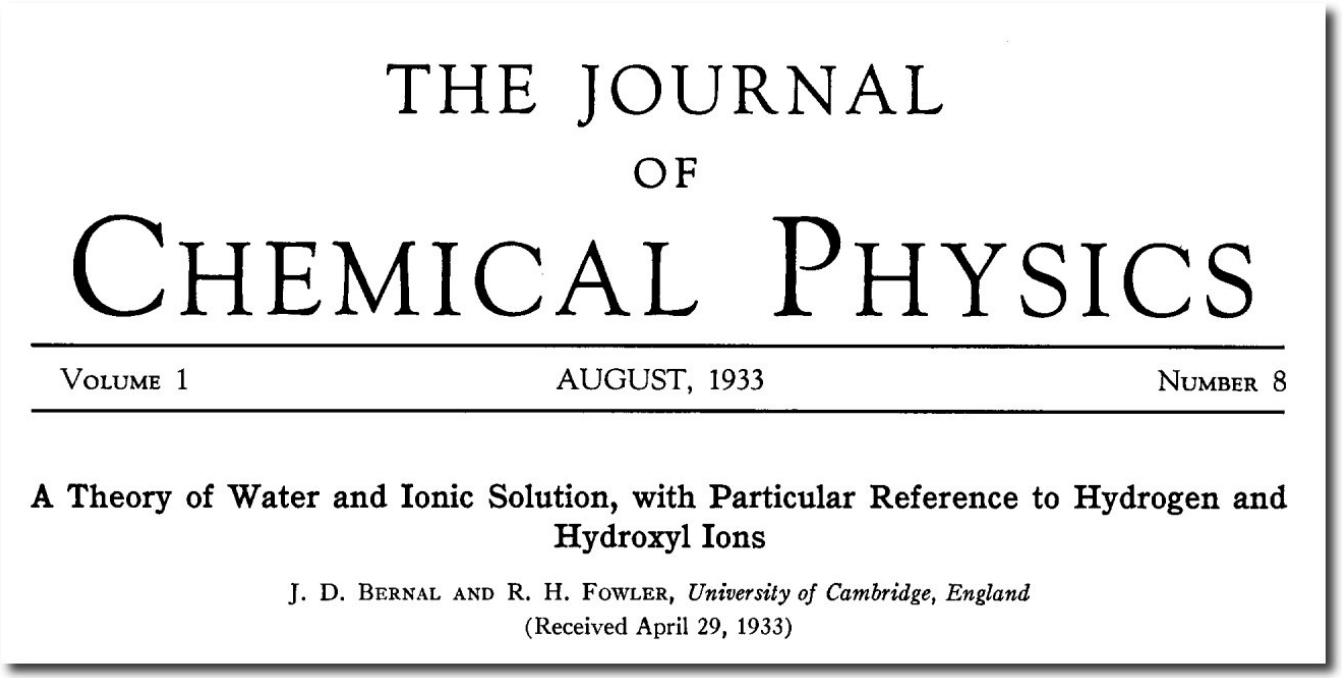
The precise analogy with ice: Bernal-Fowler (1933) Ice rules



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VOLUME 1 AUGUST, 1933 NUMBER 8

A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions

J. D. BERNAL AND R. H. FOWLER, *University of Cambridge, England*
(Received April 29, 1933)

- Oxygens in ice-I_h form a wurtzite (tetrahedral) lattice, with an O-O distance of 2.76 Å
- The 0.95 Å OH bond of H_2O is retained in ice-I_h
- Each oxygen must have two H at 0.95 Å and two at 1.81 Å, but *which two* ?

Class 14: Spin and charge ice [contd.]

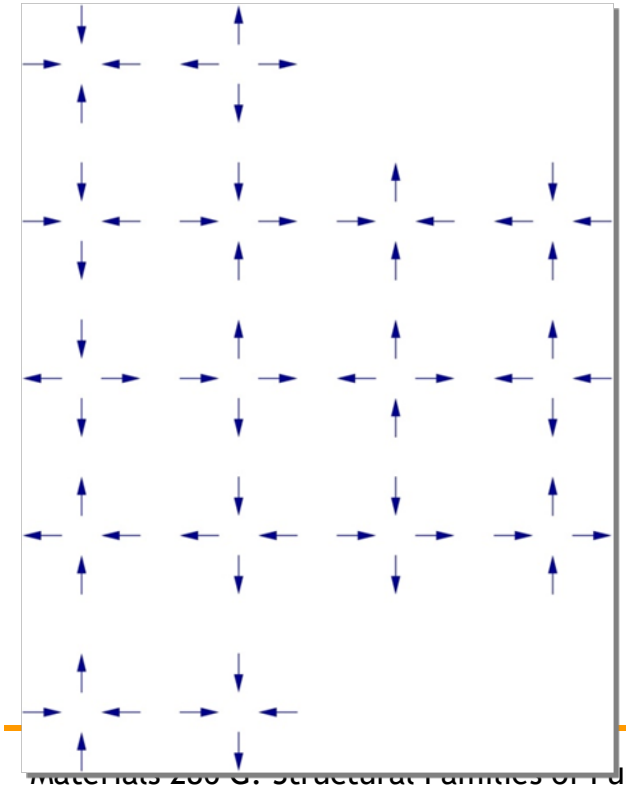
Pauling (1935): Ice-I_h has *residual entropy*

[Contribution from the Gates Chemical Laboratory, California Institute of Technology, No. 506]

The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

By Linus Pauling

16, 4-vertex models:



