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Neutron scattering studies of spin ices and spin liquids

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Abstract. In frustrated magnets, competition between interactions, usually due to incompatible lattice and exchange geometries, produces an extensively degenerate manifold of groundstates. Exploration of these states results in a highly correlated and strongly fluctuating cooperative paramagnet, a broad classification which includes phases such as spin liquids and spin ices. Generally, there is no long range order and associated broken symmetry, so quantities typically measured by neutron scattering such as magnetic Bragg peaks and magnon dispersions are absent. Instead, spin correlations characterized by emergent gauge structure and exotic fractional quasiparticles may emerge. Neutron scattering is still an excellent tool for the investigation these phenomena, and this review outlines examples of frustrated magnets on the pyrochlore and kagome lattices with reference to experiments and quantities of interest for neutron scattering.

1. PREAMBLE

In physics, a frustrated system is one in which all interactions cannot be simultaneously minimized, which is also to say that there is competition amongst the interactions. Frustration is most commonly associated with spin systems [1], where its consequences can be particularly well identified, but is by no means limited to magnetism. Frustrated interactions are also relevant in certain structural problems [2–6], colloids and liquid crystals [7], spin glasses [8], stripe phases [9, 10], Josephson junction arrays [11], stellar nuclear matter [12, 13], social dynamics [14], origami [15], and protein folding [16], to name a few.

Interest in frustrated spin systems stems from the idea that conventional order will be suppressed by the frustration, and an unconventional state will appear in its place. For example, Anderson proposed that in high temperature superconductors, antiferromagnetic Néel ordering would be replaced by a resonating valence bond state (RVB) [17], which would host the superconductivity on doping. If the RVB state could be promoted by enhancing frustration, a route to high(er)-T_c materials might appear. This has never been realized, and understanding the character of the “unconventional” states, particularly the quantum spin liquid, which emerge in frustrated magnets is usually the objective of current studies.

Extensive reviews of topics in frustrated magnetism can be found in the books edited by Lacroix, Mendels and Mila [1], and by Diep [18]. Topics recently reviewed in the literature include quantum spin liquids [19, 20]; various aspects of spin ice [21–23]; rare earth pyrochlores [24], spinels [25]; and spin ices and kagome spin liquids have their own chapters in Ref. [1]. In the following, I present a brief

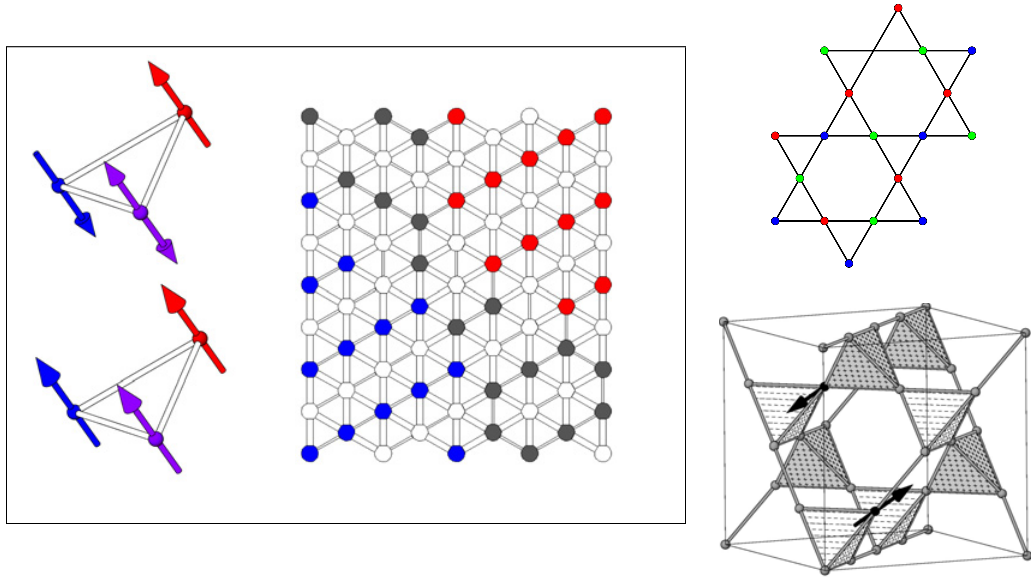

Figure 1. Left: ferromagnetically coupled spins on single triangles are unfrustrated, while antiferromagnetic coupling is frustrated. Note that the frustration greatly increases the degeneracy of the groundstate. The groundstate of a triangular lattice antiferromagnet has many groundstates constructed by ensuring that the local groundstate is realized on every triangle. These states may be ordered, but the vast majority are disordered. Right: the kagome and pyrochlore lattice, two and three-dimensional corner sharing triangles.

overview of frustrated magnetism, followed by examples on the pyrochlore (spin ice and quantum spin ice) and kagome lattices (spin liquids).

2. FRUSTRATION

The canonical example of frustration is the triangular lattice Ising[1] antiferromagnet [26]. On a single triangle, it is not possible for all pairwise interactions to be minimized - in the ground state, one spin will point up and two down (or vice-versa), such that one magnetic interaction is unsatisfied. This imparts a significant degeneracy, as an individual antiferromagnetic triangle has six ground states, while the ferromagnet conversely has just two (all up or all down). The interesting question concerns the ground states of the entire lattice of triangles. Because of the frustration, the ground state of the whole system must also be governed by some compromise condition. Generally, provided that every plaquette[2] of the lattice is individually in a ground state, a global ground state is achieved [27, 28]. However, the inherent degeneracy of the individual plaquettes means that an enormous number of states can be constructed, most of them disordered [26]. These states form an extensive manifold of degenerate groundstates (i.e. the number of groundstates scales with the system size) in which a small number of ordered states are far outweighed by the disordered ones. Although the most direct way to produce a frustrated magnet is

[1] Spins on lattices may have different dimensionalities d - we call spins with $d = 1$, which is to say that they are confined to point parallel or antiparallel to a particular direction, Ising spins; $d = 2$, spins which may rotate freely within a plane are XY-spins; and $d = 3$, where the spins may orient freely in space, we describe as Heisenberg or continuous.

