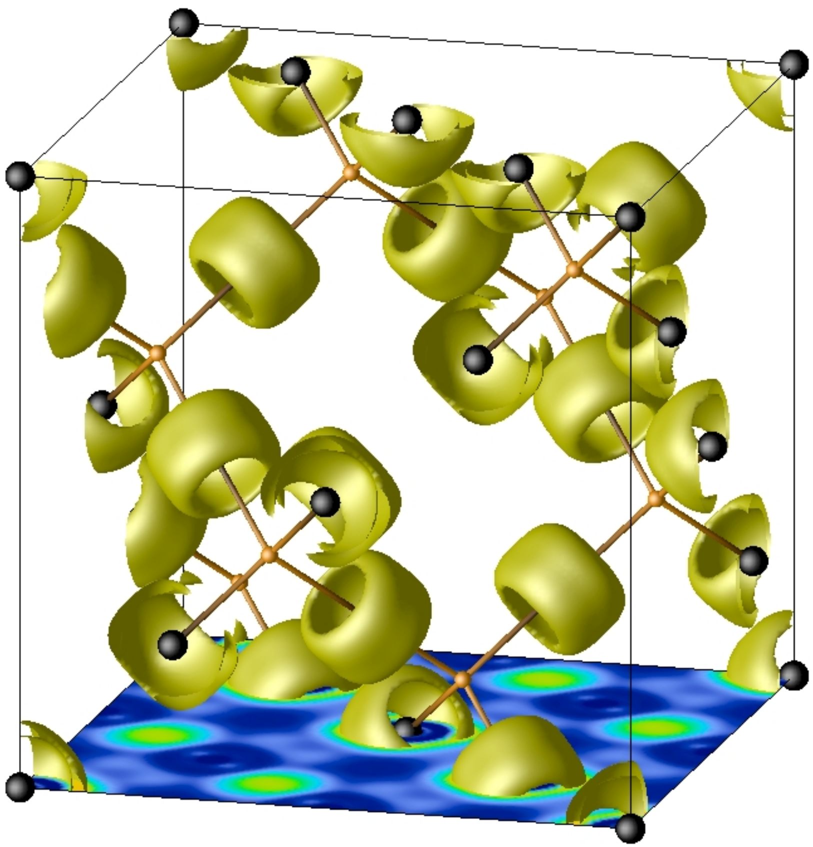
Lone pairs in the solid state: Frustration

$Bi_2Ti_2O_6O'$, the pyrochlore analogue of perovskite $PbTiO_3$, is cubic down to 2 K. [Hector, Wiggin, *J. Solid State Chem.* **177** (2004) 139]

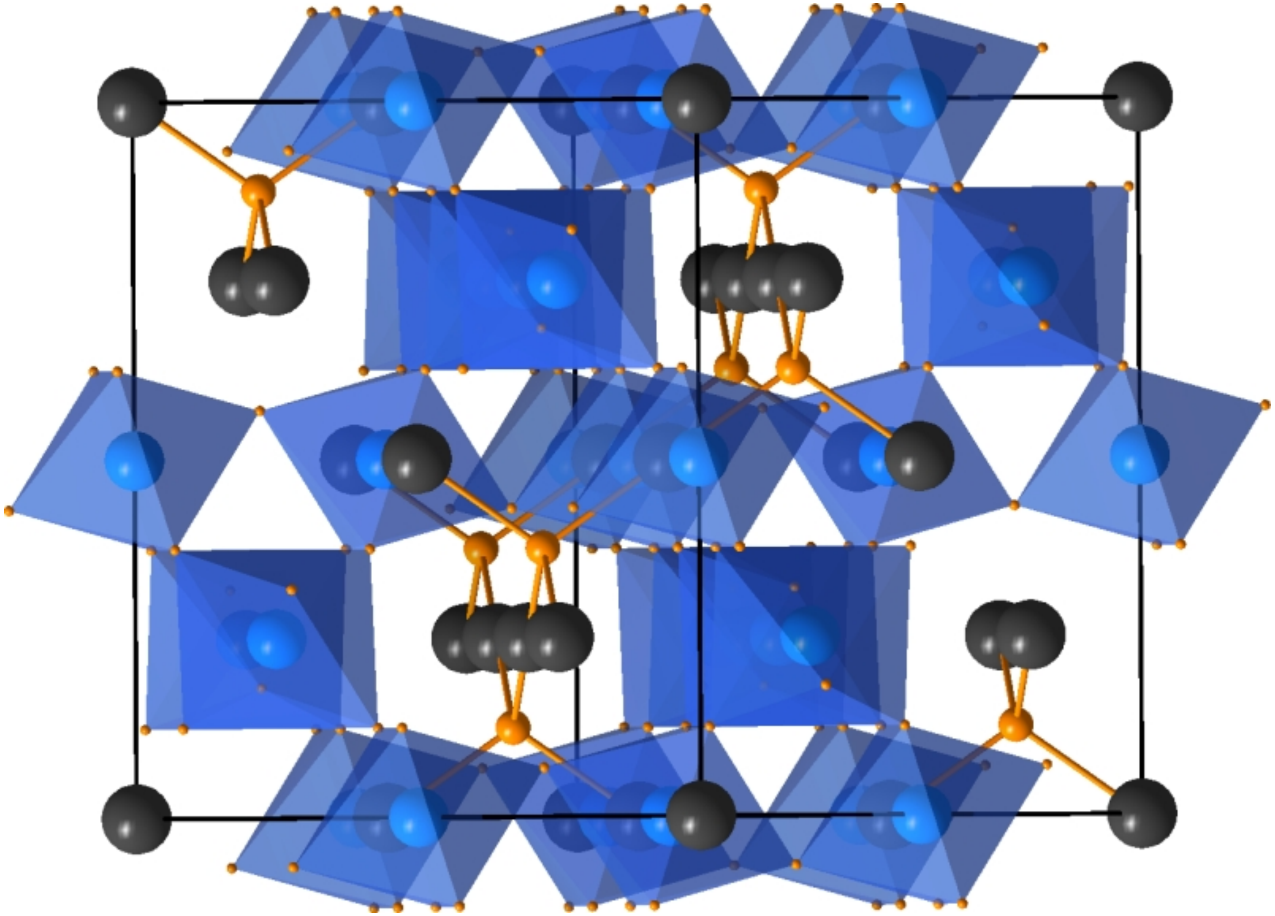
Question: Is the absence of a phase transition related to the frustrated topology of the pyrochlore lattice ? Is BTO a manifestation of *charge ice*?