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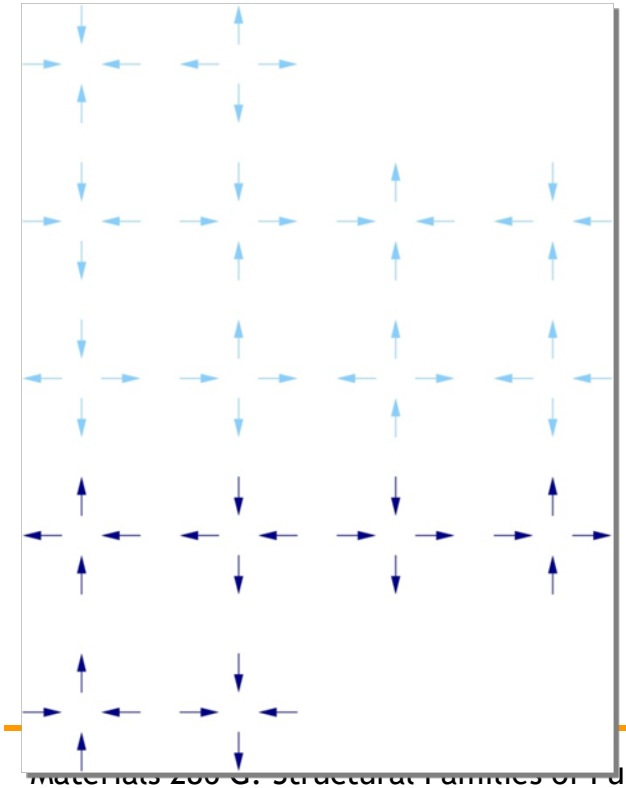
The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement

By Linus Pauling

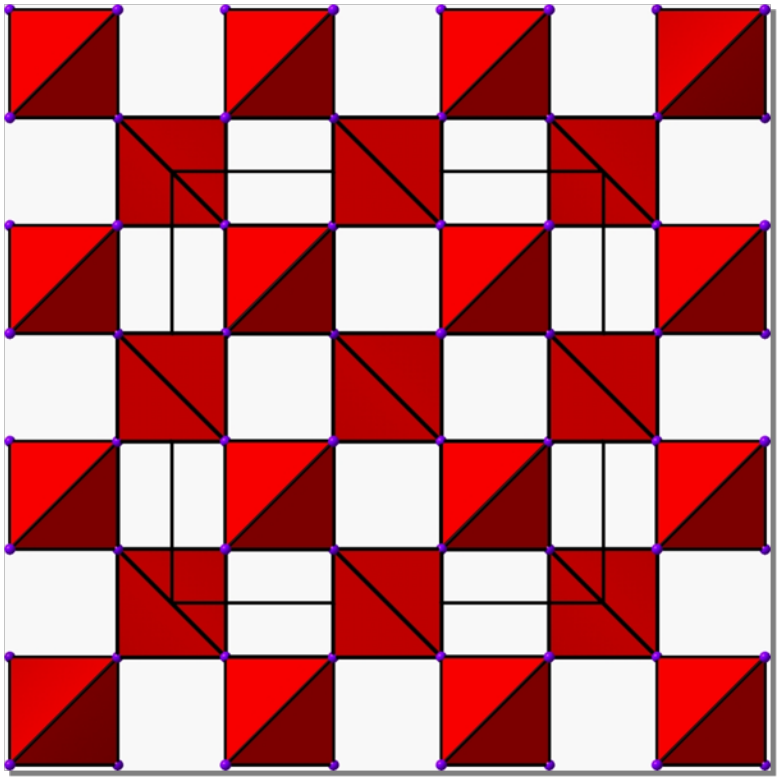
6 ways of arranging H around O so that ice rules are obeyed. Each bond has a 1/2 probability that the proton is is in an aceptable position.

$S = k_B \ln W$ and
$W = (6)(1/2)(1/2) = 3/2$

calculated: 0.80 cal/K/mol
measured: 0.82 cal/K/mol

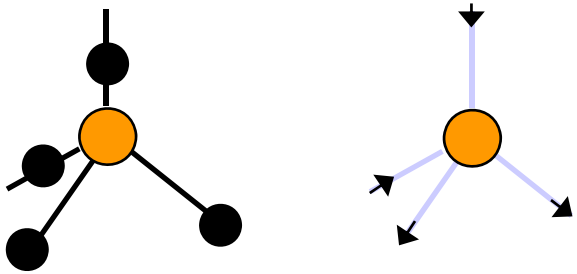


Class 14: Spin and charge ice [contd.]



