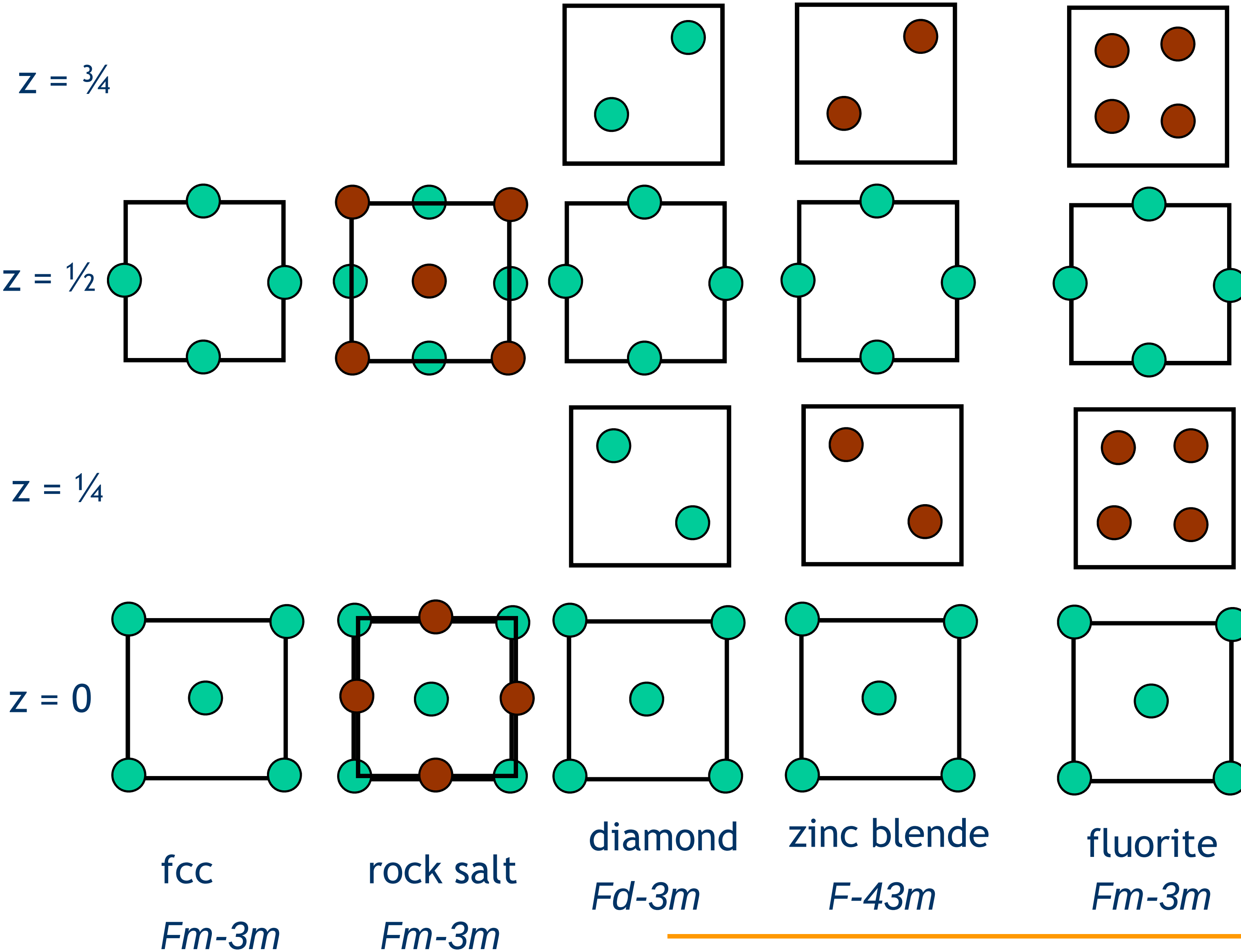
Class 13: Fluorite, Pyrochlore, Murataite, ice



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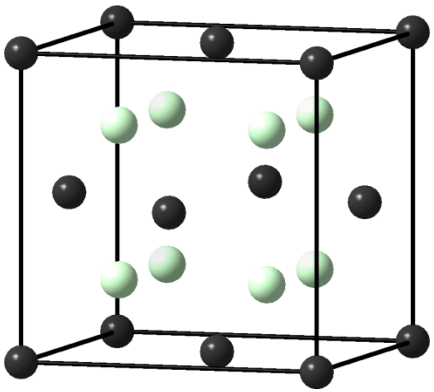
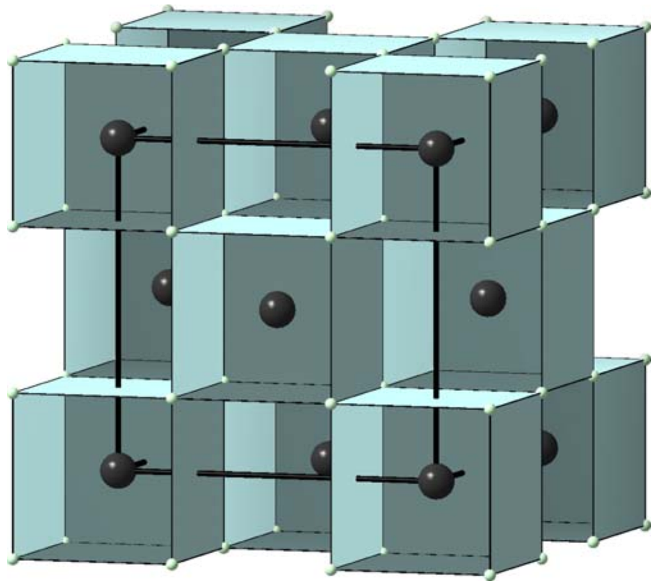
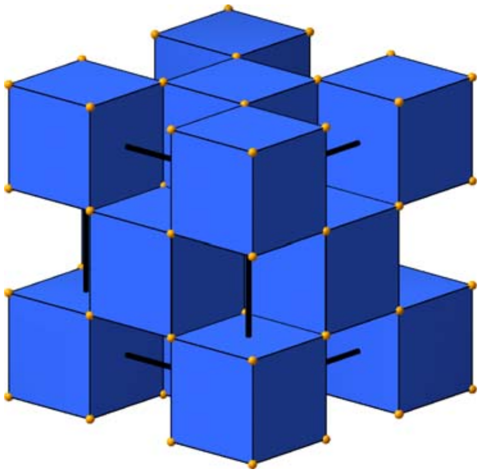




