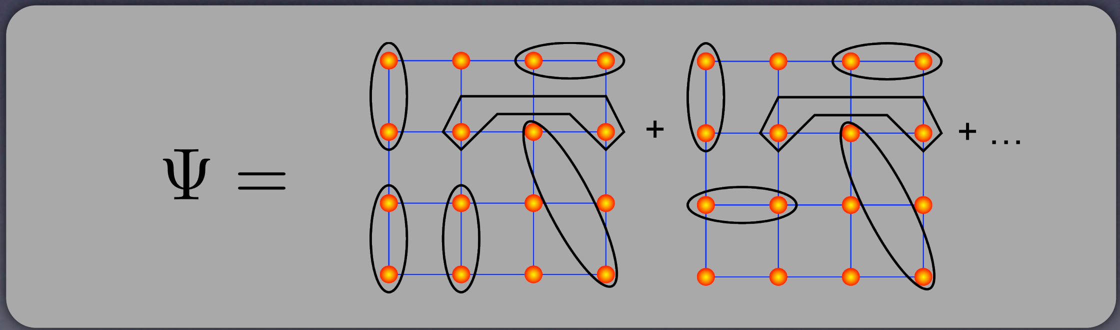
Quantum Spin Liquids

Ultimate frustration?

- Can quantum fluctuations prevent order even at T=0: f=∞?
- Many theoretical suggestions since Anderson (73)
  - "Resonating Valence Bond" QSL states



Variational methods

- Probably the most flexible and physical approach which has a good success record in theoretical physics is the variational wavefunction
- Pioneered by PW Anderson, who suggested "RVB" state for the triangular antiferromagnet (he was wrong, obviously!)
- Idea: best state for two spin-1/2 spins is a "Valence Bond" (VB), just a spin singlet

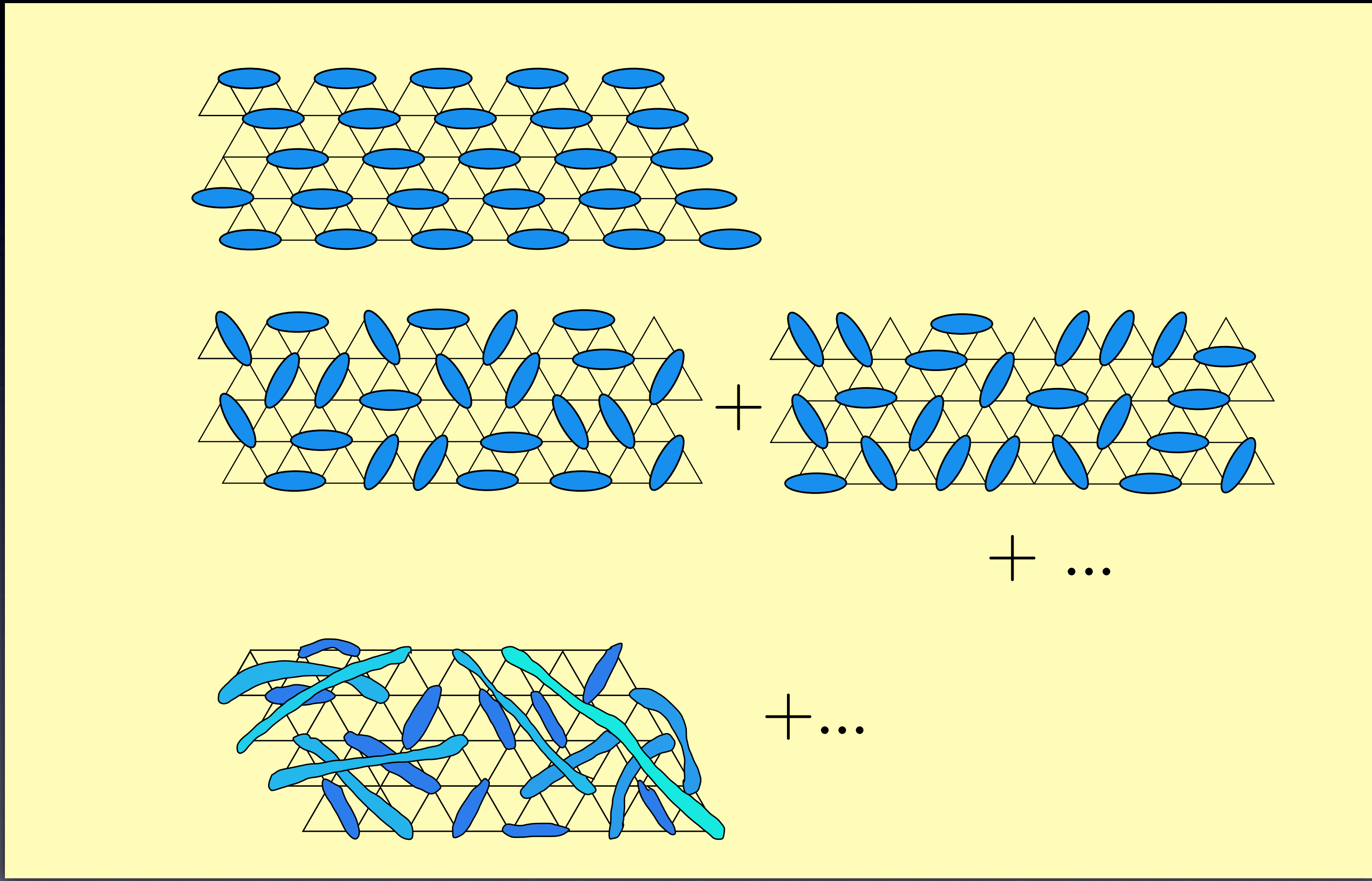
$$|VB\rangle = \frac{1}{\sqrt{2}} \left(| \uparrow\downarrow\rangle - | \downarrow\uparrow\rangle \right)$$

VB states

VBS

Short-range RVB

Long-range RVB



General expectations for VB states

- Formation of a VB creates a gap to excite those two spins
  - Long-range VBs are more weakly bound, so with long-range VBs there need not be a spin gap for the system as a whole
  - But generally the susceptibility will be suppressed by VB formation
  - Excitations associated with moving VBs can have low energy but do not carry spin

The "landscape"

- As you can imagine, the number of RVB variational wavefunctions is vast
- It is now clear that the number of distinct Quantum Spin Liquid (QSL) *phases* is also huge
  - e.g. X.G. Wen has classified *hundreds* of different QSL states all with the same symmetry on the square lattice (and this is *not* a complete list!)
  - This makes it difficult to compare all of the states
  - and there may be many states with similar energies

Slave particles

- One approach to constructing variational wavefunctions is to begin with a state with free particles, and *project* it back to a spin wavefunction
  - Use a reference Hamiltonian

$$H_{ref} = \sum_{ij} \left[t_{ij} c^{\dagger}_{i\alpha} c_{j\alpha} + \text{h.c.} + \Delta_{ij} c^{\dagger}_{i\uparrow} c^{\dagger}_{j\downarrow} + \text{h.c.} \right]$$

  - Project

$$|\Psi_{var}\rangle = \prod_i \hat{P}_{n_i=1} |\Psi_{ref}\rangle$$

Spinons and gauge theory

- It is usually believed that to such a wavefunction there corresponds an effective theory in which the $c_i, c_i^\dagger$ fermions are elevated to "almost" real quasiparticles: spinons
- However they generally carry a gauge charge and interact with associated gauge fields that reflect the projection
  - Note that a gauge transformation of the c_i does not change the projected wavefunction

Gauge theories

- All the known (in theory) QSL states seem to have some underlying gauge structure
  - This is probably necessary because of the non-locality of spinons
- Various gauge structures are possible, most commonly U(1) and Z_2
- Also different spinon "band structures" are possible - gapped, Dirac, Fermi surface...
- These gross features are connected to "Projected Symmetry Group" structure (perhaps Sachdev will discuss?)