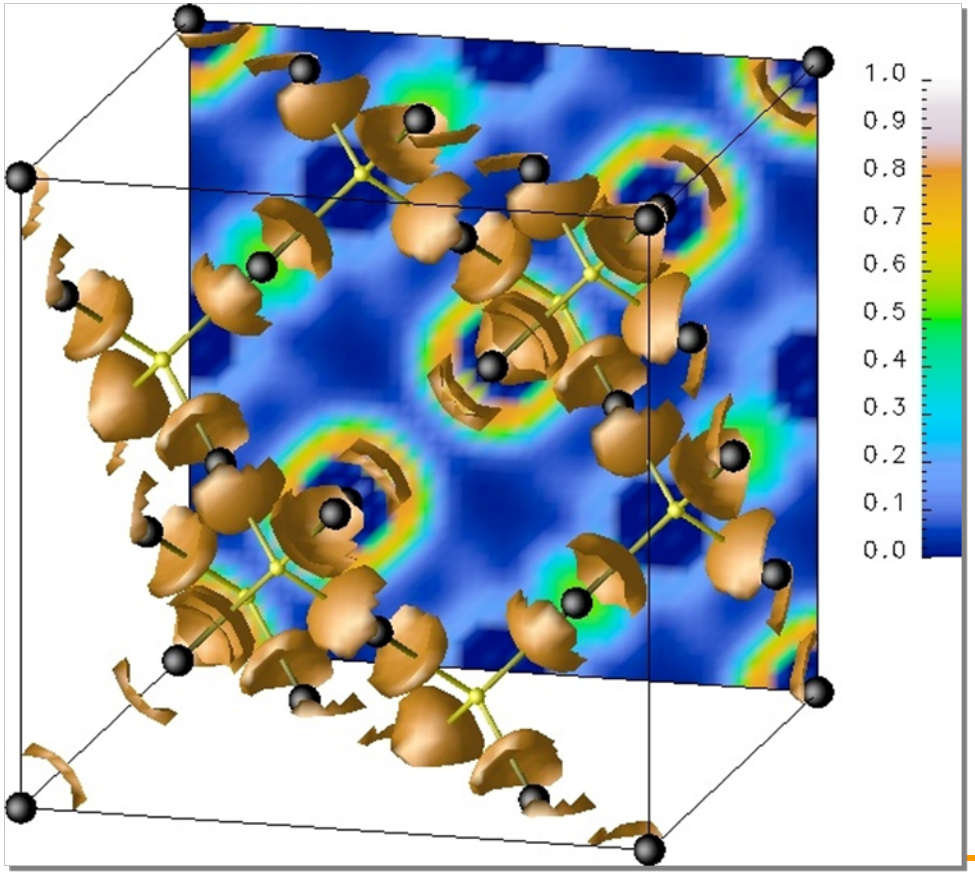
The A atom network of connected A_4 tetrahedra in $A_2B_2O_7$ is *frustrated* with respect to certain kinds of magnetic ordering. Similarities with the crystal structure of ice I_h: the notion of *spin ice.*

Bramwell, Gingras, *Science* **294** (2001) 1495.