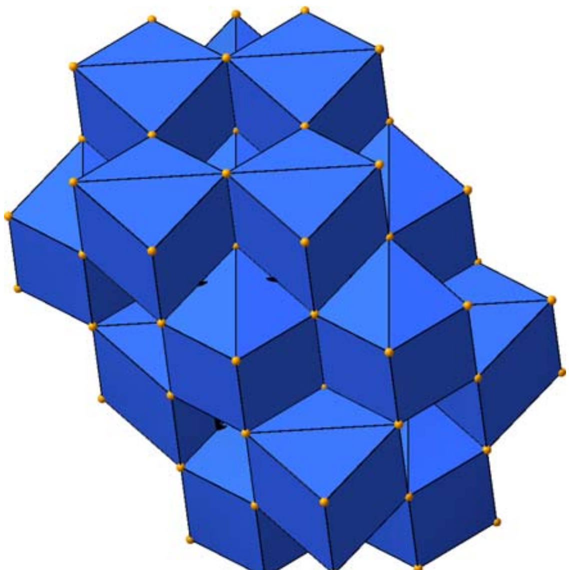
Views of the fluorite CaF_2 structure [Gerlach 1922]. Ca is 8-coordinate and F is 4-coordinate. Many oxides: UO_2, PrO_2, CeO_2, stabilized, cubic ZrO_2 and HfO_2...
Uses: CeO_2 is an oxide ion conductor. HfO_2 and ZrO_2 are important structural materials. UO_2 is "yellowcake"

Stabilized zirconia:

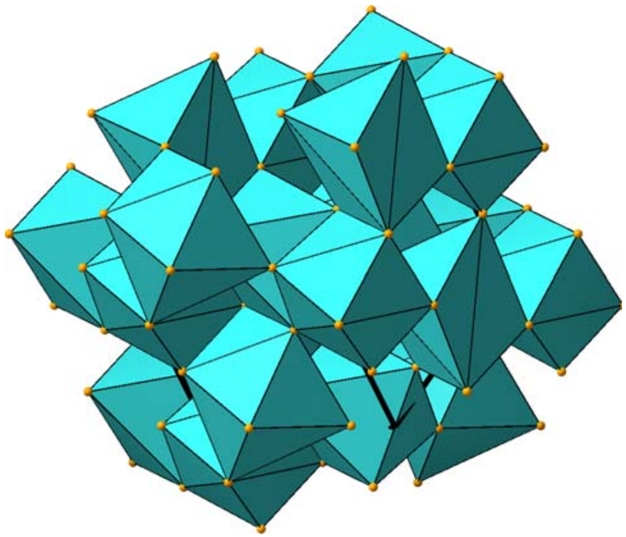
cubic



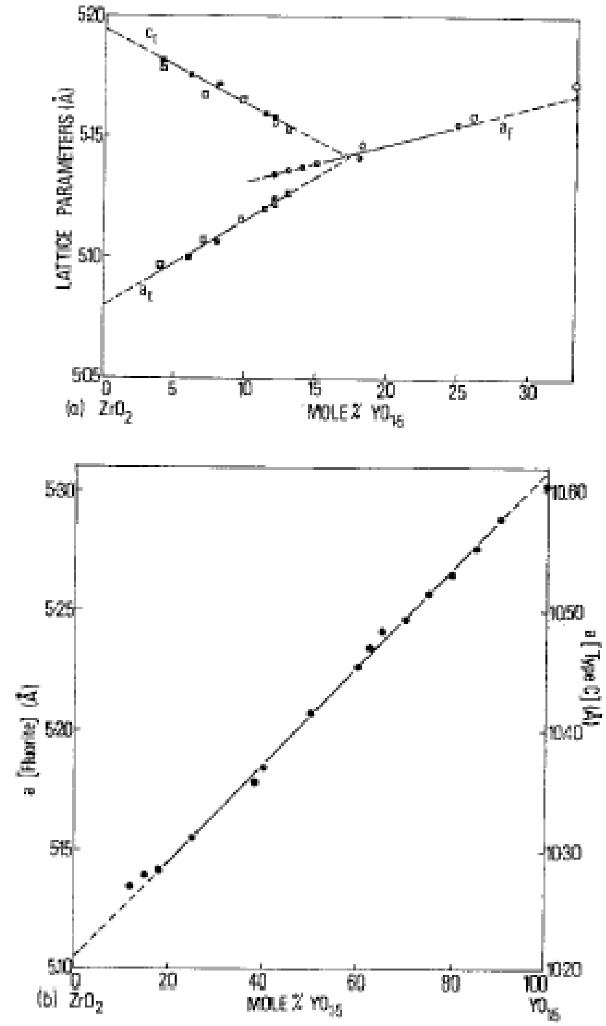
tet

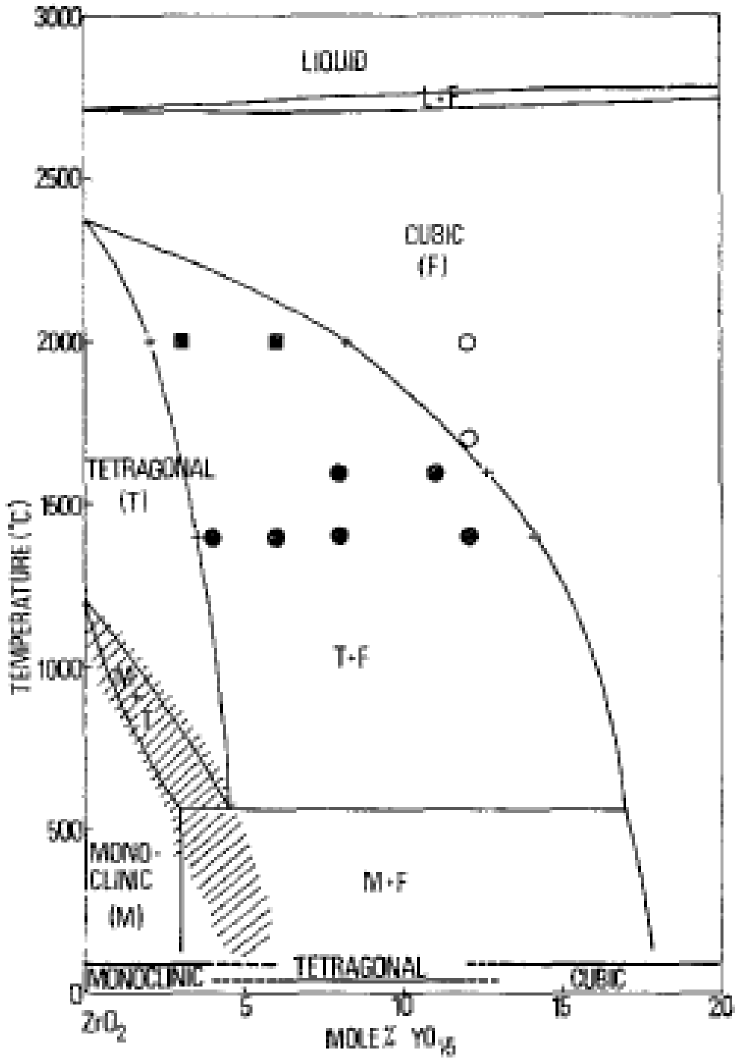


mono
baddeylite



stabilization with Y_2O_3



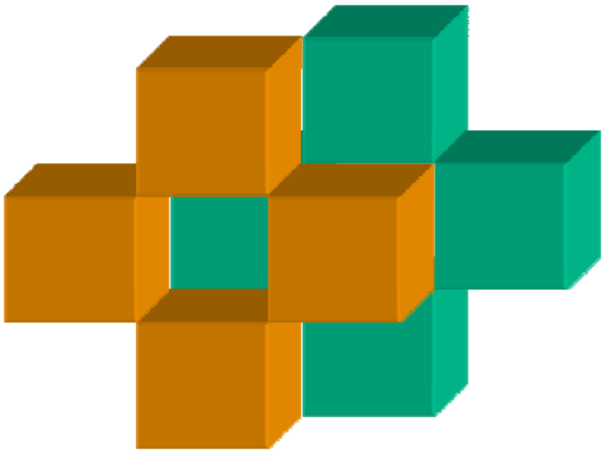


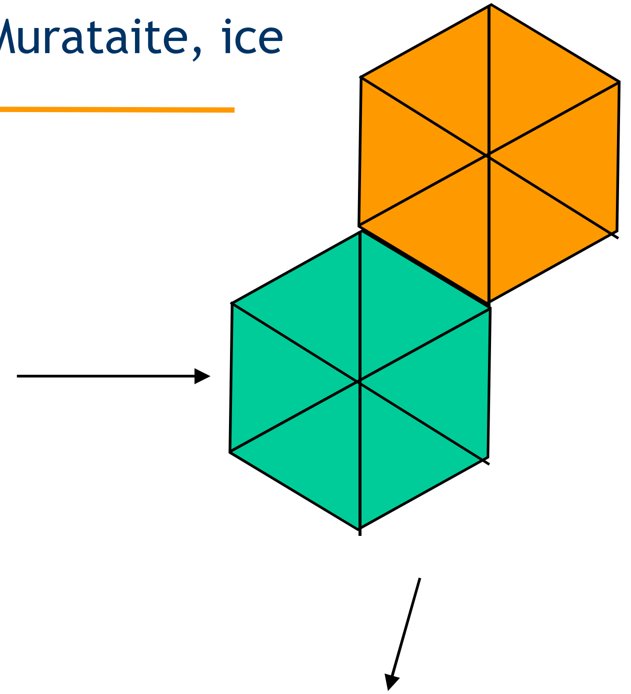
H. G. Scott,
Phase relationships in the zirconia-yttria system
JOURNAL OF MATERIALS SCIENCE 10 (1975) 1527-1535

Fluorite oxides are highly radiation tolerant because they are able to accomodate point defects easily: *Science* **289** (2000) 748.