[2] An isolated unit of a geometrically frustrated lattice such as a single triangle or tetrahedron is sometimes called a plaquette or a simplex.

to identify a system with antiferromagnetic interactions on a lattice based on triangular units, this is not the only way to generate frustration. For example, bipartite lattices with antiferromagnetic interactions are unfrustrated, since the partition into two sublattices, each with neighbors only drawn from the other, means that any spin can always be antiparallel to all its neighbors. However, introduction of further neighbor exchanges which compete with the main exchange interaction can create important frustration effects in bipartite lattices such as the diamond lattice [29], as well as in 1-dimensional systems [30].

Conventional magnets[3], in which the number of groundstates is limited to the small number of symmetry-related, long-range ordered groundstates are compatible with the Third Law of Thermodynamics, which requires the entropy of the system to vanish as $T \to 0$. On the other hand, in a simple, frustrated, spin model such as the triangular Ising antiferromagnet, where the number of groundstates is extensive, and there is no way to resolve the degeneracy, the entropy will persist to zero temperature. In general, the spins of a frustrated magnet become strongly correlated at a temperature corresponding to the energy scale of the dominant interaction, i.e. the Curie-Weiss temperature. Because of the frustration, ordering does not occur at this temperature, so the correlated state persists to lower temperature than "expected". This part is generically called a cooperative paramagnet [31], a term which spans many specific behaviors, including classical and quantum spin ices and spin liquids. Usually this region is signified by the extension of the Curie-Weiss law below the expected ordering temperature. The persistence of the Curie-Weiss law can be used as a simple way to quantify the frustration of a compound - the frustration index is the ratio θ_{CW}/T_N. No real material threatens the third law, but, as in the RVB/Hi-T_c example, the conflict is at the root of the original interest in frustrated magnets since it may drive the emergence of an unconventional order parameter. In a real system, a much smaller energy scale is eventually reached and a normally small effect such as a further neighbor exchange or magnetoelastic coupling (e.g. as in $ZnCr_2O_4$ [32]) becomes relevant and drives an ordering transition. Alternatively, the system may fall out of equilibrium, in which case all bets about the Third Law of Thermodynamics are off.

The current main interest in frustrated magnetism could probably be summarized as the identification of a genuine spin liquid. This would be a magnetic system in which the groundstate has no broken symmetries. Pragmatically, it may be defined as a magnetic state in which the spin correlations remain short ranged, and a gapless continuum of spin excitations exists, as in a liquid [33, 34]. However, the detailed usage in theory is more complicated, and conflicting definitions seem to exist (gapped, gapless, with or without spinons etc.) [19]. While conventional ordered phases can be classified and described by the Landau paradigm of broken symmetry, by which a local order parameter can be defined, spin liquids are examples of "topological order" [35], and are now classified by the topological properties of their groundstate wavefunctions. Other examples of topological materials are the FQHE and ^{3}He [36–38]. Integer valued topological quantum numbers characterize topological states, which are are robustly protected and can offer remarkable reproducibilty and stability, as in the case of FQHE voltage standards or Josephson junction flux quantization. In this context, spin liquids are interesting systems for topologically protected quantum computing. Connection between exotic many body theory and experiment is still developing, but some concrete consequences are established – local measurements cannot detect the development of the topological ordering (i.e. that the system is not any longer a simple paramagnet); but in the absence of conventional long range order, and associated bosonic excitations, correlations with an emergent gauge structure and unconventional fractional quasiparticle excitations are possible. While the topological invariants characterizing the topological order remain inaccessible, the spin correlations and excitations of frustrated magnets can be studied directly, and this offers essential experimental information in the search for a spin liquid.

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[3] I refer several times to "conventional magnets", by which I imply a magnetic material with a well ordered lattice and unfrustrated exchange geometry, resulting in long range order with associated broken symmetry and magnon excitations.

In the following, I will introduce emergent gauge structure and fractional quasiparticles and exemplify their study by neutron scattering. I will begin with spin ice, which is sometimes admitted as a "classical spin liquid", and allows a clearer exposition of both. Then I will progress to quantum spin ice (which is actually a quantum spin liquid), and then to spin liquids on the kagome lattice. The objective is to provide an understanding of what a spin liquid is, and the reasons they have become so interesting, while calling attention to various types of neutron scattering experiment which are useful in the field of frustrated magnetism. The basis of these techniques is described at length in other chapters by Enderle, Chapon, Stewart and Raymond. It is important to remember that the bibliography is not exhaustive, most especially with respect to other techniques which have been applied to these examples.

3. SPIN ICE

Spin ice [21–23, 39] has acquired a central place in frustrated magnetism, in part because it is relevant to many frustrated magnets on the pyrochlore lattice and in part because some good model materials exist, providing clean realizations of the theories and spurring their development. Current interest in spin ices is certainly motivated by studies of their dynamics, which are generally agreed to be controlled by emergent magnetic monopole excitations, the first example of a fractional quasiparticle in a three dimensional magnet [40].