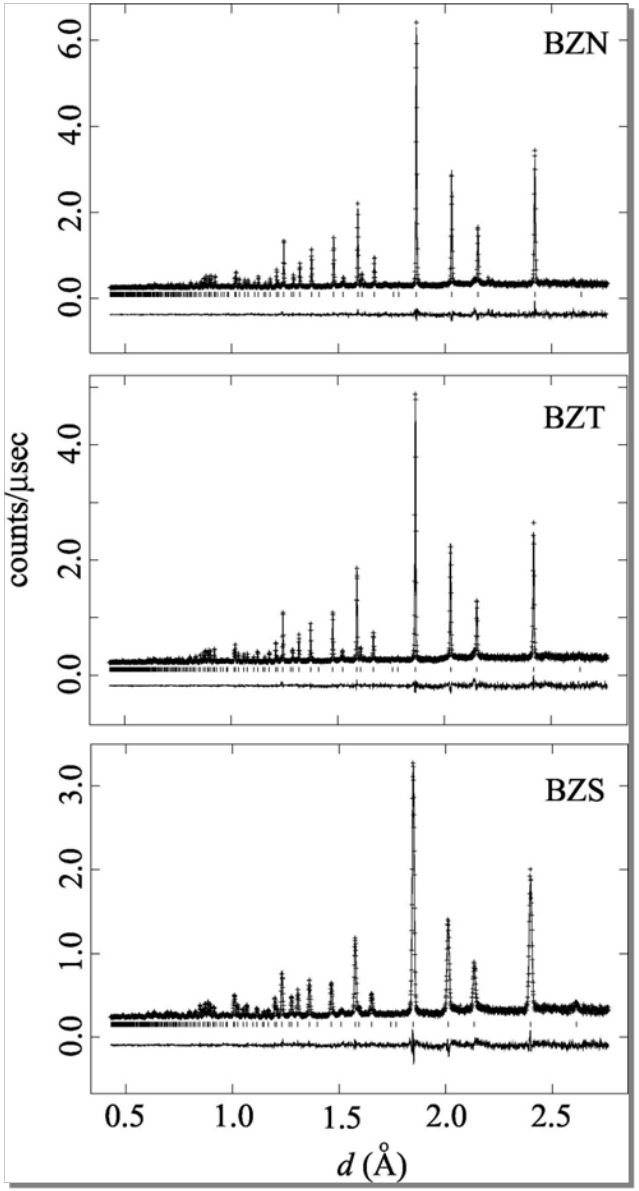
ice spin ice

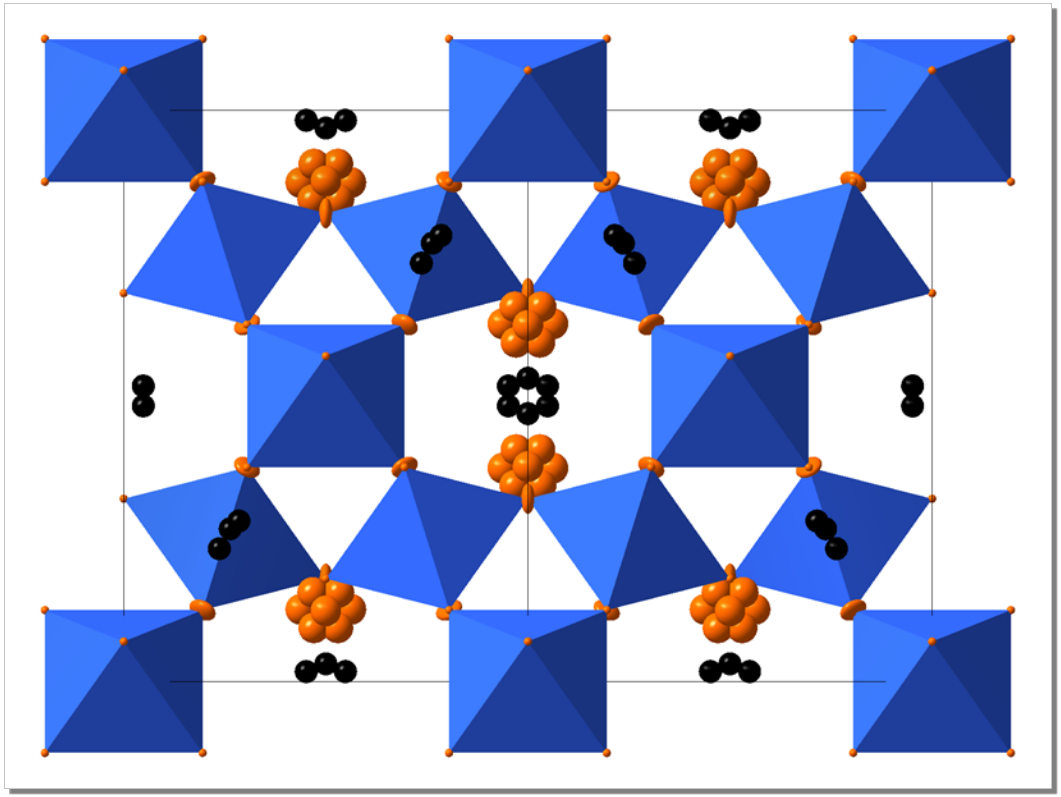
$Pb_2Sn_2O_6$: An ice analog [$Pb_2Sn_2O_6\square$: $Pb_2\square$ is similar to H_2O]
"lead-tin yellow"
Morgenstern-Badarau, Michel, *Ann. Chim.* **6** (1971) 109.



The Pb^{2+} are like H in H_2O. In which direction should they distort ?

Class 14: Spin and charge ice [contd.]

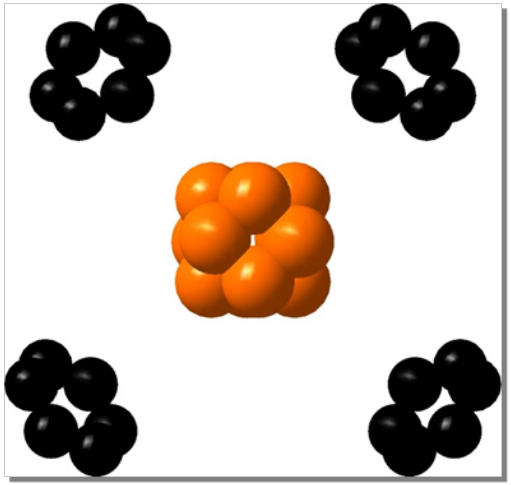


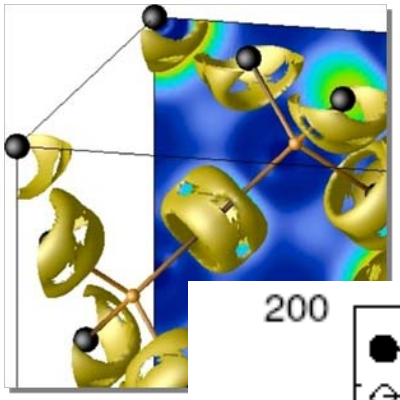


Understanding structural details through neutron diffraction:

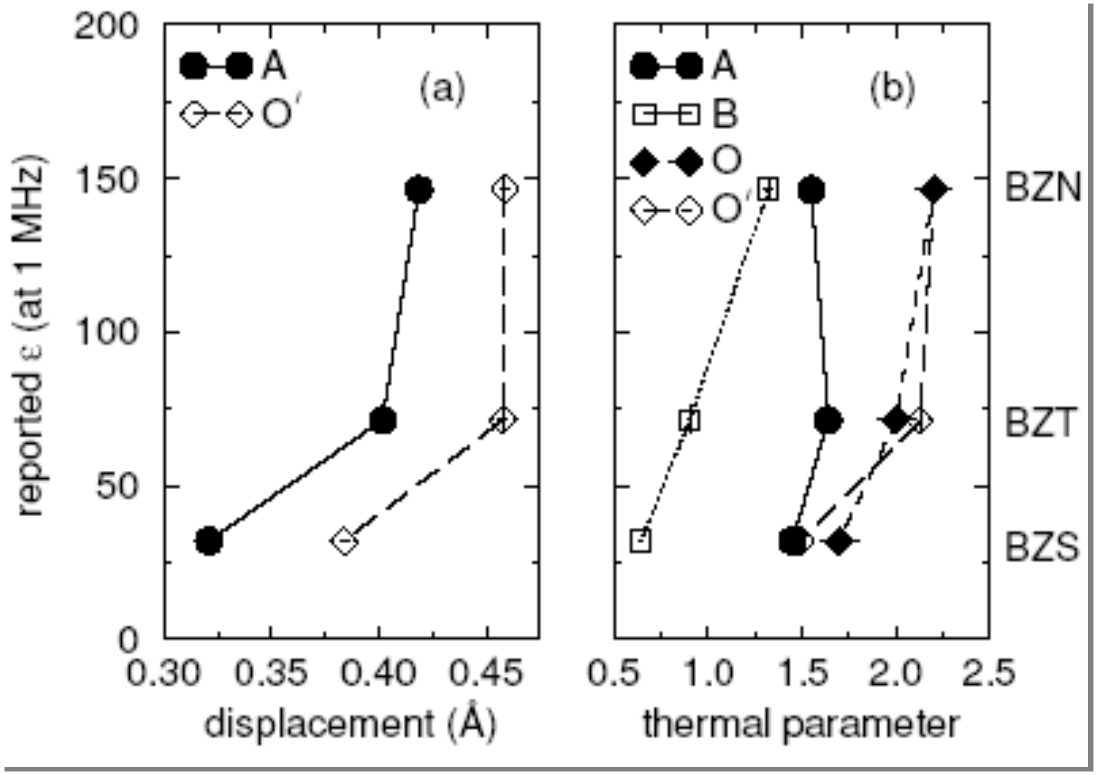
$Bi_{1.5}Zn_{0.5}B_{1.5}Zn_{0.5}O_7$ [*B* = Nb (BZN); Ta (BZT); Sb (BZS)]

