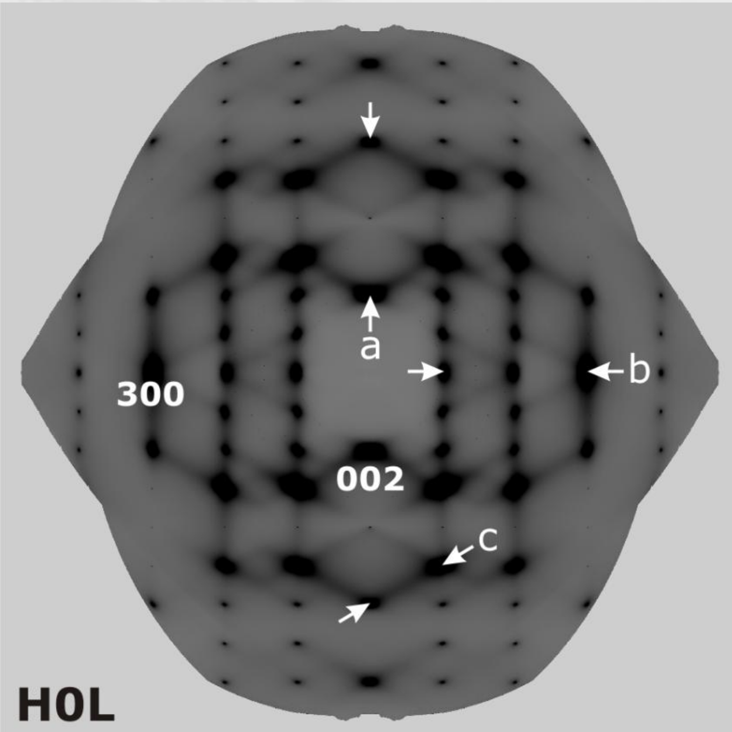


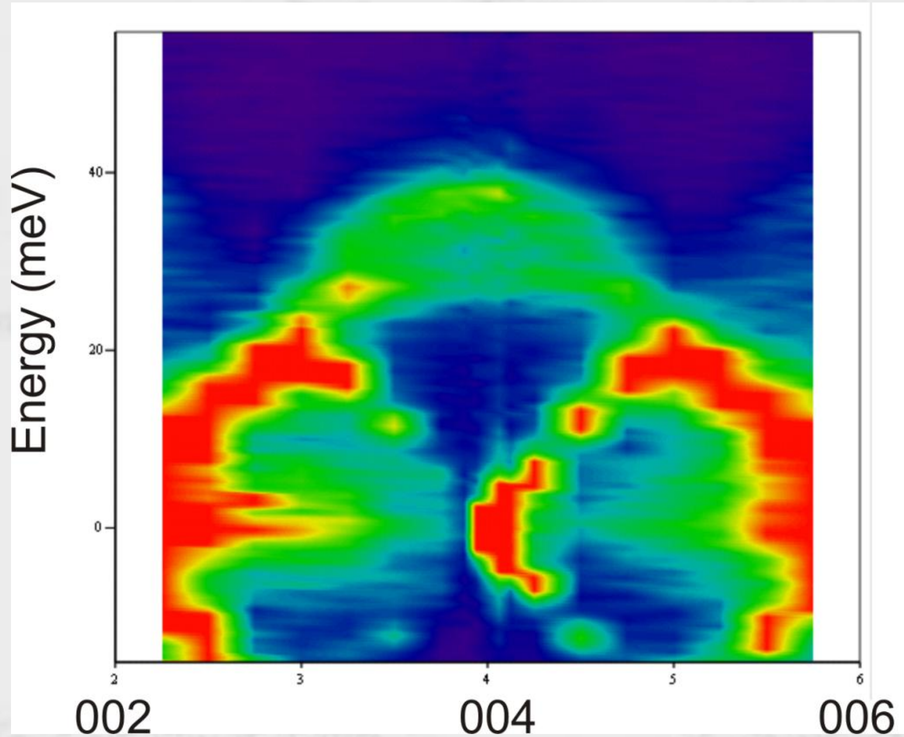


path **b**

ice Ih 175 K

First data on phonon dispersion / ID28

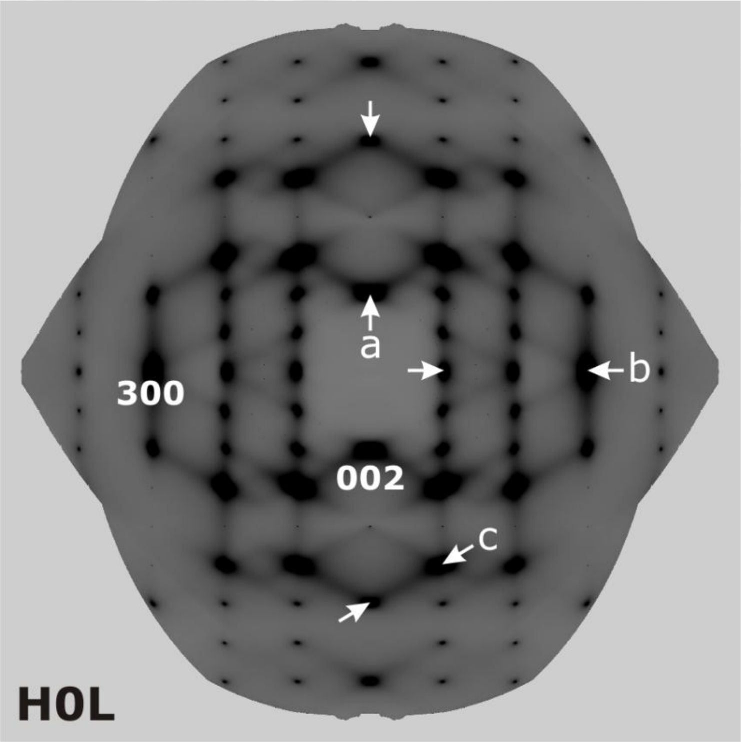


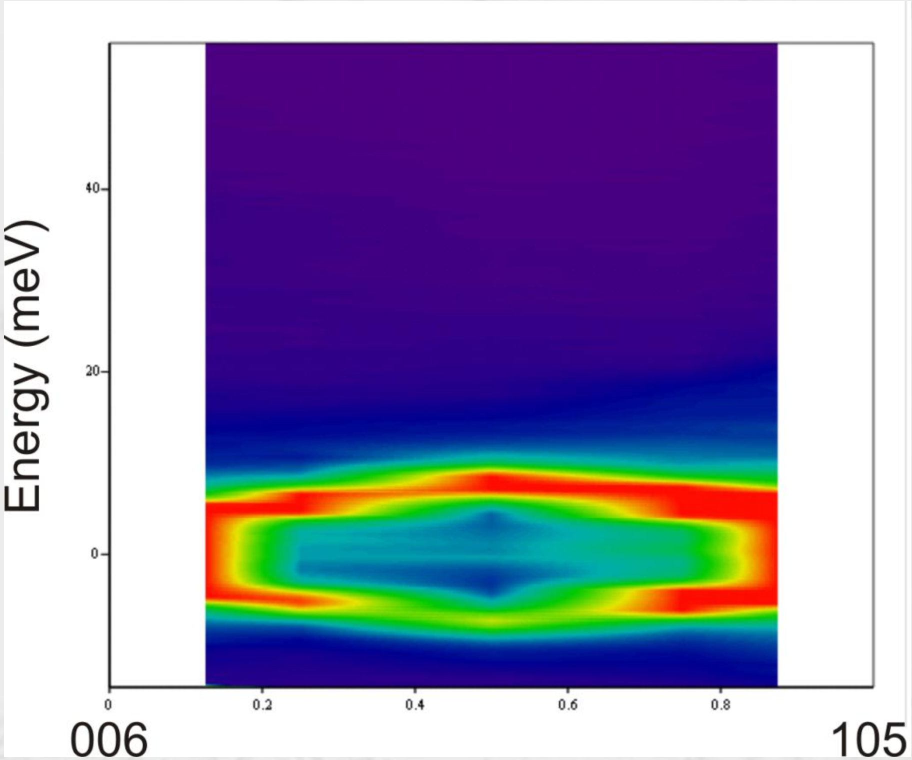


path **a**

ice Ih 175 K

First data on phonon dispersion / ID28



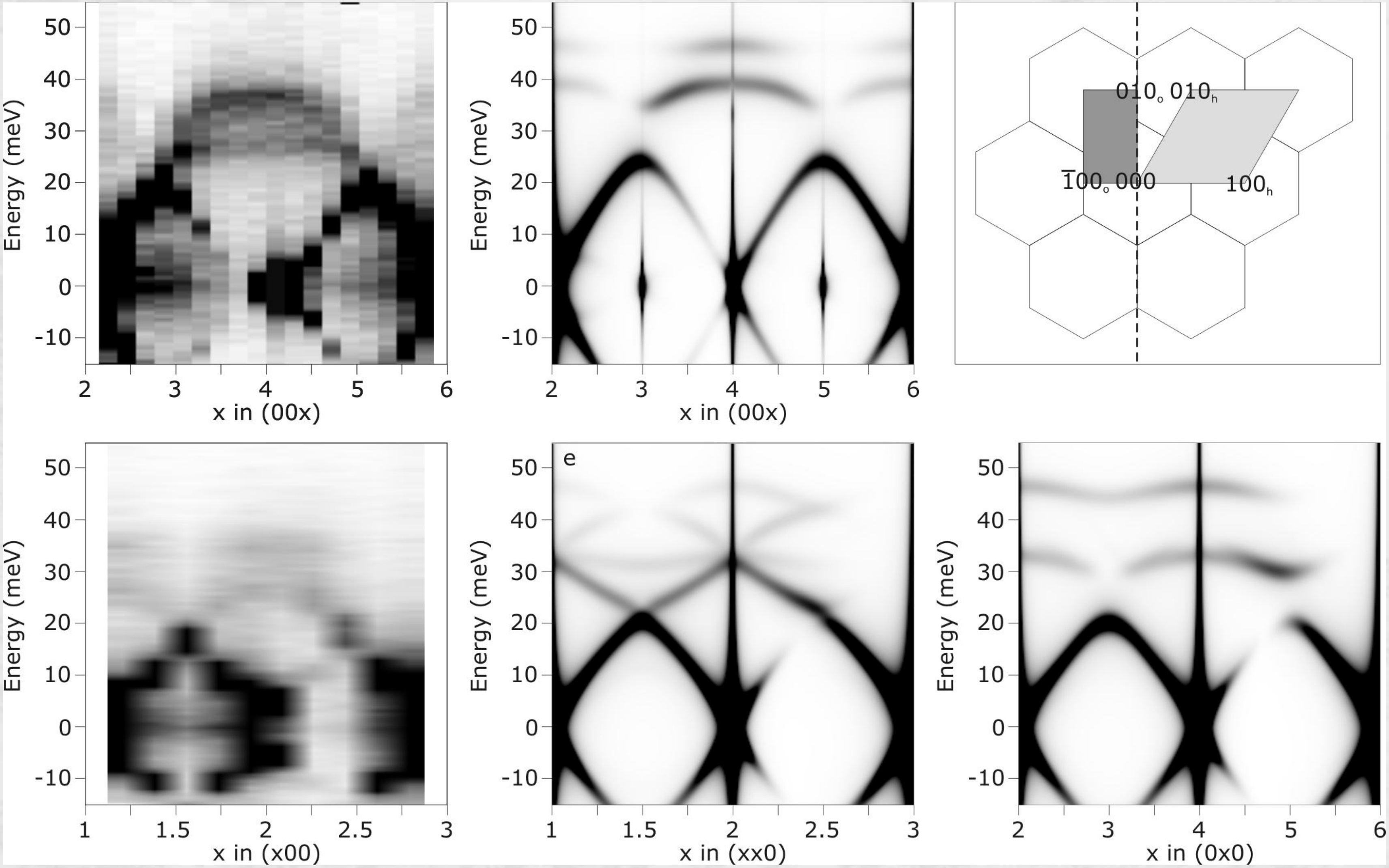


path **c**

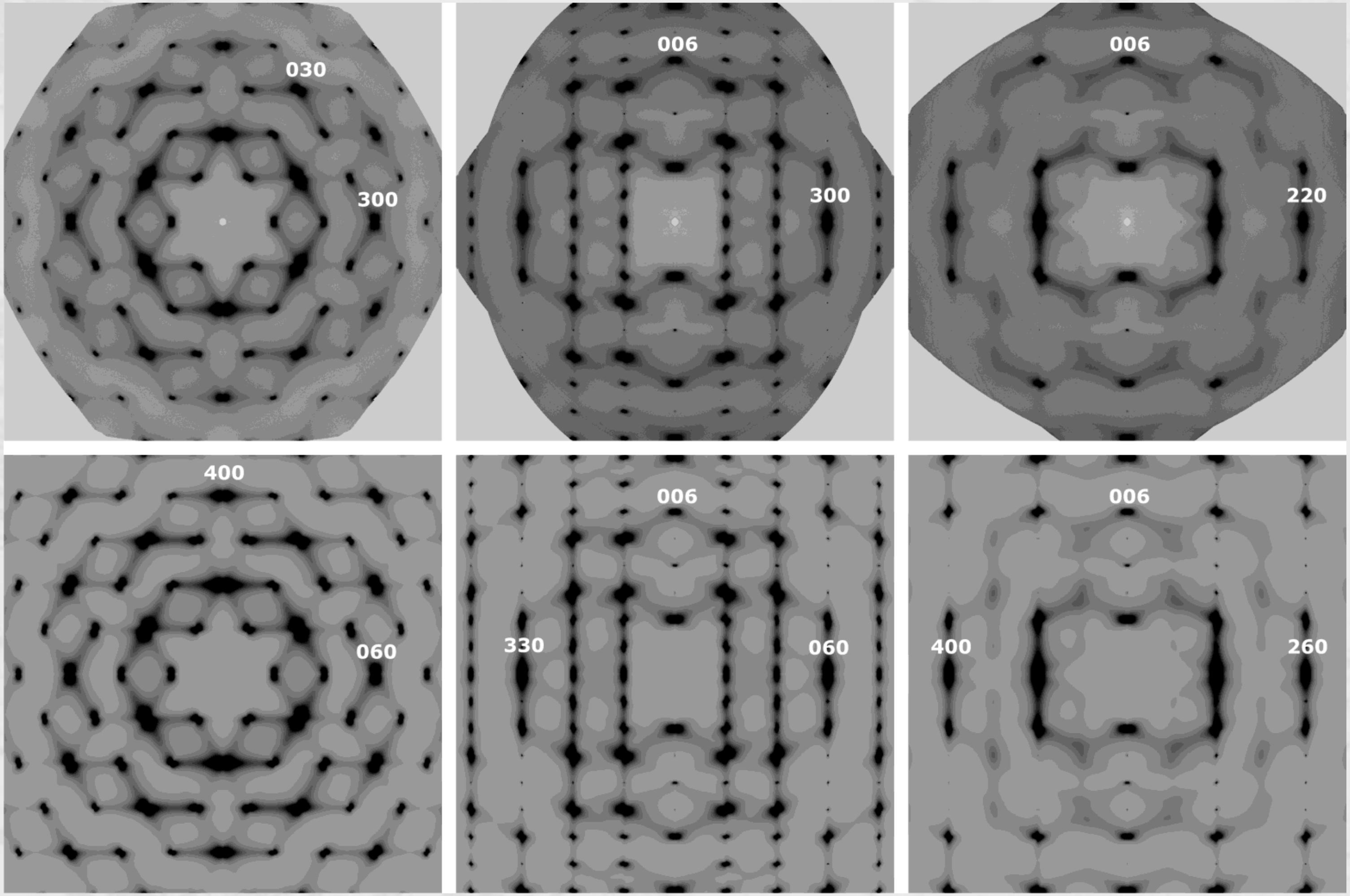
ice Ih 175 K

inelastic scattering is largely dominating