3.1 Spin ice mapping and materials

Early neutron scattering experiments on $Ho_2Ti_2O_7$ by Bramwell and Harris established that the spins in this material were highly anisotropic, and preferred local groundstates in which two spins point in and two spins point out of each tetrahedron of the pyrochlore lattice. They realized that there is a mapping between the under-constrained hydrogen-bonded network of water molecules in ice, and the spin configurations in the $\langle 111 \rangle$-Ising ferromagnet on the pyrochlore lattice [41–43] (see Fig. 2), and coined the name spin ice. Consequently, both the ice and spin ice have statistically identical ground state manifolds and entropy, as shown by integration of specific heat measurements [44–46]. Because mappings can be made between "two-in-two-out" Ising spins with ferromagnetic coupling, and "two-up-two-down" Ising spins with antiferromagnetic coupling[4] [42, 43, 47–49] the form of spin correlations obeying the ice rules becomes an important result in both pyrochlore ferromagnets and antiferromagnets [48–52].

A small number of spin ice materials exists, and only $Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ are currently available as large single crystals for neutron experiments [53–56]. Other possible spin ices are $Ho_2Sn_2O_7$ [57] and $Dy_2Sn_2O_7$, $Ho_2Ge_2O_7$ [58], $Dy_2Ge_2O_7$ [59, 60] and $CdEr_2Se_4$ [61], which are currently only available as powders. Although all have the relevant entropy, this is not a definitive indicator of emergent gauge structure[5]. Recent developments in the reverse Monte Carlo technique have shown that it is very effective in modeling the spin correlations of frustrated magnets [63] and application to powder neutron diffraction from samples of $Ho_2Ge_2O_7$ suggest that does indeed have spin correlations of the required form [58].

[4] These uniaxial antiferromagnetic spins do not respect the cubic symmetry of the pyrochlore lattice so have no physical realization, but the mapping can be used for pseudo-spins representing individual components of higher dimensionality spin systems.

[5] For example the "stuffed" spin ice $Ho_{2+x}Ti_{2-x}O_{7-x/2}$ has a very similar entropy but strongly modified spin correlations, this can be understood since the Pauling estimate is based on a single tetrahedron, and will capture the entropy whether the ice rules are propagated coherently (spin ice) or disrupted by disorder (stuffed spin ice) [62].

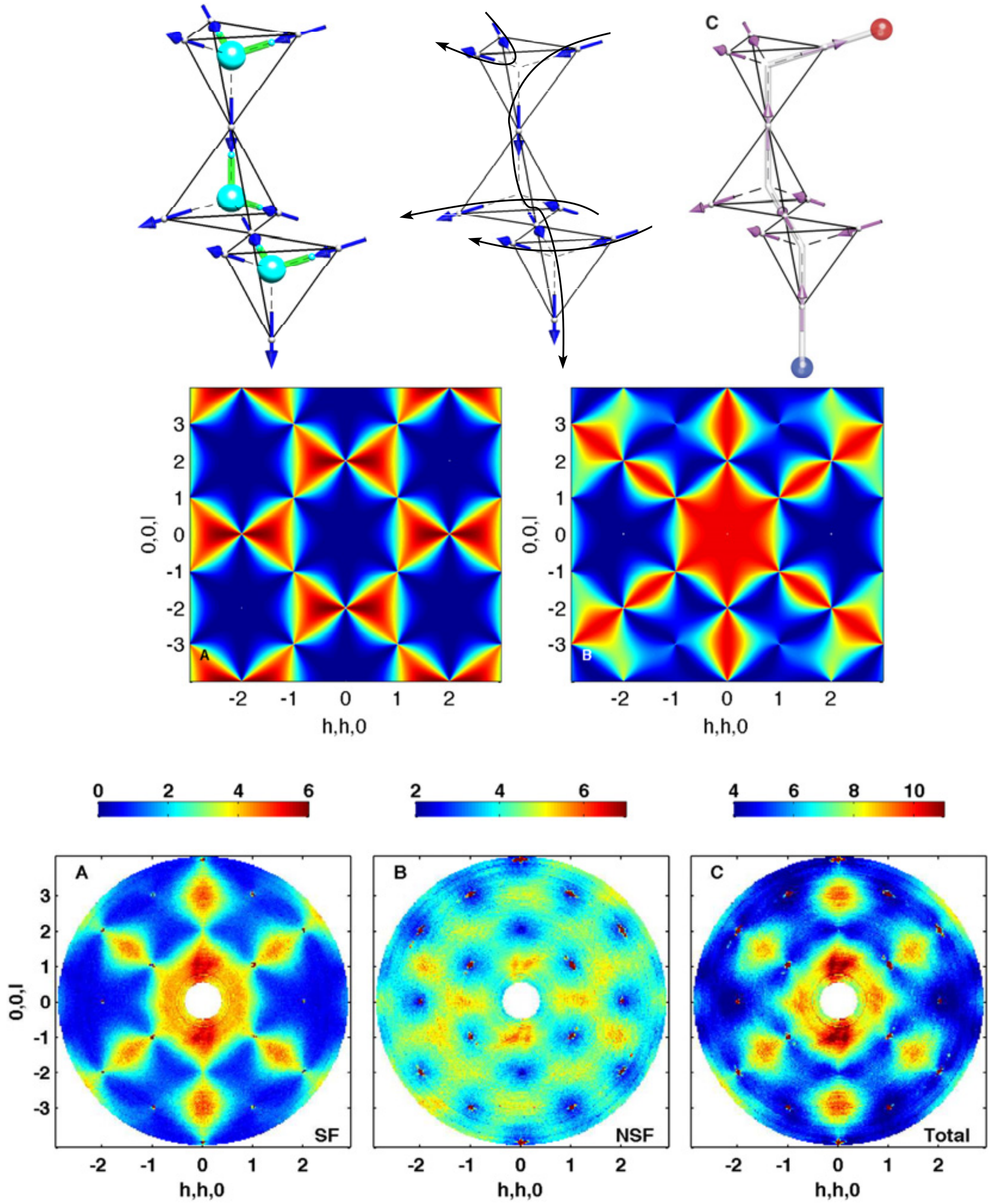

Figure 2. Top row: sketches of mapping of diamond ice and spin ice (water molecules in cyan/green); coarse graining of spin ice spins to a non-divergent field; unbound monopole defects made by flipping first the lowest spin to create a pair, and then subsequent flips along the highlighted path (the Dirac string). Middle row: diffuse scattering expected from dipolar correlations in the pyrochlore Heisenberg antiferromagnet (left) and ⟨111⟩ Ising ferromagnet (right) – the two are related by a mapping and have identical correlation functions, but different structure factors, hence pinch points at the same wavevectors but of different appearance (calculated following [22]); Bottom row: polarized neutron scattering data from $Ho_2Ti_2O_7$ showing the pinch points in the spin flip channel, other correlations in the NSF and hidden pinch points in the total [72].

