What is Spin Ice?

Spin Ice is a macroscopic phenomenon that occurs in geometrically frustrated systems. Geometrically Frustration is due to the spatial configuration of atoms. Two dimensional examples are the triangular lattice and the Kagome lattice. The Kagome lattice is a corner-shared triangular lattice. Recently, there has been much interest in these frustrated systems. In particular, the most studied example is the three-dimensionally frustrated Pyrochlore lattice (Fig.1).
The oxides $A_2B_2O_7$ have such a lattice. In these materials, the structure consists of pyrochlore lattices for the *A* and *B* sites which are interpenetrating. In this material group, there are compounds that show "spin ice" behavior. "spin ice" materials have macroscopically degenerate ground states down to almost zero temperature and because of this, they have a residual entropy. At first glance, this behavior appears to break the third law of thermodynamics. (The entropy should be zero at zero temperature.)

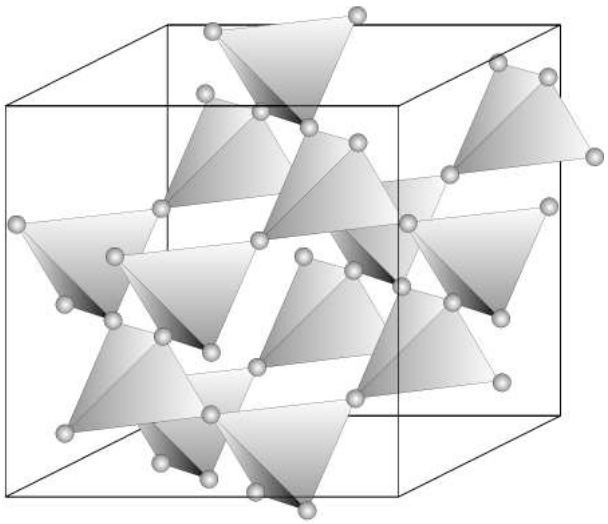

Fig.1 Pyrochlore lattice
This lattice consists of corner-shared tetrahedron. Atoms reside on the vertices of each tetrahedron.

So far, "spin ice" behavior has been observed in $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ and possible candidates are $Ho_2Sn_2O_7$ and $Dy_2Sn_2O_7$. The *A* and *B* atoms both form separate pyrochlore lattices (see Fig.1). However, the *A* site is occupied by a rare-earth metal and the *B* site is occupied by a transition metal. At the *B* site we use Ti^{4+} or Sn^{4+} since they have no spin and thus are nonmagnetic. Therefore, only the *A* site plays an important role in magnetic properties of these compounds.

The spins of *A* ion reside on the vertices of tetrahedron in the lattice (open circle of Fig.1). The spins have Ising anisotropy directed to the center of tetrahedron from the vertices and since there is an effective ferromagnetic interaction between nearest neighbor spins, the stable spin configuration is two-spins inward and two-spins outward from the tetrahedron. Thus, in each tetrahedron, there are ${}_4C_2 = 4!/2!2! = 6$

configurations, and because of this degeneracy there is a residual entropy.

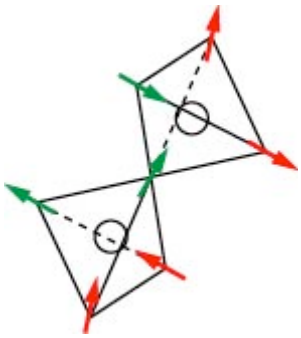

Fig.2 Spin configuration in a spin ice

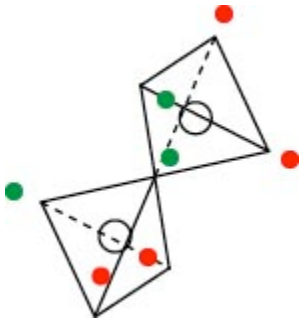

Fig.3 Proton ordering in water ice

The solid of H_2O also has same corner-shared tetrahedral network. In ordinary ice, O^{2-} ions reside on the center of tetrahedron (black open circle) and H^+ ions reside near the vertices of the tetrahedron (red and green circle) (Fig.3). In Fig.3, the O^{2-} ion is surrounded by four H^+ ions. The two bonds between H^+ and O^{2-} ions are covalent (red) and the other two are hydrogen bonds (green). However, the bond length of hydrogen bond is longer than that of covalent bond. If we consider the covalent and hydrogen bonds to be spins pointing inwards and pointing outwards, respectively, this situation is analogous to our spin system (Fig.2). This is the reason why the system in Fig.2 is called "spin ice". The 2-spins inward and 2-spins outward rule is called "ice rule".