Phonon dispersion: experiment vs. calculation



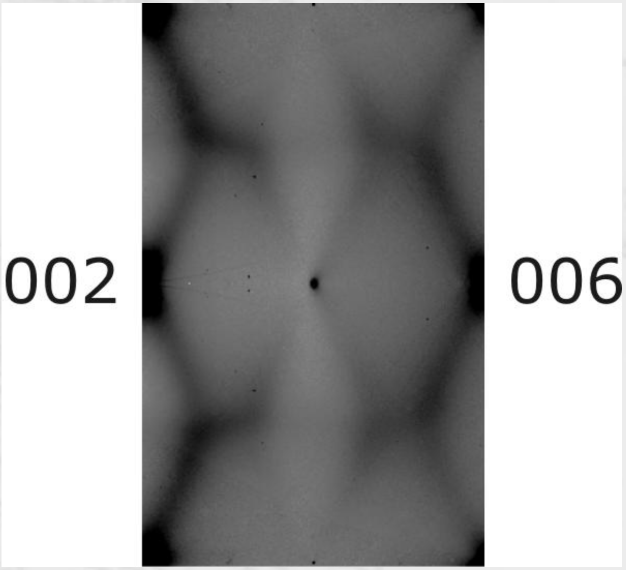
X-ray thermal diffuse scattering: modelling

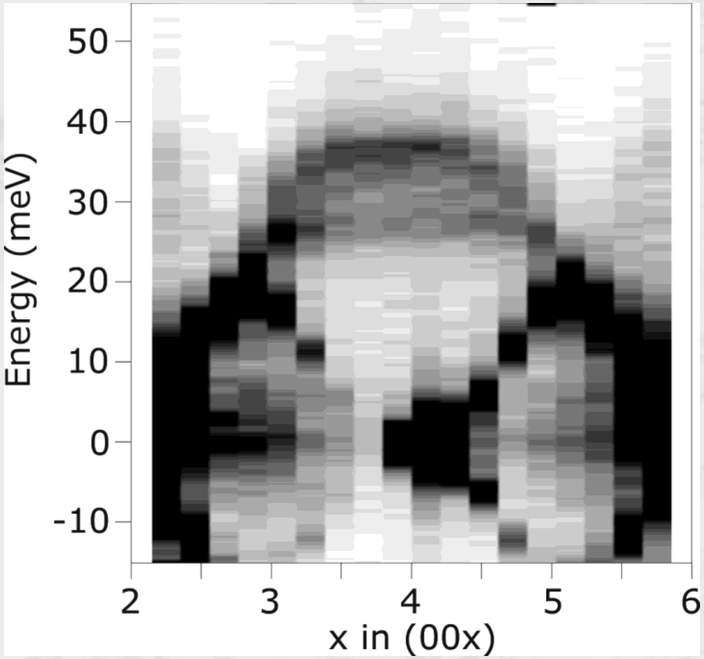


CASTEP package + ESRF developments

B. Wehinger, A. Mirone

Hydrogen in the inelastic x-ray scattering



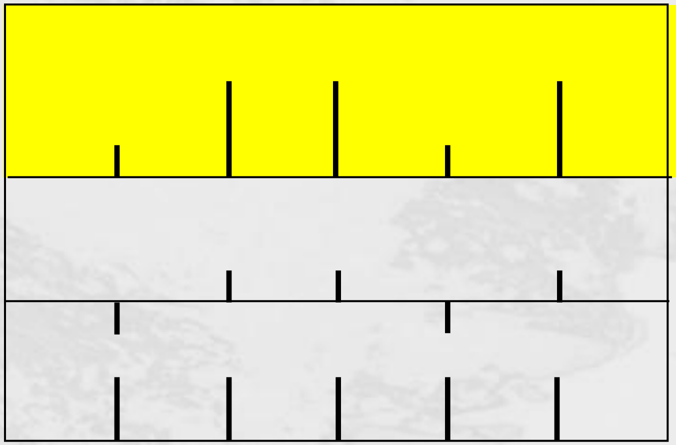


the same acoustic phonons are much weaker for (004-x) than for (004+x)

- the asymmetry disappears if the scattering from hydrogen is switched off

Imaging the disorder?