3.2 Dipolar spin ice Hamiltonian and diffuse scattering in spin ices

$Ho_2Ti_2O_7$ and $Dy_2Ti_2O_7$ were first understood microscopically, and neutron scattering was key to this. The crystal field scheme of $Ho_2Ti_2O_7$ was obtained by inelastic neutron scattering experiments [64], and extended to $Dy_2Ti_2O_7$. The first excited crystal field states are separated by a very large energy gap, so that at low temperatures, the magnetic moments are very well approximated by classical Ising spins pointing in or out of the tetrahedra (see also polarized neutron scattering measurements of the local site susceptibility [65]).

Because the magnetic moments of both Ho^{3+} and Dy^{3+} are very large, the dipolar interaction plays an important role. A detailed microscopic Hamiltonian, the so-called dipolar spin ice model [46, 66–68] was constructed using all available parameters of the materials. A key part of its development was its comparison, by use of Monte Carlo simulations, with diffuse neutron scattering measurements of the spin correlations [46, 68, 69]. Thermodynamic properties were also reproduced. It now includes the dominant dipolar interaction, and competitive superexchange interactions extending to third-nearest neighbour distance. The dipolar spin ice Hamiltonian can be written as

$$\mathcal{H}_{DSM} = \sum_{n=1,3}(-J_n \sum_{\langle ij \rangle} \mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}) + Dr_{nn}^3 \sum_{j>i} \frac{\mathbf{S}_i^{z_i} \cdot \mathbf{S}_j^{z_j}}{|r_{ij}|^3} - \frac{3(\mathbf{S}_i^{z_i} \cdot \mathbf{r}_{ij})(\mathbf{S}_j^{z_j} \cdot \mathbf{r}_{ij})}{|r_{ij}|^5} \tag{3.1}$$

where J_i is the ith near neighbour superexchange between spins S_j and S_k. Surprisingly, the dipolar interaction does not lead immediately to long-range order. On a single tetrahedron, the ground state is still given by the ice rules, and in fact the long-range part of the dipolar interaction is almost perfectly self-screened [70, 71]. This was formalized in the concept of projective equivalence, which implies that the near neighbour spin ice model (FM $\langle 111 \rangle$ spins) and dipolar spin ice model have essentially identical eigenvalue spectra and, therefore, spin correlation functions.

3.3 Emergent Gauge structure

This spin correlation function provides an example of emergent gauge structure [22, 48, 49, 71]. If the spins of a spin ice are coarse grained to a field (at zero temperature, where the ice rules are obeyed on all tetrahedra), this field will be non-divergent - it can be seen that the configuration of a single tetrahedron is non-divergent, and since all the tetrahedra are in two-in-two-out states, the field obtained is globally non-divergent (i.e. $\nabla.\mathbf{M} = 0$). Because the ice rule groundstates are degenerate, the free energy is determined only by the entropy [22, 48, 49], which will be maximized by states with zero magnetization (once a finite magnetization is introduced in a coarse-graining volume, it puts considerable constraints on the configuration of field lines in adjoining cells, at cost of entropy) and this results in a free energy of form $F_{\text{tot}}(\mathbf{M}(\mathbf{r}))/T = \text{const} + \int d^d r K |\mathbf{M}(\mathbf{r})|^2/2$. These two conditions resemble the non-divergence criterion and energy of a free field with no charges, such that a system where these transformations can be made is known as a Coulomb phase[6] [73–76].

The clearest illustration of why the excitations of spin ice can be considered as emergent magnetic monopoles can be obtained from the dumbbell model introduced by Castelnovo *et al.* [23, 40]. The magnetic dipole moments of the rare earth ion are replaced by small dumbbells with opposite magnetic charges at either end. The charges lie at the centre of the tetrahedra (on the sites of a diamond lattice), and Castelnovo *et al.* showed that the dipolar spin ice Hamiltonian can be rephrased in terms of these charges, so that a global two-in-two-out state is one in which the magnetic charges of the dumbbell model sum to zero at every diamond lattice point. Reversing a dumbbell (or flipping a spin) creates

[6] A Coulomb phase is any material where the local degrees of freedom can be coarsegrained into a non-divergent field and other examples include dimer models and pyrochlore antiferromagnets, it is in spin ice that the relationship between spins and field is particularly clear.

an imbalance of magnetic charge on two adjacent tetrahedra. These ice rule defects can hop apart by subsequent flips of spins/dumbbells, which restore the local ground state at intervening tetrahedra. As they do so, we see that the original flipped dipole has been fractionalized into monopoles. Because the real spins interact through space, via the dipolar interaction, these magnetically charged defects also interact, and the form of the interaction is a Coulomb interaction. A similar picture with non-interacting monopoles was developed by Rhyzkin [77].