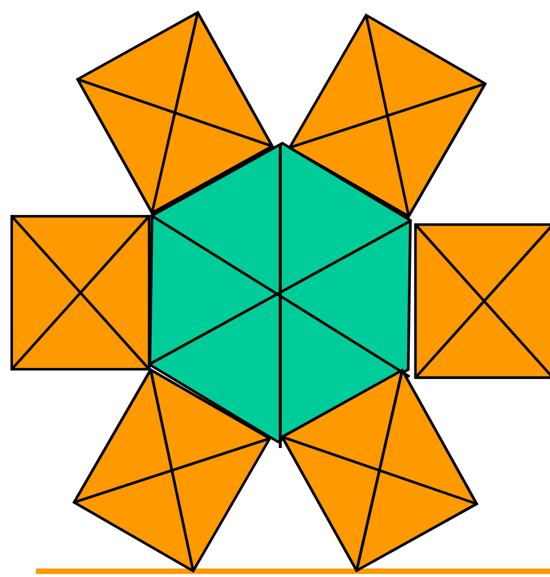
Class 13: Fluorite, Pyrochlore, Murataite, ice

Fluorite





8 coordination + 8 coordination

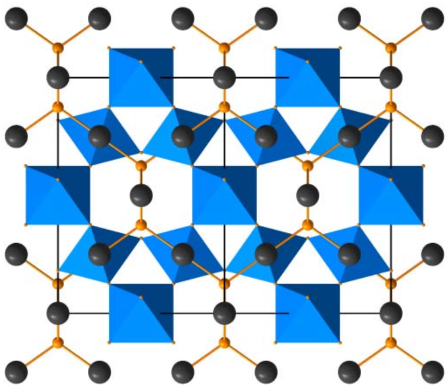


Pyrochlore

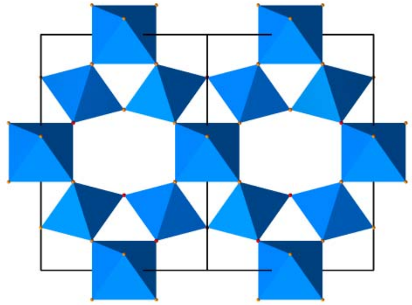
$A_2B_2O_8 \rightarrow A_2B_2O_7$

8 coordination + 6 coordination

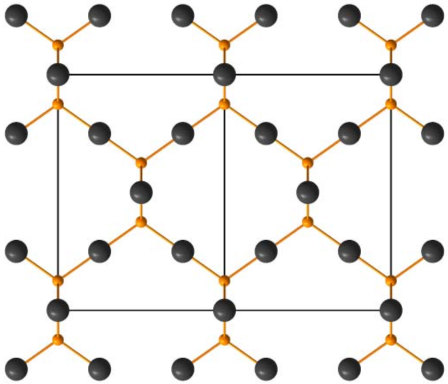
Pyrochlore views:



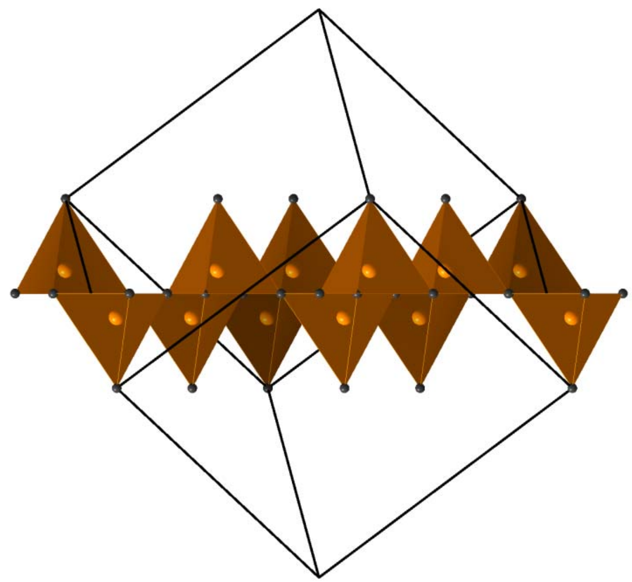
$A_2B_2O_6O'$



B_2O_6



A_2O'



Stellated *Kagomé* lattice of B_4 tetrahedra. The central atom is O′. This is a motif found in spinel as well.

A wide variety of pyrochlore structures are known: A can be Ca, Cd, Tl, Pb, Bi, Ln etc. B can be transition metals as well as main group elements. The A and B sites can be mixed. O′ can be absent, or can be F^-, OH^- etc.

Pyrochlores can be insulating, metallic, magnetic ...

The standard reference: Subramanian *et al.* Prog. Solid State Chem. **15** (1983) 55.

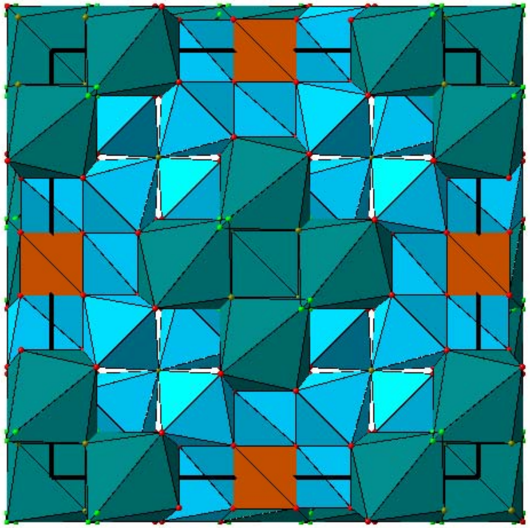
For unusual phase relationships in pyrochlores, see Vanderah *et al.* Eur. J. Inorg. Chem. (2005) 2895.