The Bi_2O' network in $Bi_2Ti_2O_6O'$, and the associated lone pair ELFs:

Seshadri, *Solid State Sci.* **8** (2006) 259.

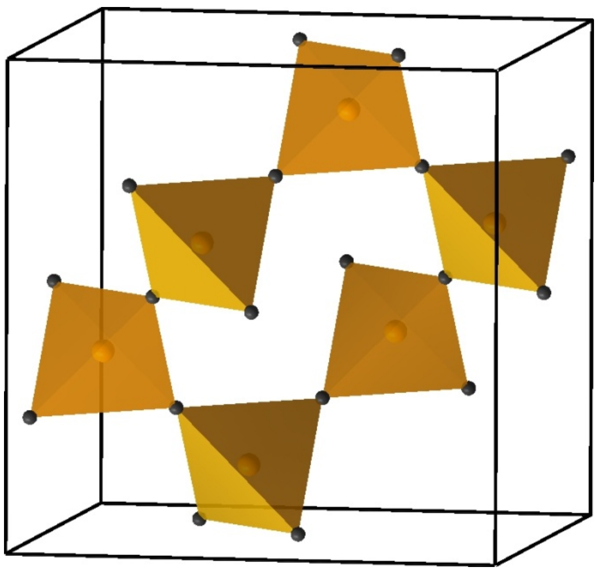
Lone pairs in the solid state: Frustration

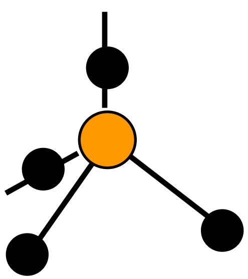


The cubic (*Fd-3m*) structure of pyrochlore (CaNa)Nb_2O_6F [$A_2B_2O_7$ or $A_2B_2O_6O'$] The A site often has lone-pair cations (Pb^{2+} or Bi^{3+}). Polar materials in this structure type are rare however.

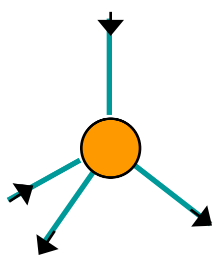
Lone pairs in the solid state: Frustration

The more familiar *spin ice*





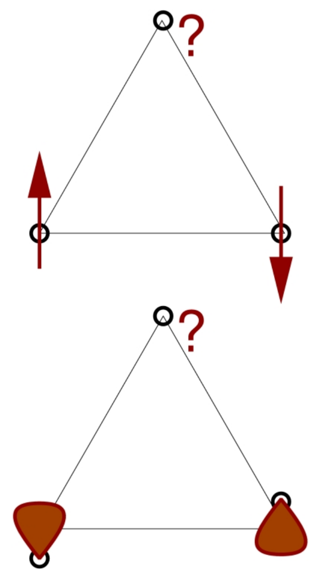
ice



spin ice

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.*



Well-known frustration of spins on corners of triangles.

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

Lone pairs in the solid state: All about ice

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

THE JOURNAL OF CHEMICAL PHYSICS

VOLUME 1 AUGUST, 1933 NUMBER 8

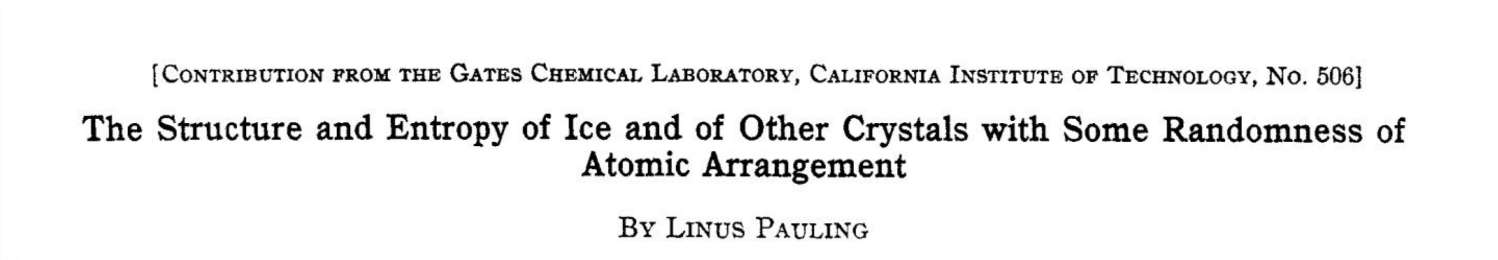
A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions

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 ?*

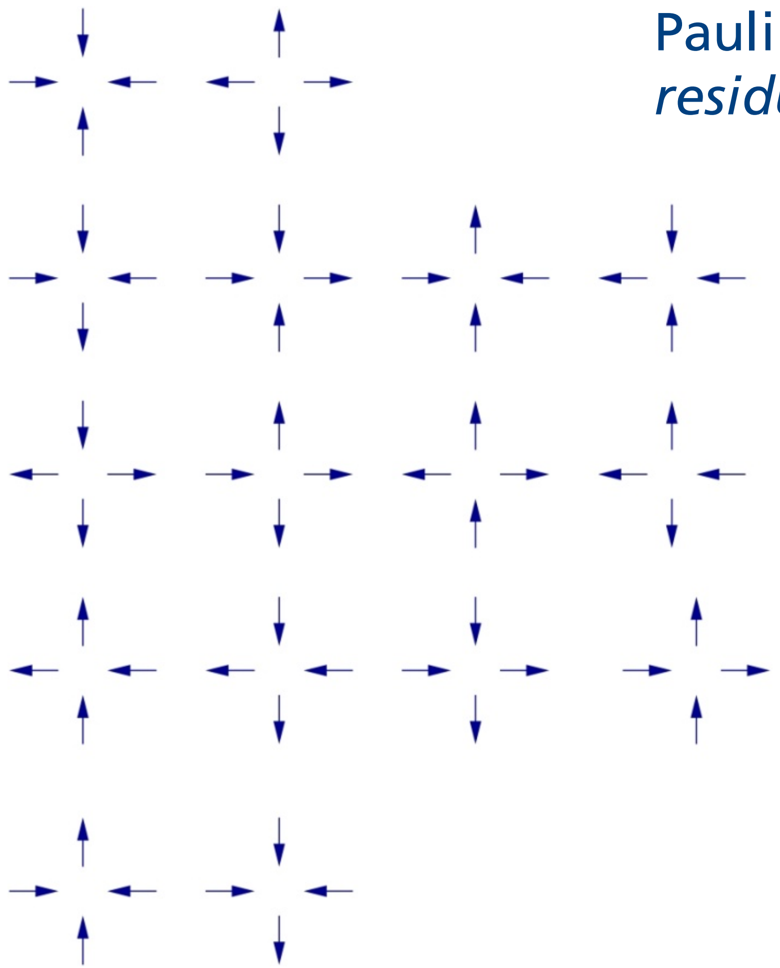
Lone pairs in the solid state: All about ice


[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 ways of arranging H around O.



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

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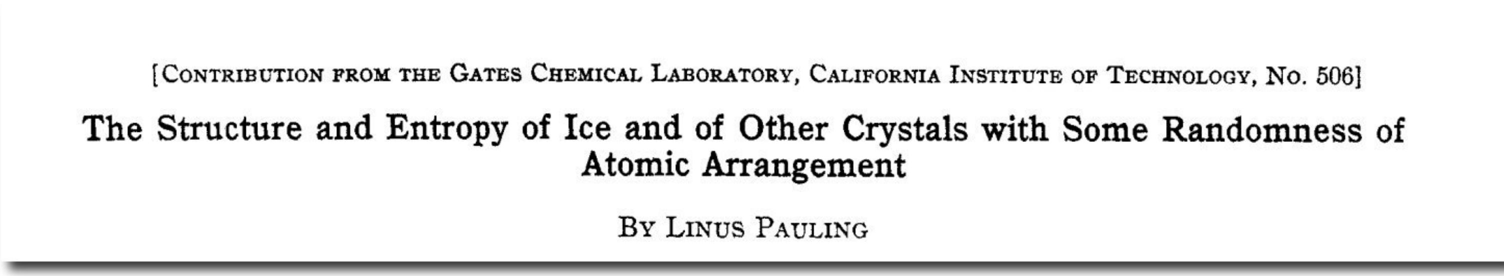
Lone pairs in the solid state: All about ice

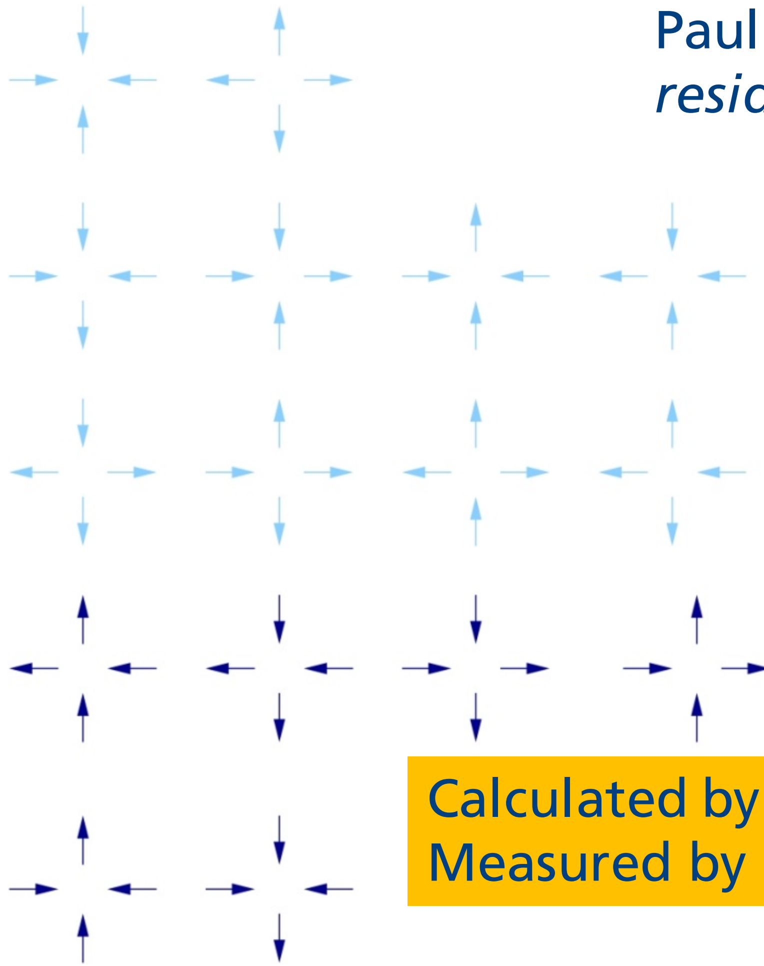

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 506]