3.4 Dipolar correlations and pinch points in pyrochlore magnets

As a direct consequence of the non-divergent condition on the spin configurations, the spin correlations acquire the spatial form of the dipolar interaction. This has specific ramifications in the diffuse scattering - ice rule obeying fluctuations of all lengthscales are still allowed. Short-wavelength, ice-rule obeying fluctuations correspond to reversal of a short loop of spins, such as a hexagon in the pyrochlore lattice. Such a fluctuation contributes scattering intensity at or near the zone boundary. Long wavelength fluctuations, which are ultimately magnetization fluctuations, are also possible, and they contribute scattering at the zone centre. Loops on all lengths are possible, so scattering extends from the zone centre to the zone boundary. However, other wavevectors have no intensity at all (precisely speaking, at zero temperature where there are no defects), as they correspond to fluctuations or correlations forbidden by the ice rules. The distinctive signature of this situation is a pinch point, a sharp bow-tie-like feature in the diffuse scattering [78, 79]. These considerations are true for ice rule obeying spins, irrespective of how those ice rules are established – in spin ices, dipolar describes the form of the correlations, as well as their interactions. Pinch points can also be observed in actual ices, for example the two-dimensional ice copper formate tetradeuterate (CFTD) [80–82] (the situation in real ice is less clear [83, 84]). In theory, the pinch point is a singularity, but at finite temperature, will always be rounded by defects, and by neutron scattering resolution.

The existence of a mapping between the spin correlation functions of the nearest neighbor spin ice model and the pyrochlore Heisenberg antiferromagnet, and the projective equivalence [71] between the former and the dipolar spin ice model implies that the spin correlations of a (real) spin ice should have the dipolar form expected for ice rule models on the pyrochlore lattice, with associated pinch point scattering. Furthermore, these dipolar correlations are an implicit ingredient in the monopole picture. Indeed, the pinch points are clearly visible in certain calculations, typically near neighbor spin ice models which neglect the dipolar interaction [46, 85, 86]. However, unpolarized diffuse scattering measurements of $R_2Ti_2O_7$ showed strong scattering at the zone boundaries suggestive of cluster-like correlations. Self-organization of frustrated spin systems on the pyrochlore lattice into independent strongly bound hexagonal clusters has been an ongoing theme in the study of spinels, where a characteristic diffuse scattering response was originally observed in $ZnCr_2O_4$ [87], and subsequently in $MgCr_2O_4$ [88], $HgCr_2O_4$ [89], $CdFe_2O_4$ [90] and $CdCr_2O_4$ [91]. Although it was concluded in Ref. [68] that microscopic clusters do not dominate the spin correlations of $Dy_2Ti_2O_7$, in part because they should strongly modify the entropy, the absence of pinch point scattering in real spin ices was puzzling.

In spin ice, a second type of diffuse scattering experiment has resolved this problem, at least partially. Polarized neutron scattering shows clearly that the total scattering contains pinch points and allows a simple interpretation of their invisibility in the previous experiments [72, 92] in terms of of ice rule and non-ice rule correlations. Although the existence of these pinch points implies that the correlation function is indeed dipolar, as required, their reduced intensity relative to a simple ice-rule model (which leads to them being hidden in the total scattering by contributions arising from other correlations) remains an open question in the study of spin ices, as it implies the unweighting of certain types of ice-rule obeying states. Similarly in spinels, an alternative interpretation to the cluster-like correlations is given by Conlon and Chalker [52] in terms of further neighbour exchanges, which modify the power-law correlations of the minimal model of a Heisenberg pyrochlore antiferromagnet.

3.5 Dirac strings

In the original prediction of magnetic monopoles by Dirac, $\nabla \cdot \mathbf{B} = 0$ is maintained by an object known as the Dirac string, a quantized string-like singularity bringing the requisite magnetic flux back into the monopole [93, 94]. In a spin ice, the overturned line of dipoles left by the hopping of a monopole was also named a Dirac string. The two are not directly analogous, because the spin ice has a network of indistinguishable strings (see Henley [22] for full details), which are continuously rearranged [95]. In an instantaneous snapshot of the sample, no string segment joining two monopoles can be uniquely assigned as the Dirac string. When a magnetic field is applied along the [001] direction a long range ordered phase is produced, with the same two-in-two-out configuration on every tetrahedron [96] (possibly by a topological transition known as a Kasteleyn transition [97]). All the strings are extended, parallel to the field, and propagating monopoles now trail an identifiable string. Along the string, the ice rules are still obeyed, so the energetic cost comes only from the creation and interaction of the monopoles at its ends, and the growth of the string against the field. At moderate temperatures and fields, small numbers of monopoles can be created, and their strings are visible in the fully polarized background. Although the monopoles diffuse along the field direction, they make a random walk in the plane perpendicular to it, which can also be biased by tilting the field. Specific diffuse scattering patterns associated with these two cases were both observed and calculated, showing that spin ice does indeed have interacting quasiparticle excitations [86].

To be a truly emergent description [38, 98, 99], the underlying microscopic physics should become irrelevant, so that spin ice materials can be described just by an effective theory of the quasiparticles, in this case, a Coulomb gas of magnetic charges. Much further theoretical work investigating the utility, limits and further further implications of this picture has appeared [95, 100–108]. Experimental techniques such as neutron scattering in applied fields [109] as well as susceptibility [95, 110–112], magnetization [113–115], μSR [116, 117], NMR [102], and thermal conductivity [118, 119] have been applied.