Murataites:

Urusov et al. Dokl. Earth Sci. 401 (2005) 315: Synthetic “murataites” as modular members of a pyrochlore-murataite polysomatic series.

The fluorite is a 3D chessboard of regular cubes. The pyrochlore has one half of the cubes replaced by octahedra, and one eights of the anions missing. The pyrochlore can be constructed by making the coloring the fluorite chessboard. This is a 2x2x2 ordering.

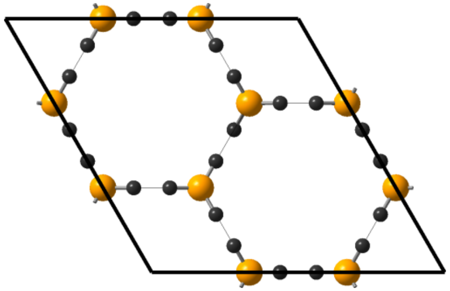
More complex 3x3x3 ordering gives the murataite.

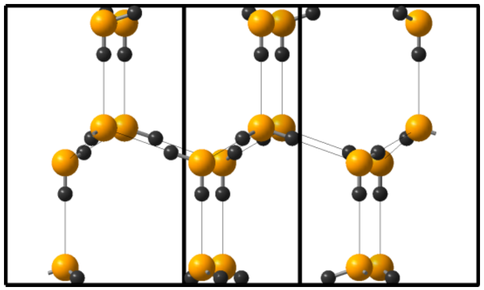


A Theory of Water and Ionic Solution, with Particular Reference to Hydrogen and Hydroxyl Ions, J. D. Bernal and R. H. Fowler, *J. Chem. Phys.* **1** (1933) 515-548.

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

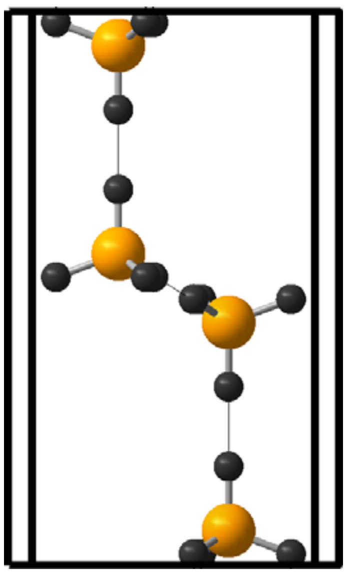
Atom	#	OX	SITE	x	y	z	SOF
O	1	-2	6 c	0.3333	0	0.0625	1.
O	2	-2	6 c	0.6667	0	0.9375	1.
H	1	+1	6 c	0.3333	0	0.174	1.
H	2	+1	6 c	0.438	0	0.026	1.
H	3	+1	12 d	0.772	0.105	0.975	1.





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

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 $P6_3/mmc$

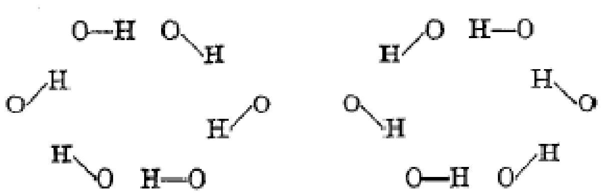
O	1/3	2/3	0.06226(8)	
H1	1/3	2/3	0.178(3)	[Occ. = 0.5]
H2	0.439(3)	0.878(3)	0.020(3)	[Occ. = 0.5]

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.

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.

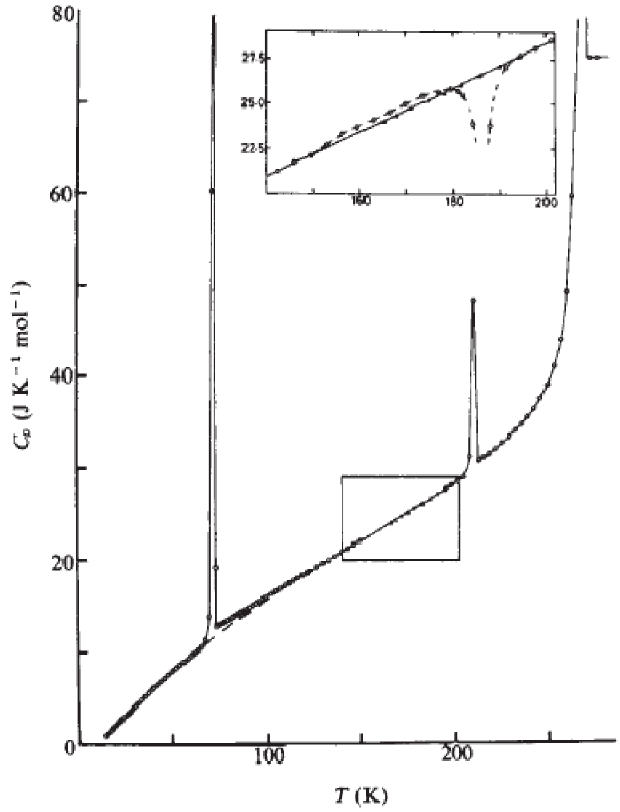
Also see: Residual entropy of square ice, E. H. Lieb, Phys. Rev. **162** (1967) 162.