Gross low-E features from gauge theory

- **How low?**
- U(1) states
  - spinons unpaired
  - strong gauge fluctuations
  - spinons must be gapless in d=2
  - stable in d=3 at T=0 only
- Z_2 states
  - spinons paired
  - weak gauge fluctuations
  - stable in d=2 at T=0
  - T>0 Ising transition in d=3

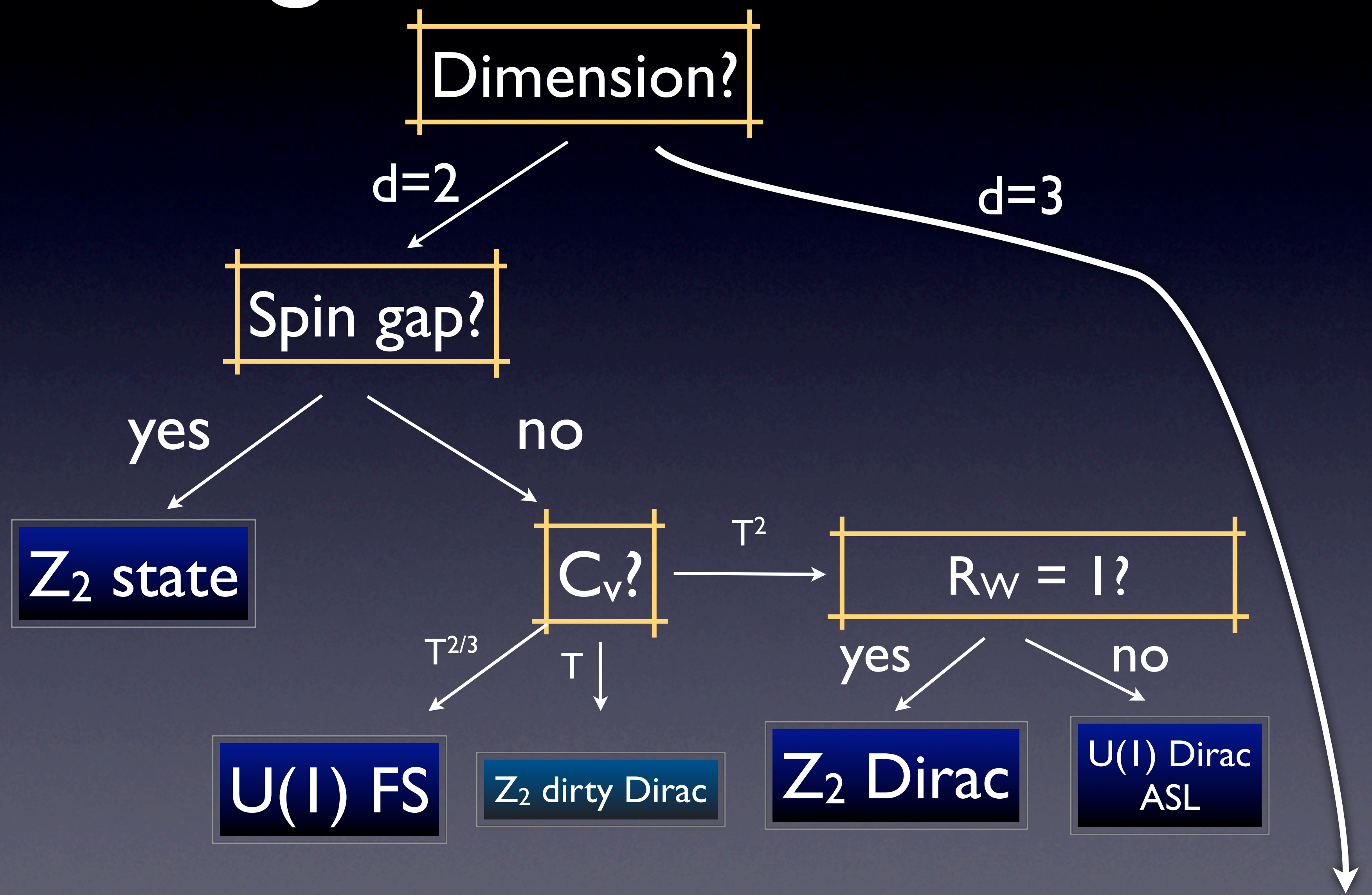
Search for QSLs

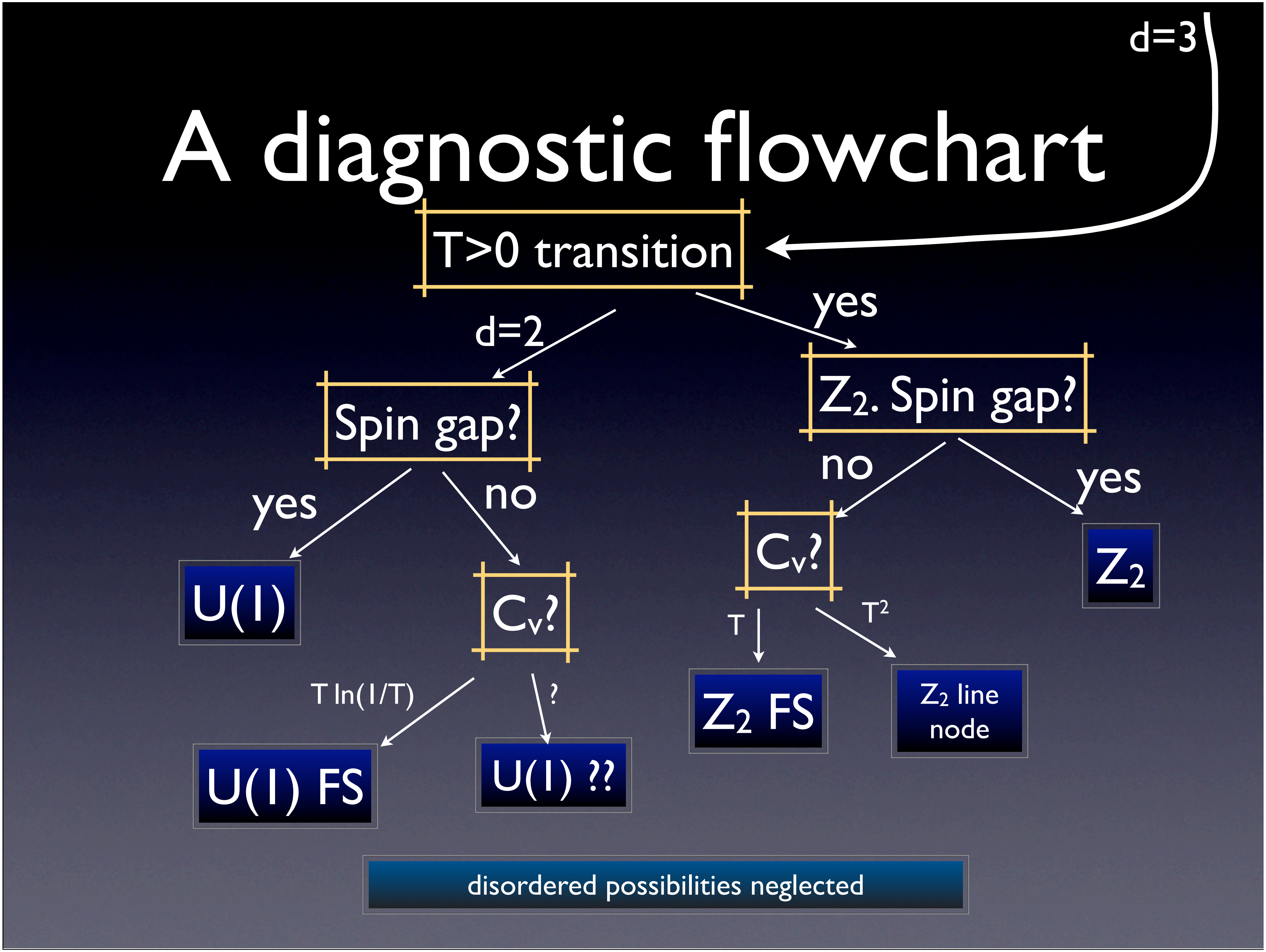
- Where do we look?
  - Spin-1/2 frustrated magnets
  - Intermediate correlation regime (near the Mott transition)

