The frustrating quest for a perfect quantum kagome antiferromagnet

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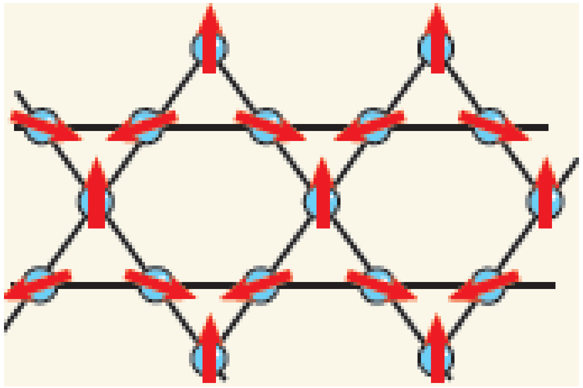
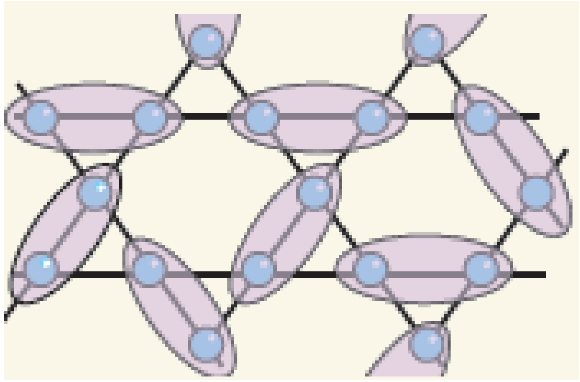
Workshop dedicated to Igor Dzyaloshinskii on the occasion of his 80th birthday

September 9th 2011

Outline

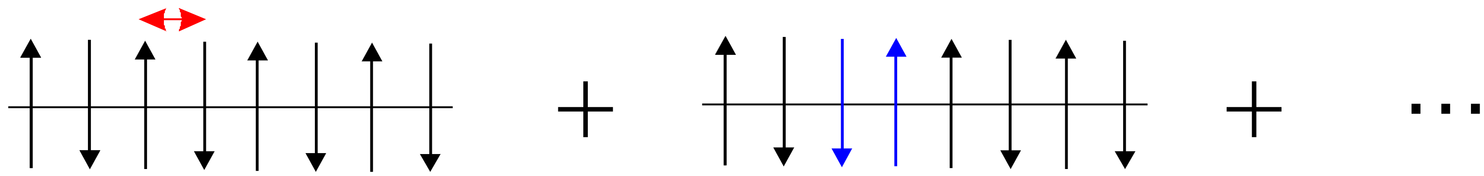
- Motivation: why are QKAFMs interesting ?
- Classical kagome antiferromagnets: S = 5/2
  - Jarosites
- Quantum kagome antiferromagnets: S = ½
  - Volborthite and Herbertsmithite



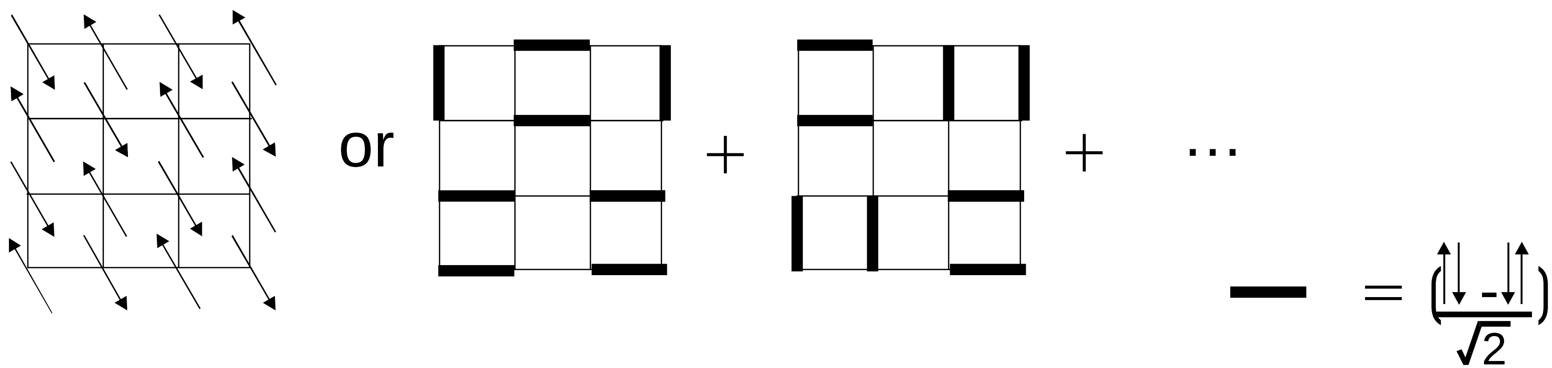


Opening a very old can of worms

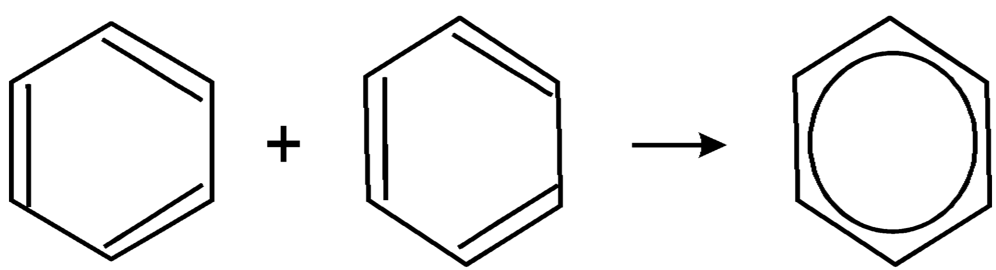
- 1920's - conventional (now Néel) ground state debated



- 1980's – question reopened with high-T_c cuprates

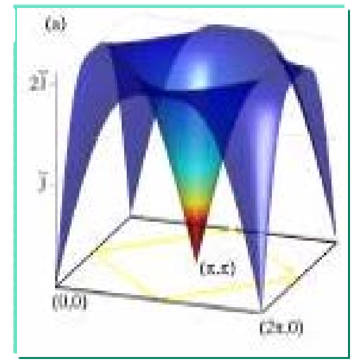


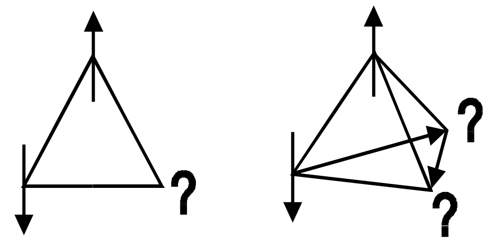
- = RVB (resonating valence bond) or spin fluid ground state

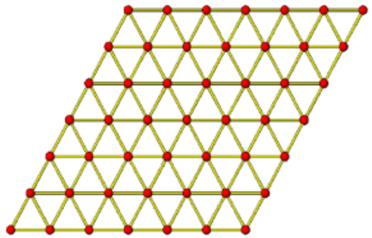


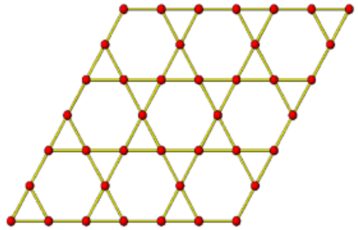
Classical or not?

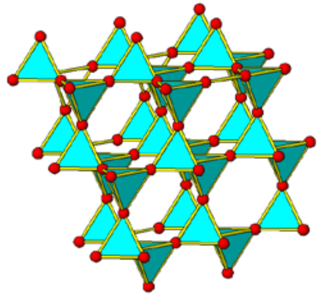
- Classical model works well most of the time
- Quantum fluctuations more significant for
  - Small spin (S= ½)
  - More spin degrees of freedom (Heisenberg)
  - Fewer neighbours - chains and planes
- Further destabilisation through frustration

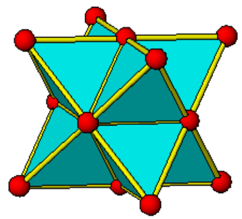




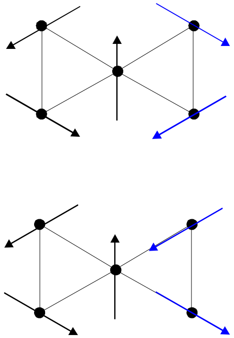






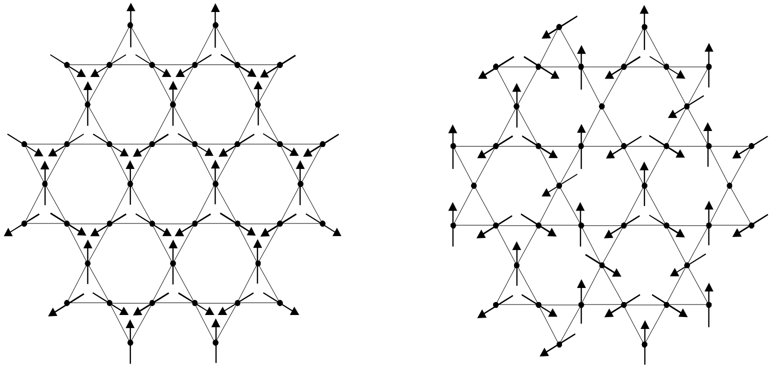


Kagome antiferromagnets: model systems



- Many possible degenerate ground states
  - vertex-sharing does not convey spin information uniquely
  - Thermal fluctuations select coplanar states by ‘order through disorder’
  - But what is the ‘order’: spin nematic, conventional LRO?