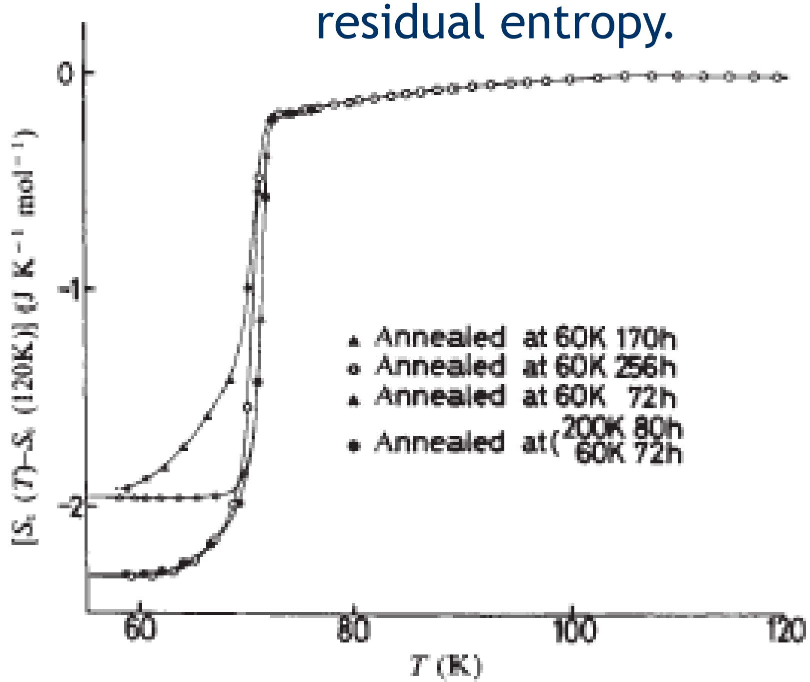
http://link.aps.org/abstract/PR/v162/p162

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

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

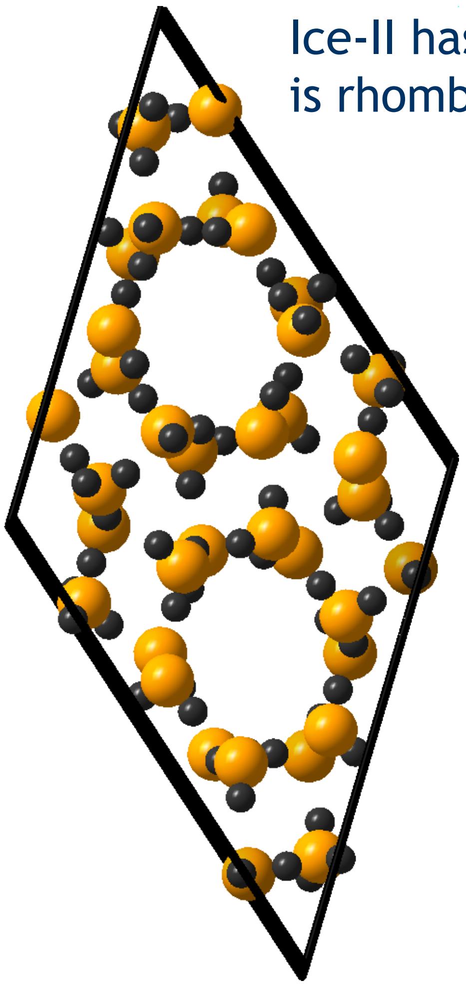
Phase transition near 80 K to an ordered structure with decreased residual entropy.



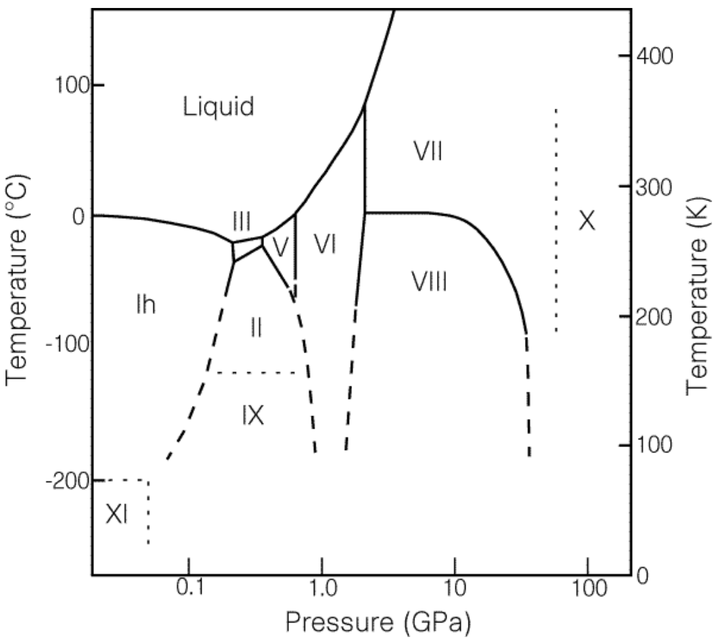


H2O doped with 0.1 mol dm^{-3} of KOH

Ordering hydrogens though pressure: The many phases of ice.