Search for QSLs

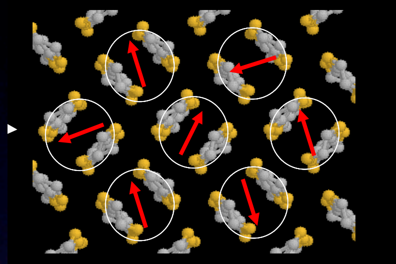
- $1/f = T_c = 0$: no ordering (magnetic or otherwise!)
- No spin freezing (hysteresis, NMR, μSR)
- Structure of low energy excitations
  - $\chi(T)$, $C_v(T)$, $1/T_1$, κ, inelastic neutrons
  - theoretical guidance helpful!
- Smoking gun?

A diagnostic flowchart



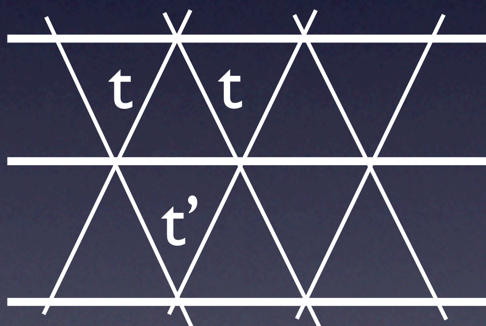

A diagnostic flowchart
d=3
T>0 transition
d=2
yes
Spin gap?
Z_2. Spin gap?
yes
no
no
yes
U(1)
C_v?
C_v?
Z_2
T
T^2
T ln(1/T)
?
Z_2 FS
Z_2 line node
U(1) FS
U(1) ??
disordered possibilities neglected

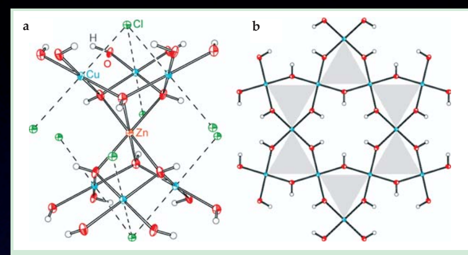
S=1/2 Materials



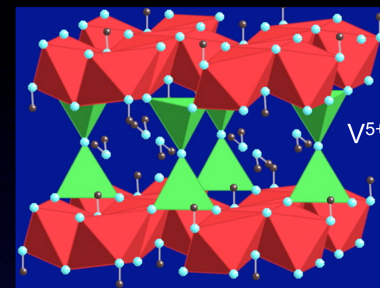
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$

EtMe$_3$Sb[Pd(dmit)$_2$]$_2$

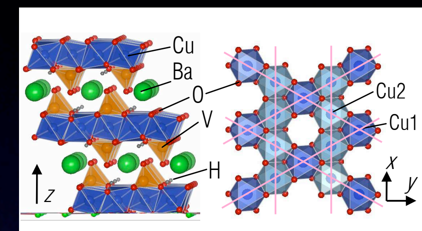




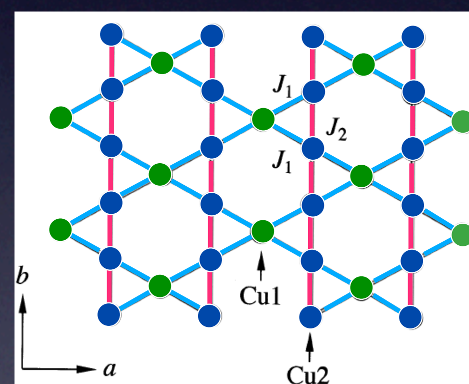
herbertsmithite

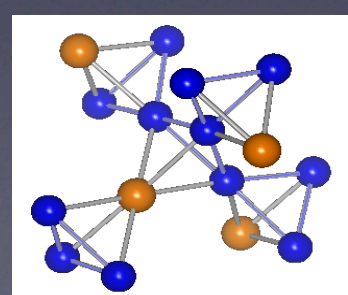


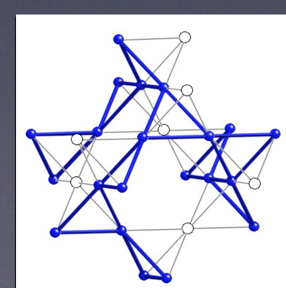
volborthite



vesignieite







Na$_4$Ir$_3$O$_8$

S=1/2 Candidates

material	lattice	ground state	f
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$	≈triangular	QSL?	$>10^3$
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	≈triangular	QSL?	$>10^3$
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	kagome	QSL?	$>10^3$
Cu$_3$V$_2$O$_7$(OH)$_2$ · 2H$_2$O (volborthite)	a-kagome	AF? Glass?	≈100
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesigniete)	a-kagome	QSL?	>100
Na$_4$Ir$_3$O$_8$	hyperkagome	QSL?	$>10^3$

S=1/2 Candidates

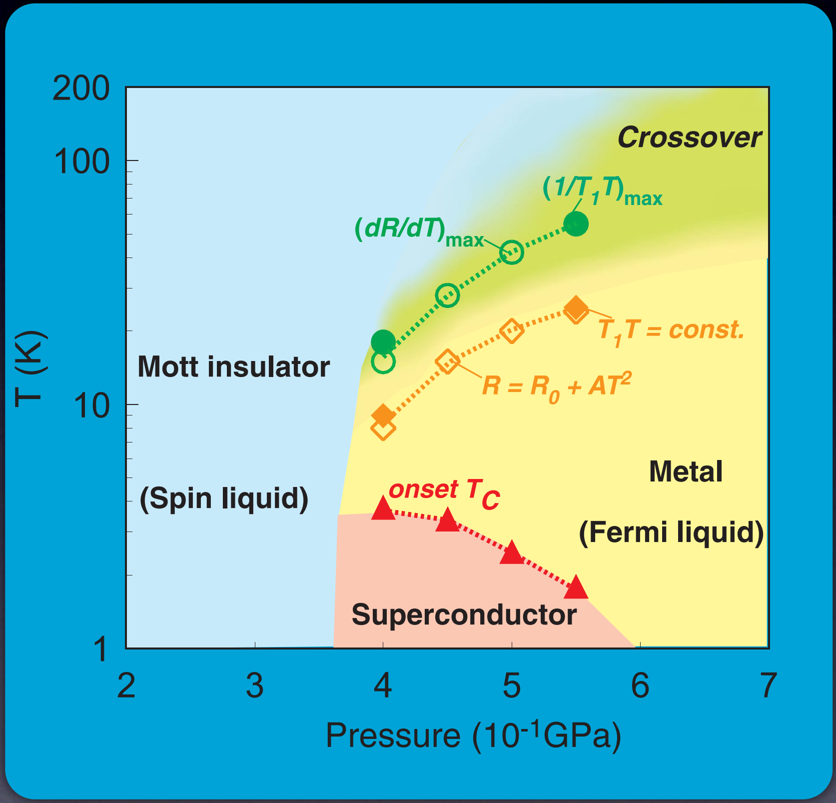
material	lattice	[illegible]	f
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$	≈triangular	[illegible]	>10^3
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	≈triangular	[illegible]	>10^3
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	kagome	[illegible]	>10^3
Cu$_3$V$_2$O$_7$(OH)$_2$ · 2H$_2$O (volborthite)	a-kagome	AF? Glass?	≈100
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesigniete)	a-kagome	QSL?	>100
Na$_4$Ir$_3$O$_8$	hyperkagome	QSL?	>10^3