Class 14: Spin and charge ice [contd.]

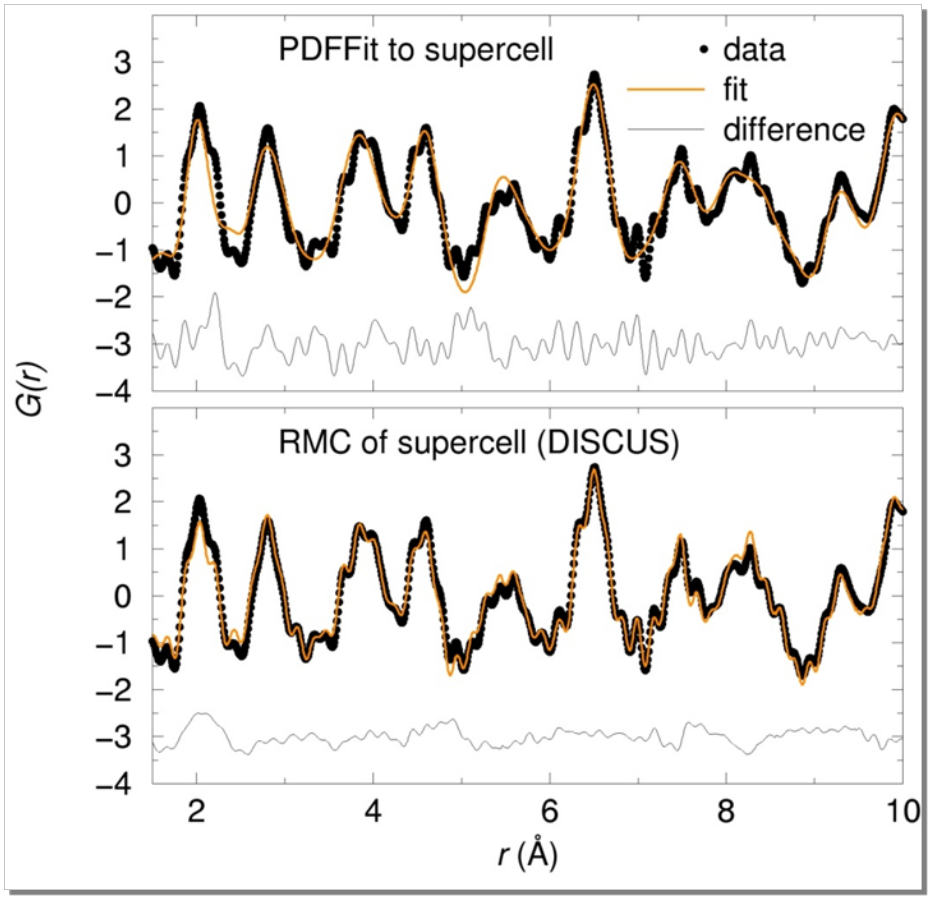




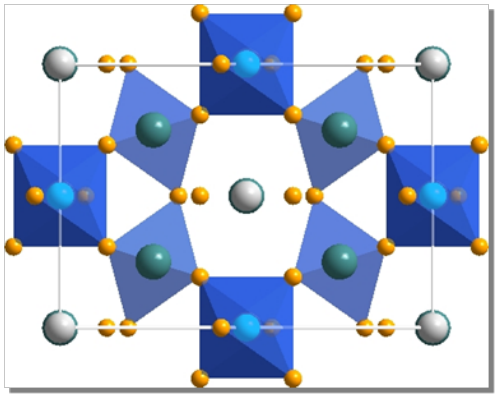
$O'Bi_4$ units show considerable disordering: *incoherent displacements*



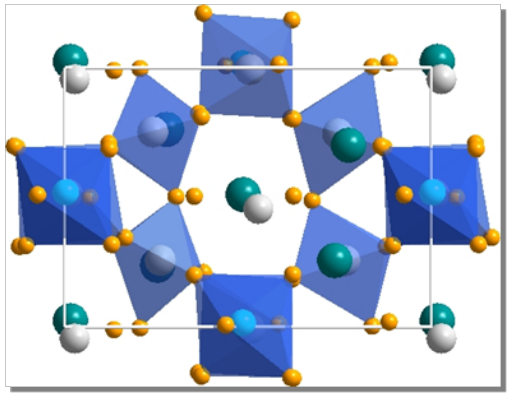
Class 14: Spin and charge ice [contd.]