Disorder-related diffuse scattering

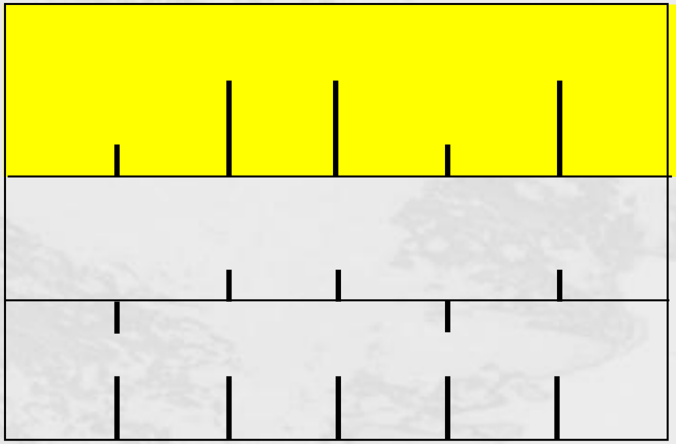


ρ with occupation disorder

$= \Delta\rho \longrightarrow$ diffuse scattering

$+ \langle\rho\rangle \longrightarrow$ Bragg scattering

Disorder-related diffuse scattering



f_i

$= f_i - f_{ave} \longrightarrow$ diffuse scattering

$+ \; f_{ave} \longrightarrow$ Bragg scattering

$$I_{diff}(\mathbf{Q}) = I_{tot}(\mathbf{Q}) - I_{Bragg}(\mathbf{Q})$$

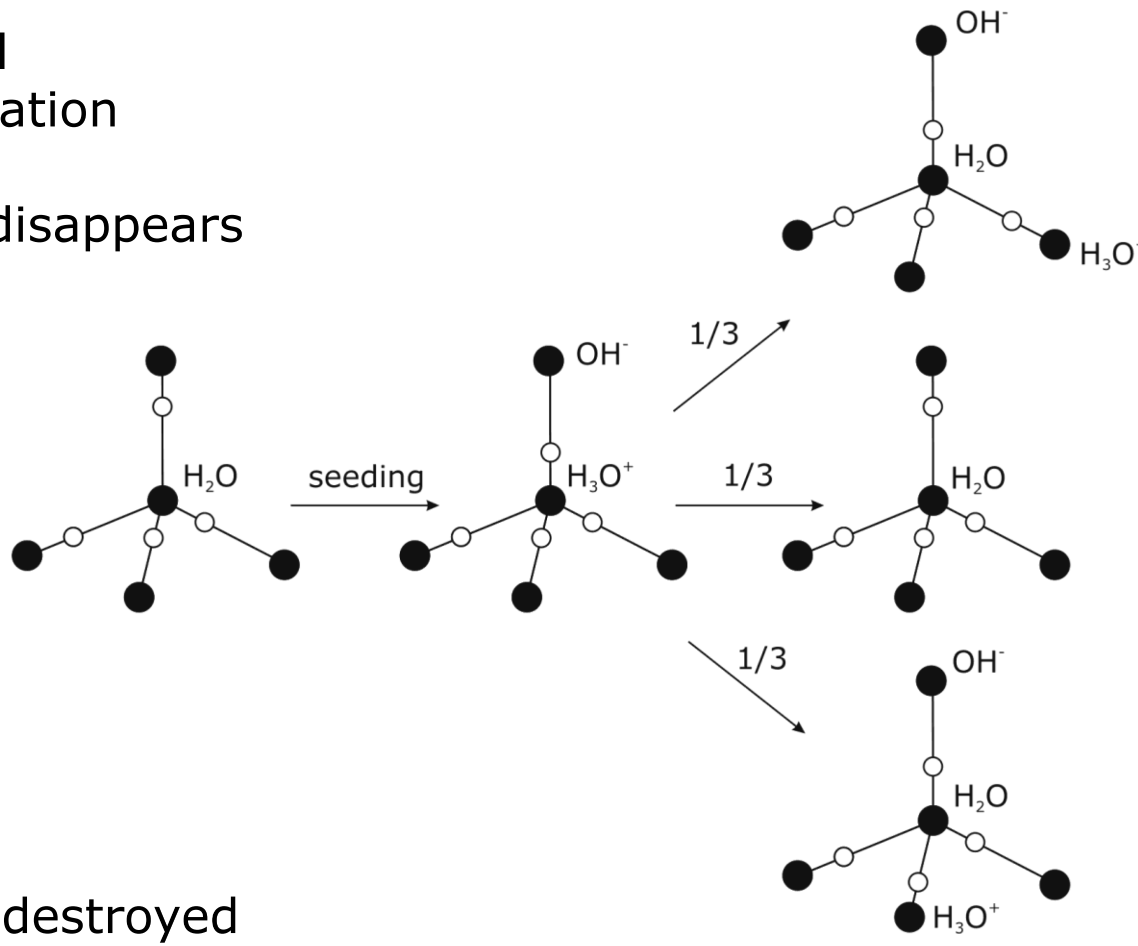
$$I_{tot}(\mathbf{Q}) = \sum_i \sum_j f_i(\mathbf{Q}) f_j^*(\mathbf{Q}) \exp\left(2\pi i \mathbf{Q}\left(\mathbf{R}_i - \mathbf{R}_j\right)\right)$$

$$I_{Bragg}(\mathbf{Q}) = \sum_i \sum_j f_{ave}(\mathbf{Q}) f_{ave}^*(\mathbf{Q}) \exp\left(2\pi i \mathbf{Q}\left(\mathbf{R}_i - \mathbf{R}_j\right)\right)$$

$$I_{diff}(\mathbf{Q}) \approx \sum_i \sum_j \left(f_{ave}(\mathbf{Q}) - f_i(\mathbf{Q})\right)\left(f_{ave}^*(\mathbf{Q}) - f_j^*(\mathbf{Q})\right) \exp\left(2\pi i \mathbf{Q}\left(\mathbf{R}_i - \mathbf{R}_j\right)\right)$$

Building the disorder

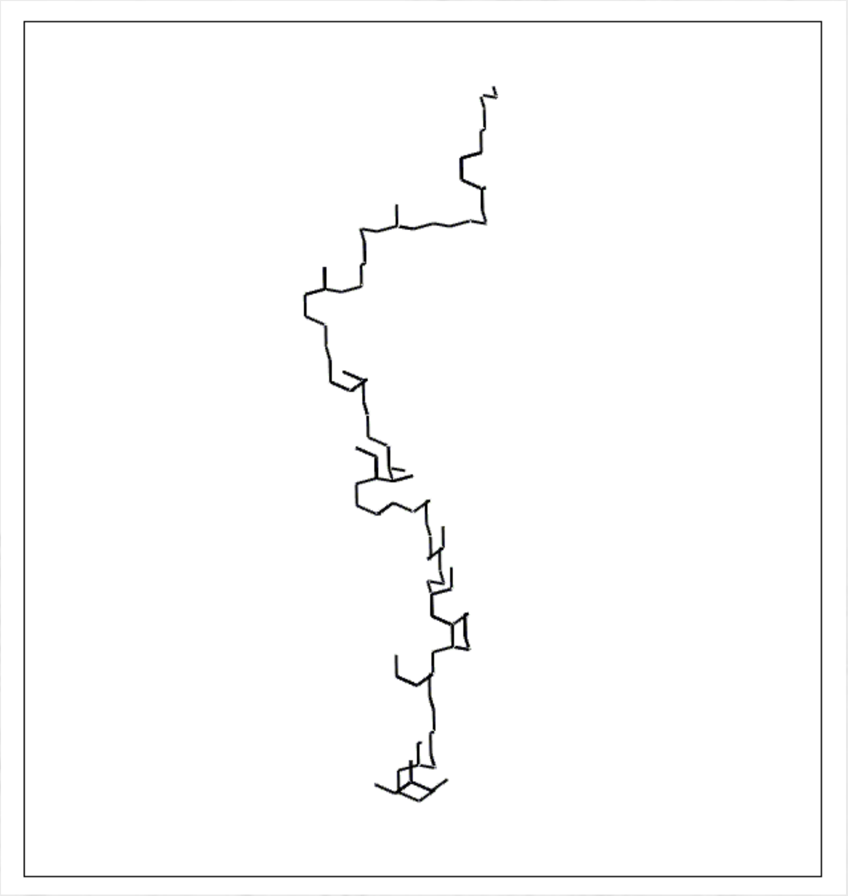
start: ordered ice crystal
- H_3O^+/OH^- defect generation
- random proton walk
finish: when the defect disappears



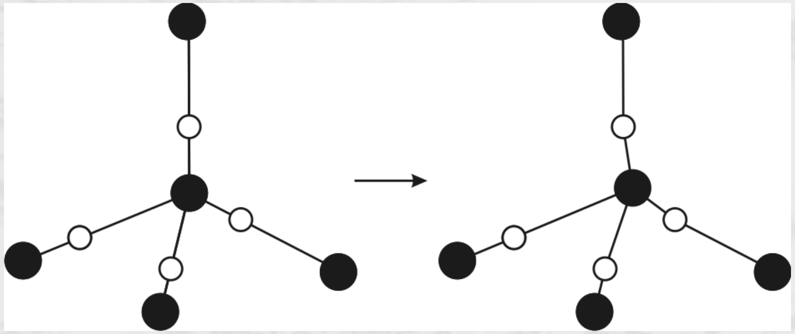
repeat until the order is destroyed

Disorder in ice Ih

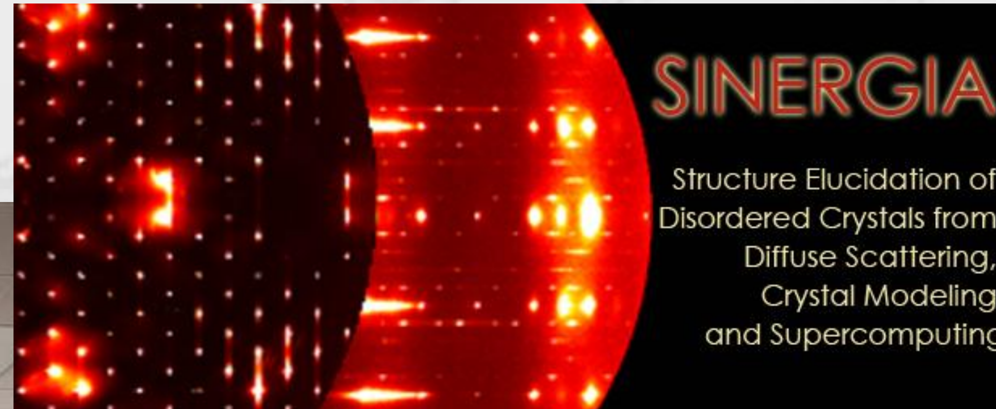
arrangement of atoms is still governed by **ice rules**



local symmetry of oxygen position is broken ⇒
oxygen is displaced (along the H_2O bisector?)
- can we see that with x-ray diffuse scattering?



Data manipulation & modelling



ORNL's Petascale Jaguar Supercomputer

...or just a desktop

Fast&easy approach

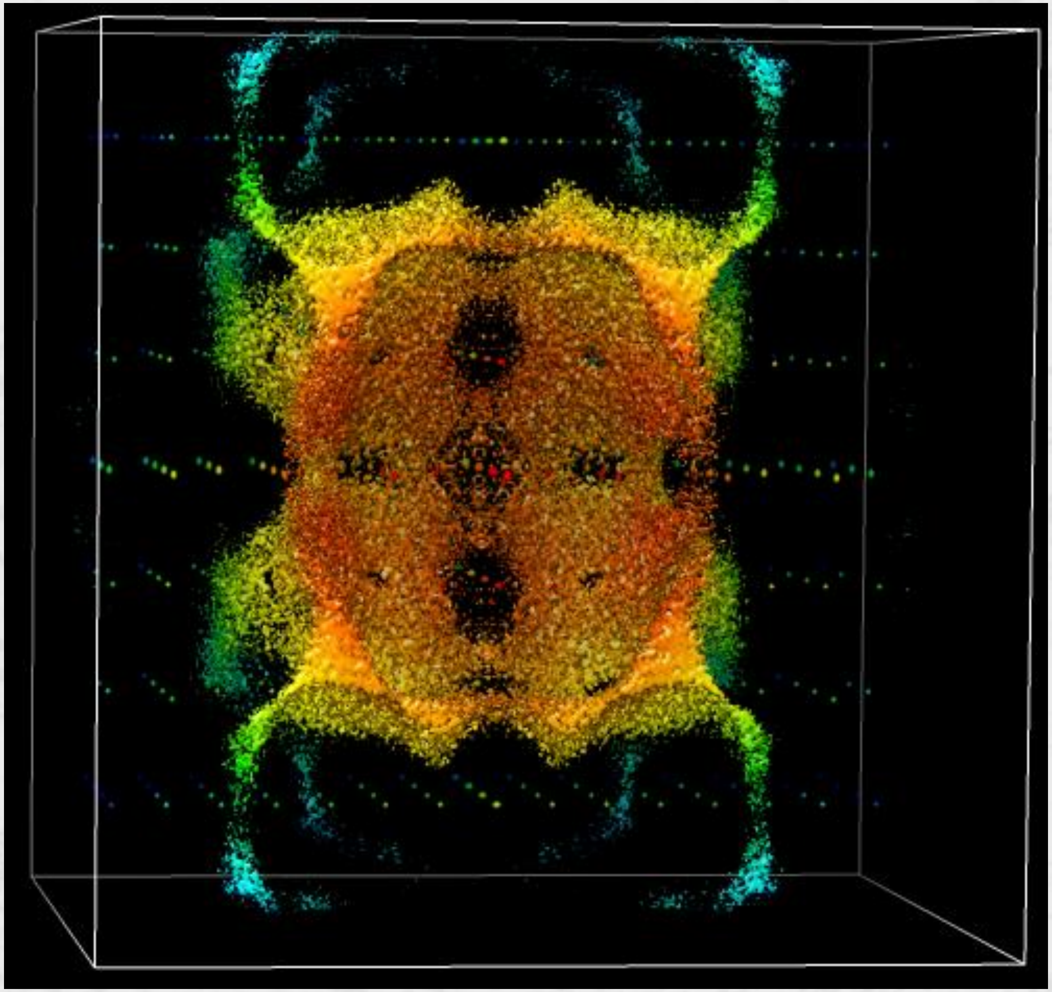
- limit the displacements by the discrete set
  (32 for H and 48 for O)
- generate the binary arrays 0/1 for all the lattices
- take the fast fourier transform FFT(NlnN instead of N^2!)
- sum up the FFTs with corresponding structure factors
- take the square to get the intensity

~5 s for the array generation (2^{21} = 2097152 water molecules)

<10 s for 1 reciprocal cell unit (including f(Q)exp(-2W(Q)) generation)