S=1/2 Candidates

material	$|\Theta_{CW}|$	Type of MI	chemistry
κ-$(BEDTTTF)_2Cu_2(CN)_3$	375K	weak	organic
$EtMe_3Sb[Pd(dmit)_2]_2$	350K	weak	organic
$ZnCu_3(OH)_6Cl_2$ (herbertsmithite)	240K	strong	inorganic
$Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ (volborthite)	120K	strong	inorganic
$BaCu_3V_2O_8(OH)_2$ (vesigniete)	80K	strong	inorganic
$Na_4Ir_3O_8$	600K	weak	inorganic

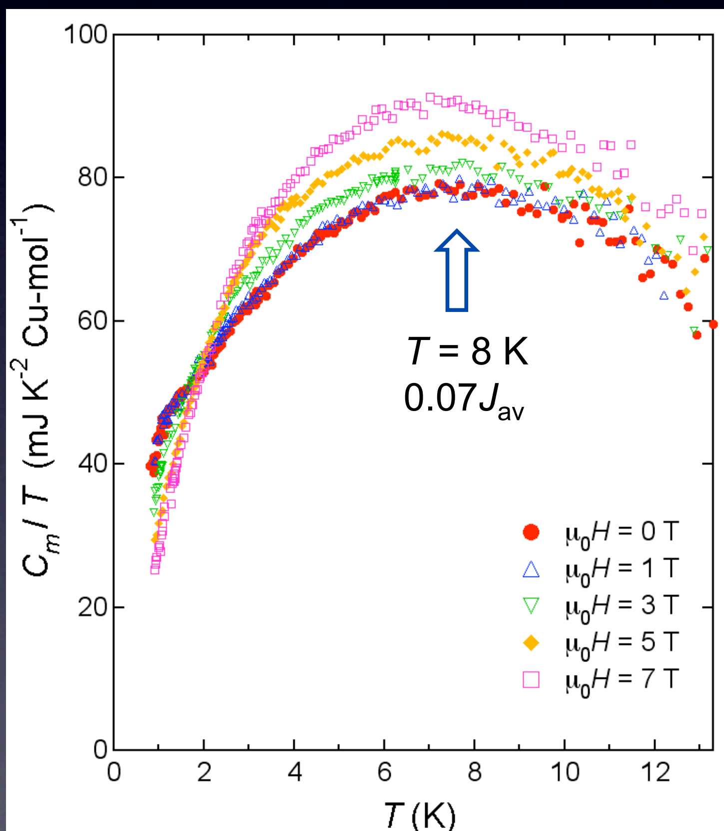
κ-(BEDT-TTF)$_2$Cu$_2$(CN)$_3$

- Material is proximate to a Mott transition
- Non-activated transport
- Optical pseudogap

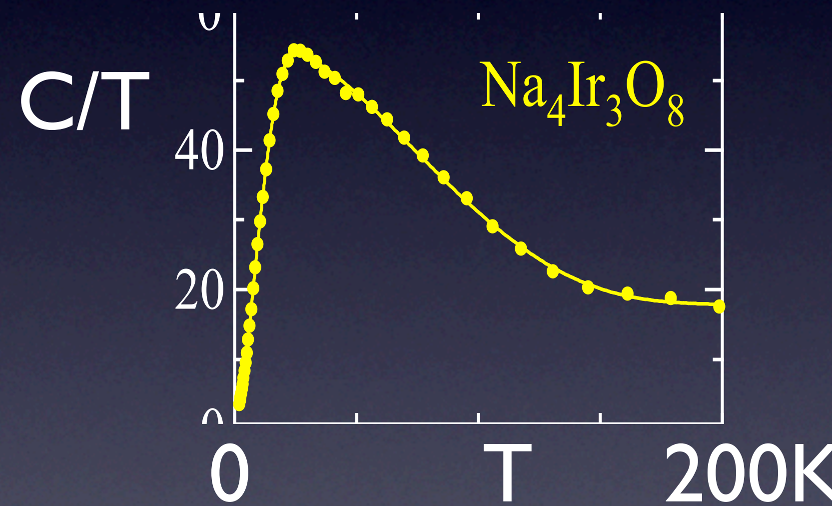


Experimental Properties

Specific Heat



volborthite (Hiroi)



Okamoto *et al*

Specific Heat

- Specific heat
  - broad peak well below $|\Theta_{CW}|$
  - approximately ~ AT^2 below the peak
  - at very low temperature ~γT
  - large variations γ=1-250 mJ/(mole-K^2)
- This clearly indicates large low energy density of states

Specific Heat

material	γ [mJ/(mole K^2)]
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$	12
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	?
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	240
Cu$_3$V$_2$O$_7$(OH)$_2$ · 2H$_2$O (volborthite)	40
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesigniete)	50
Na$_4$Ir$_3$O$_8$	1

- For the same form of Hamiltonian, γ should scale with 1/J

Specific Heat

material	γ [mJ/(mole K^2)]	$\gamma \times$ $\|\Theta_{CW}\|$/4500
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$	12	1
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	?	?
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	240	13
Cu$_3$V$_2$O$_7$(OH)$_2$ · 2H$_2$O (volborthite)	40	1.1
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesigniete)	50	0.89
Na$_4$Ir$_3$O$_8$	1	0.13

Specific Heat

material	γ [mJ/(mole K^2)]	$\gamma \times$ $\lvert\Theta_{CW}\rvert$/4500
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$	12	1
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	?	?
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	240	13
Cu$_3$V$_2$O$_7$(OH)$_2$ · 2H$_2$O (volborthite)	40	1.1
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesigniete)	50	0.89
Na$_4$Ir$_3$O$_8$	1	0.13

Specific Heat

material	γ [mJ/(mole K^2)]	$\gamma \times$ $\lvert\Theta_{CW}\rvert/4500$
κ-$(BEDTTTF)_2Cu_2(CN)_3$	12	1
$EtMe_3Sb[Pd(dmit)_2]_2$	?	?
[illegible]	[illegible]	13
[illegible] (volborthite)	[illegible]	1.1
$BaCu_3V_2O_8(OH)_2$ (vesigniete)	50	0.89
$Na_4Ir_3O_8$	1	0.13

defects!