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

BY LINUS PAULING

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

16 ways of arranging H around O. Only 6 obey the ice rules:

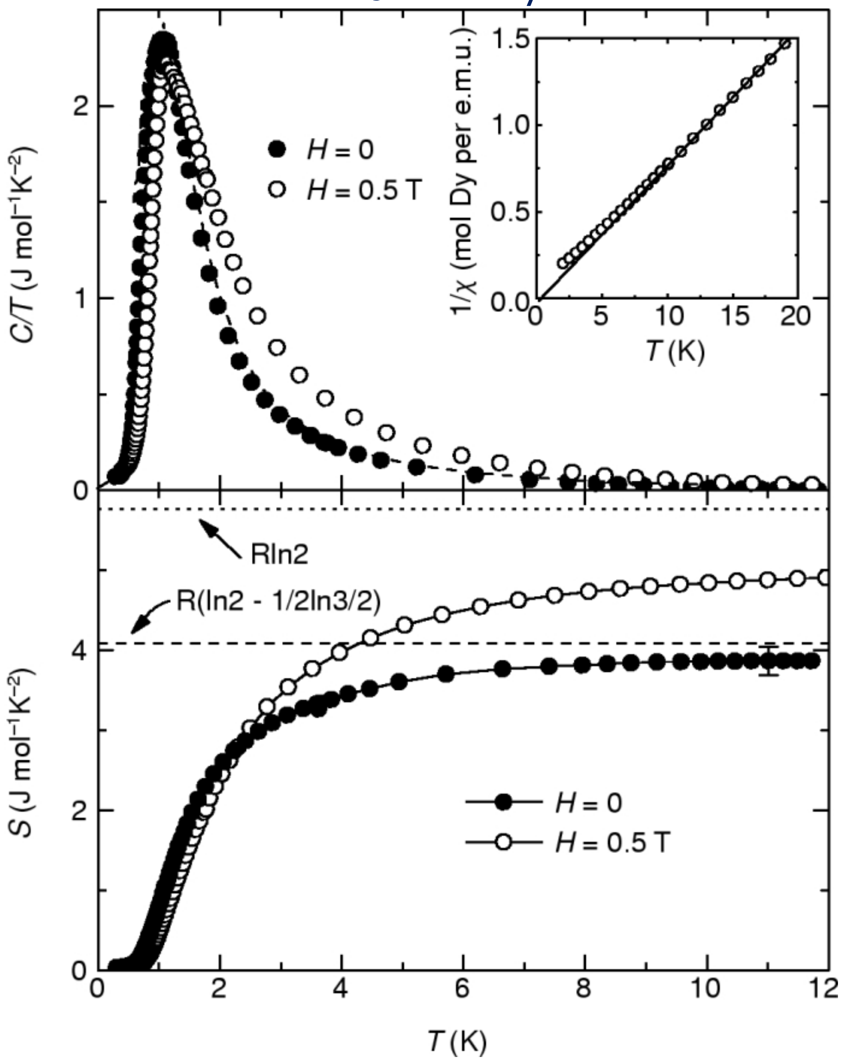


$S = k_B \ln W$ and $W = 6(1/2)(1/2) = 3/2$

Calculated by Pauling: 0.80 cal/K/mol
Measured by Giauque: 0.82 cal/K/mol

Lone pairs in the solid state: Heat capacity signatures

$Dy_2Ti_2O_7$



The incomplete ordering of spins at low temperatures in spin-ice results in characteristic heat capacity signatures.

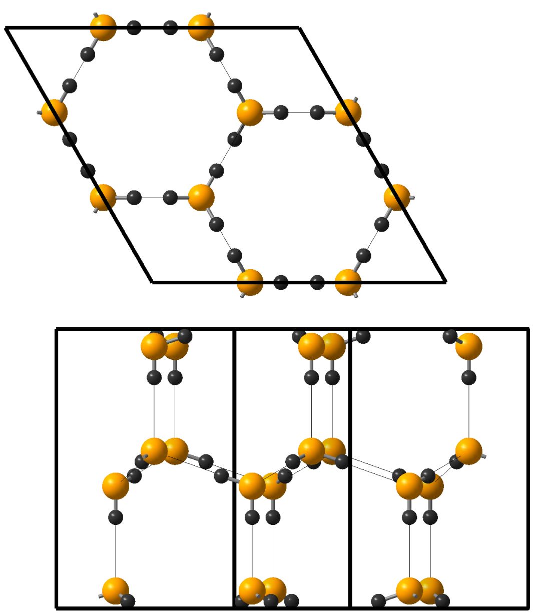
Ramirez, Hayashi, Cava, Siddharthan, Shastry, *Nature* **294** (2001) 1495.

Ice, spinels, pyrochlores and spin-ice

A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions, J. D. Bernal and R. H. Fowler, *J. Chem. Phys*. **1** (1933) 515-548.