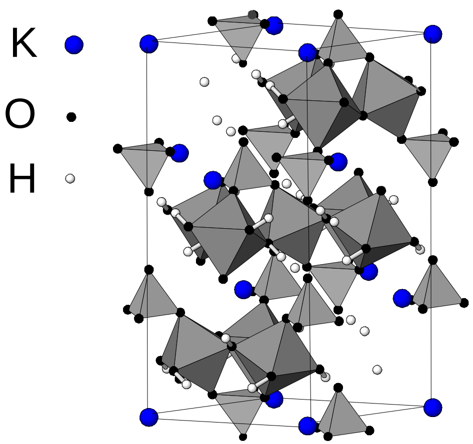
‘q = 0’

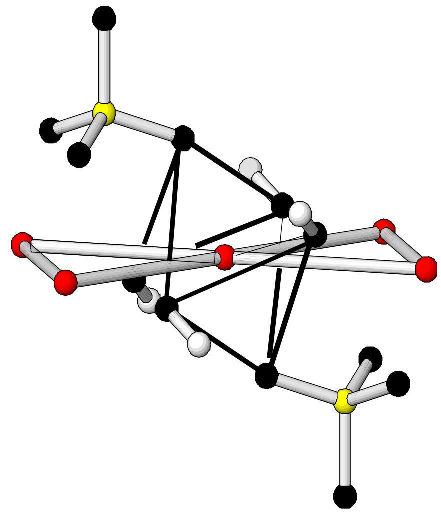


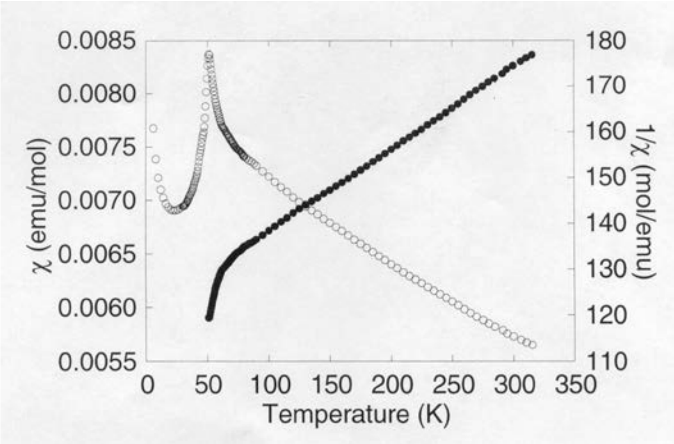
‘ √3 x √3 ‘

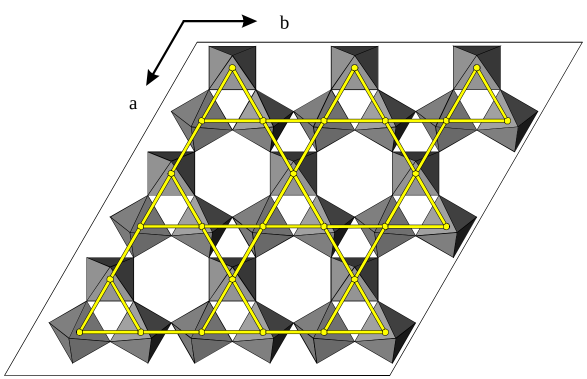
Jarosites: meet the family

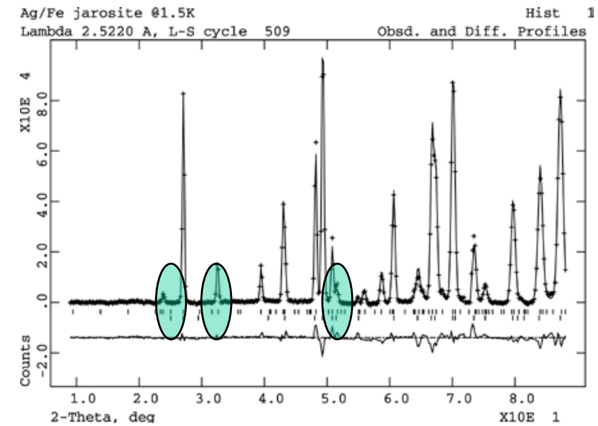
- Fe series ($AFe_3(SO_4)_2(OH)_6$) most widely studied – $S = 5/2$
  - Strong AFM exchange (θ = -700 K)
  - All show LRO (q=0) at $T_N \sim$ 60K (except A = H_3O, D_3O…see later)
  - Further terms in Hamiltonian likely – nnn exchange, ligand-field, DM terms





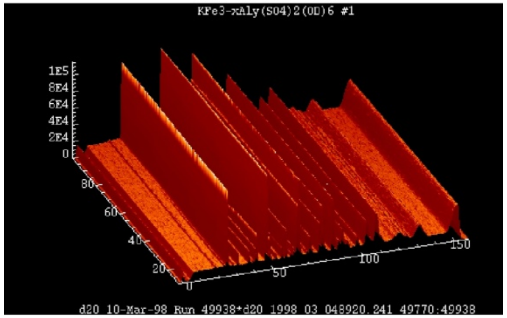


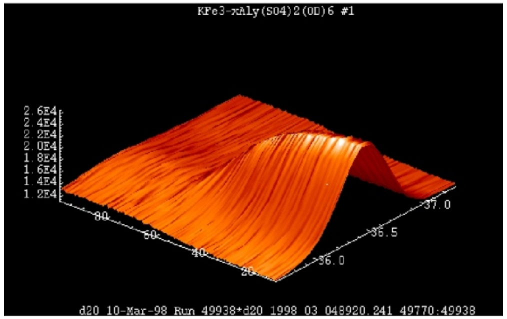


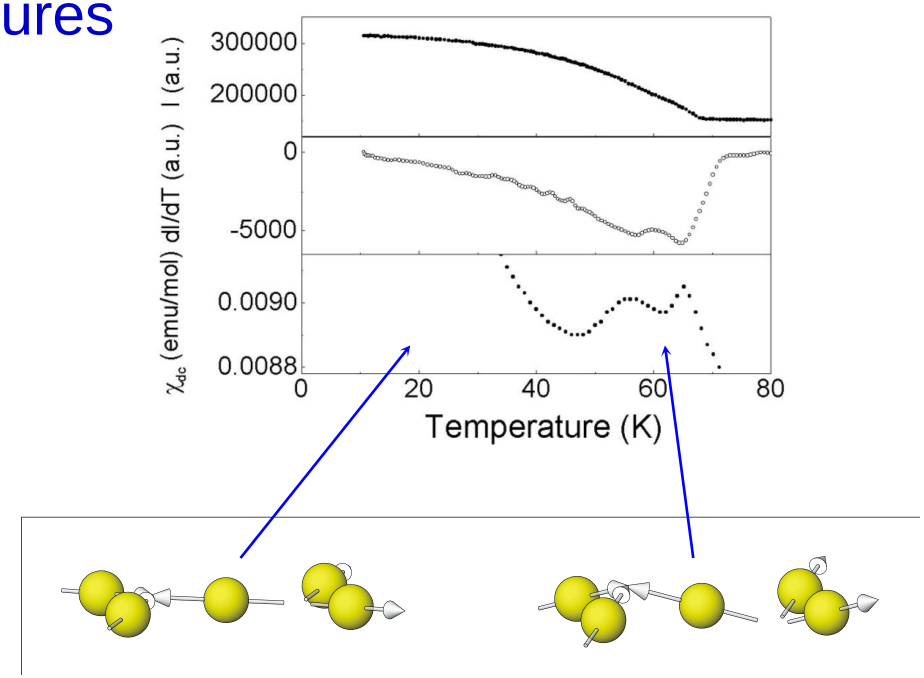


Taking a closer look at powders

- Track change in magnetisation through thermodiffraction from magnetic Bragg peak on D20 at ILL (potassium iron jarosite)
- Observe two transitions that follow features in $d\chi/dT$
- Refine symmetry-allowed structures







At 18K coplanar structure

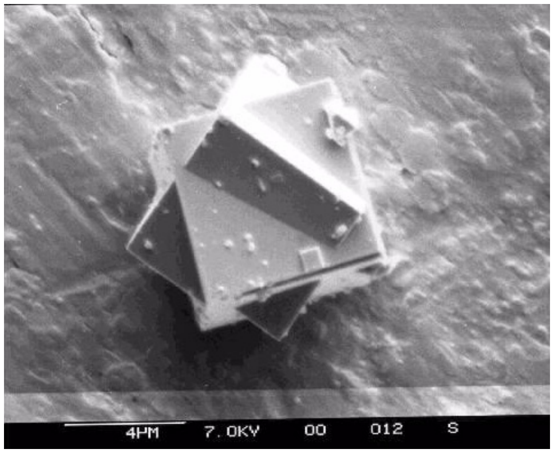
< 4° out-of-plane; 3.9μ_B

At 62K umbrella structure

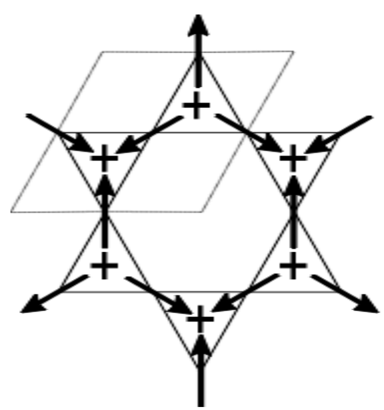
16° out-of-plane; 1.8μ_B

How coplanar is ‘coplanar’

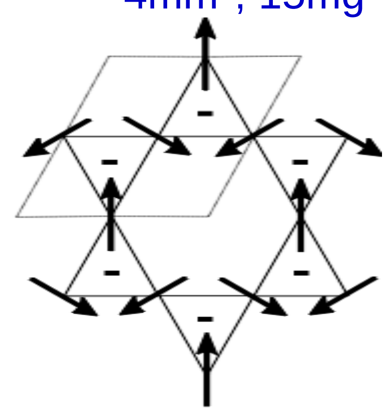
- *Zero-field* polarimetry allows *all* spin components to be determined (IN20, ILL)
- $KFe_3(SO_4)_2(OH)_6$ at 20 K has coplanar array within 1°; q =0 with +1 chirality



natural sample of $KFe_3(SO_4)_2(OH)_6$
$4mm^3$; 15mg



chirality +1



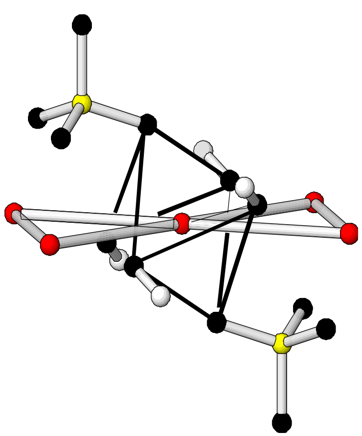
chirality -1

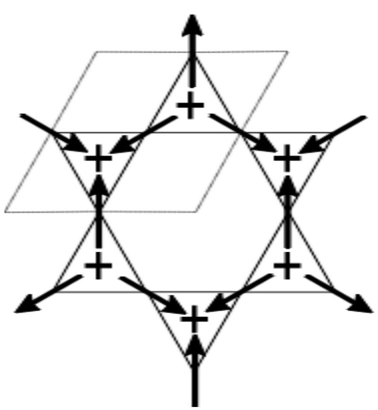
Perturbations to the simple Hamiltonian

- Other likely terms and their consequences

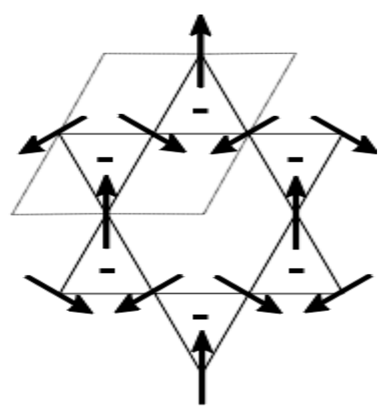
$$H = J_1 \sum_{<i,j>} S_i . S_j + D \sum_i (S_i^{z'})^2 - E \sum_i (S_i^{x'})^2 - (S_i^{y'})^2 \sum_{<i,j>} \mathrm{D}_{ij} . \mathrm{S}_i \times \mathrm{S}_j$$

  - Deviation of FeO_6 from perfect O_h allows ligand-field terms *D*, *E*
    - *D*, *E* favour q = 0 structure, with chirality depending on sign of *E*
  - Symmetry allows Dzyaloshinsky-Moriya terms D_{xy} and D_z
    - D_{xy} leads to canting of moments out of the kagome layers
    - D_z selects q = 0 structure, with chirality depending on sign of D_z
  - Further-neighbour exchange?