4. QUANTUM SPIN ICE

A quantum spin ice is, as the name suggests, a spin ice in which quantum fluctuations are possible. The most important consequence of this generalization is that the effective field theory is transformed from emergent magnetostatics on the pyrochlore lattice with monopoles, to emergent quantum electrodynamics on the pyrochlore lattice. More than one route to a quantum spin ice may be possible, but, thus far, a productive line of enquiry follows from a Hamiltonian based on symmetry-allowed nearest neighbour exchange interactions which can exist in actual rare earth pyrochlores. This Hamiltonian can be written

$$\begin{aligned}\mathcal{H}_{S=1/2} = \sum_{\langle ij \rangle} \{ & J_{zz} S_i^z S_j^z - J_{\pm}(S_i^+ S_j^- + S_i^- S_j^+) + J_{\pm\pm}[\gamma_{ij} S_i^+ S_j^+ + \gamma_{ij}^* S_i^- S_j^-] \\ & + J_{z\pm}[S_i^z(\zeta_{ij} S_j^+ + \zeta_{ij}^* S_j^-) + i \leftrightarrow j]\} \end{aligned} \tag{4.1}$$

in which the S_i^z is aligned with the local trigonal axis and γ_{ij} and ζ_{ij} are matrices relating the local coordinate frames (see Refs. [120–123] for full details). In essence, the dominant term (J_{zz}) is an Ising part which establishes the ice rules, while transverse terms allow fluctuations between the ice rule states by quantum tunneling. Experimentally, to realize this physics, one needs to reduce the importance of the dipolar interaction, and enhance quantum fluctuations. The search for QSI effects has therefore moved away from $Ho_2Ti_2O_7$ or $Dy_2Ti_2O_7$, to materials containing rare earth ions with smaller moments. At this stage investigations seek to establish the applicability of a quantum spin ice Hamiltonian in various materials.

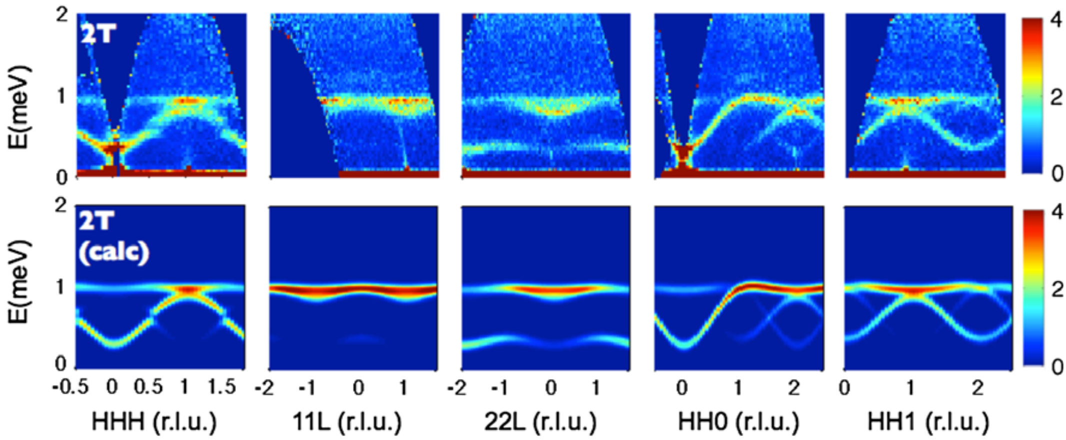

Figure 3. Fitting of spin wave dispersions in $Yb_2Ti_2O_7$ [121]. Permission required from APS.

4.1 $Yb_2Ti_2O_7$

In $Yb_2Ti_2O_7$, the dipolar interaction strength is reduced to 0.018 K, as the moment size is only $\sim 3\,\mu_B$ [124] and the moments have an XY-character. $Yb_2Ti_2O_7$ was originally thought to be a type of XY-ferromagnet on the pyrochlore lattice [125, 126], but definitive evidence of static order below a phase transition at 0.24 K remained conflicting [24, 126–128]. This was compounded by irregular existence of the phase transition in different samples [129, 130] which is now attributed to very small variations in stoichiometry [130, 131]. Above this temperature is a cooperative paramagnet phase [132, 133] has become the most popular candidate quantum spin ice [121, 124, 131, 134]. Although the magnetic moments do have an XY-character, the Ising degree of freedom and ice rule constraint can be understood to operate on an effective $S = 1/2$ associated with the two members of the ground doublet of Yb^{3+}.

The parameters of the spin Hamiltonian have been determined from different neutron scattering experiments [121, 124, 131], and also by comparison with thermodynamic measurements [134]. Using the random phase approximation, the Hamiltonian was used to calculate the energy integrated diffuse scattering [124, 131]. As in the case of the classical spin ices, the diffuse scattering provides the necessary evidence of the spin correlations which are the key to the Hamiltonian. The work of Ross *et al.* [121] employs a technique originally pioneered by Coldea *et al.* in a study of the triangular lattice $S = 1/2$ antiferromagnet $CsCuCl_4$ [135]. Because there is (ideally) no ordered phase in a frustrated magnet, the usual means of fitting spin Hamiltonian parameters – i.e. measurement and calculation of magnon dispersions – is not available. By applying a strong field, sufficient to polarize the spins completely, it is possible to enter a phase where an ordered structure with magnon excitations exists. In $Yb_2Ti_2O_7$, the parameters of the quantum spin ice Hamiltonian could be fitted to the spin wave dispersions of the field-ordered phase. The three analyses disagree amongst themselves, but the parameters of Ross *et al.* are now also supported by a calculation which reproduces the specific heat [134].