Ice-I_h: a = 7.82 Å ; c = 7.36 Å $P6_3cm$ Proton ordering not proved

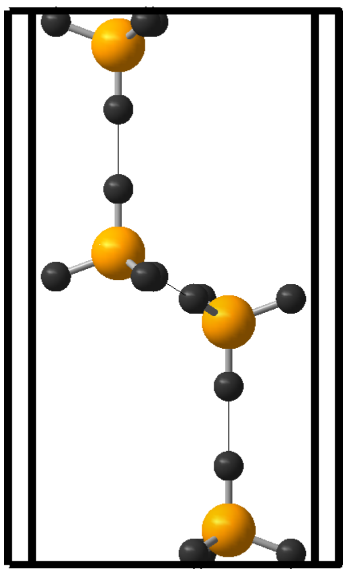
Atom	#	OX	SITE	x	y	z	SOF
O	1	-2	6 c	0.3333	0	0.0625	1.
O	2	-2	6 c	0.6667	0	0.9375	1.
H	1	+1	6 c	0.3333	0	0.174	1.
H	2	+1	6 c	0.438	0	0.026	1.
H	3	+1	12 d	0.772	0.105	0.975	1.



Views of the ordered Bernal-Fowler structure. Hydrogens positioned through guesswork.

Ice, spinels, pyrochlores and spin-ice

Actual disordered structure of Ice-I_h: $P6_3/mmc$ hexagonal diamond lattice.



Ice-I_h: a = 4.511(3) Å ; c = 7.346(3) Å $P6_3/mmc$

O	1/3	2/3	0.06226(8)	
H1	1/3	2/3	0.178(3)	[Occ. = 0.5]
H2	0.439(3)	0.878(3)	0.020(3)	[Occ. = 0.5]

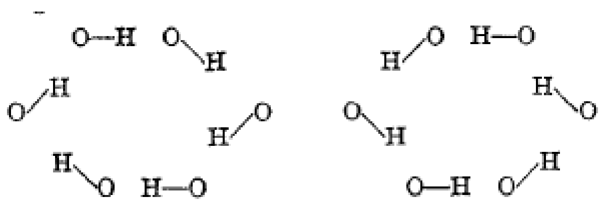
Goto *et al.* J. Chem. Phys. **93** (1990) 1412.

The Bernal-Fowler ice rules:

1) Each water molecule is oriented such that its two hydrogen atoms are directed approximately toward two of the four surrounding oxygen atoms (arranged almost in a tetrahedron).
2) Only one hydrogen atom is present on each O-O linkage.
3) Each oxygen atom has two nearest neighboring hydrogen atoms such that the water molecule structure is preserved.

Ice, spinels, pyrochlores and spin-ice

Linus Pauling and residual entropy:
The Structure and Entropy of Ice and of Other Crystals with Some Randomness of Atomic Arrangement, L. Pauling, *J. Am. Chem. Soc.* **57** (1935) 2680-2684. Also see hardcopy handout.



degenerate configurations of hydrogen in ice

There are N molecules in a mole of ice. A given molecule can orient itself in six ways satisfying condition 2. However, the chance that the adjacent molecules will permit a given orientation is $^1/_4$; inasmuch as each adjacent molecule has two hydrogen-occupied and two unoccupied tetrahedral directions, making the chance that a given direction is available for each hydrogen of the original molecule $^1/_2$, and the chance that both can be located in accordance with the given orientation $^1/_4$. The total number of configurations for N molecules is thus $W = (^6/_4)^N = (^3/_2)^N$.

The residual entropy of ice, extrapolated to 0 K is $S = R\ln(3/2)$

Proved by Giaque.

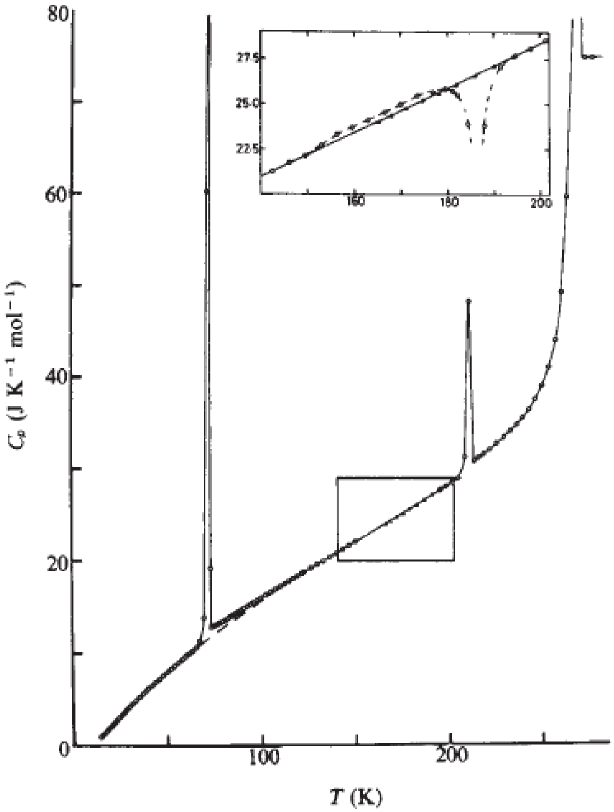
Also see: Residual entropy of square ice, E. H. Lieb, Phys. Rev. **162** (1967) 162.
http://link.aps.org/abstract/PR/v162/p162