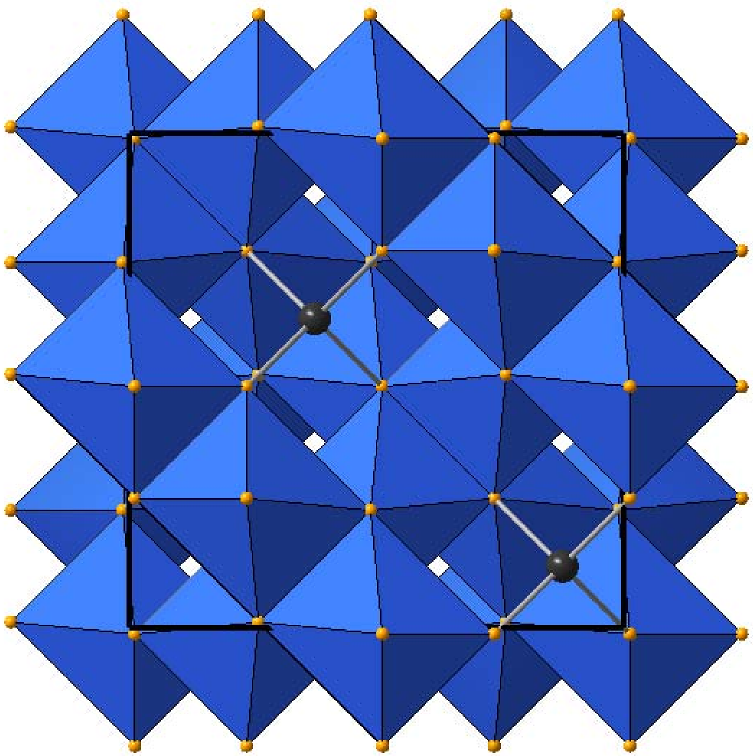


Ice-II has all H(D) atoms located at 80 K. The structure is rhombohedral.



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 $MgAl_2O_4$

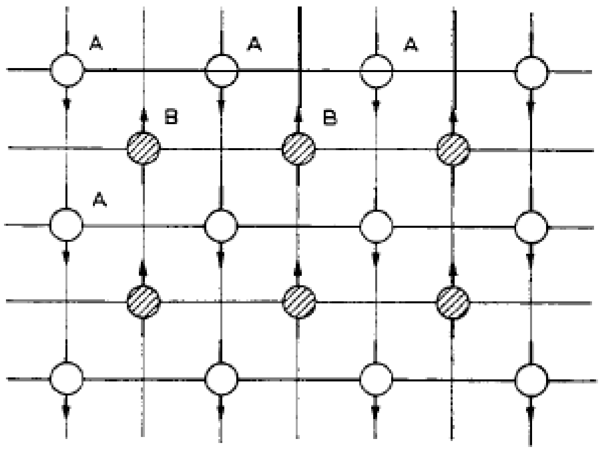
A are tetrahedral with O and B are octahedral

"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.

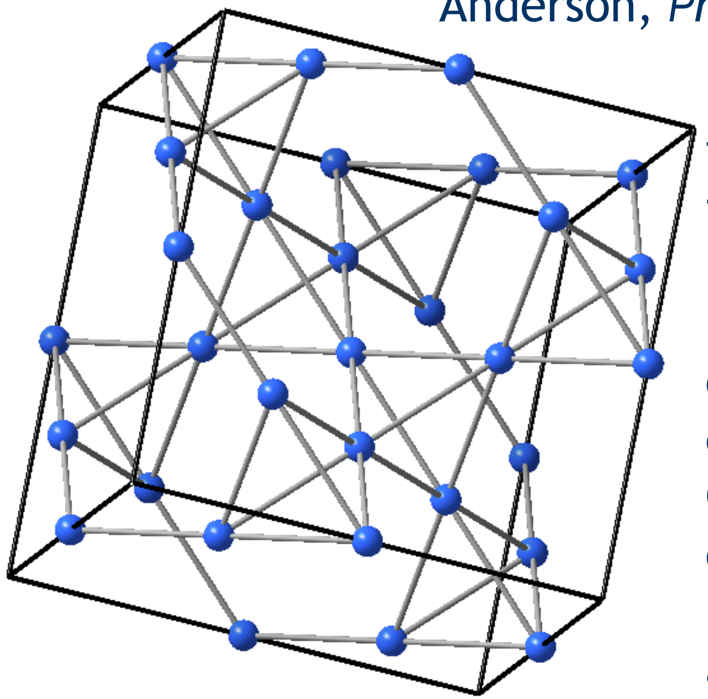
Magnetite or lodestone, from which the term *magnetism* derives, is actually a ferrimagnetic spinel.



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

Spinel magnetism and ice:

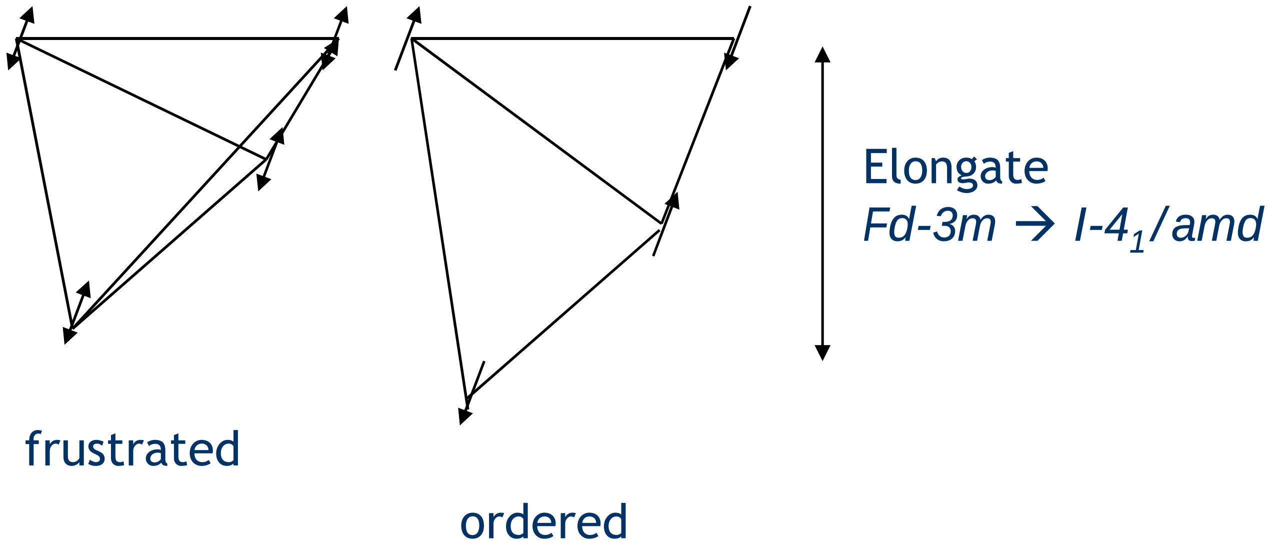
Ordering and Antiferromagnetism in Ferrites, P. W. Anderson, *Phys. Rev.* 102 (1956) 1008.