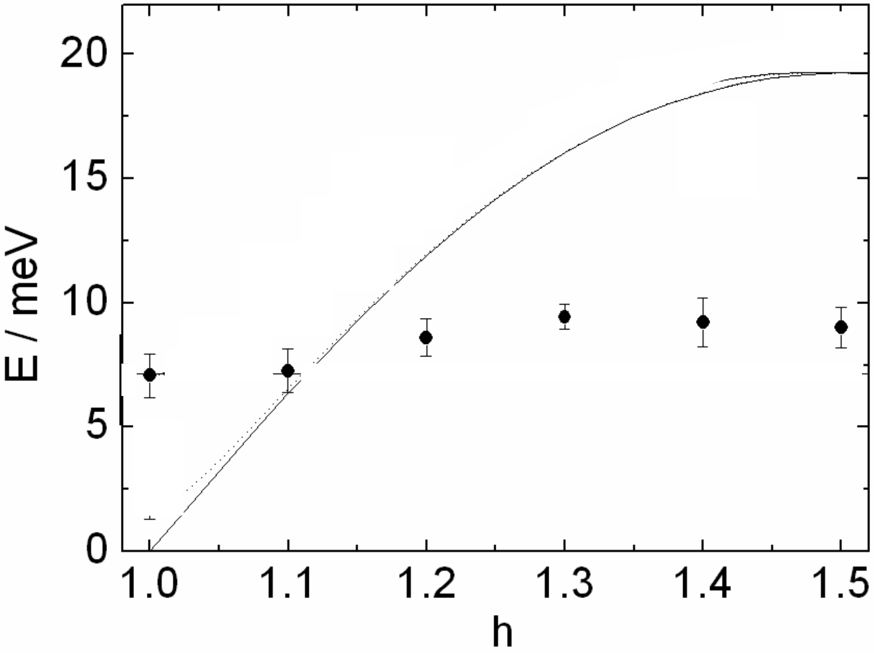
chirality +1



chirality -1

Spin-wave dispersion

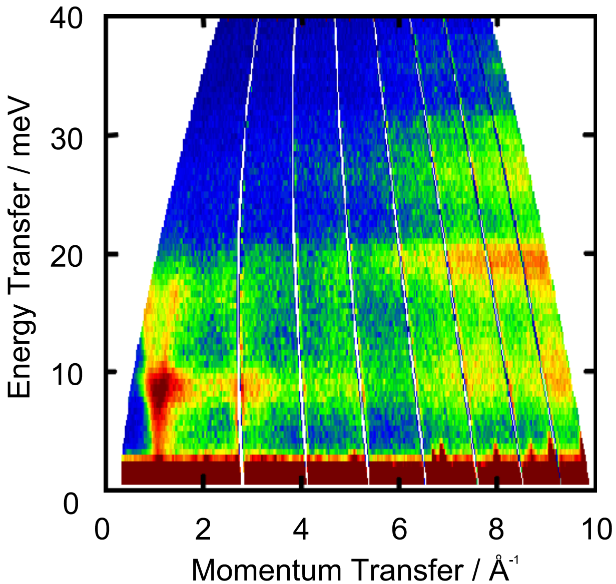
- Measure J and perhaps further terms in the Hamiltonian through measurement of spin-wave dispersion
  - Use natural crystal again (*i.e.* protonated sample, poor BG) on IN8 at ILL
  - Mainly observe one flat branch – intensity makes phonon unlikely
  - Further significant terms in the Hamiltonian present

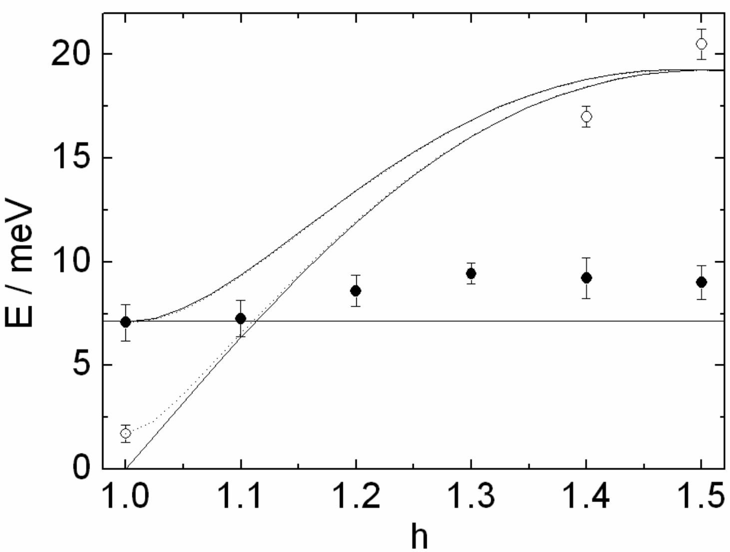


Rare insight from powder data

- Complementary data from deuterated powder on MARI at ISIS
  - Low-dimensionality and low background reveals dispersion plus flat mode
  - Data fitted *either* to ‘ligand field’ *or* ‘DM’ model compatible with known structure
    - J_1 = 3.50(3) meV, D=0.47(2) meV, E = 0.038(2)
    - J_1 = 3.33(5) meV, D_z=0.21(1) meV, and $|D_{xy}|$=0.10(2) meV from canting limit of 1° (Coomer *et al*, JPCM **18** (2006) 8847)

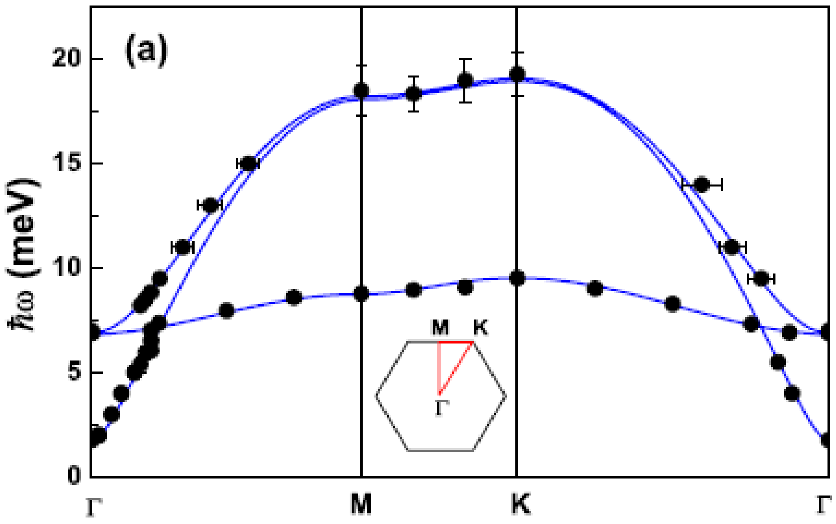
$$H = J_1 \sum_{<i,j>} S_i . S_j + D\sum_i (S_i^{z'})^2 - E\sum_i (S_i^{x'})^2 - (S_i^{y'})^2 \sum_{<i,j>} \mathrm{D}_{ij}.\mathrm{S}_i \times \mathrm{S}_j$$





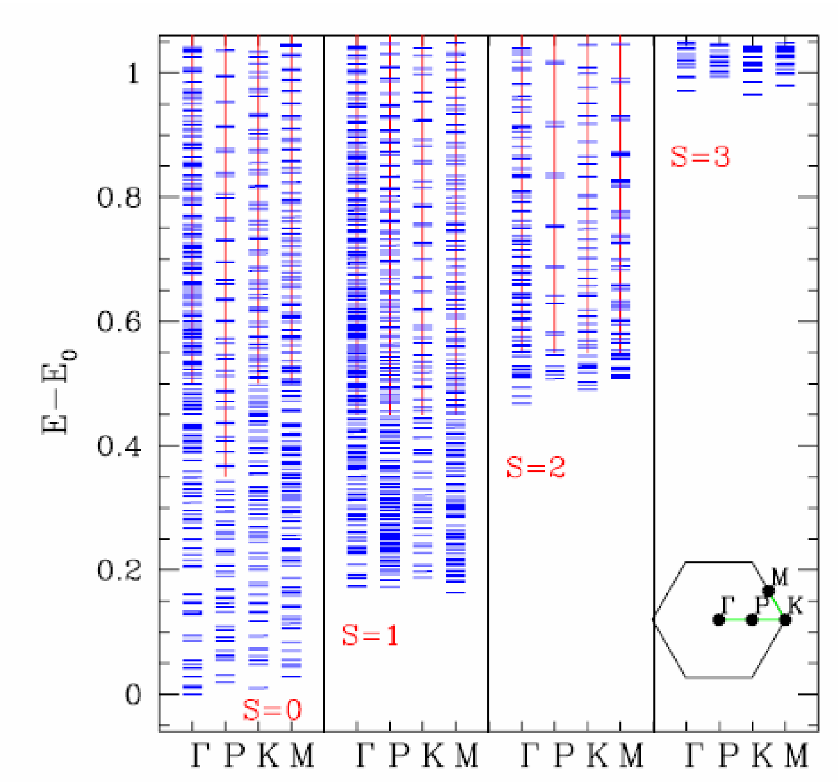
Coup de grace – best crystal data

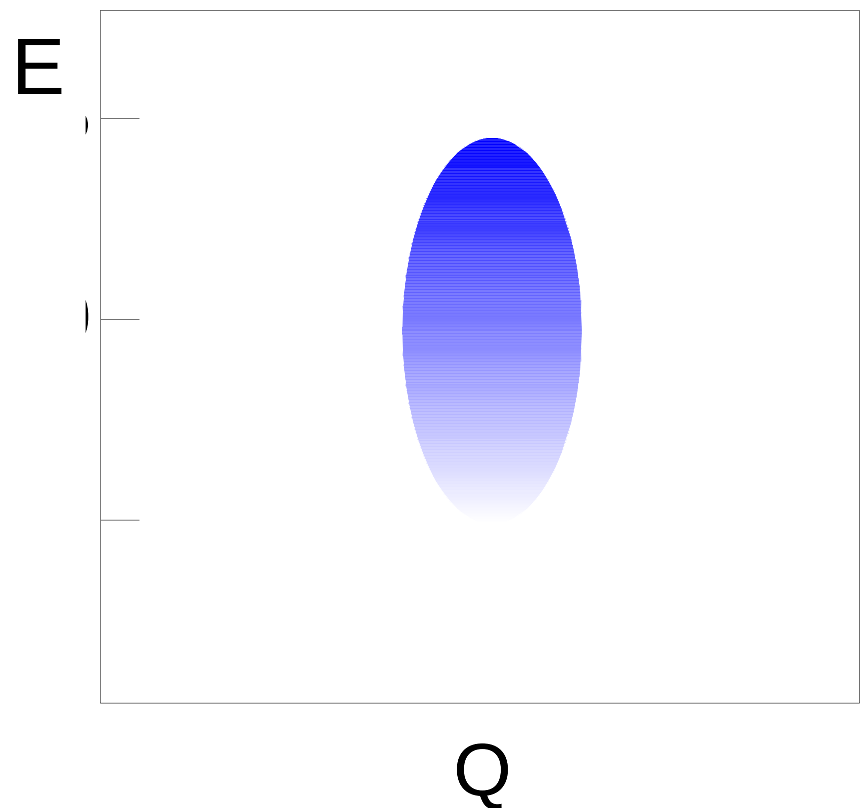
- Arguably best work now done on *synthetic* single crystal
  - (Matan et al, PRL **96,** 247201 (2006); Yildirim and Harris, PRB**73** (2006)214446)
- All terms in Hamiltonian compatible with spin structure, excitations and thermodynamics
  - Nnn J_2 necessary (e.g. small dispersion of 'flat' mode)
  - DM term alone works slightly better than LF terms alone (but both probable)