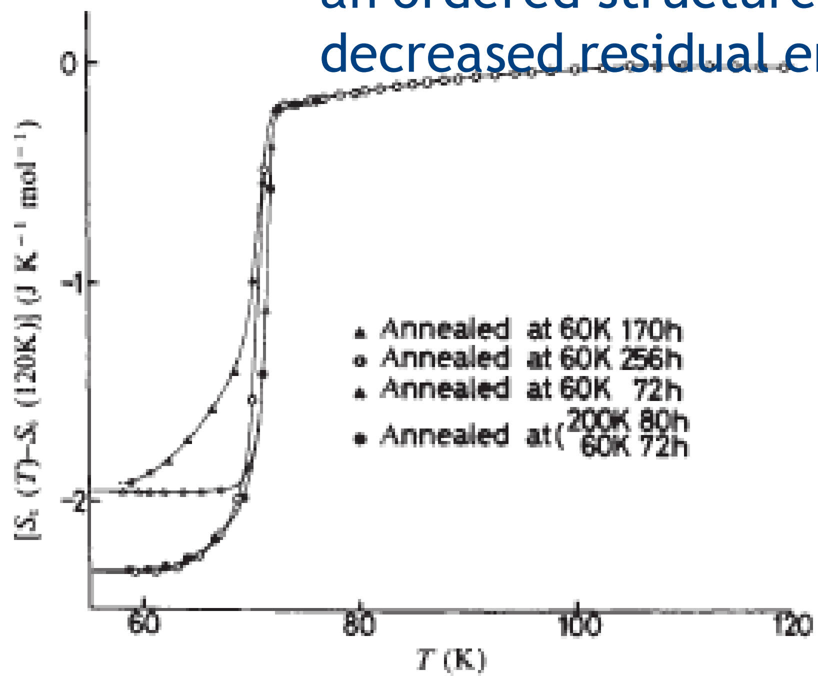
Ice, spinels, pyrochlores and spin-ice

How to order the hydrogens in ice: add OH^-

Phase transition in KOH-doped hexagonal ice, Y. Tajima et al. Nature 299 (1982) 810.

Phase transition near 80 K to an ordered structure with decreased residual entropy.

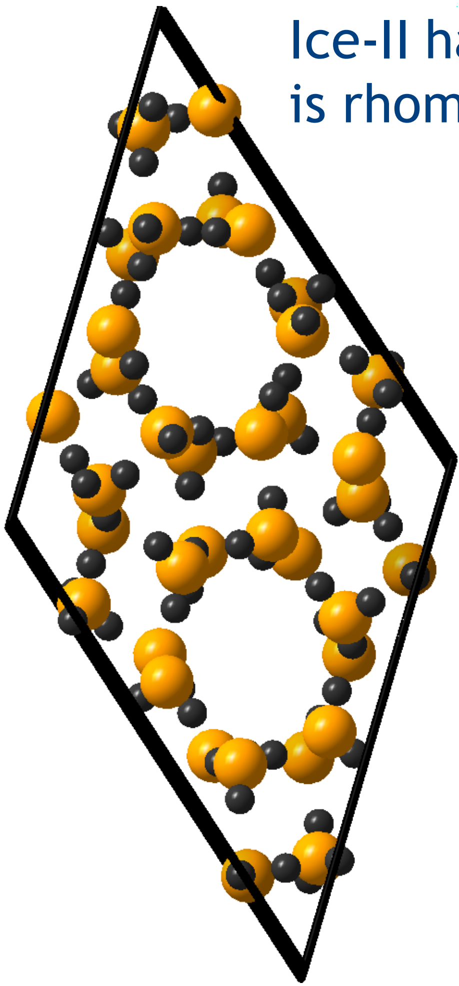




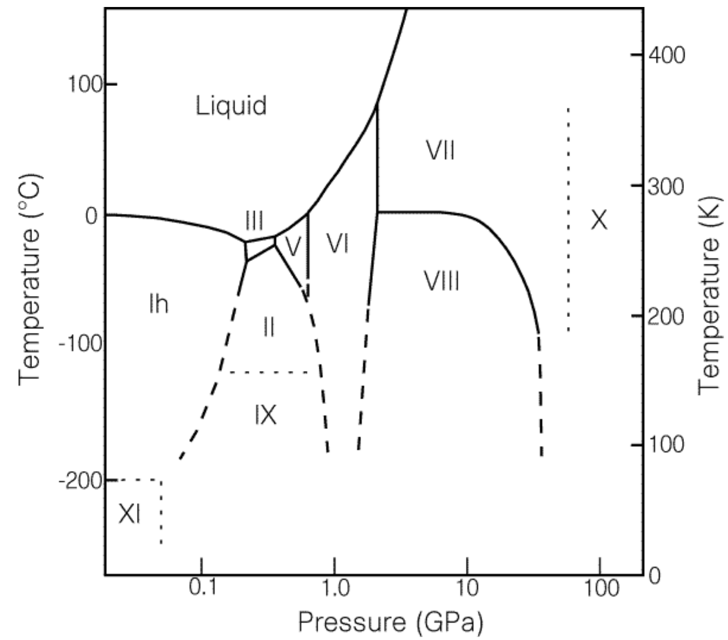
H2O doped with 0.1 mol dm^{-3} of KOH

Ice, spinels, pyrochlores and spin-ice

Ordering hydrogens though pressure: The many phases of ice.