4.2 $Pr_2X_2O_7$

While $Pr_2Ti_2O_7$ does not have the pyrochlore structure, several other compounds of Pr^{3+} are available, which do. These are $Pr_2X_2O_7$, with X=Sn [136], Zr, Hf, or Ir. $Pr_2Ir_2O_7$ is metallic and has a very different behavior, involving an anomalous Hall effect for conduction electrons moving in a background

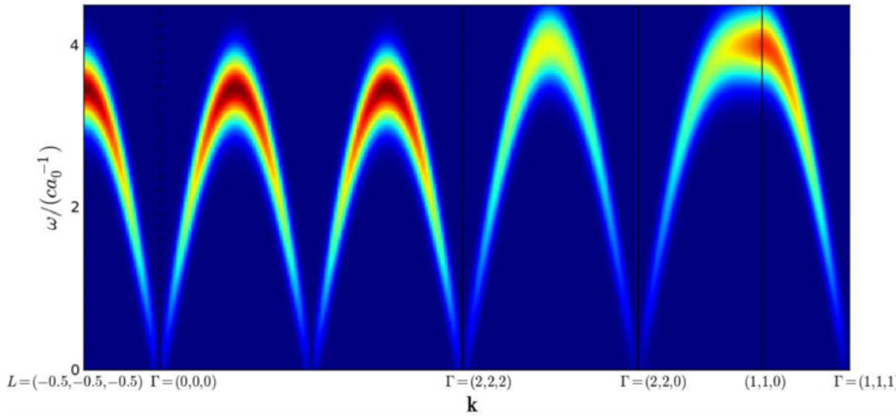

Figure 4. Predicted dispersion and structure factor of pyrochlore photons [123]. Permission required from APS.

of correlated, non-collinear spins [137]. The first three are insulators and appear more relevant to quantum spin ice. The dipolar interaction strength in $Pr_2Sn_2O_7$ is estimated at 0.13 K [138], and the crystal field scheme suggests that the moments are Ising-like, pointing in or out of the tetrahedra, again due to a doublet groundstate. Susceptibility [139], powder diffraction and spectroscopy measurements show diffuse scattering with a spin ice-like form, but accompanied by significant dynamics which are absent in classical spin ices [138]. There is an important difference between Pr^{3+}, which is a non-Kramers ion, and Yb^{3+} which is a Kramers ion. It is suggested that the stability of quantum spin liquid phases in the phase diagram of the QSI Hamiltonian will be enhanced for the non-Kramers case [140], and higher multipole degrees of freedom may also become important [141, 142], which may lead to interesting magnetoelastic effects [143]. So far, experimental work has been limited to powder samples of $Pr_2Sn_2O_7$, but large crystals of $Pr_2Zr_2O_7$ are now available, and preliminary reports [144] describe it as an exchange spin ice, another possibility of Eq. (4.1).

4.3 $Tb_2Ti_2O_7$

Many neutron scattering studies of $Tb_2Ti_2O_7$ have been made [24], but a detailed account of its behaviour is outside the scope of this review. However, $Tb_2Ti_2O_7$ is also discussed in terms of quantum spin ice, but does not fall within the framework described above. Although the Tb^{3+} ions ostensibly have Ising-doublet groundstates (though this is also debated currently), the next excited state is at a low energy of $\sim$1.5 meV, while the above discussion relates to materials with excited states which are well separated from the groundstate. The route to quantum spin ice in $Tb_2Ti_2O_7$ is therefore different, possibly involving virtual crystal field excitations which renormalize the antiferromagnetic exchange [145]. It is interesting to speculate that more than one route to a quantum spin ice can exist, as suggested by the comparison of works on $Yb_2Ti_2O_7$, $Pr_2X_2O_7$ and $Tb_2Ti_2O_7$, or that in different structure types, quite different (rare earth) ions might work, as in the case of classical spin ices in pyrochlores (so far Ho^{3+} or Dy^{3+} based) and spinels (so far Er^{3+} based).

4.4 Quantum spin ice phenomenology

Phase diagrams for the Hamiltonian in terms of the different exchange interactions have been obtained [122, 140], and contain various exotic phases, some of which are ordered. Introduction of small transverse terms to the classical spin ice immediately produces a $U(1)$ quantum spin liquid, which is also called a quantum spin ice. In a quantum spin ice, processes forbidden in classical spin ices, such as the tunneling of a hexagonal loop of spins, are allowed. On the other hand, the quantum spin ice still has ice-like correlations underlying it, so one can still think of a notional magnetic field with $\nabla.\mathbf{B} = 0$ (which is again the coarsegrained description of local degrees of freedom in a Coulomb phase). The emergence of this gauge structure means that one can also write the related vector potential. Then, unlike in the classical spin ice, the quantum fluctuations introduce fluctuations in this vector potential, so that an emergent electric field can also be identified, and the whole theory is governed by an emergent Maxwell action [74, 120, 123].

The excitations of a quantum spin ice are spinons, which are deconfined quasiparticles, closely related to the monopoles of the classical theory. The spinons are gapped, but a gapless dispersive excitation should also be present. This is the photon mode of the emergent electrodynamics. It is a linearly dispersing mode, so a T^3 contribution to the heat capacity is expected [120]. It should also be visible to neutron scattering experiments, and the properties of the magnetic photon have been further elucidated by Benton *et al.*, who make extensive predictions of its properties in this context [123]. They find that the photon has a distinctive structure factor whose intensity increases with energy; and that the pinch points, which are an important feature of a classical spin ice, are expected to be increasingly suppressed as the temperature is decreased. The bandwidth for photon excitations in $Yb_2Ti_2O_7$ is suggested to be of order 0.1 K [123], possibly putting it in reach of high resolution neutron spectrometers. The phase transition in $Yb_2Ti_2O_7$ is suggested to be a Bose-Einstein condensation of monopolar spinons. Detailed experimental investigation of this scenario is expected [131].