Ideal ordered supercell

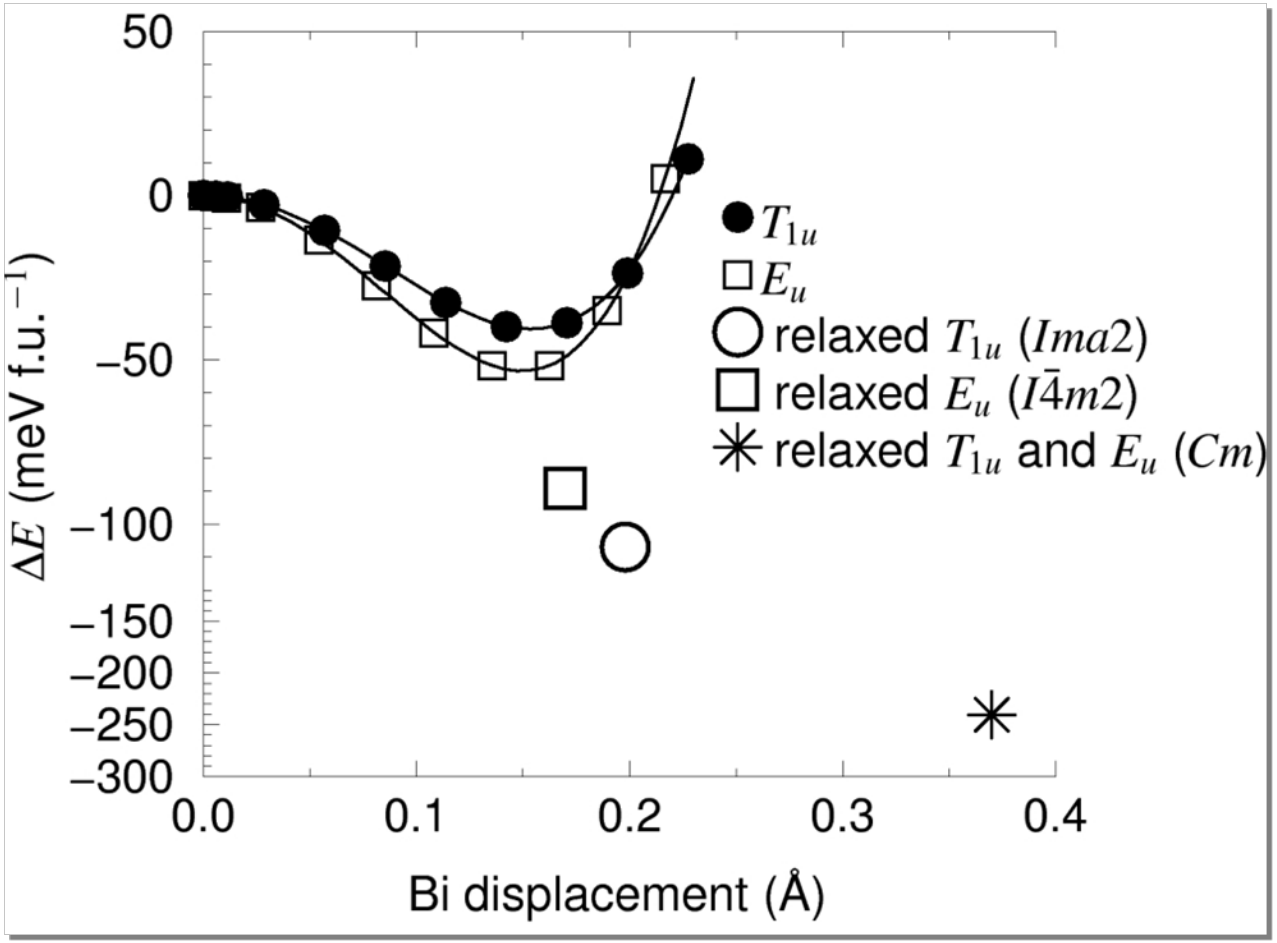


RMC structure



$Bi_{1.5}ZnNb_{1.5}O_7$: Incoherent displacements associated with the lone pair active Bi^{3+} can be followed using real-space neutron techniques (NPDF, Los Alamos).

$Bi_2Ti_2O_7$: Compute instabilities — calculations by Craig Fennie and Karin Rabe (Rutgers) suggest that it is potentially a ferroelectric with $P \sim 40\ \mu C/cm^2$.