Now introduce low spin…

- Theory generally indicates some form of singlet ground state
  - Still not clear what is the *precise* nature of the SGS
  - Gapped or gapless with respect to triplets?
  - What might we see with neutrons?

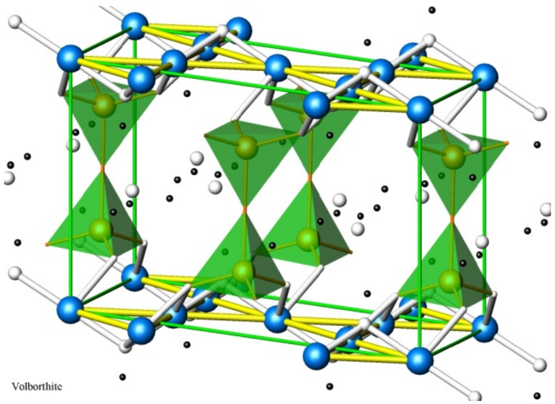


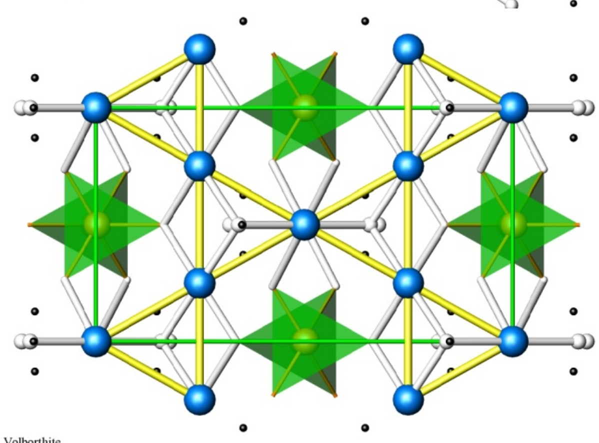


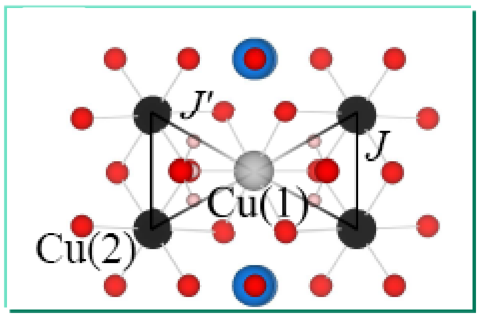
e.g. Sindzingre and Lhuillier, EPL 88 (2009) 27009

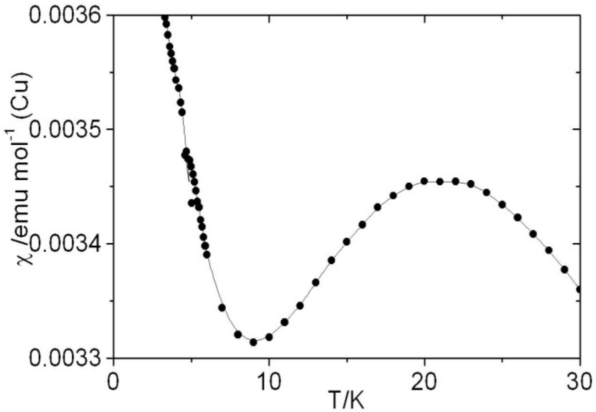
Real cases: (i) Volborthite

- Volborthite ($Cu_3V_2O_7(OH)_2 2H_2O$) - kagome Cu^{2+} layers ($S = ½$)
  - Significant afm coupling ($|\theta| \cong$ 115 K, $J \cong$ 90K), cusp in χ near 20 K
    - Hiroi *et al*, JPSJ 70 (2001) 3377; Bert et al PRL 95 (2005) 0783203
  - Note: small (orthorhombic) distortion - bond lengths 3.03 and 2.93 Å
  - Two distinct Cu sites
  - No magnetic lro down to 20 K



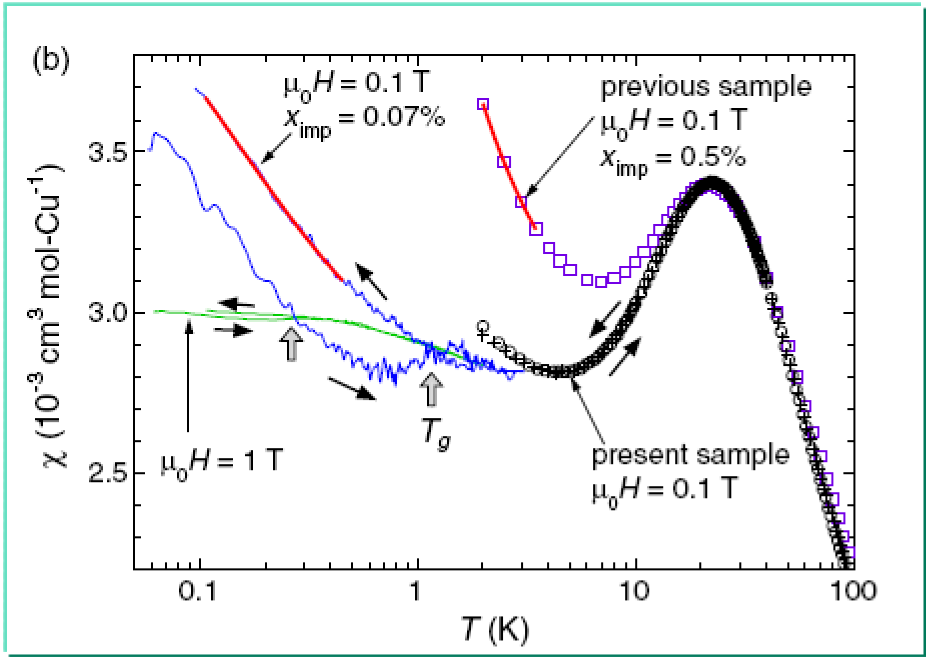


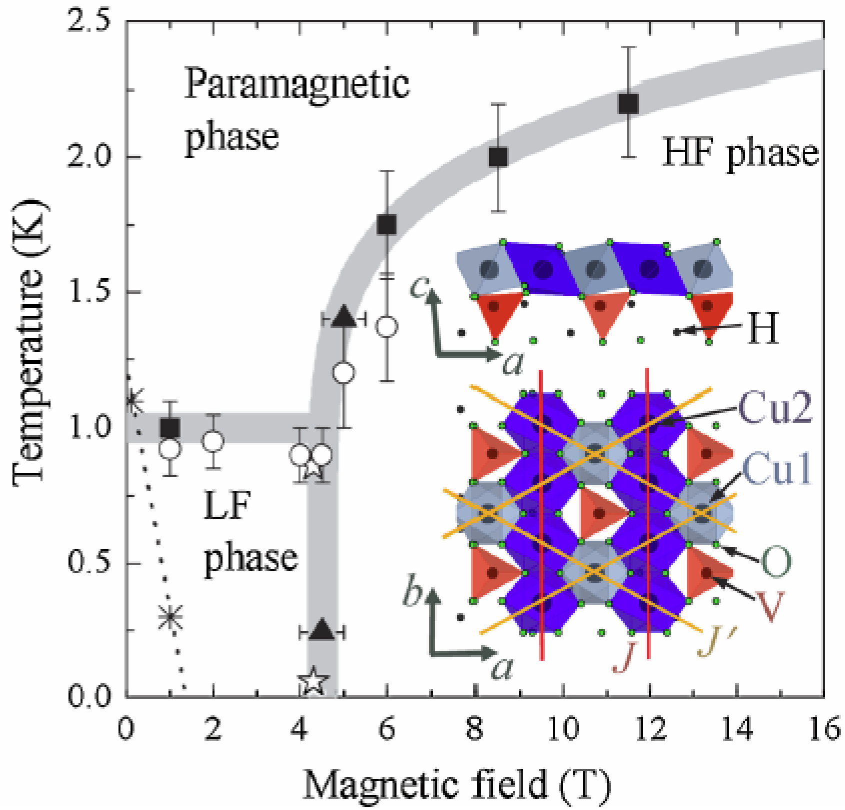




Imperfections

- Susceptibility, ^{51}V nmr and μSR data very sensitive to composition
  - Typical preparation yield 1% non-magnetic entity on Cu^{2+} site; achieve 0.07% (Yoshida *et al*, PRL 103 (2009) 077207)
- ^{51}V nmr (*ibid*) indicates spin transition near 1 K
  - Below approx 1 K there are two timescales of fluctuation, one extremely small (100 x $1/T_2$)
  - High-field phase above 4.5T