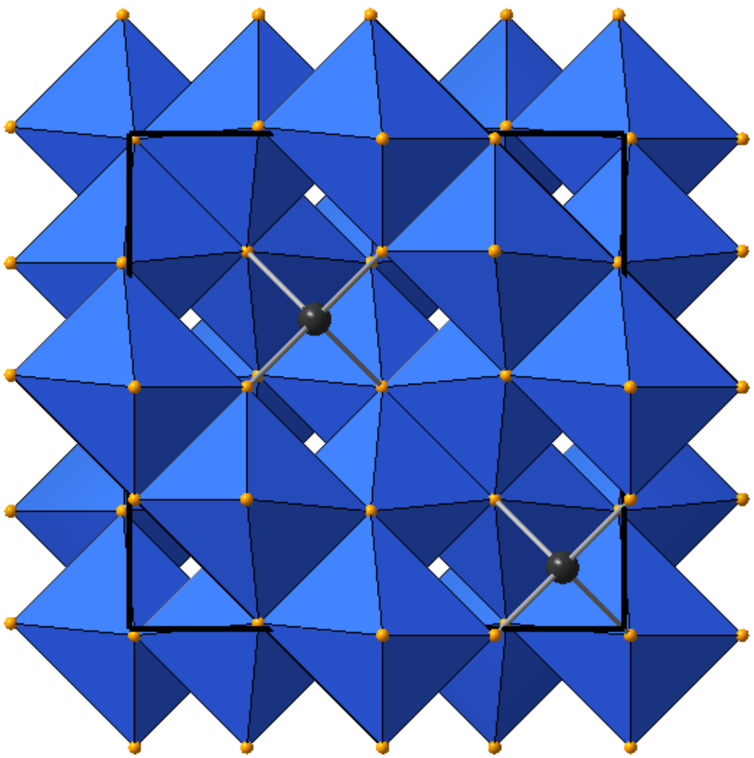


Ice-II has all H(D) atoms located at 80 K. The structure is rhombohedral.



The structure of a new phase of ice, C. Lobban, J. L. Finney, and W. F. Kuhs, Nature 391 (1998) 268

The spinel structure: $MgAl_2O_4$ *Fd-3m* (diamond) a ~ 8.5 Å



A	1/8	1/8	1/8
B	1/2	1/2	½
O	0.264	0.264	0.264*

* in $MgAl_2O_4$

A are tetrahedral with O and B are octahedral

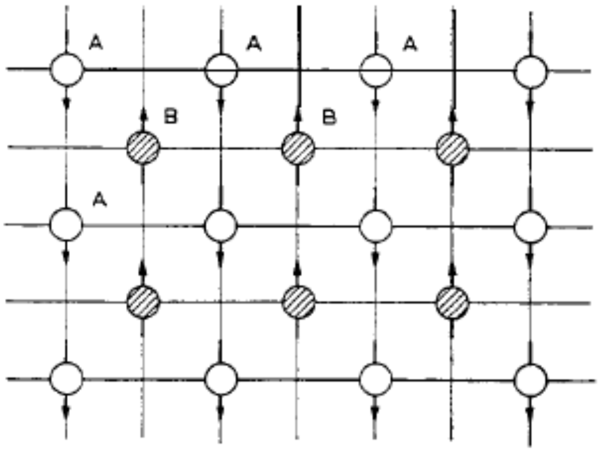
"Starting with an array of oxygens in ccp, we insert Al in certan octahedral interstices and Mg in certain tetrahedral interstices, the selection ofn interstices being made in such a way that the repeat distance along each axis is double what it would be for the ideal close packing..."

Megaw

Magnetism in spinels: Ferrimagnetism

In the spinel structure, unlike perovskite and pyrochlore, both A and B ions can be magnetic (1st row transition metals). They could with each other antiferromagnetically, but there is a net moment because they do not cancel one-another.

Magnetite or lodestone, from which the term *magnetism* derives, is actually a ferrimagnetic spinel.

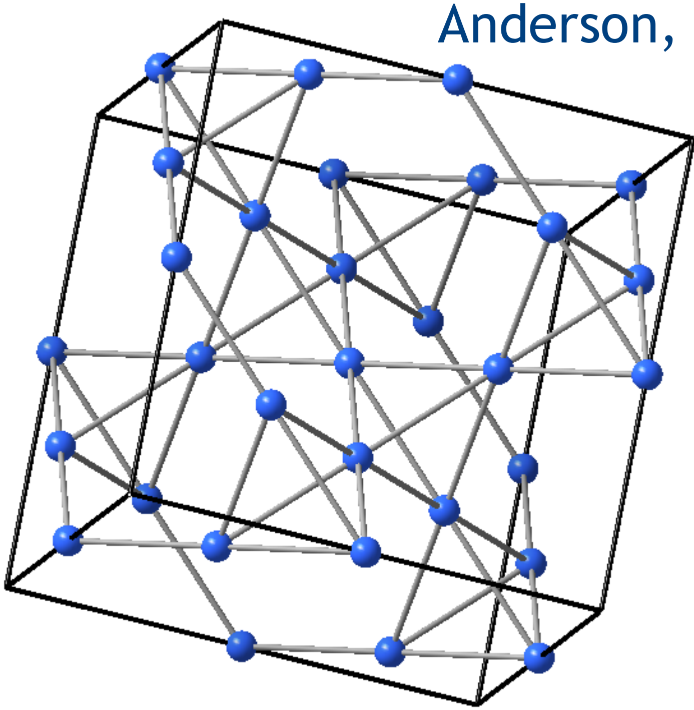


From Louis Néel's 1970 Nobel lecture (nobel.s

Ice, spinels, pyrochlores and spin-ice

Spinel magnetism and ice:

Ordering and Antiferromagnetism in Ferrites, P. W. Anderson, *Phys. Rev.* 102 (1956) 1008.



"The octahedral sites in the spinel structure form one of the anomalous lattices in which it is possible to achieve essentially perfect short-range order while maintaining a finite entropy. In such a lattice nearest-neighbor forces alone can never lead to long-range order, while calculations indicate that even the long range Coulomb forces are only 5% effective in creating long-range order. This is shown to have many possible consequences both for antiferromagnetism in "normal" ferrites and for ordering in "inverse" ferrites."

The spinel B sites form a network of corner-connected tetrahedra. Antiferromagnetism is *frustrated*.