tempting to think non-zero γ is intrinsic at least to 2d systems

Susceptibility

- All the materials show approximate Curie-Weiss form, with some saturation at low T
  - In some cases there is a peak
  - Values of the low-T susceptibility vary within a range of only about 10
- Is this intrinsic? Or is it related to disorder or spin-orbit coupling?
  - In a S=1/2 system, SOI = Dzyaloshinskii-Moriya interactions

$$H_D = \sum_{ij} \vec{D}_{ij} \cdot \vec{S}_i \times \vec{S}_j$$

Susceptibility

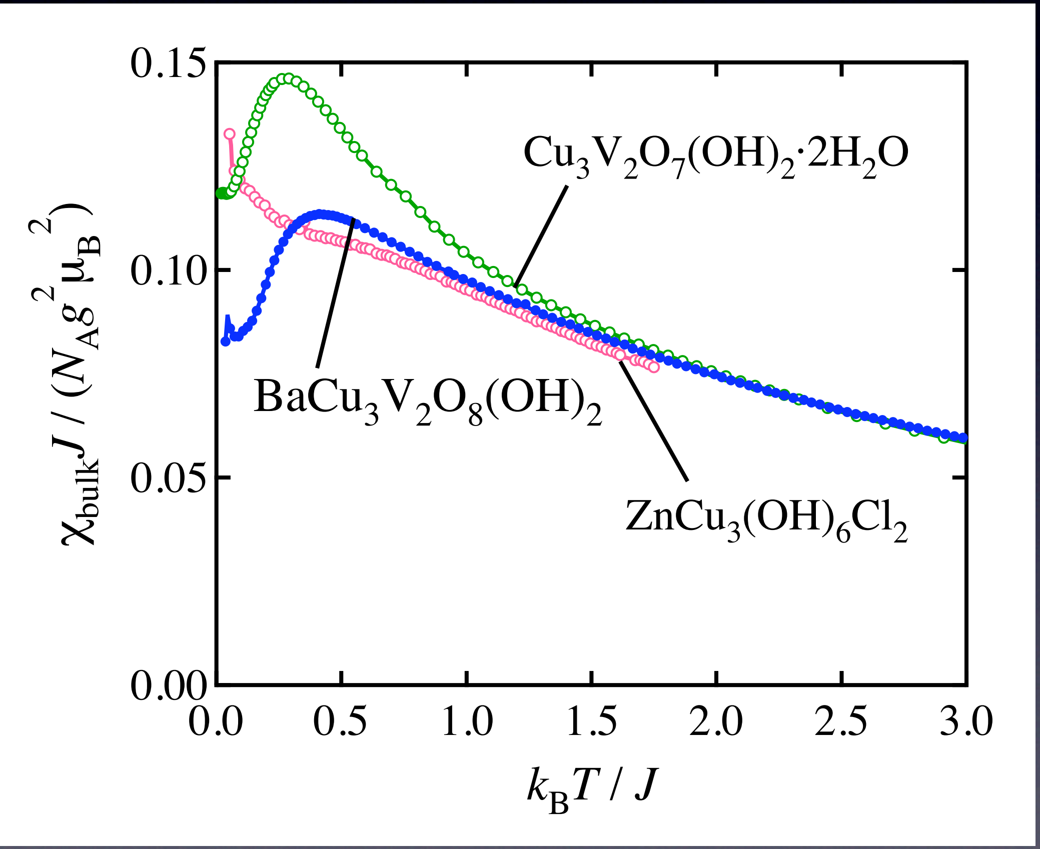
material	χ (T=0) [10^{-4} emu/mole]
κ-$(BEDTTTF)_2Cu_2(CN)_3$	3
$EtMe_3Sb[Pd(dmit)_2]_2$	4
$ZnCu_3(OH)_6Cl_2$ (herbertsmithite)	5 (from ^{17}O)
$Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ (volborthite)	30
$BaCu_3V_2O_8(OH)_2$ (vesigniete)	25
$Na_4Ir_3O_8$	10

- For the same form of Hamiltonian, χ should scale with 1/J.

Susceptibility

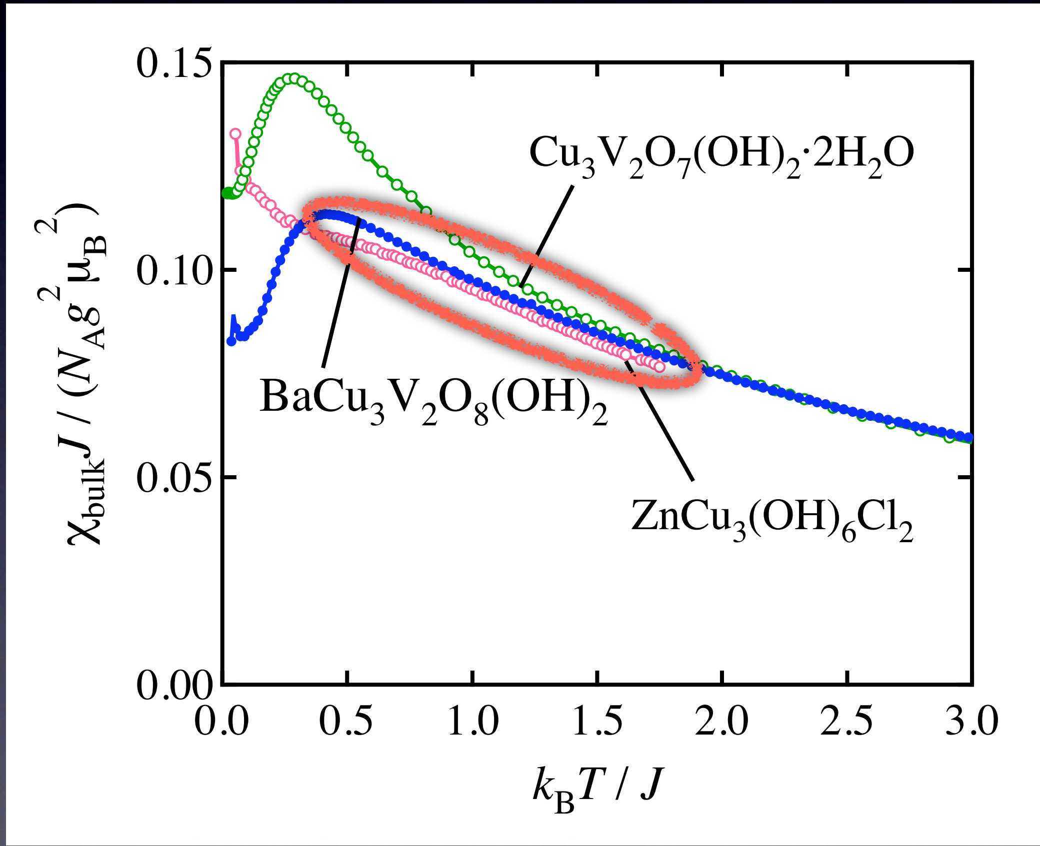
material	χ (T=0) [10^{-4} emu/mole]	$\chi \times |\Theta_{CW}|/1125$
κ-$(BEDTTTF)_2Cu_2(CN)_3$	3	1
$EtMe_3Sb[Pd(dmit)_2]_2$	4	1.2
$ZnCu_3(OH)_6Cl_2$ (herbertsmithite)	5 (from ^{17}O)	1.1
$Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ (volborthite)	30	3.2
$BaCu_3V_2O_8(OH)_2$ (vesigniete)	25	1.8
$Na_4Ir_3O_8$	10	5.3

Scaled Kagome Susceptibilities



Hiroi

Scaled Kagome Susceptibilities



Hiroi

Agreement here suggests herbertsmithite and vesignieite have similar intrinsic hamiltonians

What about VB states?