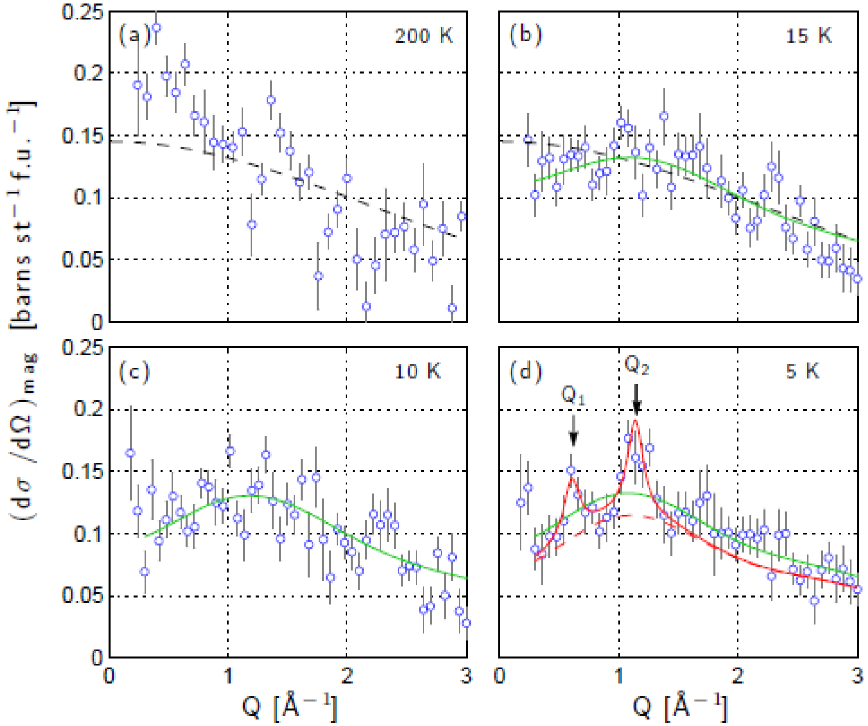




NS from volborthite - map S(Q)

- Elastic and inelastic NS measurements on D-compound on D7 (ILL)
  - ‘Perdeuterated’ sample 99 % D - incoherent scattering still significant
  - 200 K (~ 2J) magnetic S(Q) ~ Cu^{2+} form factor
  - Broad feature seen at lower T: n-n model at 15 K - $\xi \sim r_{Cu\text{-}Cu}$ (33 % of S(S+1))
  - Sharper features appear at lower T: Q_1 = 0.65(3) $Å^{-1}$; Q_1 = 1.15(5) $Å^{-1}$; $\xi \sim 8\, r_{Cu\text{-}Cu}$

Nielsen et all, arXiv: 1001.2462v2 (2011)

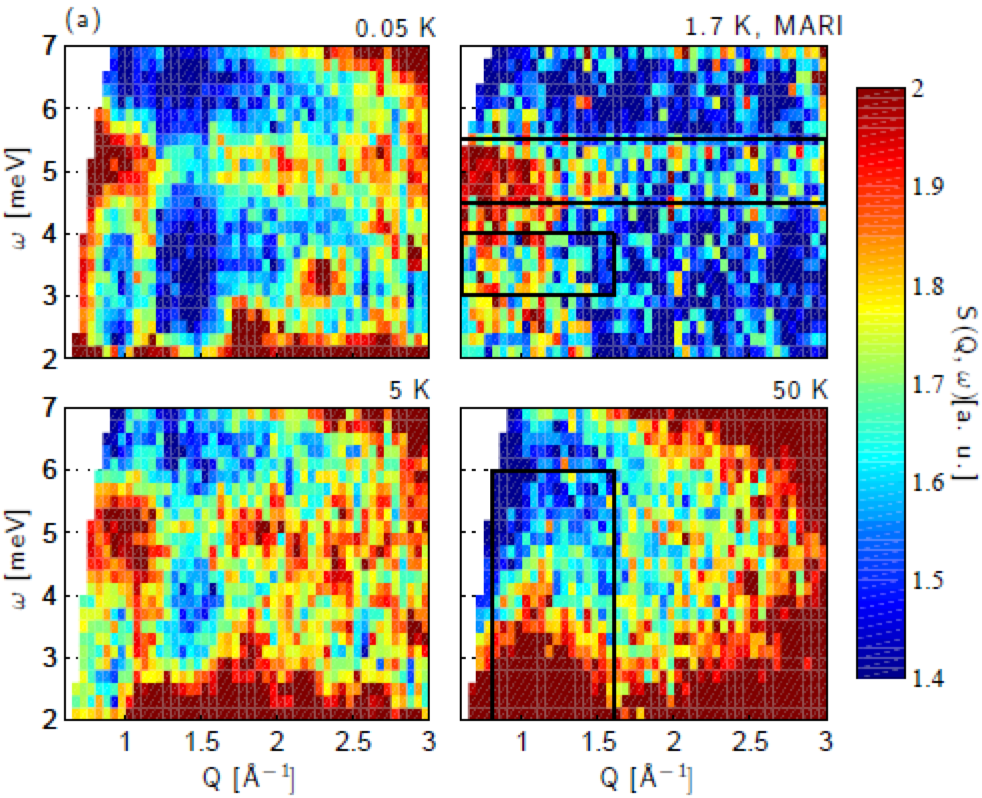


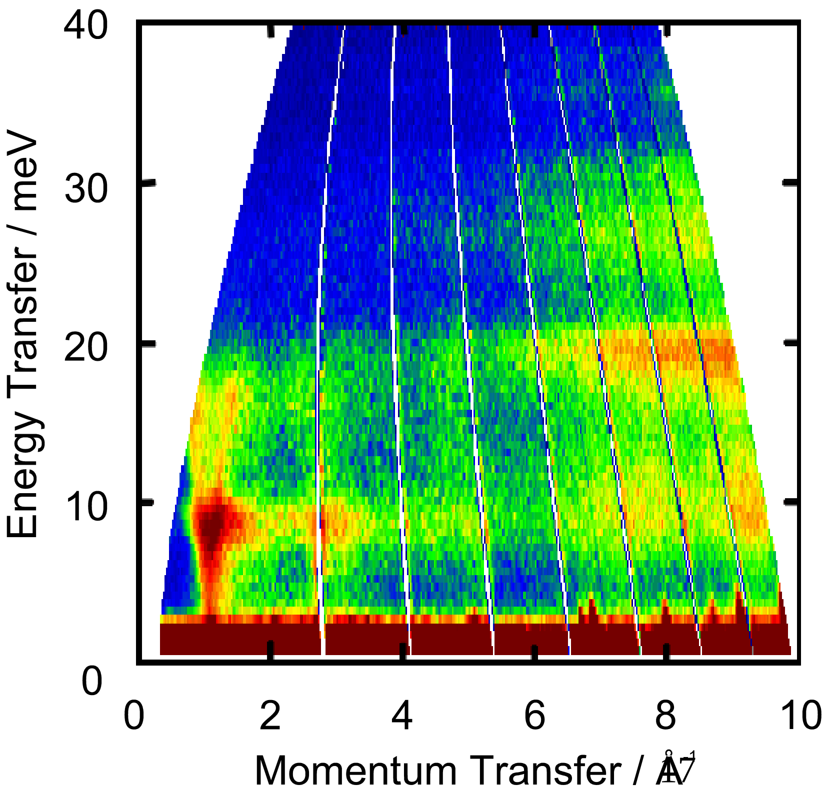
NB: no current models for static correlations in Volborthite (various combinations of J_1, J_2, DM) predict Q1

NS from volborthite - map S(Q), S(Q,ω)

- INS used to map S(Q,ω) vs T (IN4 at ILL, MARI at ISIS)
- Flat mode ~ 5 meV: singlet-triplet excitation from defects ??

- Lower-temperature dispersive mode appears similar to spin-waves
- c.f. potassium jarosite

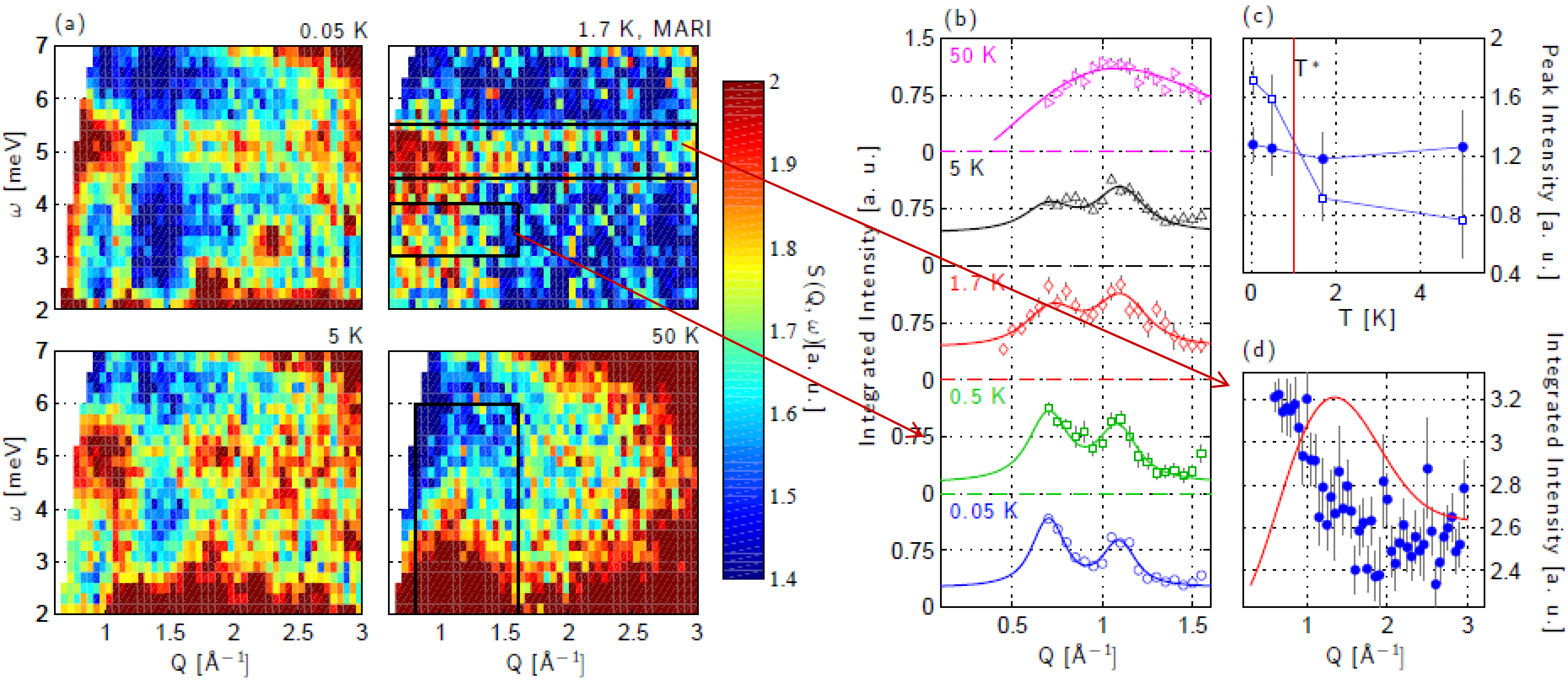




Nielsen et all, arXiv: 1001.2462v2 (2011)

NS from volborthite - map S(Q), S(Q,ω)