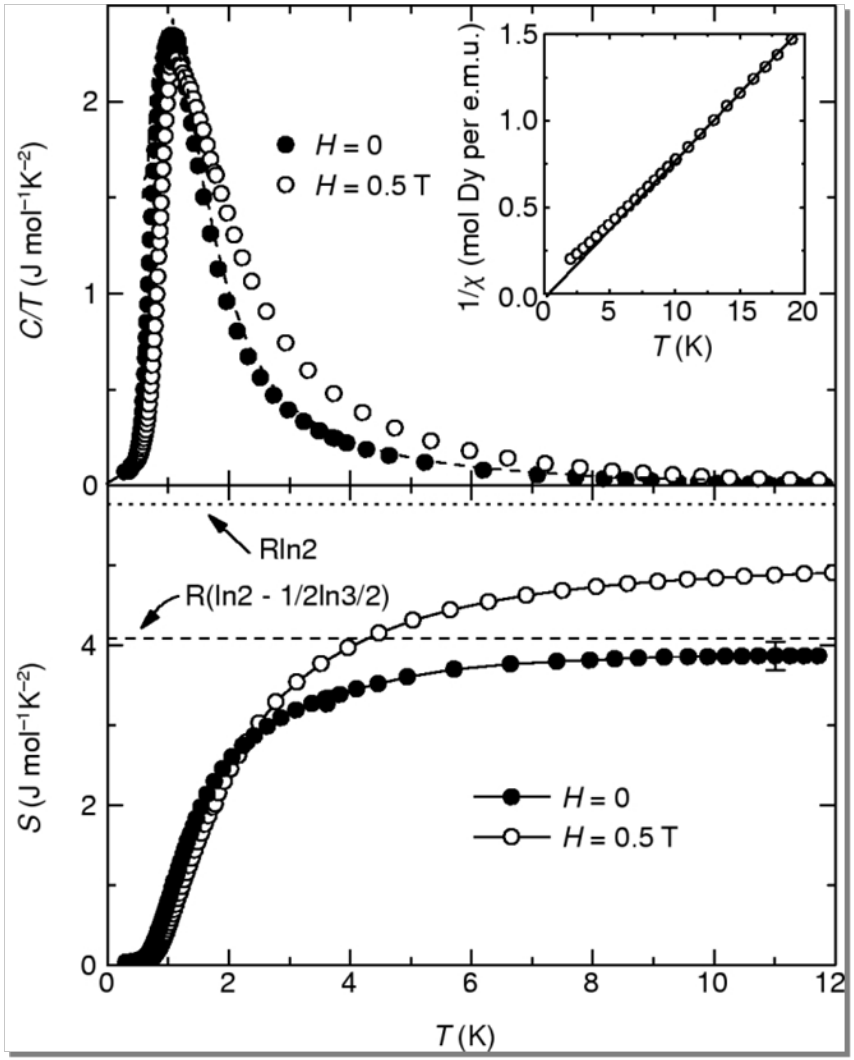


Class 14: Spin and charge ice [contd.]

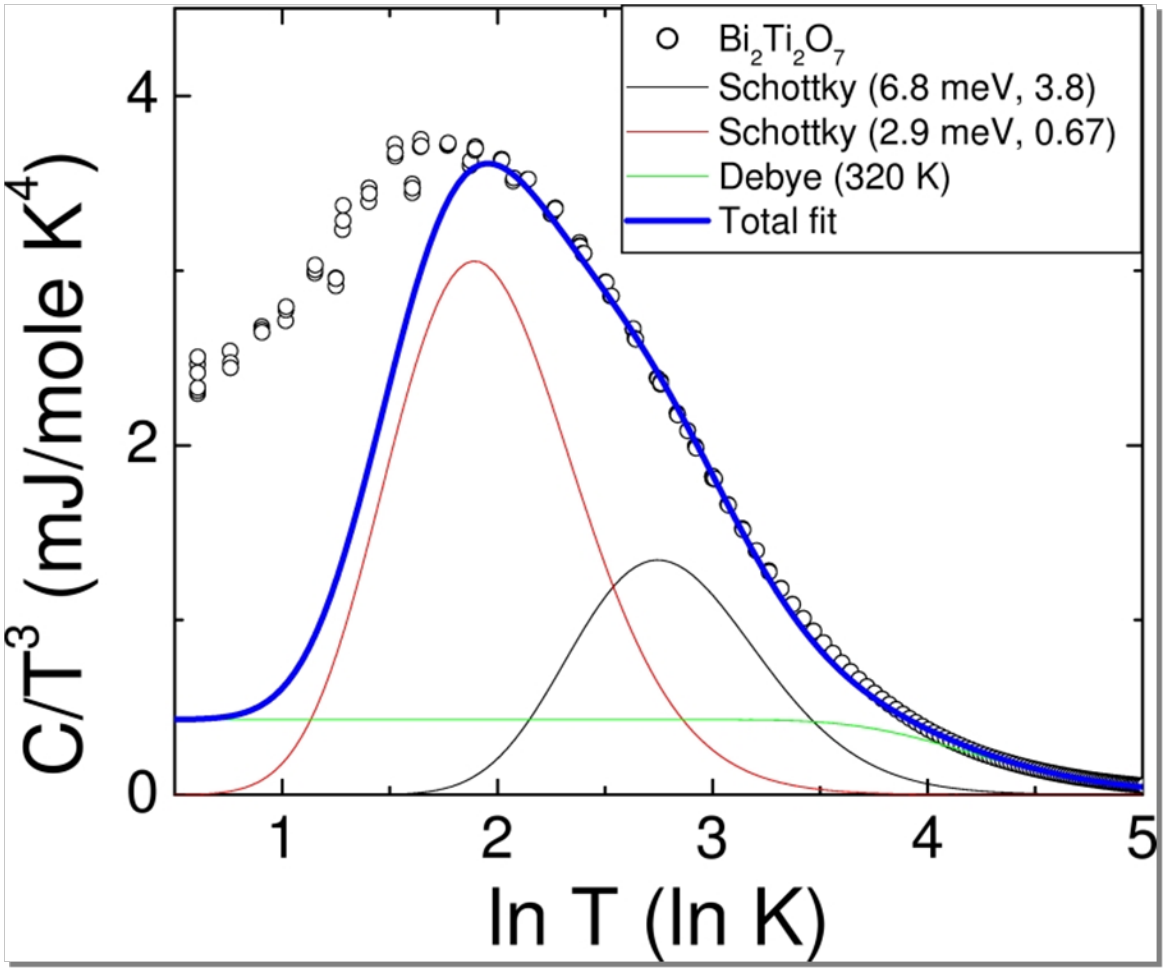
$Dy_2Ti_2O_7$

The residual entropy:

Ramirez, Hayashi, Cava, Siddharthan, Shastry, *Nature* **294** (2001) 1495.