5. KAGOME SPIN LIQUIDS

Amongst possible two dimensional frustrated spin systems, theoretical and experimental interest has become almost completely focussed on the $S = 1/2$ kagome Heisenberg antiferromagnet. The classical Heisenberg antiferromagnet on the kagome lattice is already very interesting. In theory it supports an emergent gauge structure, dispersive excitations [146, 147] and an order-by-disorder transition [148, 149]. Unfortunately, no especially good model system for experimental studies exists. Considerable investigations were made of jarosite minerals [150–153], and recently materials based on the langasite structure have appeared [154]. For the $S = 1/2$ system, the most promising experimental realizations are again provided by natural or synthetic mineral samples based on the clinoatacamite structure [155]. In the parent material, there is an approximate pyrochlore lattice, which contains two crystallographic sites. When zinc is substituted on one of these sites, isolated kagome planes result. This stoichiometry is known as herbertsmithite (γ-$Cu_3Zn(OH)_6Cl_2$) [156], and also of interest are kapellasite [157] (a polymorph) and magnesium derivatives of both [158–161]. Sample quality is hotly debated, with the possibility of dilution of the kagome sites, and/or interlayer magnetic atoms which compromise the two-dimensionality. Although samples of ever higher-quality are now appearing [162], and even single crystals [163], reported experiments have so far been limited to powders.

A very interesting quantity which can generally be extracted from neutron scattering experiments on powder samples is a scaling collapse of the generalized susceptibility. If $\chi(\omega, T)$ can be collapsed onto a universal function which depends only on the temperature, the system is said to exhibit E/T scaling, which implies that all microscopic parameters relating to the sample have become irrelevant. Quite diverse systems exhibit E/T scaling, either in theory or experiment, including certain heavy fermion materials [164, 165] and cuprates [166–169]. It may be associated with disorder, or with the close proximity of a quantum critical point. A valence bond liquid is predicted close to a quantum critical point between Néel order and a valence bond solid phase [170], both of which are relevant groundstates for spin systems on the kagome lattice.

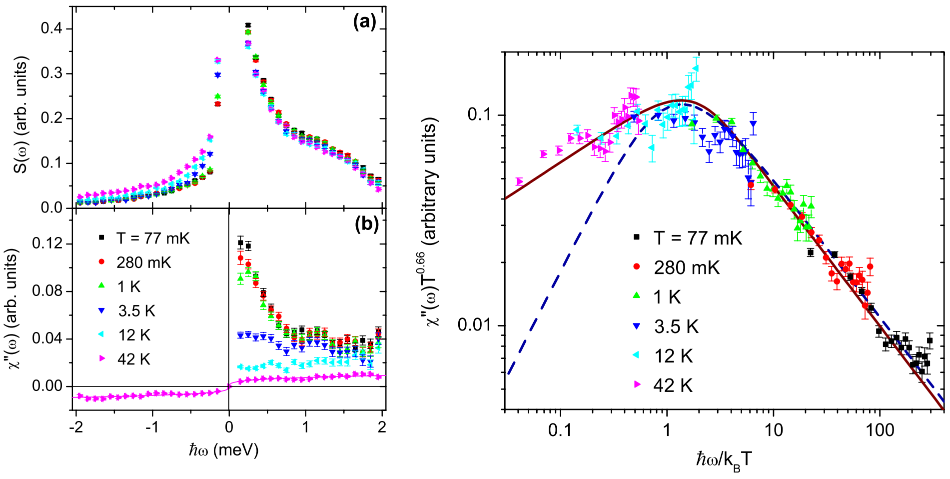

Figure 5. Scaling collapse of χ_ω in herbertsmithite [172]. Permission required from APS.

As is often the case in frustrated magnets, magnetic fluctuations centered at the elastic line, gapless at typical neutron scattering resolution, and enhanced at some wavevector are observed. If the energy dependence of the intensity is a Lorentzian function, relaxation is exponential with a single characteristic timescale and no E/T scaling will be possible [171]. Non-Lorentzian energy dependence suggests multiple timescales, and the possibility of scaling. A method of making the collapse using powder inelastic neutron scattering data is described by Helton *et al.* [172], for herbertsmithite and similar investigations have been made in kapellasite [173] and deuteronium jarosite [153].

In Herbertsmithite, $\chi(\omega, T)$ scales onto the same function that is observed in heavy fermions [172]. However, this is only true for the low-energy part of the susceptibility. An ingenious analysis of higher energy data by de Vries *et al.* [174], which provides a useful means of separating magnetic and phonon intensity, suggests that there are scale free fluctuations, but they are completely temperature independent. In contrast, neither deuteronium iron jarosite or kappellasite shows a true scaling collapse. The former is a large-spin system which undergoes a freezing transition at 22 K, so is not thought to be near to a quantum critical point. In kappellasite, the fluctuations are peaked at a quite unexpected wavevector. In herbertsmithite, they appear at a momentum transfer of 1.25 Å^{-1}, characteristic of the near neighbour distance in the kagome lattice, while in kappellasite they appear at 0.5 Å^{-1} [173]. This suggests that the fluctuations in kappellasite are associated with a different groundstate, and in fact the wavevector is characteristic of the so-called cuboc2, a non-coplanar state formed by competing interactions [173, 175]. Again, a quantum critical point is not expected, rationalizing the absence of scaling. The possibility that Herbertsmithite, the "best" $S = 1/2$ kagome spin liquid, is close to a quantum critical point is intriguing, and hopefully the scaling collapse will be verified with new high quality samples.

6. CONCLUSION

Neutron scattering experiments on powders and single crystals are excellent ways to investigate frustrated magnets. The character of the magnetic moments is accessible, particularly in rare earth base systems such as the pyrochlores, by crystal field spectroscopy. In the absence of long range order, modeling of diffuse neutron scattering can be used to propose and refine Hamiltonians or obtain empirical information about spin correlations. Excitation spectra in field-induced ordered phases may equally be used for this purpose. Finally, direct evidence of the emergent gauge structure and fractional quasiparticles may be obtained from diffuse scattering and spectroscopic studies respectively. The spin liquid currently holds an important role in condensed matter physics, as a host of emergent phenomena, perhaps associated with an underlying topological order. While much progress is anticipated, even in the well studied examples described here, the great diversity of frustrated magnets means that the study of new materials and lattices will also be illuminating, and it should not be forgotten that there must be life beyond the pyrochlore and kagome lattices.

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