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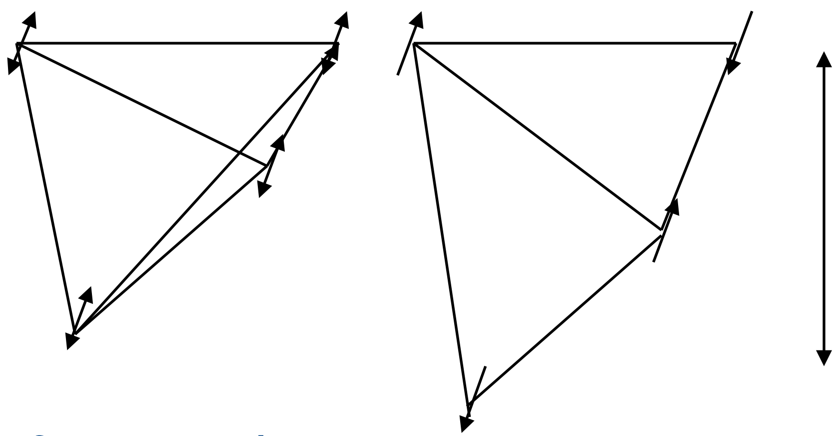
Ice, spinels, pyrochlores and spin-ice

Getting rid of frustration: Structural distortions in $ZnCr_2O_4$ and ZnV_2O_4:



frustrated

ordered

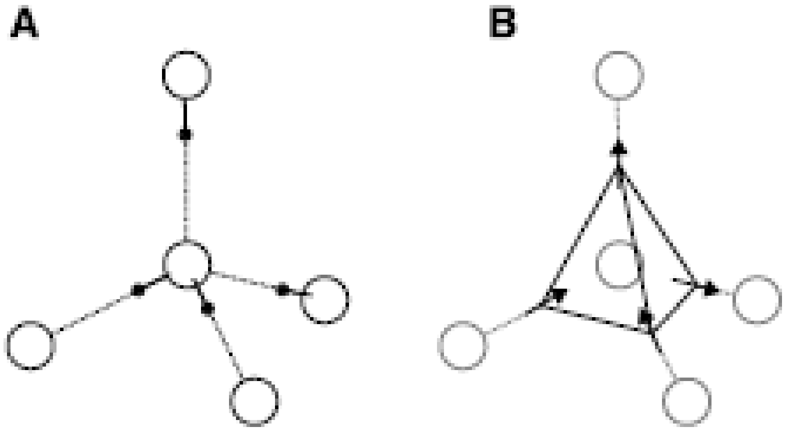
Elongate

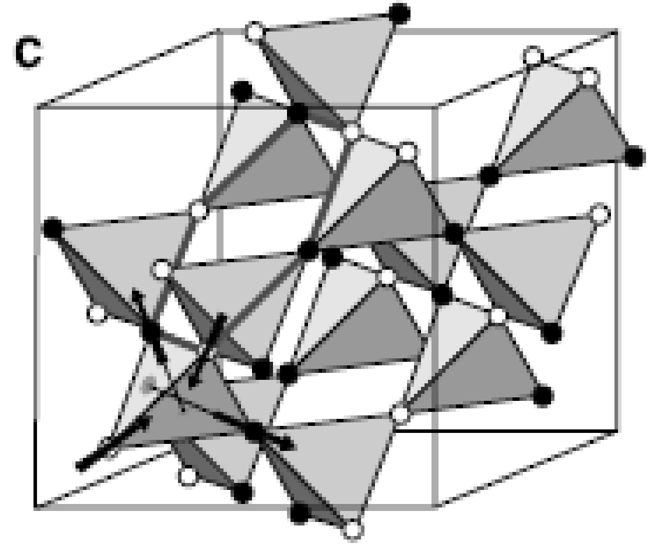
Fd-3m → *I-4₁/amd*

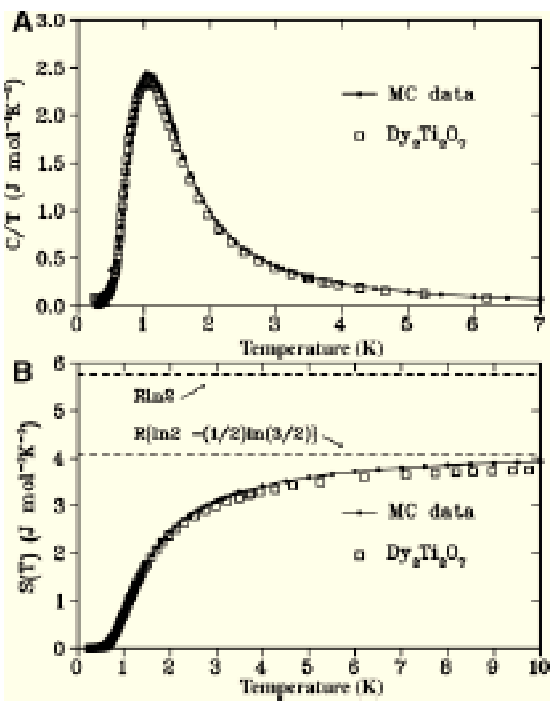
Crystallographic and magnetic structure of ZnV_2O_4: Structural phase transition due to spin-driven Jahn-Teller distortions, M. Reehuis, A. Krimmel, N. Büttgen, A. Loidl and A. Prokofiev, Eur. Phys. J. B 35, 311-316 (2003).

Ice, spinels, pyrochlores and spin-ice

Spin ice in pyrochlores: $Dy_2Ti_2O_7$







S. T. Bramwell and M. J. P. Gingras, *Science* **294** (2001) 1495.