- Both VBS and RVB states are constructed from VBs, and hence should have a suppressed susceptibility
  - in fact, nearly all states that have been proposed for frustrated magnets have a vanishing susceptibility as T goes to 0
  - but this is not the case in experiment!

How important is SOI?

- Wilson ratio $$R = \frac{4\pi^2 k_B^2 \chi_0}{3(g\mu_B)^2\gamma}$$
  - R>>1 is an indication of SOI enhancing χ
    - in general χ(T=0) is always non-zero with SOIs, even if there is a full gap (in that case, $\chi \sim D^2/\Delta^3$)
  - R~1 is characteristic of free fermions carrying spin

Wilson Ratio

material	R
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$	~1
EtMe$_3$Sb[Pd(dmit)$_2$]$_2$	?
ZnCu$_3$(OH)$_6$Cl$_2$ (herbertsmithite)	not intrinsic
Cu$_3$V$_2$O$_7$(OH)$_2$ · 2H$_2$O (volborthite)	6
BaCu$_3$V$_2$O$_8$(OH)$_2$ (vesigniete)	4
Na$_4$Ir$_3$O$_8$	70

increasing SOI

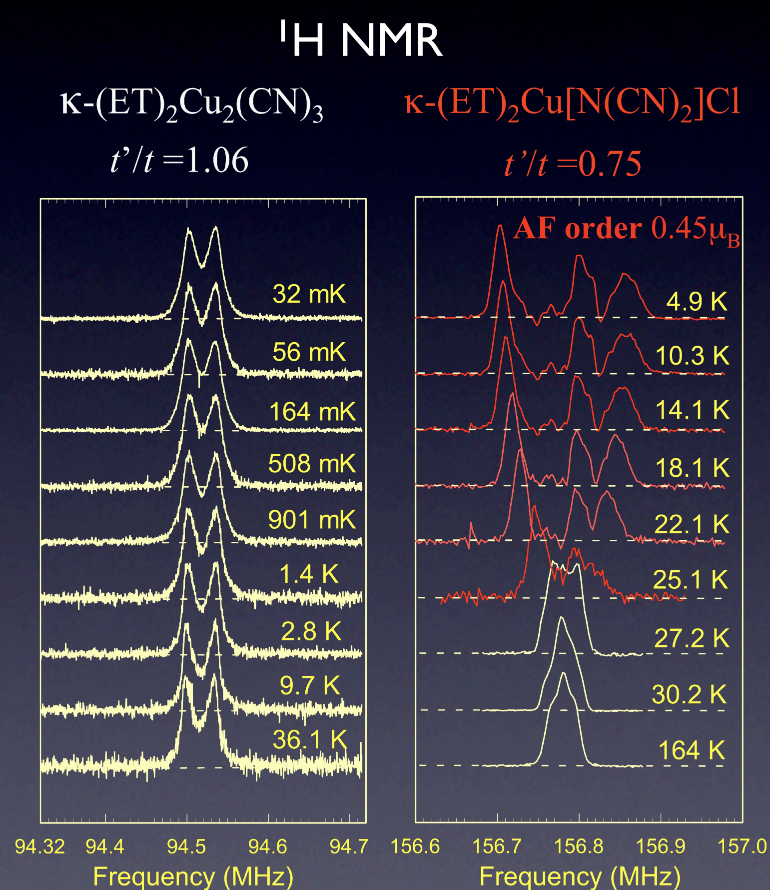
Wilson Ratio

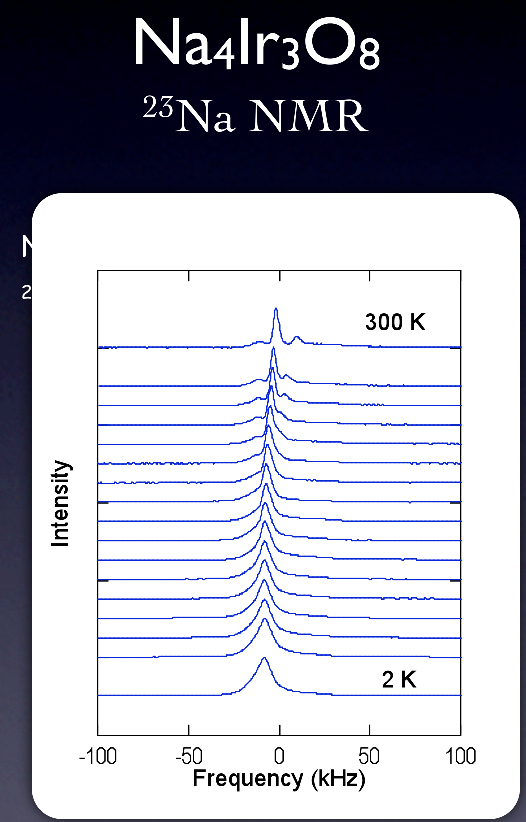
material	R	estimated D/J
κ-$(BEDTTTF)_2Cu_2(CN)_3$	~1	2%
$EtMe_3Sb[Pd(dmit)_2]_2$	?	2%
$ZnCu_3(OH)_6Cl_2$ (herbertsmithite)	not intrinsic	5-10%
$Cu_3V_2O_7(OH)_2 \cdot 2H_2O$ (volborthite)	6	5-10%
$BaCu_3V_2O_8(OH)_2$ (vesigniete)	4	5-10%
$Na_4Ir_3O_8$	70	O(1)

NMR/NQR/μSR

- Local probes
  - lineshape can tell if there are any static moments, even if not ordered
  - relaxation rate gives information on density of low energy states (dynamic local spin susceptibility)