- repeat the generation of model crystal if less noice is needed

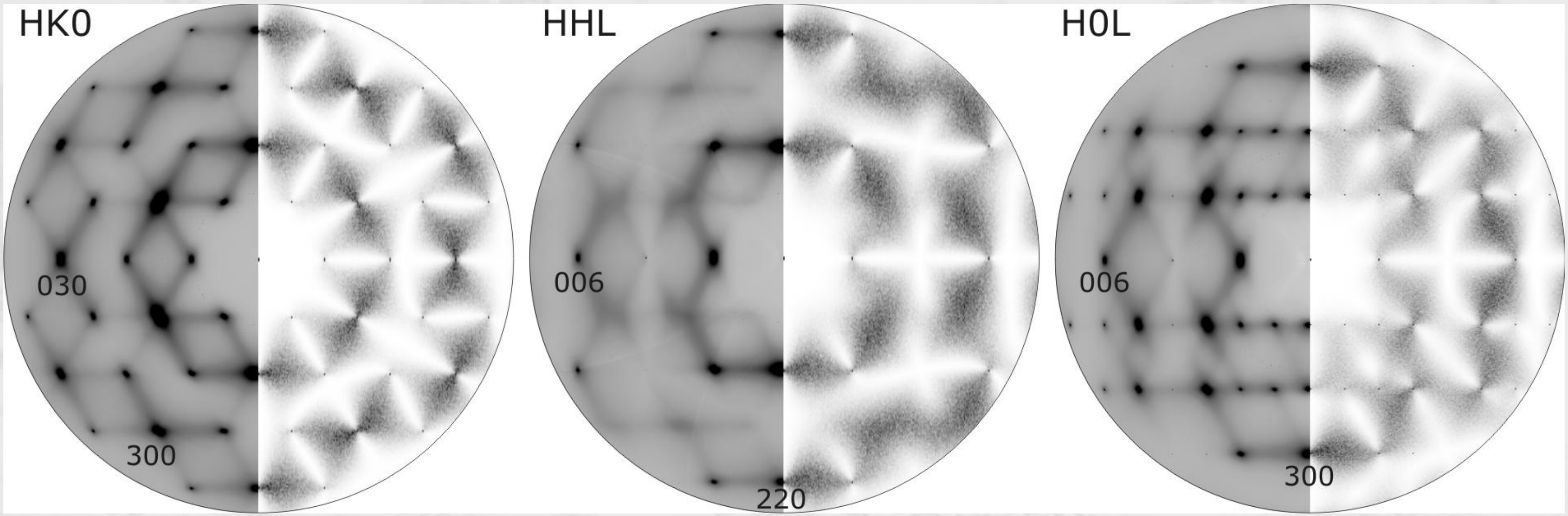
Model 3D neutron scattering from ice Ih



4 hours of single-core processor

4 clusters generated

Dynamic and static components of diffuse scattering

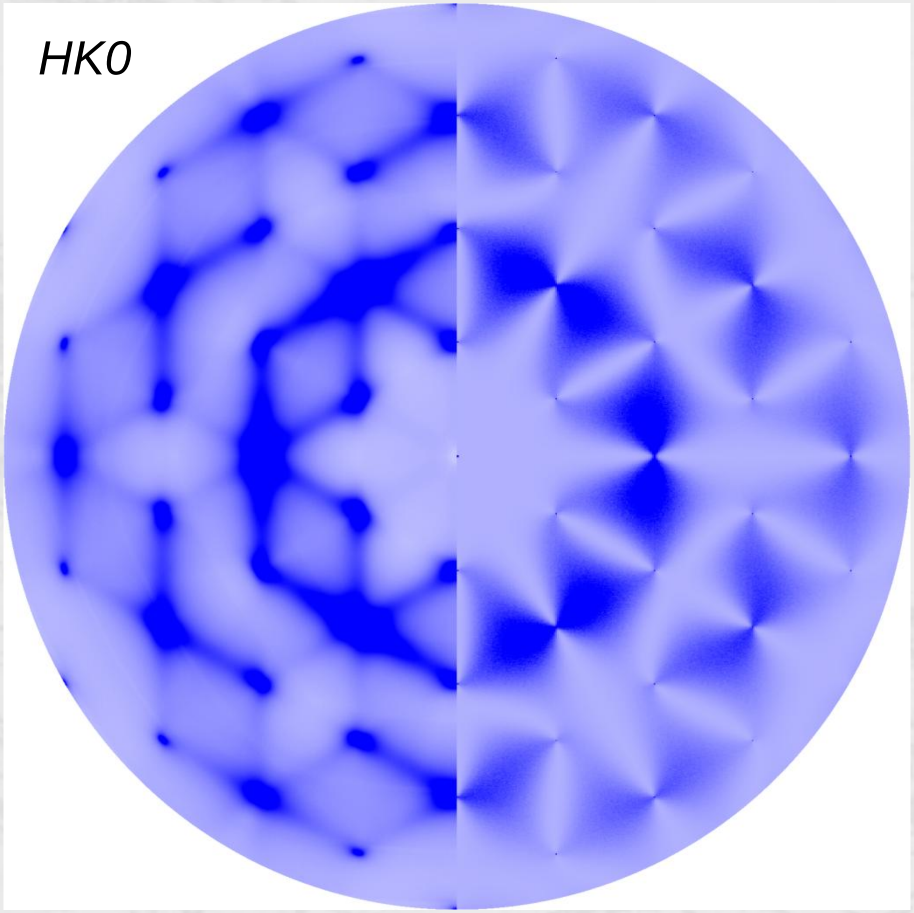


exp *ice rules model*

exp *ice rules model*

exp *ice rules model*

Dynamic and static components of diffuse scattering



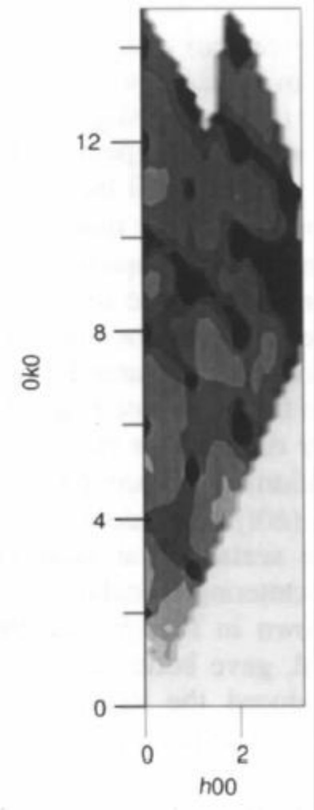
experiment *ice rules model*

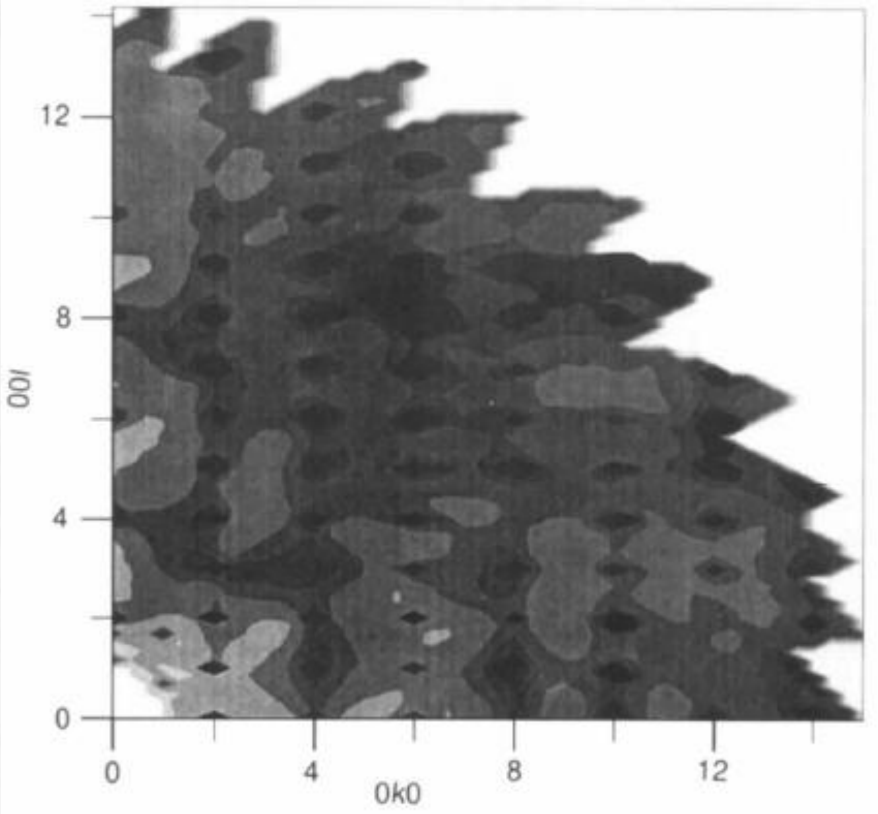
static component is strong exactly where thermal diffuse scattering is strong ⇒ diffuse x-ray scattering is useless in the study of static disorder in ice

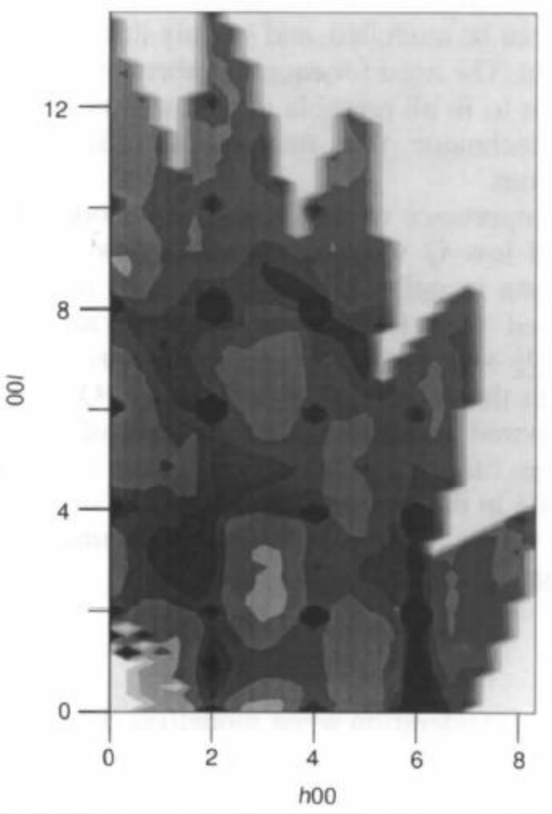
components can be separated only in the inelastic scattering

ESRF Christmas card 2012 !!