We can estimate the value of the residual entropy. If we assume that each tetrahedron is independent, then Each spin has 2 configurations (in and out). In each tetrahedron, there are $2^4 = 16$ possible configurations and among those, 6 configurations satisfy the ice rule. So, the ratio of stable configurations is 6/16 in each tetrahedron. When the system has N spins, there are $N/2$ tetrahedrons. Therefore, the number of spin-ice configurations is $2^N\ (3/8)^{N/2}$ and the expected value of residual entropy is $S_0 = k_B \ln(2^N(3/8)^{N/2}) = R/2\ln(3/2)$. (This is the Pauling method.)

In Fig.4, we show the entropy of $Dy_2Ti_2O_7$ in zero magnetic field and in magnetic fields of 0.5 T and 1 T. The spin entropy can be found by integrating the spin contribution to the specific heat (C_s). We get the spin contribution of specific heat by simply subtracting the lattice contribution from the total specific heat.

$$\Delta S(T) = \int_{T_0}^{T} \frac{C_s(T)}{T} dT$$

In Fig.4, the entropy at 40 K does not reach $R\ln 2$. The difference between $R\ln 2$ and this value is almost same as the expected value from Pauling method ($S_0 = R/2\ln(3/2)$). Under magnetic field, the energy of the spins parallel to the field is

smaller than those antiparallel and thus, the magnetic field lifts the ground state degeneracy. This behavior is observed in our experiment.

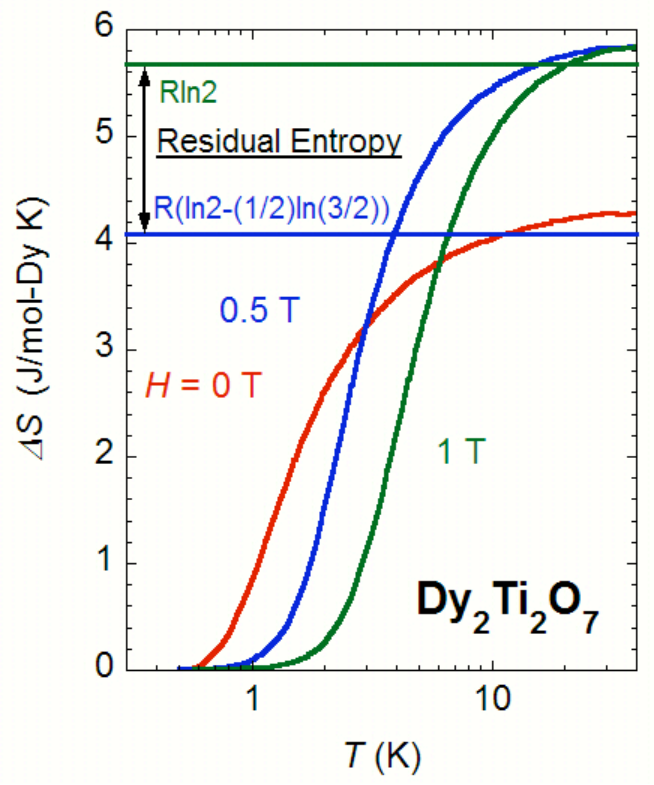

Fig.4 The entropy of $Dy_2Ti_2O_7$ in zero fields and in magnetic field(0.5 T and 1 T)

An important question is whether or not the spin ice state violates the Third law of thermodynamics. What actually happens is that below 1K, the spins are frozen and the system is not in thermal equilibrium. But, what lead to the phase transition to the real ground state? And how is the residual entropy released by applying the field? These are currently unsolved problems. In order to solve these problems we are investigating new material by measuring their low temperature properties.