NMR lineshapes

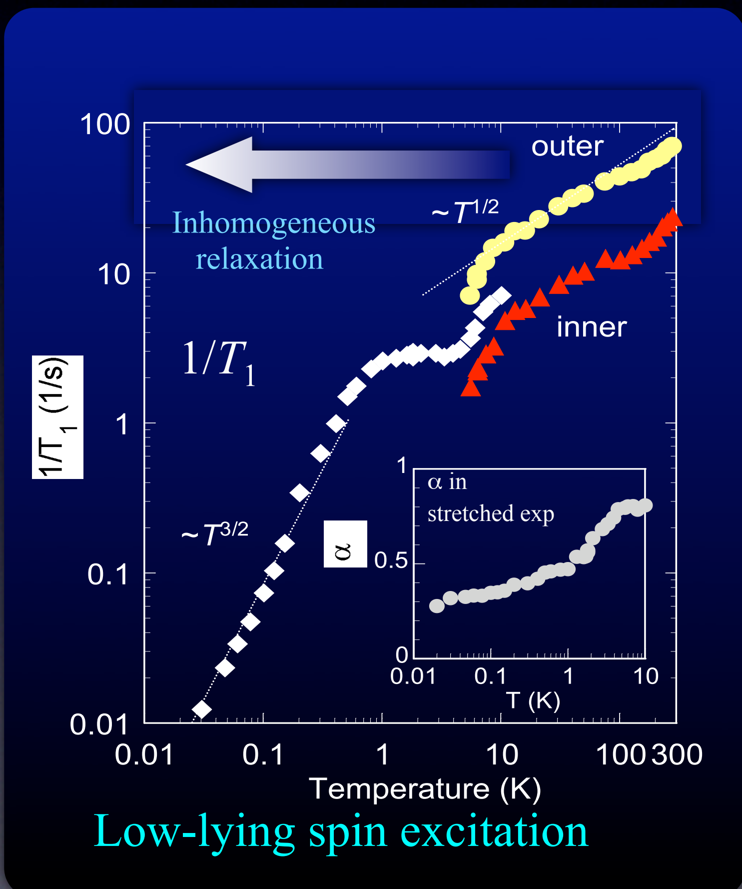




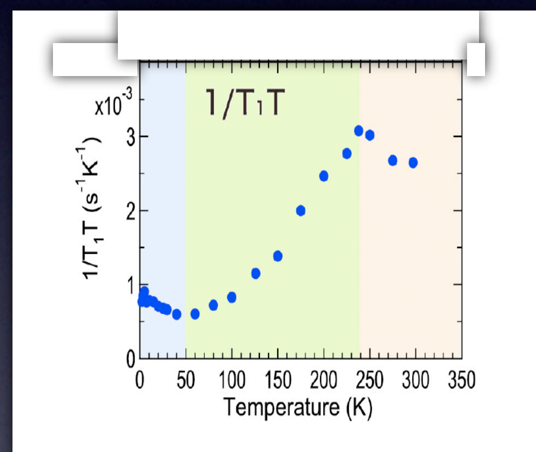
Evidence for lack of static moments

Relaxation Rate

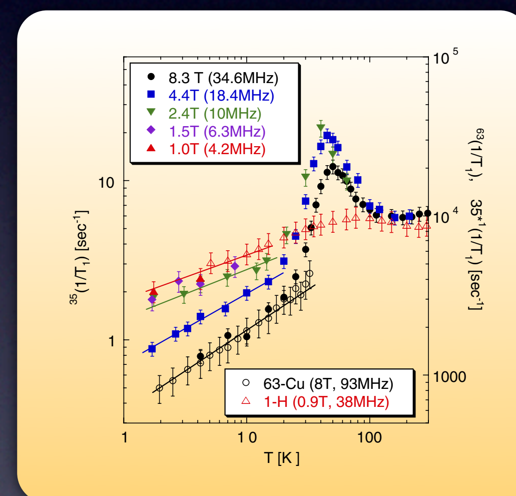
κ-(BEDTTTF)$_2$Cu$_2$(CN)$_3$



Na$_4$Ir$_3$O$_8$



herbertsmithite



Power-laws indicate gapless excitations

Theory: Organics

- “non-magnetic insulator” found by Imada from projector MC methods in triangular lattice Hubbard model
  - now confirmed by several other calculations
- But what is it? And does it correspond to experiment?

Theory: Organics

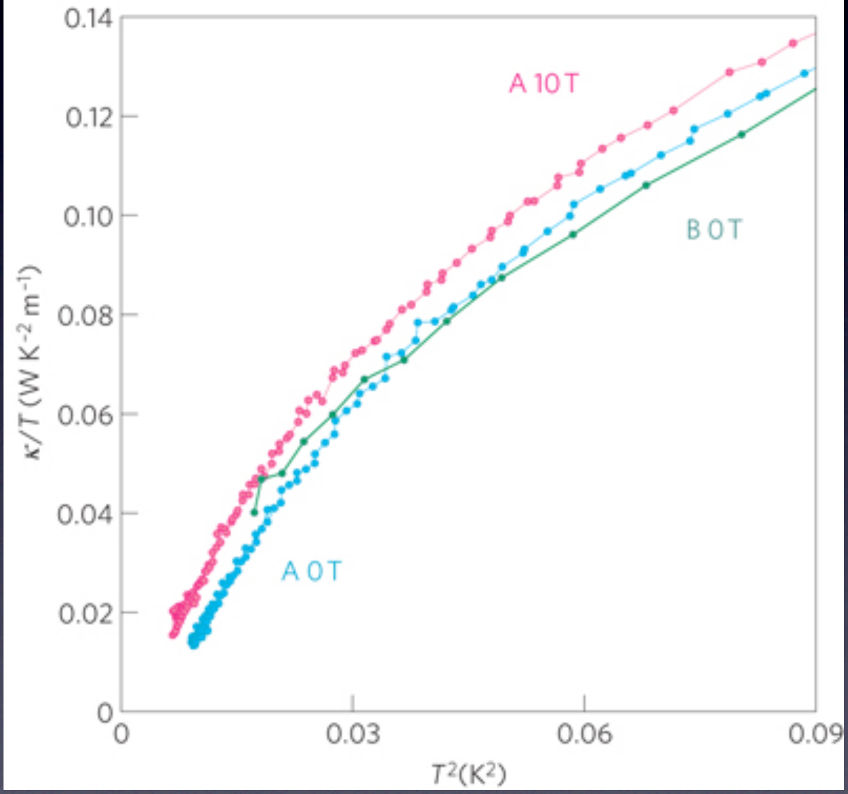
- RVB/QSL state:
  - Motrunich, Lee+Lee: (2005) “uniform RVB”
  - this is a kind of RVB state with very many (maybe a maximal number of?) long-range VBs
  - It is described by a “Fermi sea” of spinons coupled to a U(1) gauge field
- Good variational energy for triangular lattice Hubbard model
- How does it fit with experiments?

Circumstantial evidence

- No ordering ✔
- Large T=0 susceptibility ✔
- Linear specific heat ☹
  - theory predicts $C_v = AT^{2/3}$ due to gauge fluctuations
  - but if we ignore this, it seems reasonable that R=O(1)
- Power-law $1/T_1$ ✔
  - but it's not clear the actual power works

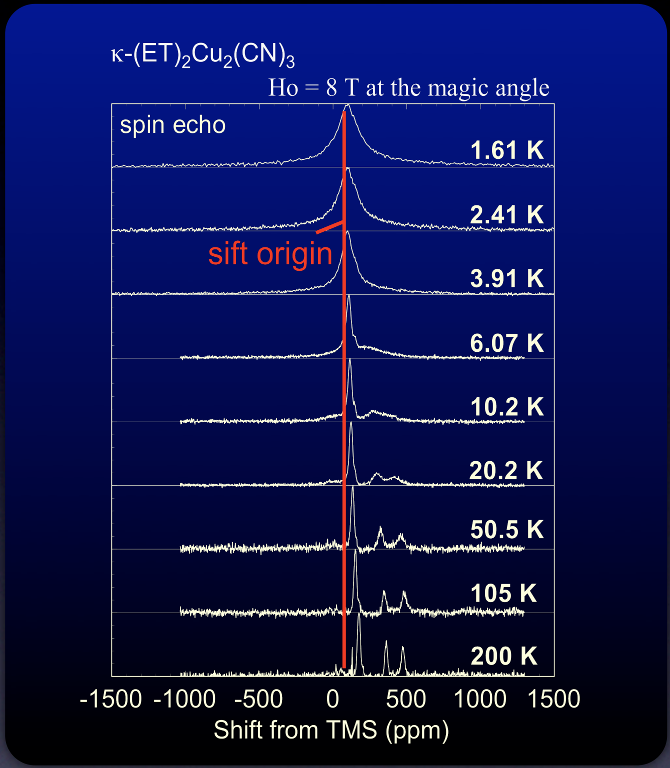
Challenges

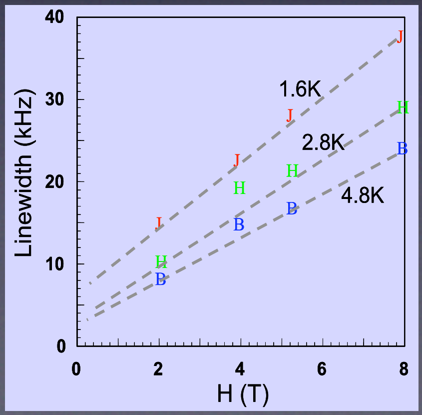
- The thermal conductivity appears to show a small gap of order 0.5K at very low temperature
- Not consistent with uniform RVB
- Is it consistent with heat capacity?