Diffuse neutron scattering in ice Ih





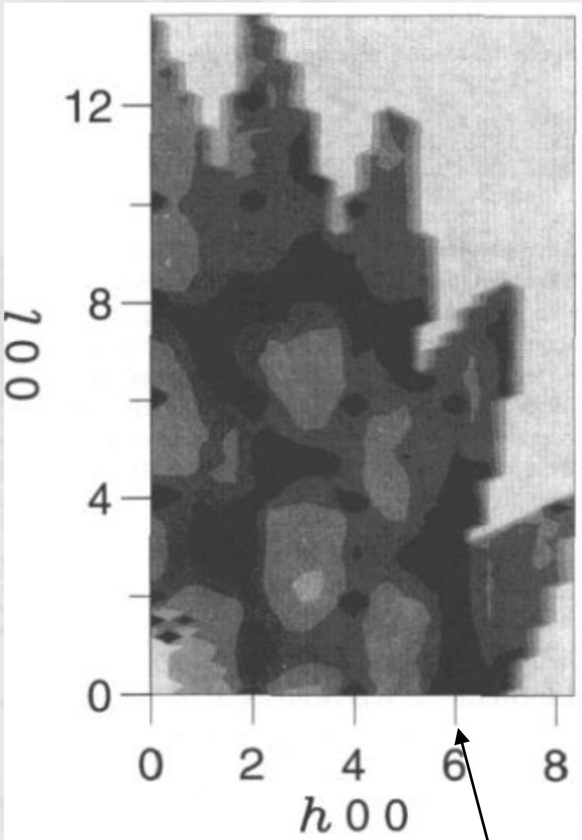


Time-of-flight Laue diffraction / ISIS

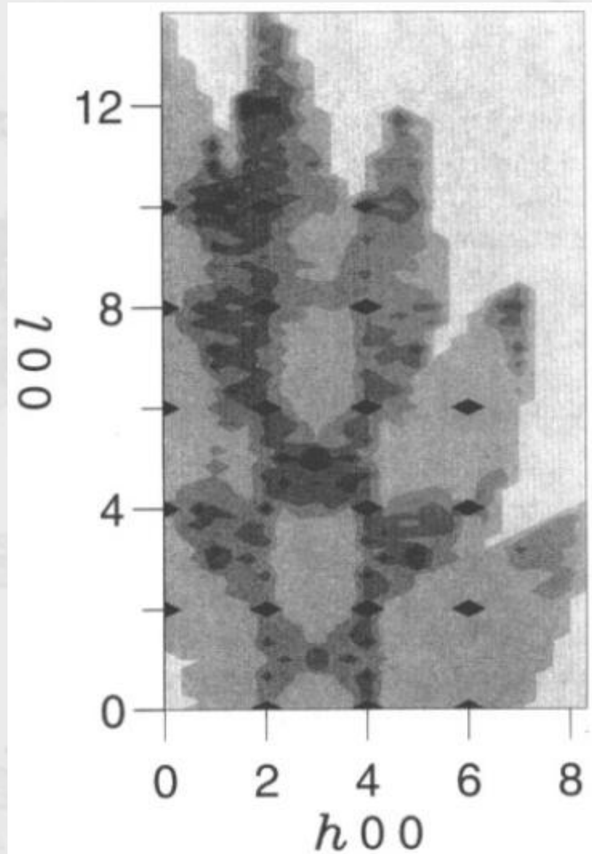
[V.M. Nield et al., Acta Crys. A 51, 763 (1995)]

