Lone pairs in the solid state: Frustration

$\text{Bi}_2\text{Ti}_2\text{O}_6\text{O}'$, the pyrochlore analogue of perovskite $\text{PbTiO}_3$, 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 $\text{Bi}_2\text{O}'$ network in $\text{Bi}_2\text{Ti}_2\text{O}_6\text{O}'$, and the associated lone pair ELFs:

The cubic \((Fd-3m)\) structure of pyrochlore \((CaNa)\)Nb\(_2\)O\(_6\)F \([A_2B_2O_7\) 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.
The more familiar 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.

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$_2$O 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?
16 ways of arranging H around O.

Pauling (1935): Ice-I$_h$ has residual entropy.
Lone pairs in the solid state: All about ice

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

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

\[ S = k_B \ln W \text{ and } W = 6(1/2)(1/2) = 3/2 \]

Pauling (1935): Ice-I_h has residual entropy
Lone pairs in the solid state: Heat capacity signatures

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

Ice, spinels, pyrochlores and spin-ice


**Ice-I_h**: $a = 7.82 \, \text{Å} \; ; \; c = 7.36 \, \text{Å} \; P6_3cm$  

Proton ordering not proved

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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]


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.

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 $W = (1/4)^N = (3/2)^N$.

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

Proved by Giaque.

Ice, spinels, pyrochlores and spin-ice

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


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

H$_2$O 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.

Ice, spinels, pyrochlores and spin-ice

The spinel structure: \( \text{MgAl}_2\text{O}_4 \) \( Fd-3m \) (diamond) \( a \sim 8.5 \text{ Å} \)

\[
\begin{array}{ccc}
A & 1/8 & 1/8 & 1/8 \\
B & 1/2 & 1/2 & 1/2 \\
O & 0.264 & 0.264 & 0.264^* \\
\end{array}
\]

* in \( \text{MgAl}_2\text{O}_4 \)

A are tetrahedral with O and B are octahedral

"Starting with an array of oxygens in ccp, we insert Al in certain octahedral interstices and Mg in certain tetrahedral interstices, the selection of 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
Ice, spinels, pyrochlores and spin-ice

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)
Ice, spinels, pyrochlores and spin-ice

Spinel magnetism and ice:


“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*. 
Ice, spinels, pyrochlores and spin-ice

Getting rid of frustration: Structural distortions in ZnCr$_2$O$_4$ and ZnV$_2$O$_4$:

Ice, spinels, pyrochlores and spin-ice

Spin ice in pyrochlores: Dy$_2$Ti$_2$O$_7$