- INS used to map S(Q,ω) vs T (IN4 at ILL, MARI at ISIS)
- Flat mode ~ 5 meV: singlet-triplet excitation from defects ? Q-dependence wrong probably intrinsic – 'weathervane' mode in SRO state, E ~ DM, J, S.
- Lower-temperature dispersive mode appears similar to spin-waves - supported in regions of SRO (stabilised by DM ?) – and more spectral weight at Q_1 below 1 K



Nielsen et all, arXiv: 1001.2462v2 (2011)

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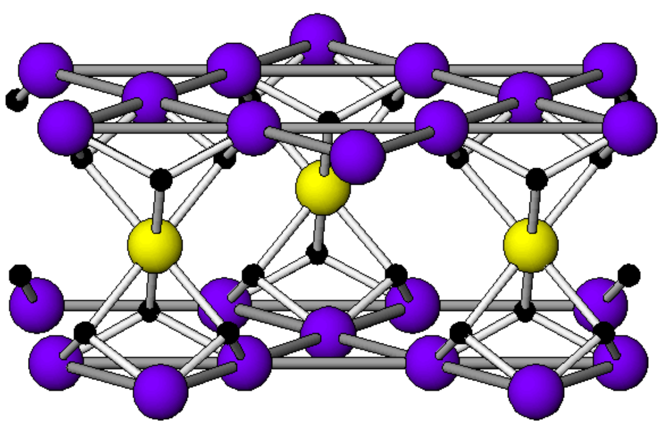
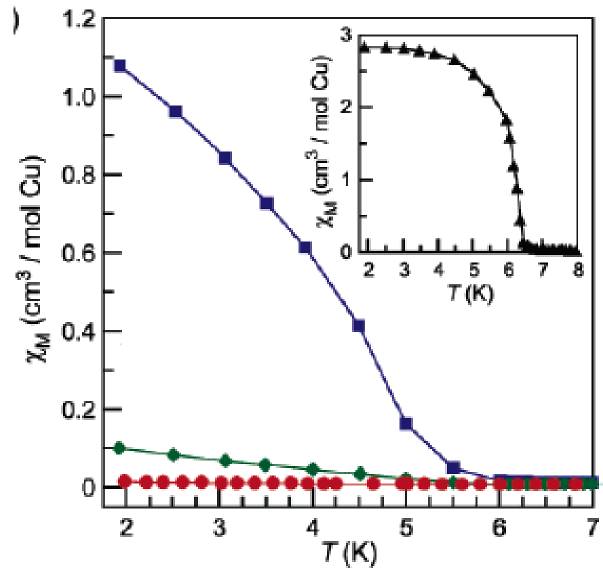
Real cases: (ii) Herbertsmithite

- Parent compound: γ-$Cu_4(OH)_6Cl_2$ - dope with Zn: $Zn_xCu_{4-x}(OH)_6Cl_2$
  - Parent compound has pyrochlore structure
  - Zn selects sites between kagome layers (no JT distortion)
  - For Cu_3Zn compound, yields undistorted kagome layers separated by Zn
    - But NB – there is generally intersite mixing – order of 5-10% deficient Cu on Cu_3 layer
  - Zn severs weak FM component of Cu-Cu exchange ($|\theta|\uparrow$ as %Zn $\uparrow$
    - Intra-plane Cu-O-Cu 119º; inter-plane Cu-O-Cu 97º
    - (Shores et al, JACS 127 (2005) 13462)

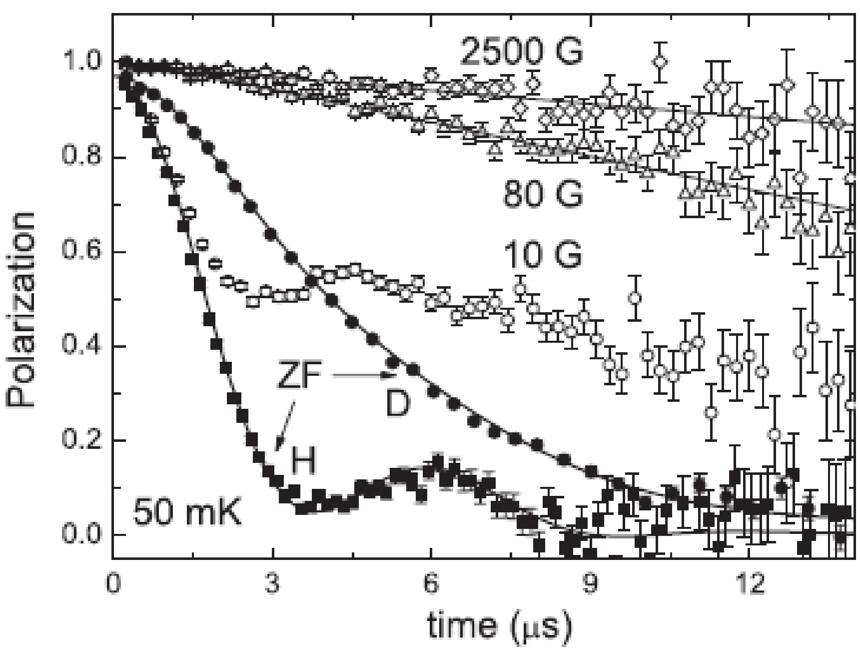
x = 0, 0.5, 0.66, 1.0

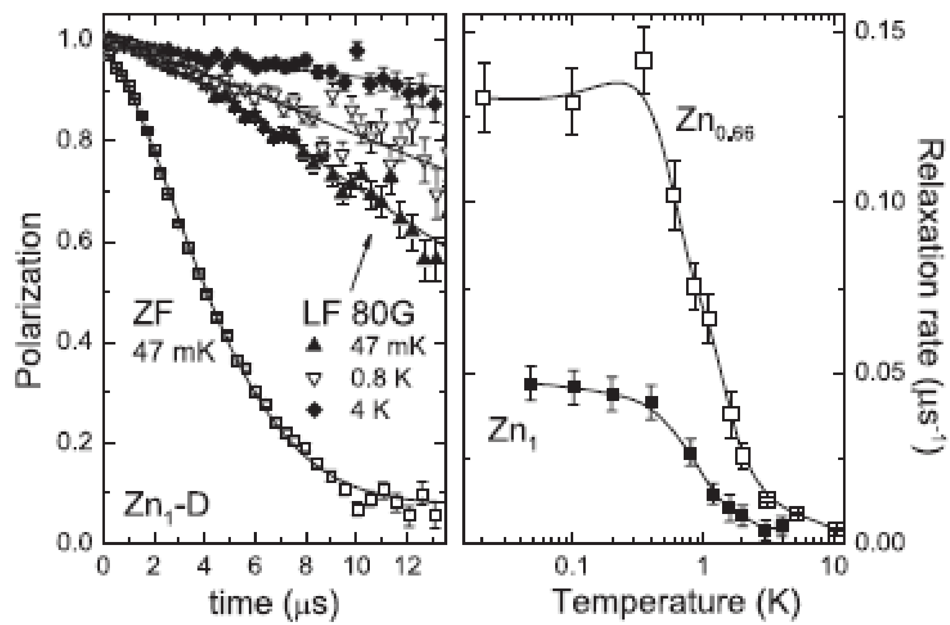




Spin freezing in paratacamite series - $Cu_{4-x}Zn_x$

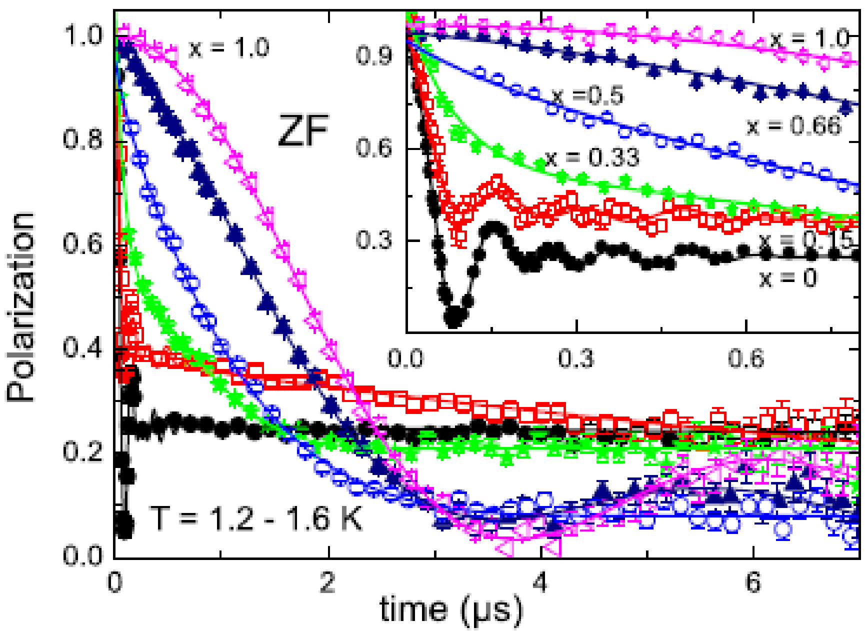
- Perform μSR measurements on $Zn_xCu_{4-x}(OH)_6Cl_2$ ($0.0 \le x \le 1$) plus some deuterated analogues (Mendels, Bert *et al*, PRL **98** (2007) 077204)
  - Oscillations in ZF for x = 1 (H) compound – attributed to OH-μ (p-μ dd)
  - No change in this frequency down to 50 mK – no electronic spin freezing
  - Additional low-frequency dynamics in long-time tail (18 G – c.f. 500 G in x = 0)
    - Slow relaxation slows down below 1 K
    - Implies most of spins are in singlet state or fluctuating too quickly for muons

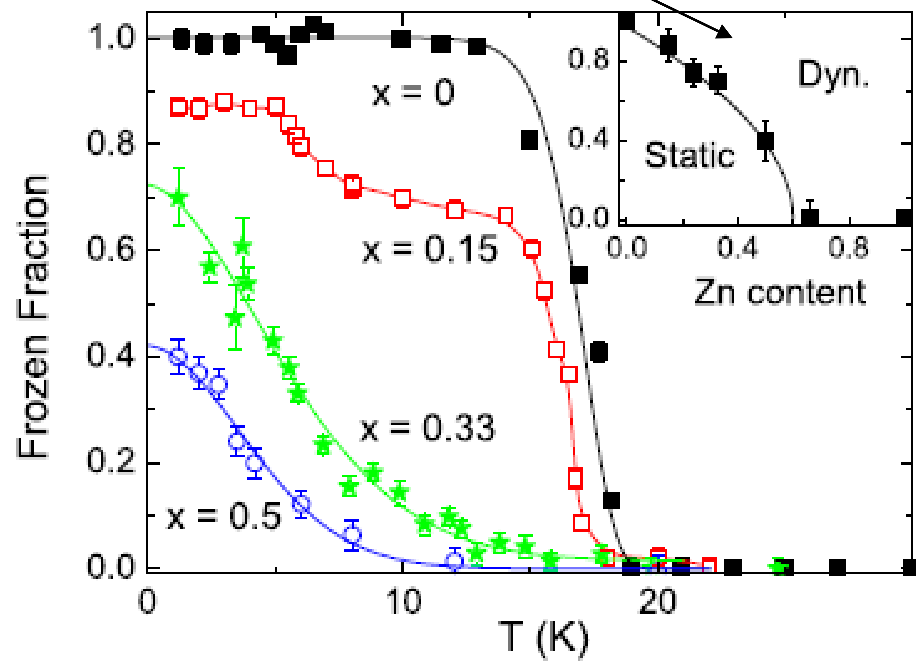




Spin freezing in paratacamite series - $Cu_{4-x}Zn_x$

- Track behaviour with x
  - For x ≤ 0.15 distinct oscillations plus paramagnetic term
  - For x = 0.33, x = 0.5 freezing transition broader and at lower T
  - Higher values of x only dynamic down to lowest T (record θ_{CW}/T_c >6000)