orthorhombic settings

Interpretation



experiment

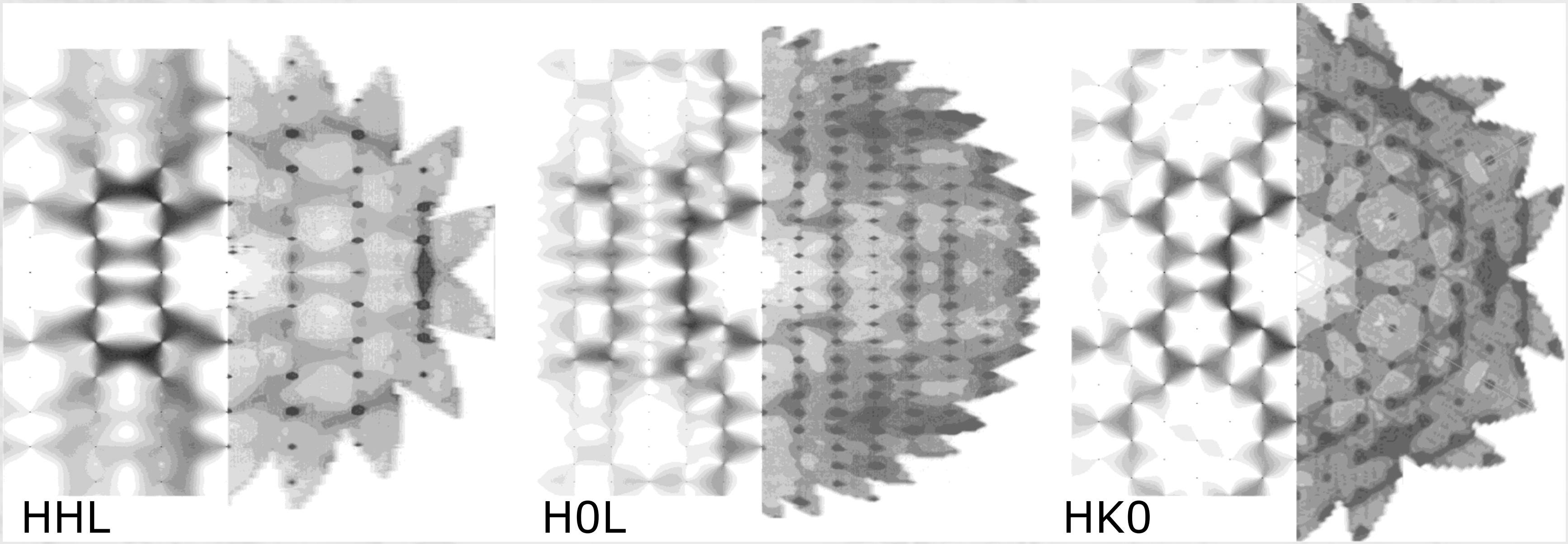


Bernal-Fowler rules only

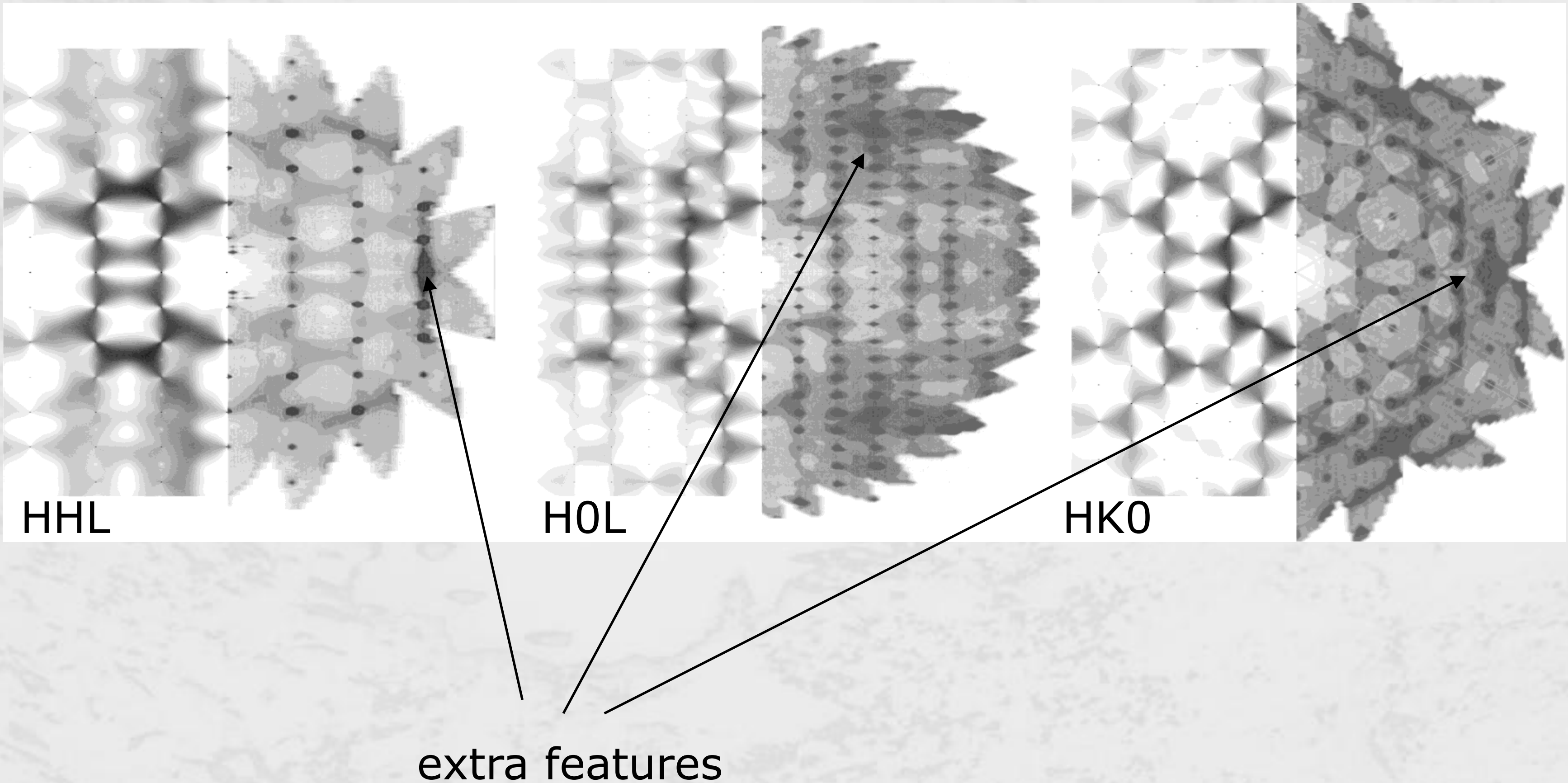
extra feature

reverse Monte-Carlo calculation produces the additional correlated displacement

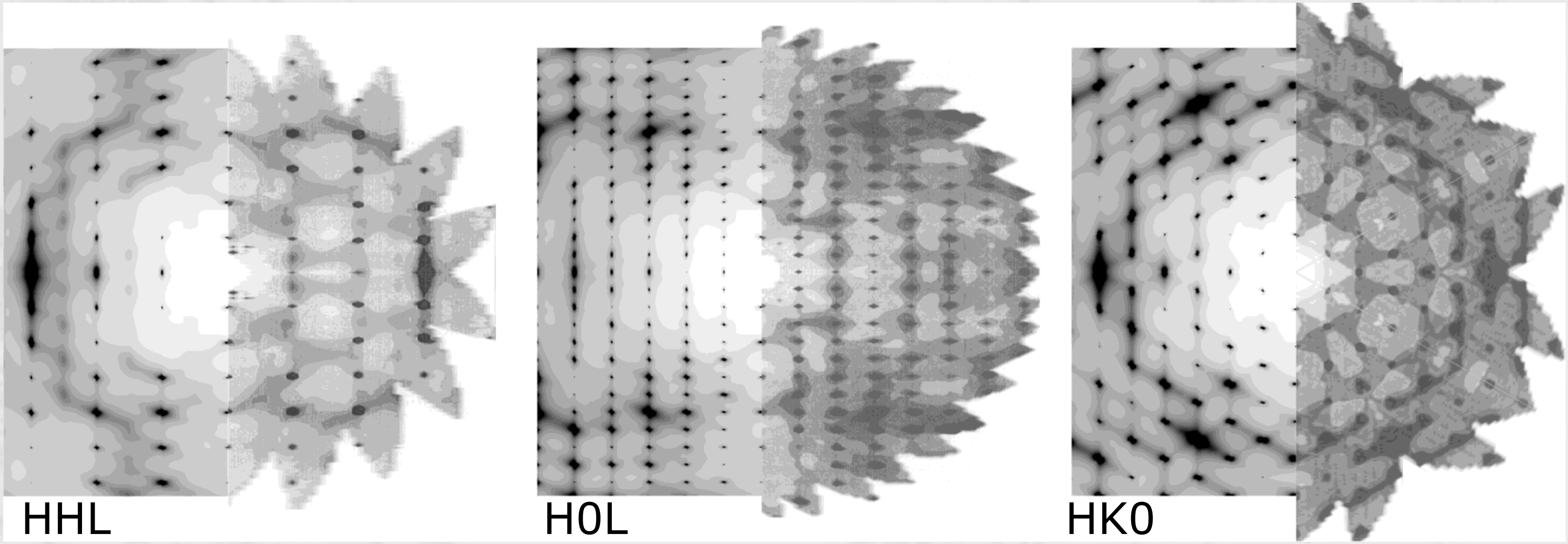
Ice rules only



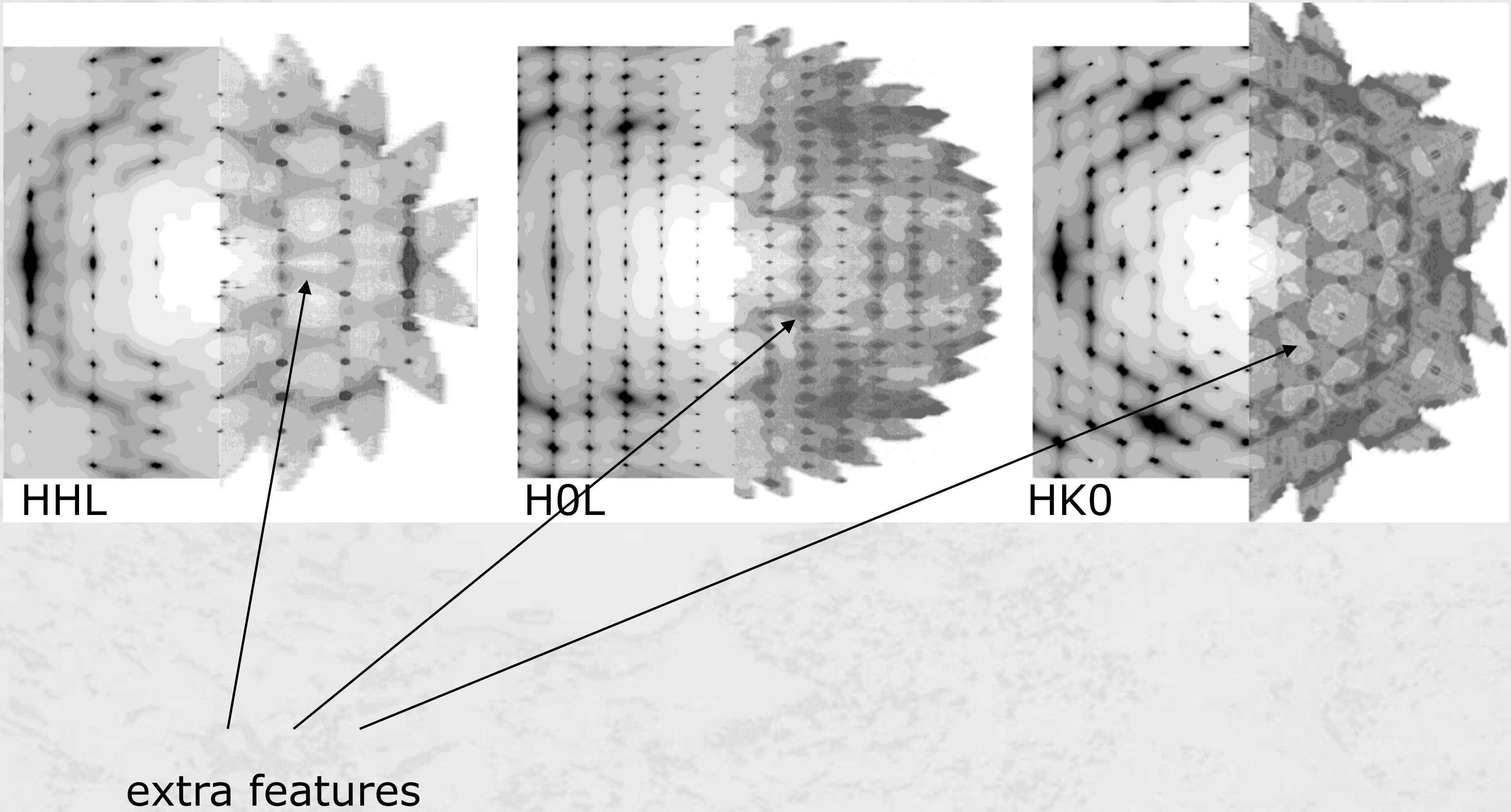
Ice rules only



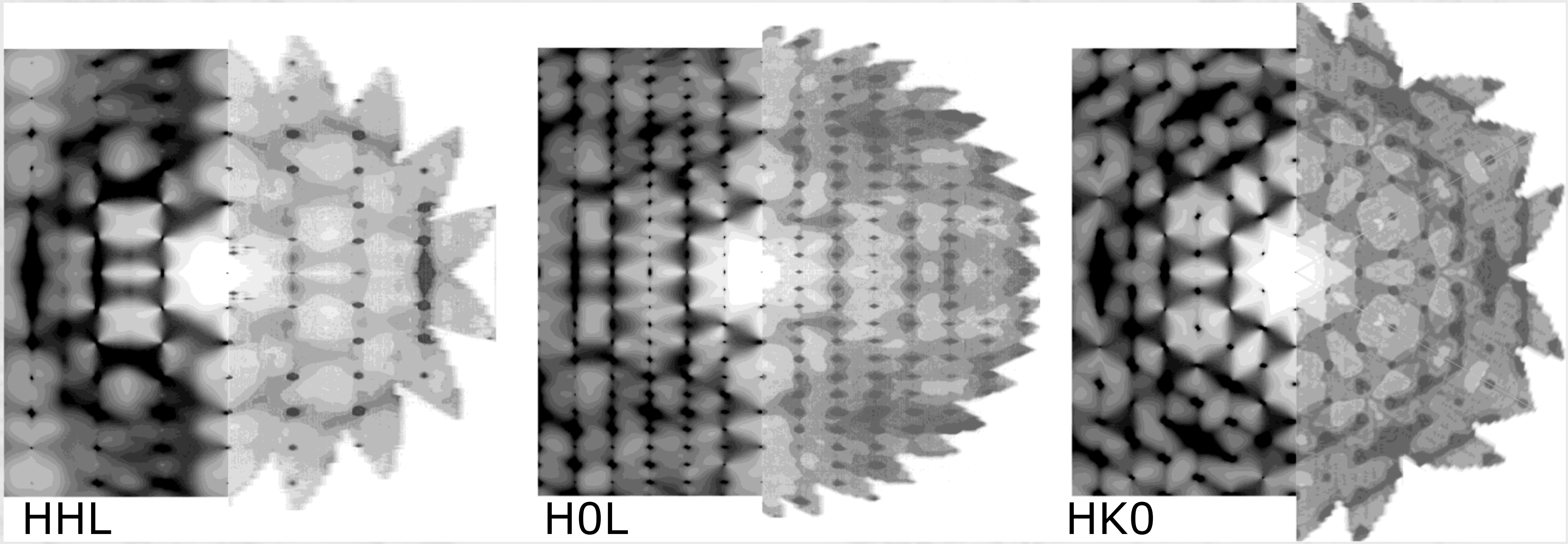
Thermal diffuse scattering only



Thermal diffuse scattering only



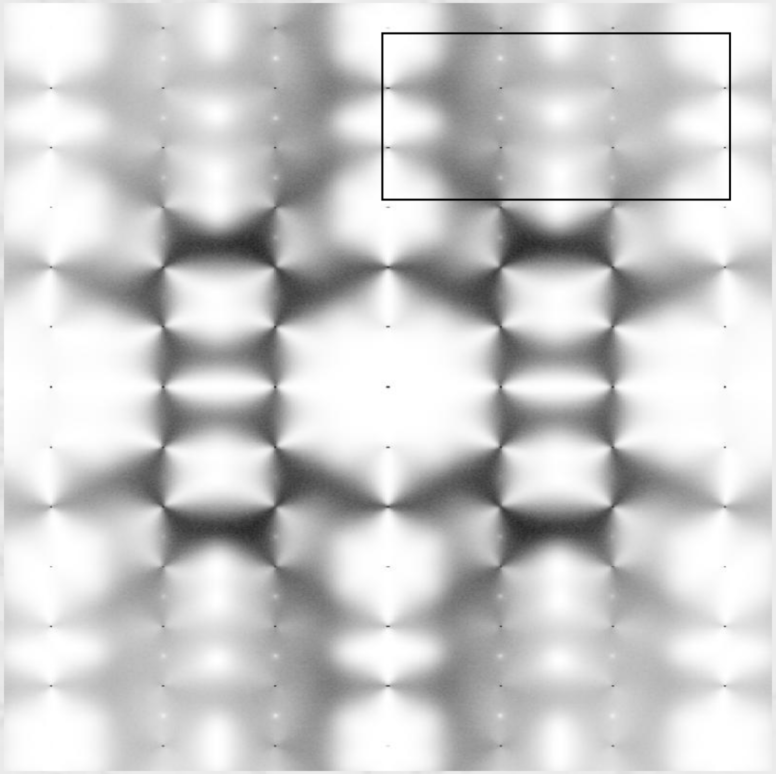
Total scattering

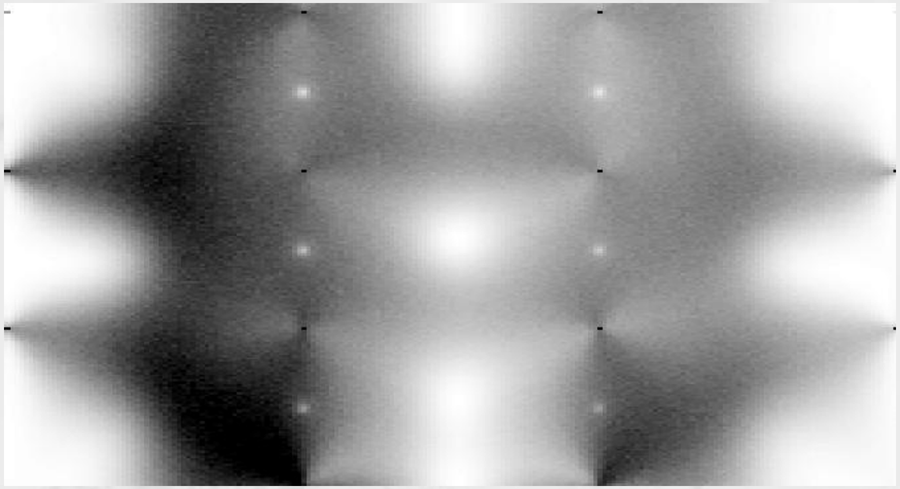


scattering pattern is better described by the sum of disorder and dynamics than by artificially introduced correlated displacements