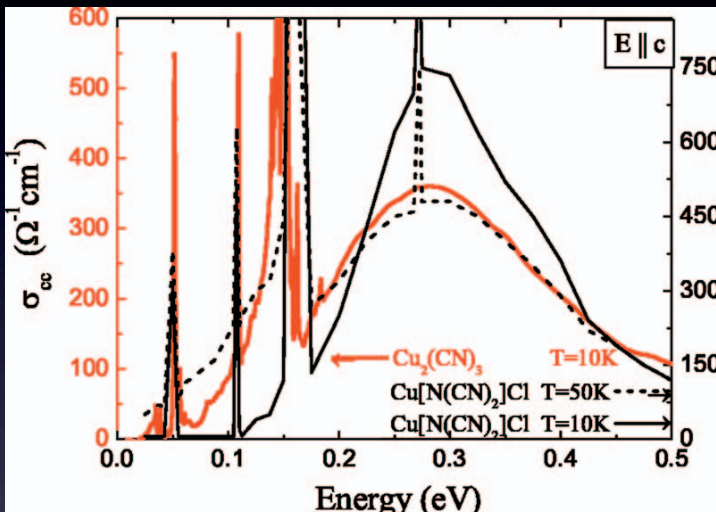
Challenges

- ^{13}C NMR: line broadening at low temperature in a field
  - indicates inhomogenous AF moments induced by field

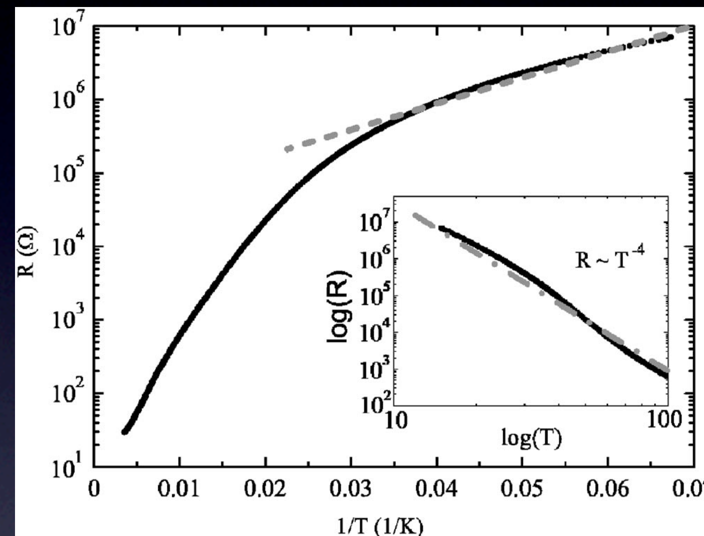




Challenges



very small or no optical gap (pseudogap)



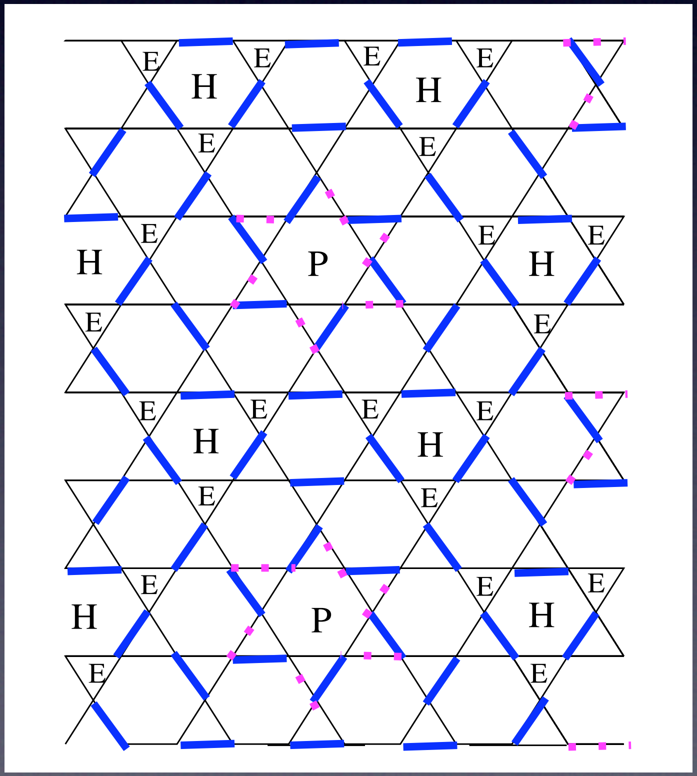
non-activated resistivity (or gap <15 meV)

Theory: Kagomes

- ED: clearly indicates a non-magnetic ground state, with a small or zero gap to triplets and/or singlets
- There are at least two competing pictures of the ideal kagome lattice
  - VBS states
    - This idea has a long history but was revived recently by Huse+Singh, and seems to be favored by most numerical approaches
    - However, one should be cautious since many approaches are biased toward short-range VBs

Marston-Zeng VBS

- 36 site unit cell with a small gap



VBS vs expt

- In any VBS state, you should have a gap for all excitations
  - seemingly at odds with specific heat and NMR $1/T_1$
  - but it is also agreed that these gaps must be very small, so the state may be highly susceptible to disorder, SOI, anisotropy
  - one needs to understand how these perturbations affect the physics to make any real comparison (or get some new expts!)

Dirac QSL

- Y. Ran *et al*, 2007: proposed an RVB state built from projected lattice Dirac fermions, based on variational wavefunctions
- This state has $C_v \sim AT^2$ and $\chi \sim BT$, and certain power-law correlations of spin, etc.
  - need to invoke impurities to explain both linear C_v and non-zero $\chi(0)$
  - But quadratic specific heat can agree over an intermediate temperature range
  - Without impurities, DM is expected to induce magnetic order

Is theory natural?

- At the moment, all the viable ideas on purely theoretical grounds involve some degree of VB formation
- However, in experiment, it is not particularly clear that this is happening
- In addition, there are in either case very few aspects of the experiments that are actually predicted correctly by the ideal theory
  - so apart from theoretical biases, it is hard to say that there is any really compelling reason to believe in these theories!

Where now?

- Incremental improvements in theory and materials could converge
- It is possible we need a radically different theory of QSLs, which might naturally explain the experiments
- It would be good to have theories that focus less on very low temperature, and more on intermediate energy physics, and are more quantitative

The Smoking Gun

- Can we devise an experiment which convincingly shows the presence of exotic excitations directly?
  - maybe inelastic single crystal neutrons - they do see spinons in 1d
  - the "Senthil experiment" to see *visons* (cannot be done on most materials)
  - Can you see $2k_F$ oscillations somehow in a Mott insulator?
  - something more clever?

Conclusions

- Frustrated magnets provide a rich variety of phenomena including a number of promising new quantum spin liquid candidates
- For QSLs, what is needed is a combined effort of innovative experimental and theoretical work, with attention of the latter paid to the former!