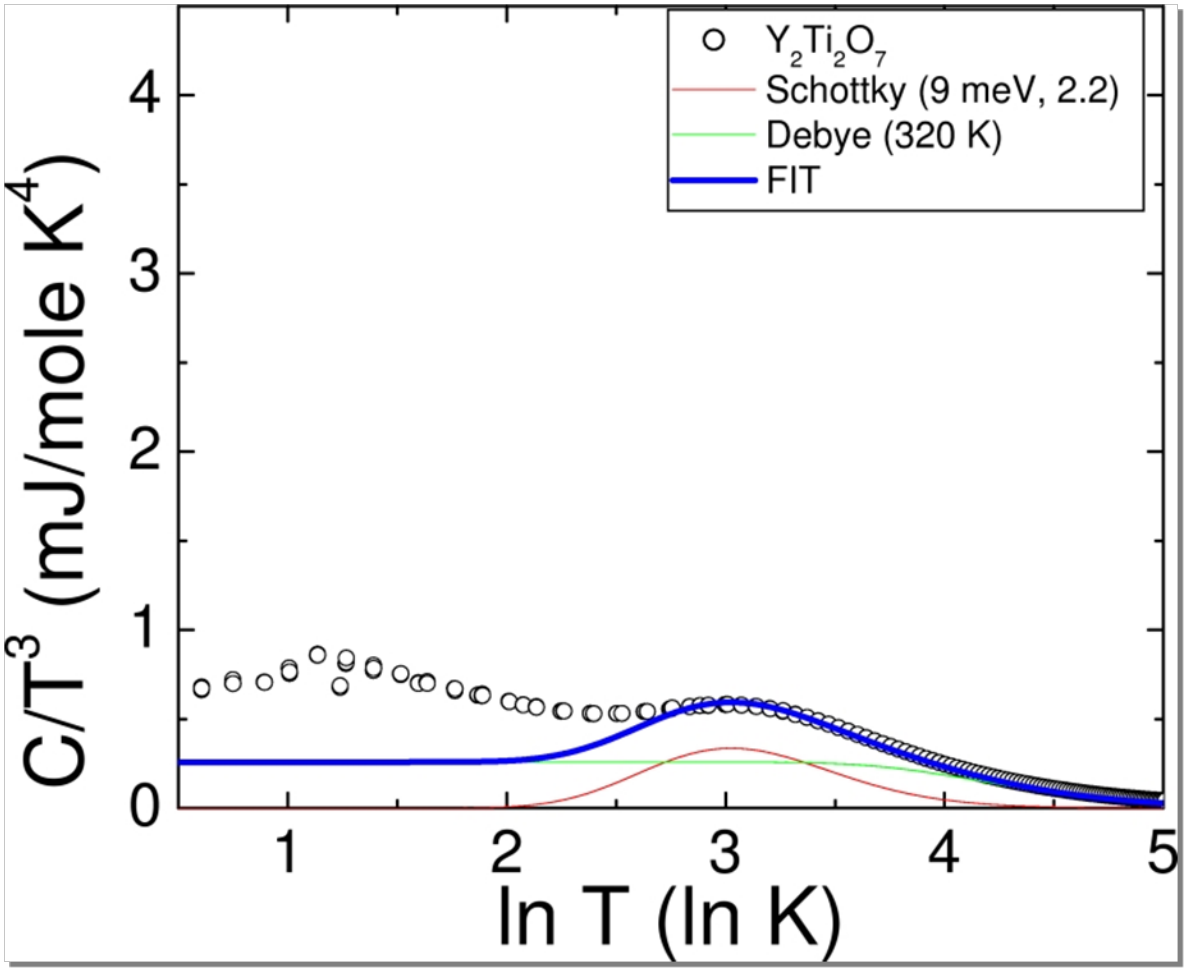


Class 14: Spin and charge ice [contd.]



$Bi_2Ti_2O_7$ does indeed have signatures in the heat capacity that suggest *local* low energy modes that do not freeze out.

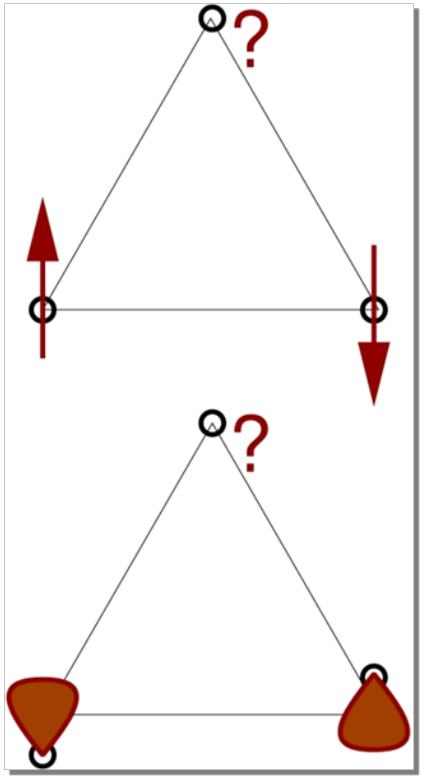
Class 14: Spin and charge ice [contd.]



$Y_2Ti_2O_7$ does not have these modes.

Conclusions:

Increasing evidence for the validity of idea that local coöperativity of off-centering can be frustrated by lattice geometry. Possibly a way of designing new high-*k* materials without phase transitions.



Na_6PbO_4