Less clear observations

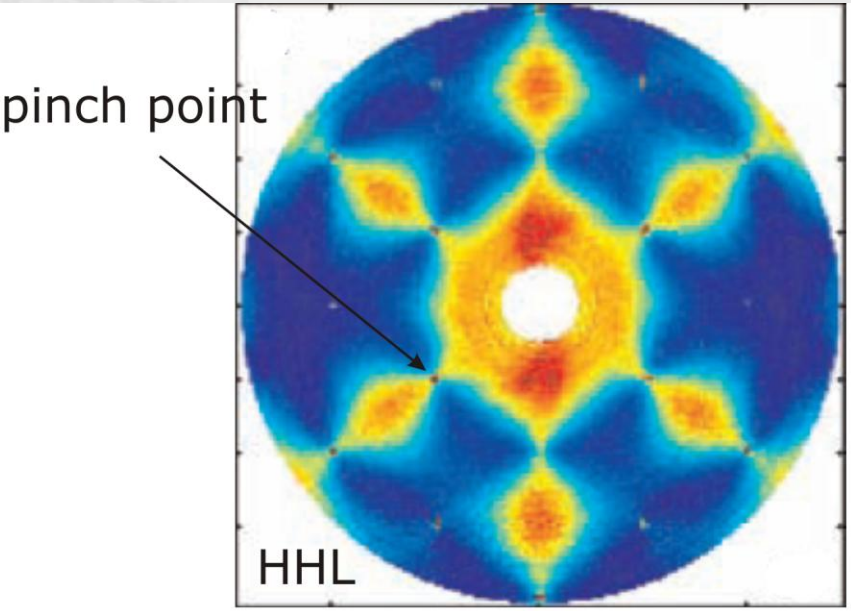
Anti-nodes of diffuse scattering



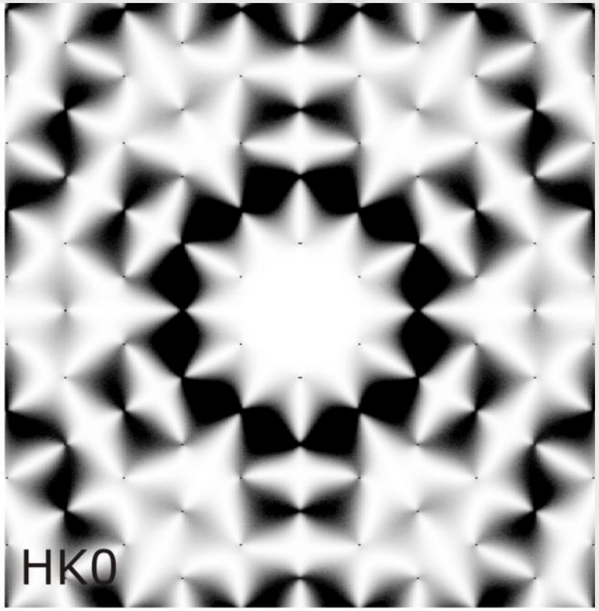


diffuse scattering "anti-nodes" are due to large-distance-forbidden configurations?

Similarity to the spin ice

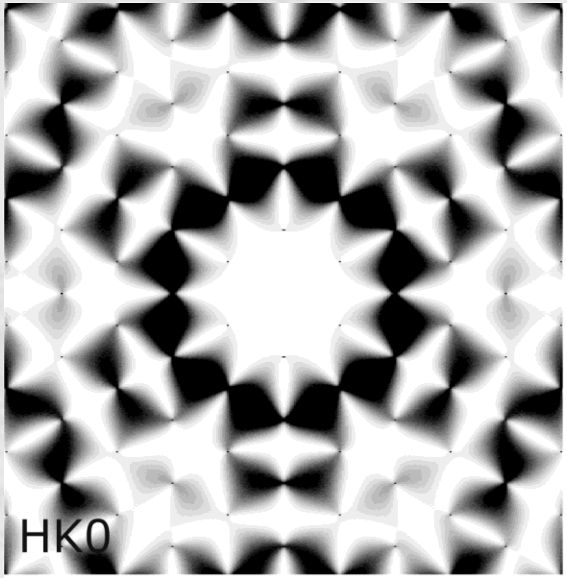


$Ho_2Ti_2O_7$
neutrons
spins

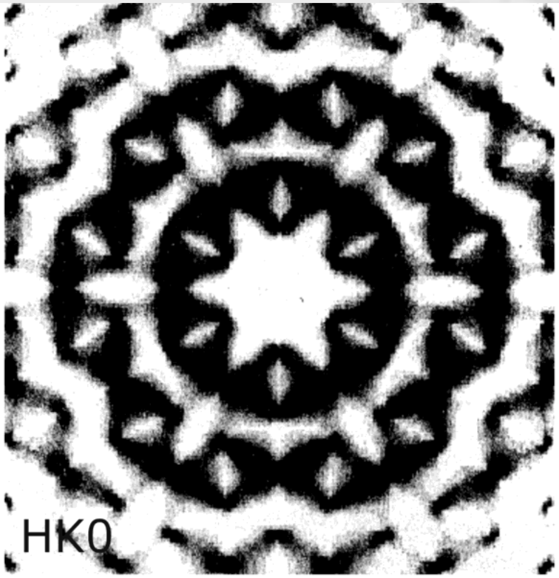


ice Ih
X-rays
oxygen shifts

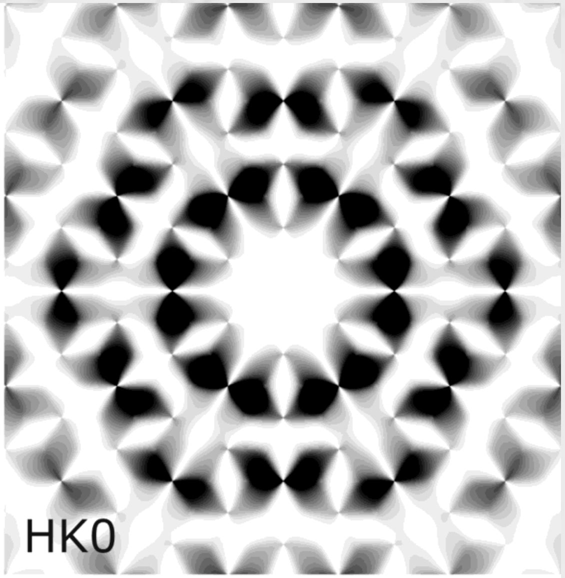
More suspicious similarity



ice Ih
X-rays
oxygen shifts



AgI
thermal
diffuse scattering



ice Ih
pseudo-TDS

static disorder

nearly flat TA dispersion

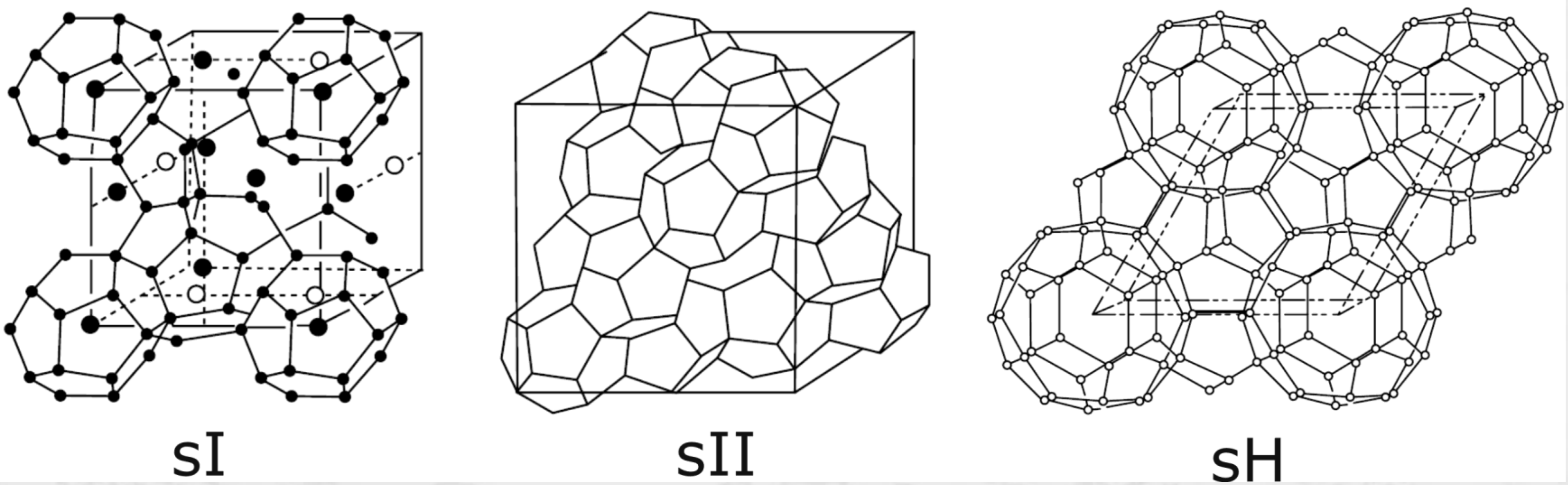
TA phonons only
n(E)/E switched off

spin ice description in terms of "dynamical matrix"?

What else?

Ice + something else

water + something + HP and/or LT -> clathrates



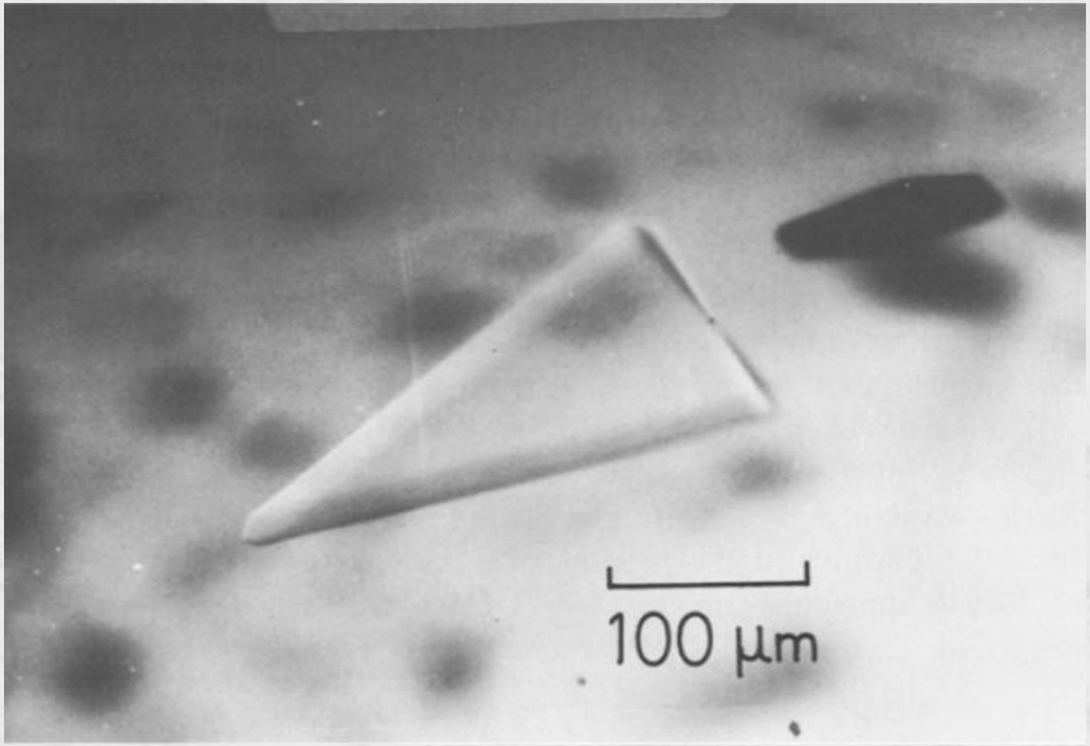
small molecules

larger molecules

...or very small

even larger molecules

Crystallography of natural air hydrates

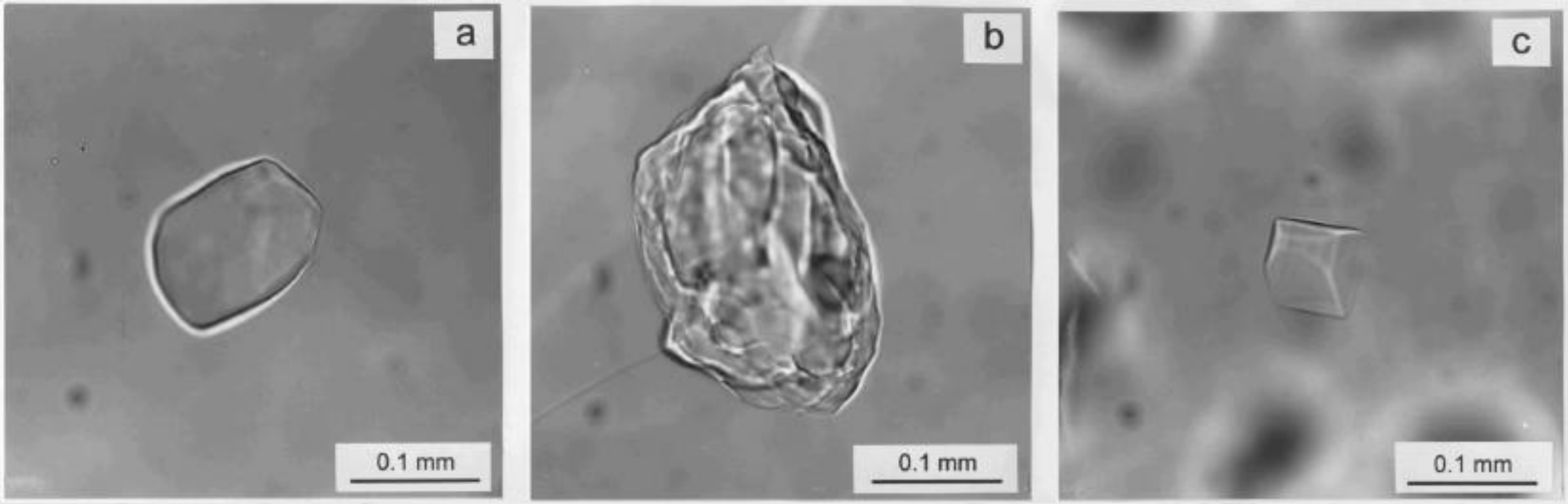


Dye-3, Greenland, 1500 m

[T. Hondoh et al., Journal of Inclusion Phenomena and Molecular Recognition in Chemistry, 8, 17 (1990)]