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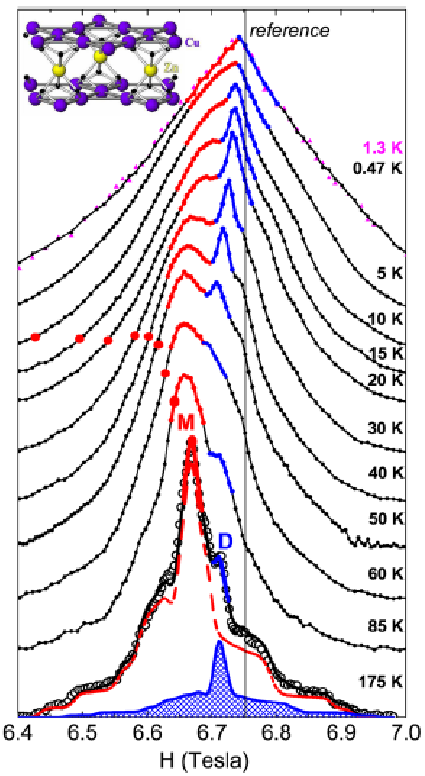
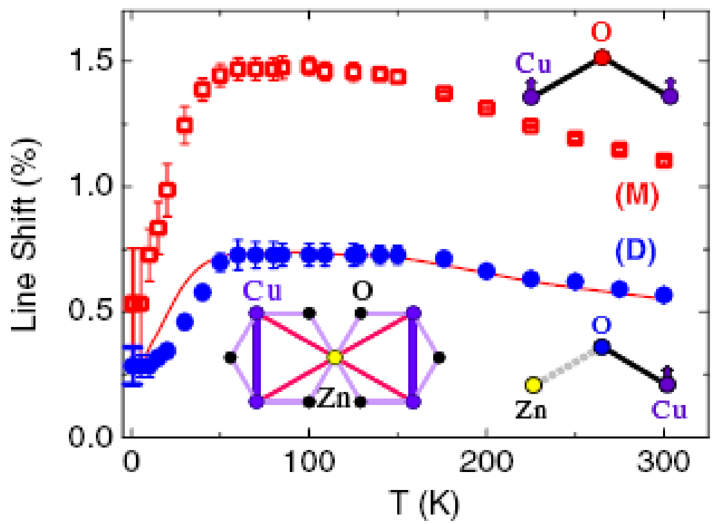
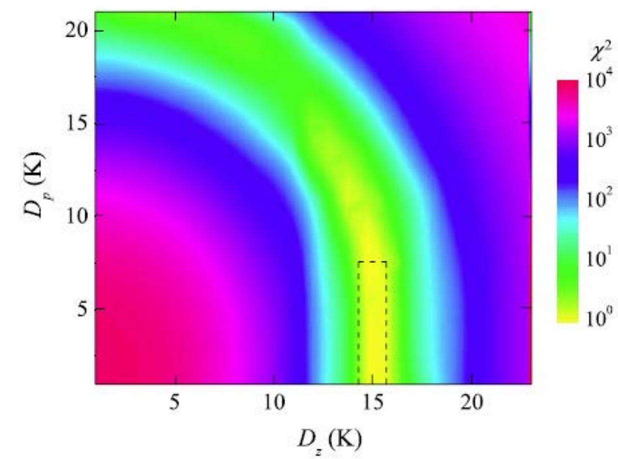
Spotting the imperfections

- ^{17}O NMR - site selective χ: observe 2 O sites, with 2 or 1 nn Cu - x % defects
  - Broad maximum in intrinsic χ of Kagome lattice at 30 K (≈ J/2) and $\chi \rightarrow$ non-zero value as T $\rightarrow$ 0 : implies non-singlet character at lowest accessed T
- High-temperature ESR – significant DM term: (D/J) ~ 0.08 (D_z ~ 15 K)
- Heat capacity and neutron data shows ~ 6% Cu^{2+} on Zn^{2+} sites



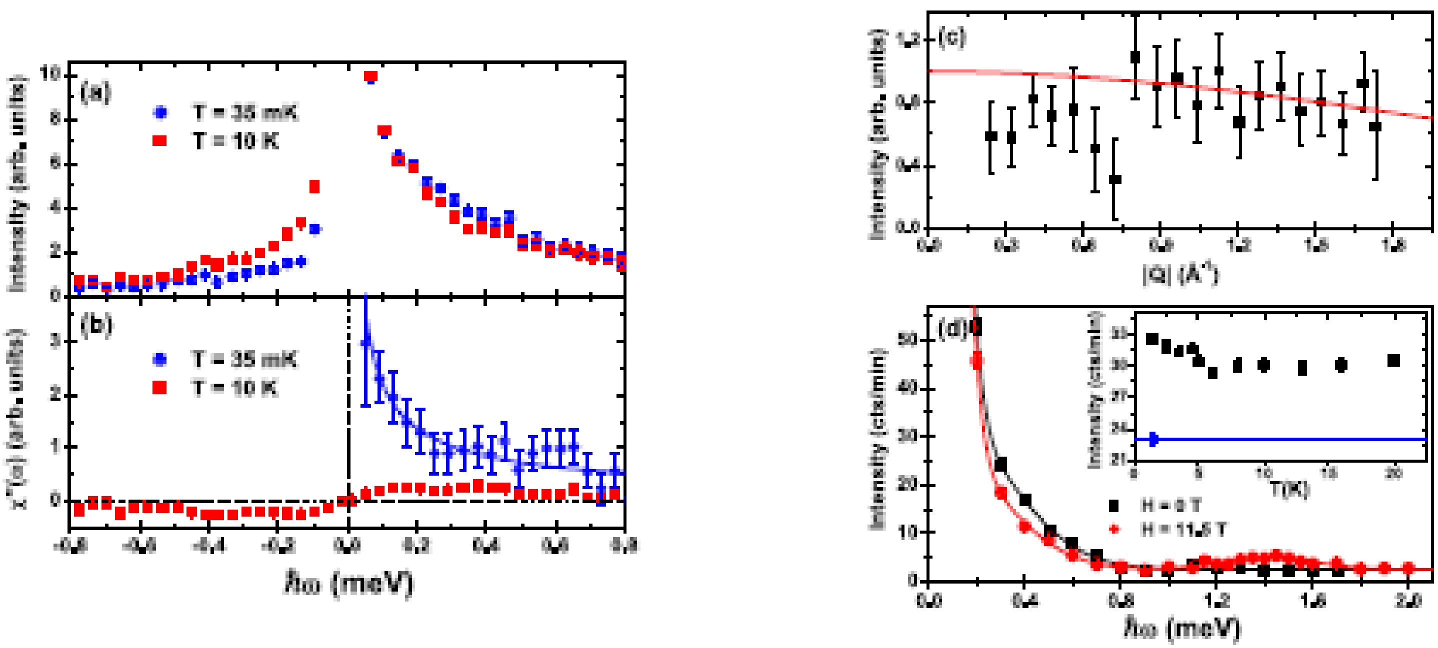




Olariu *et al*, PRL 100 (2008) 087202; Zorko *et al*, PRL 101 (2008) 026406

Neutron probe of correlations

- INS on Herbertsmithite (Helton *et al*, PRL 98 (2007) 107204)
  - Broad spectrum of low-energy excitations - no evidence of order to 50 mK or gap to 0.1 meV (J/170)
  - No particular structure in S(Q) integrated from 0.22 – 0.5 meV
  - Weak excitation seen at 1.3 K in 11.5 T (not seen in zero field)

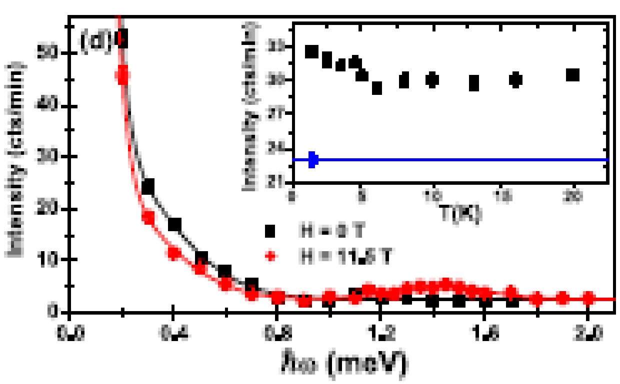


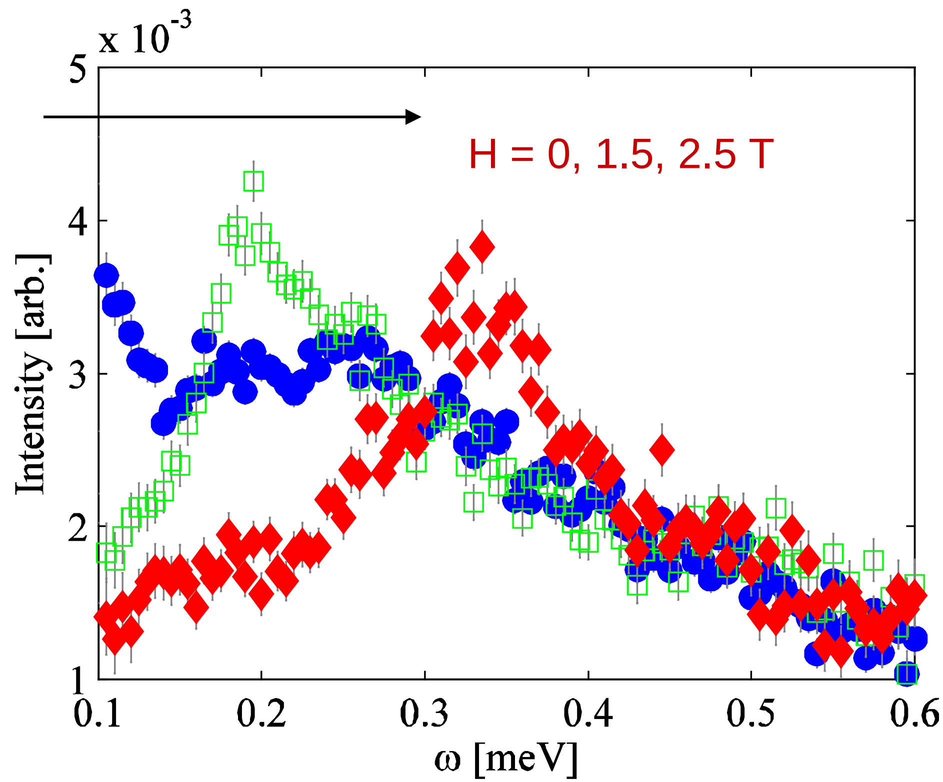
NEUTRONS FOR SCIENCE

Focussing in on low-energy feature…

- Go to higher flux and resolution
  - Measure on high-flux cold spectrometer IN5 at ILL (resolution 0.02 meV fwhm)
  - Zeeman-splitting for (impurity?) spins with g = 2