“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.”

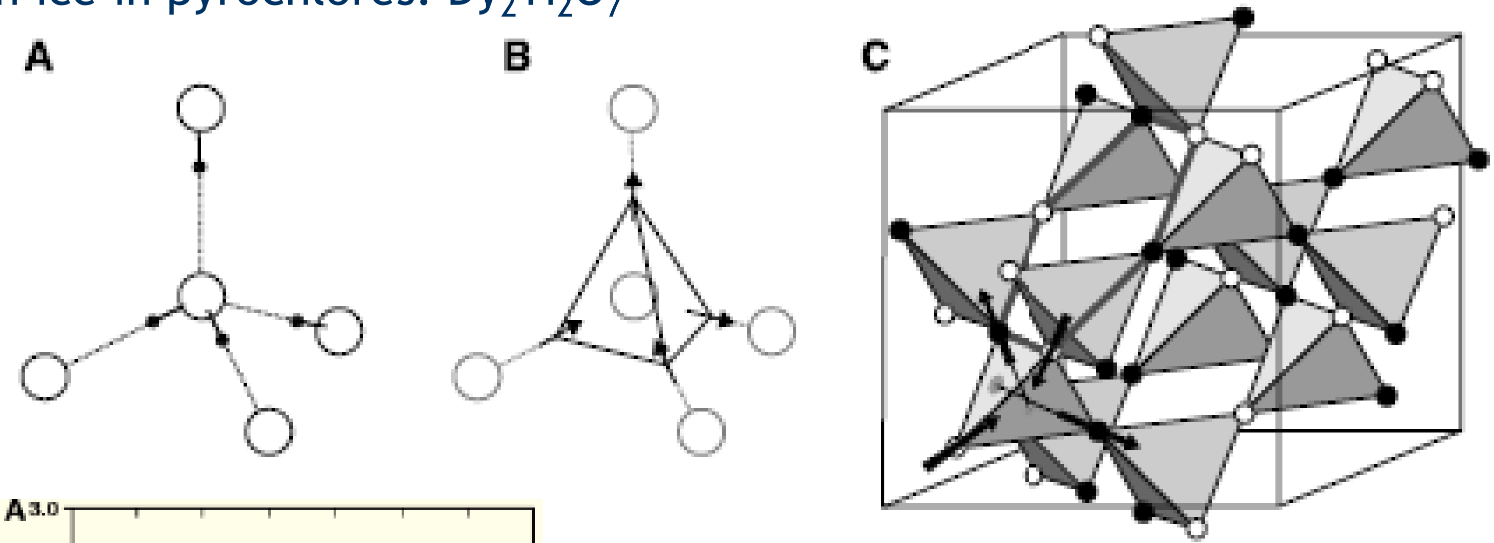
The spinel B sites form a network of corner-connected tetrahedra. Antiferromagnetism is *frustrated.*

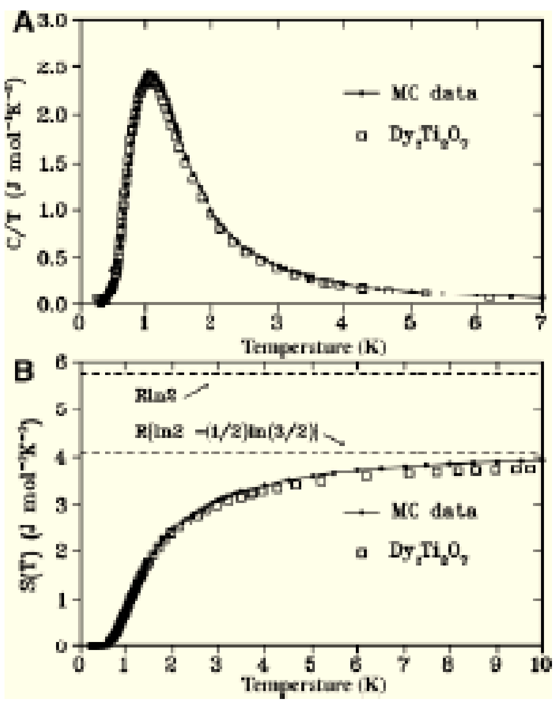
Getting rid of frustration: Structural distortions in $ZnCr_2O_4$ and ZnV_2O_4:



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).

Spin ice in pyrochlores: $Dy_2Ti_2O_7$





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