structure of type II

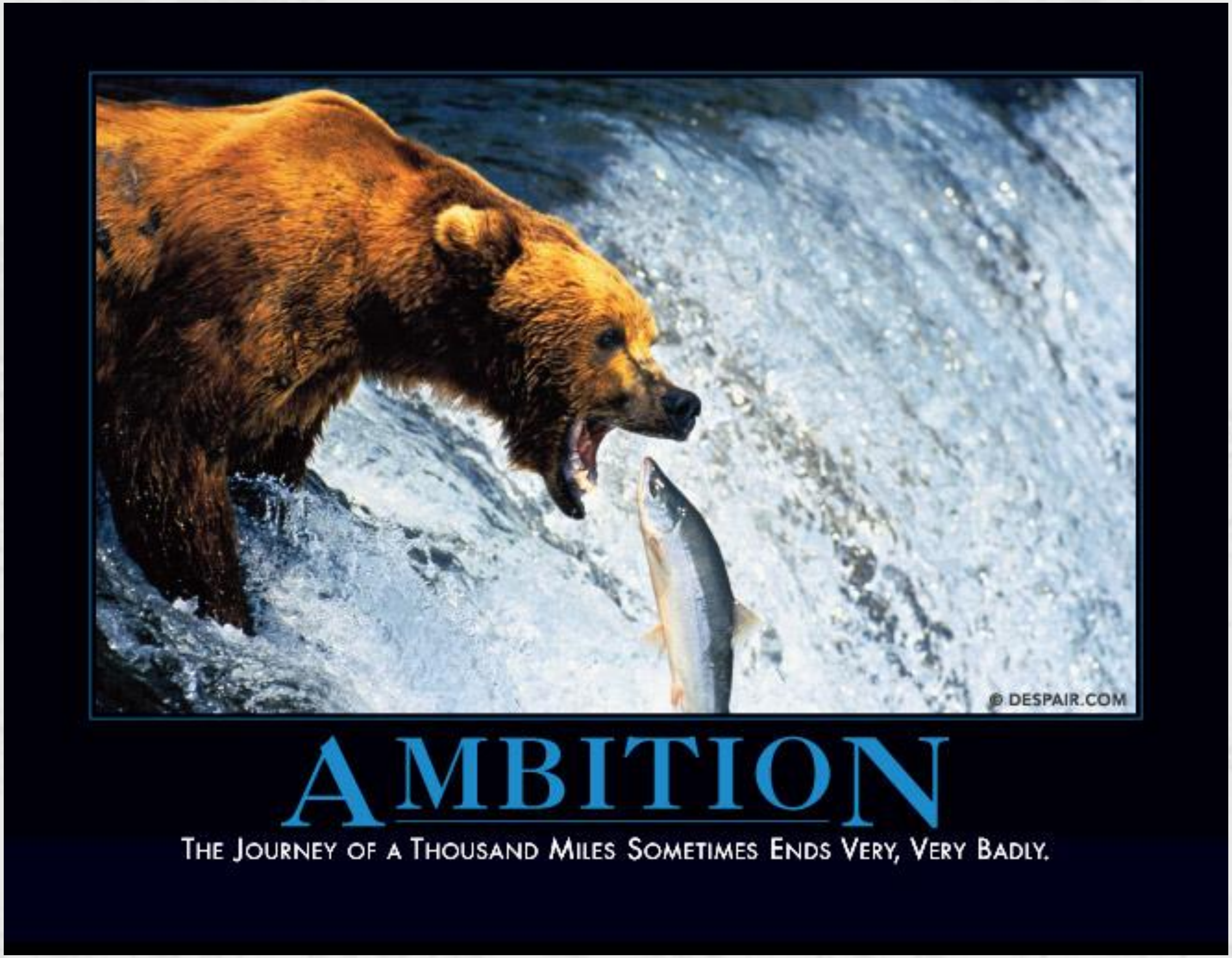
Vostok station ice core



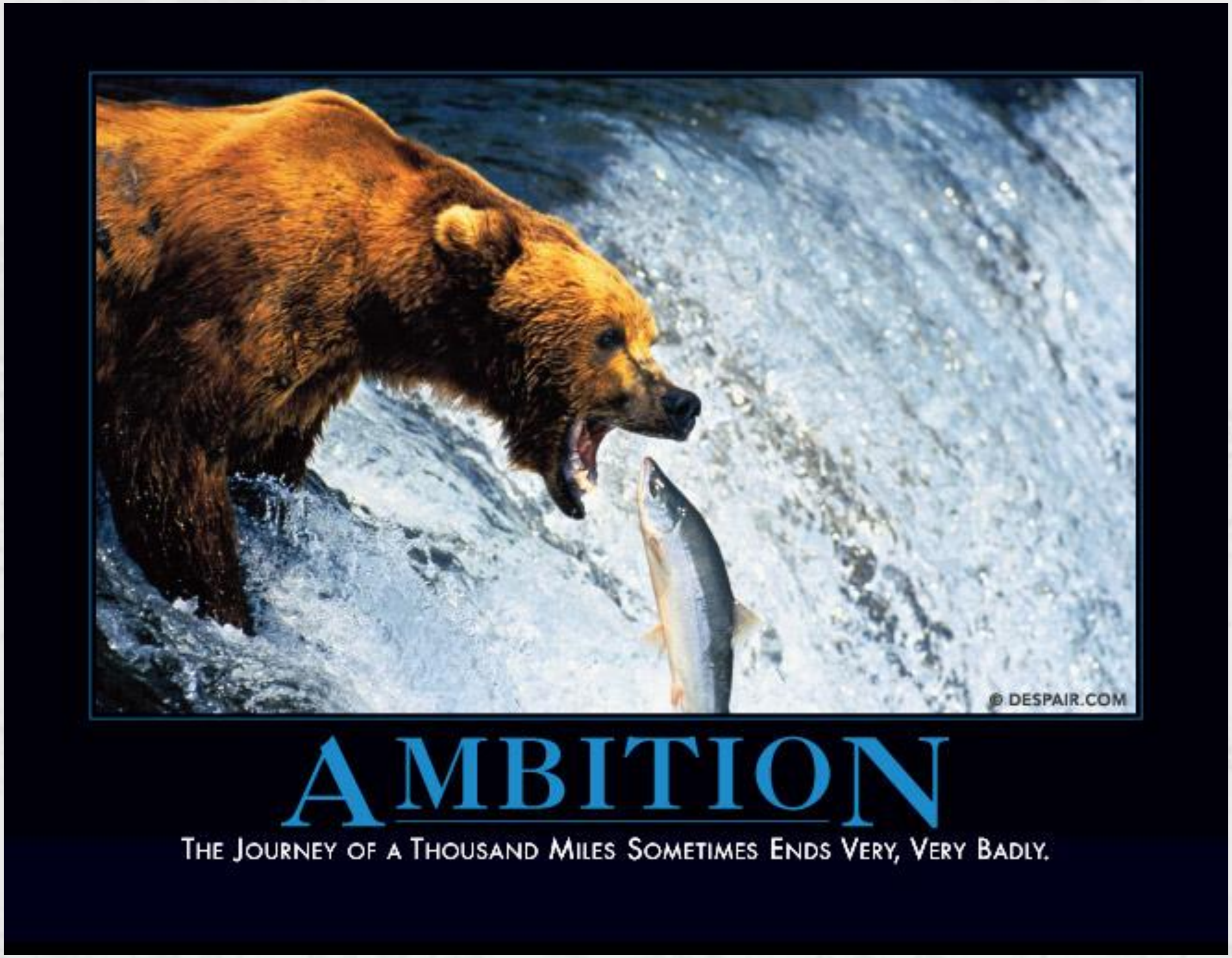
no crystallographic information available

[V.Ya. Lipenkov, Physics of Ice Core Records, Ed. T. Hondoh, Hokkaido University Press, 2000]

Many ambitious tasks remaining

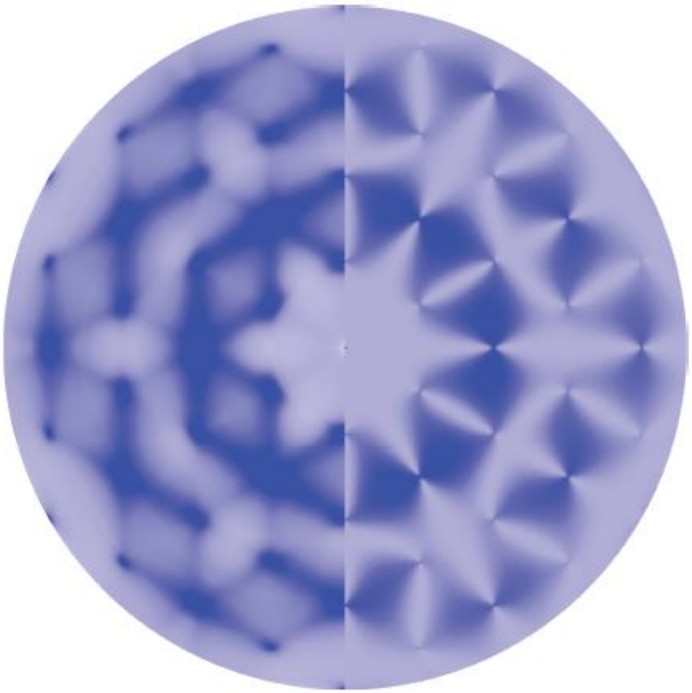


Many ambitious tasks remaining



So it goes.

[K. Vonnegut, Slaughterhouse-Five]



Diffuse x-ray scattering from a single crystal of antarctic ice extracted from the Antarctic ice sheet at a depth of 3.5 km, above the large subglacial Lake Vostok. Data taken at ID29 using a Pilatus detector.

Simulation of the x-ray scattering data from the intrinsic static disorder managed by «ice rules».

Best wishes
for the Holiday Season
and the New Year

A. Bosak, D. Chernyshov, A. Popov, D. De Sanctis, S. Bulat, V. Ezhov

Data manipulation & modelling

ORNL's Petascale Jaguar Supercomputer

...or just a desktop