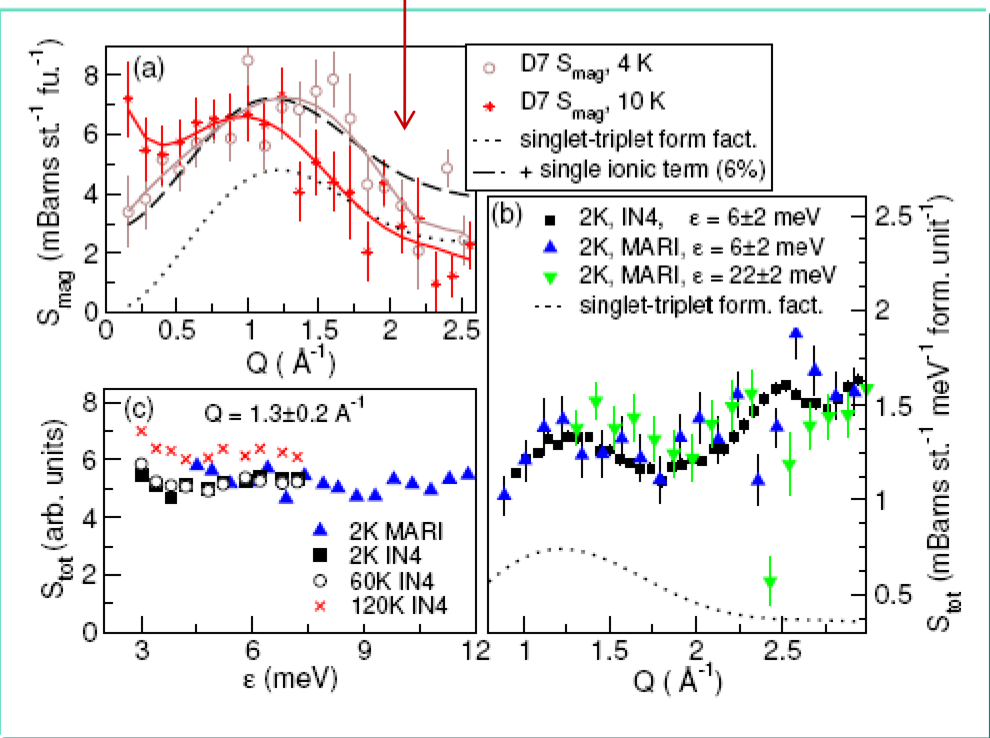
de Vries et al, Phys. Rev. Lett. 103 (2009) 237201;
similar feature in 0.66 sample studied by Lee et al, Nature Mat. 6 (2007) 853)

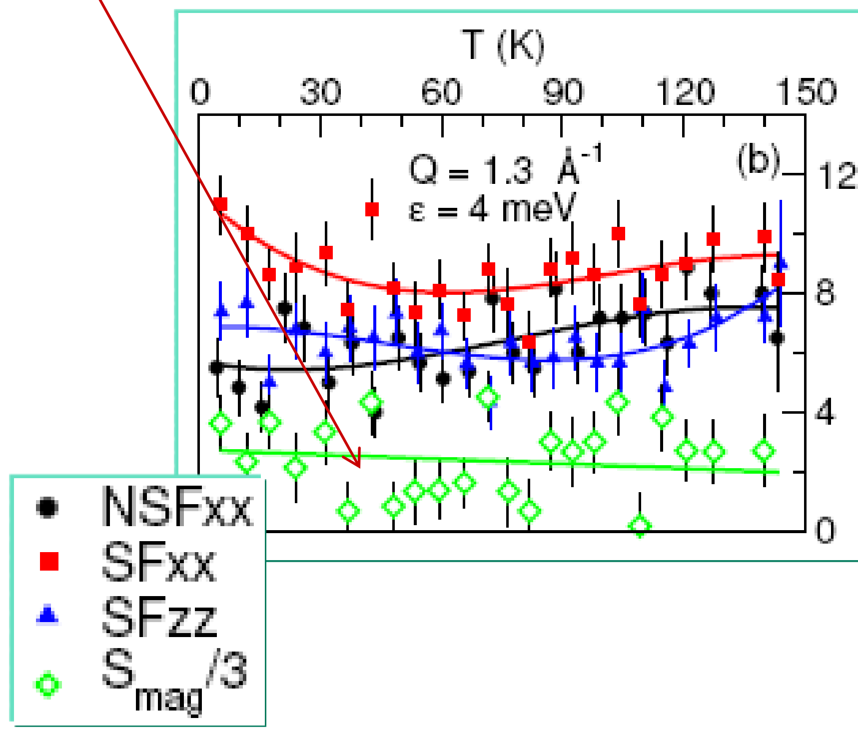




…and then up to higher energies

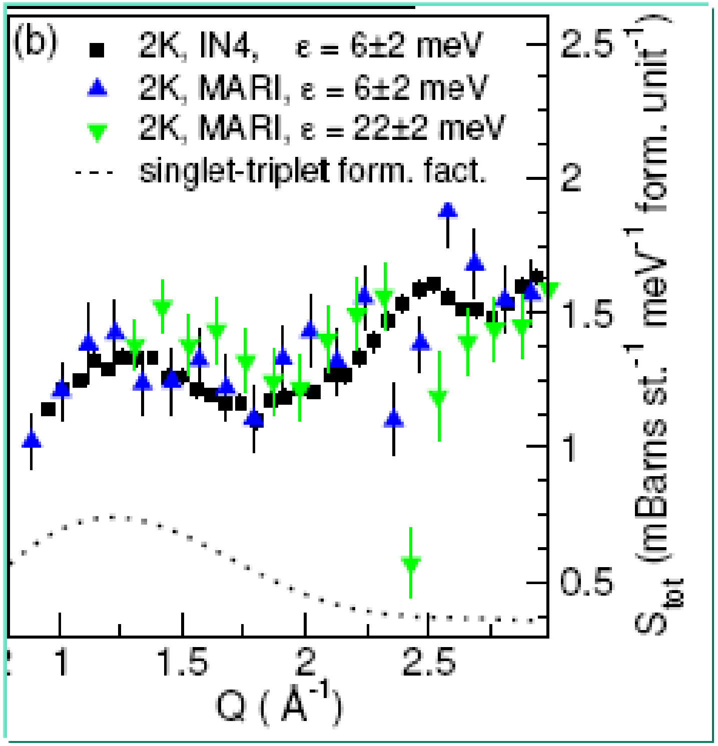
- Pick out magnetic scattering with polarisation analysis
  - Magnetic scattering on D7 instrument (integrated up to 6.5 meV energy transfer) compatible with single-triplet (AF dimer) form factor + single-ion term (6% intersite)
  - No change with temperature from 2 – 150 K !

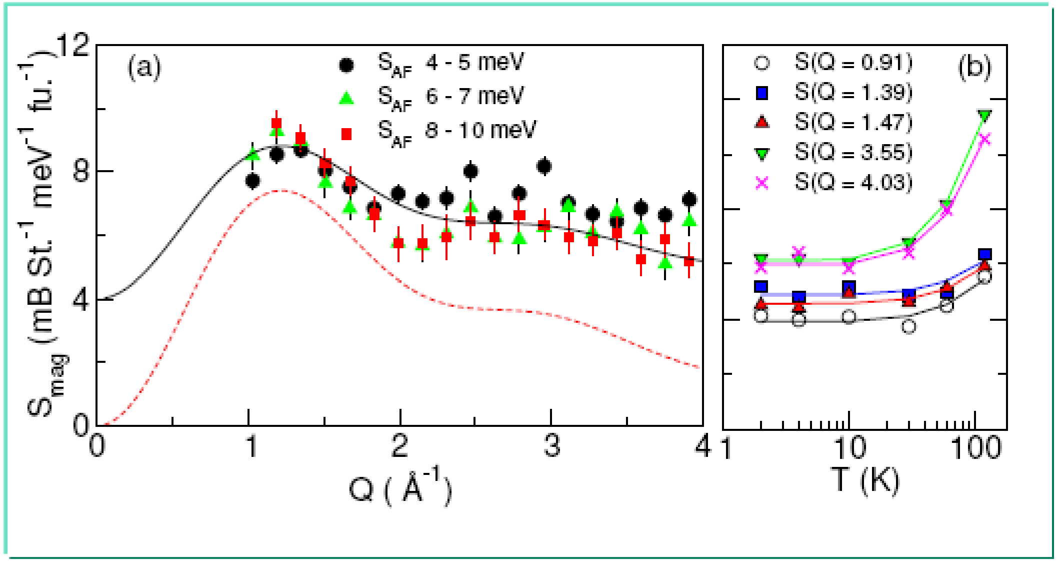




…and then up to higher energies

- Go to yet higher energies on same sample (no polarisation)
  - Up to 17.2 meV on IN4 (ILL) and 56 meV (MARI,ISIS)
  - Correct for phonons – fitting data to T-independent and T-dependent term
  - Very little change with energy to 22 meV





Summary

- Classical kagome system
  - Structure and dynamics well treated with many common perturbative terms added to the Hamiltonian - J_{nnn}, ligand field, DM terms
- Volborthite
  - No long-range order to 30 mK;
  - *Very* sensitive to impurities
  - Low temperature phase with SRO (ξ ~8 $r_{Cu\text{-}Cu}$) that supports spin waves
- Herbertsmithite
  - No spin freezing down to at least 50 mK; zero or very small singlet-triplet gap
  - Very sensitive to disorder and D
- Wish list
  - Single crystals' with control of intersite mixing
  - New systems with variable disorder, D, disorder…
  - Complementary theory – what is the ground state?

Without whom none of this would happen…

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