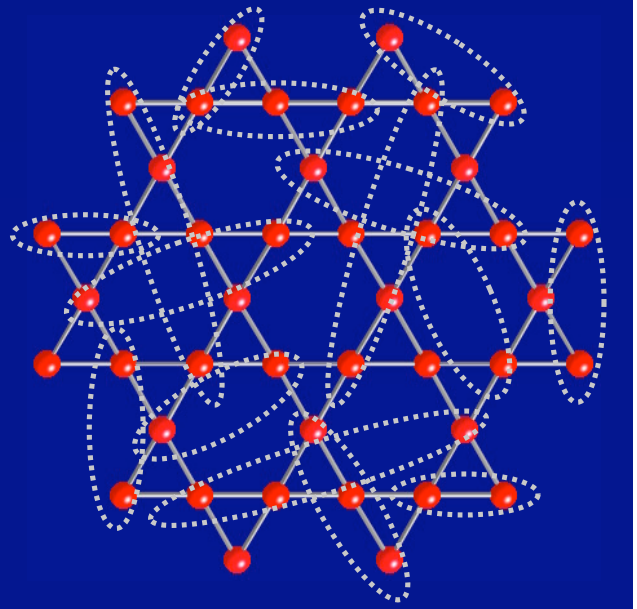
IMSS-Symposium, October 17, 2008

Magnetization “steps” in the spin-1/2 kagome lattice of volborthite

H. Yoshida Y. Okamoto



RVB state, spin liquid or what?

long-standing issue on the frustrated lattice

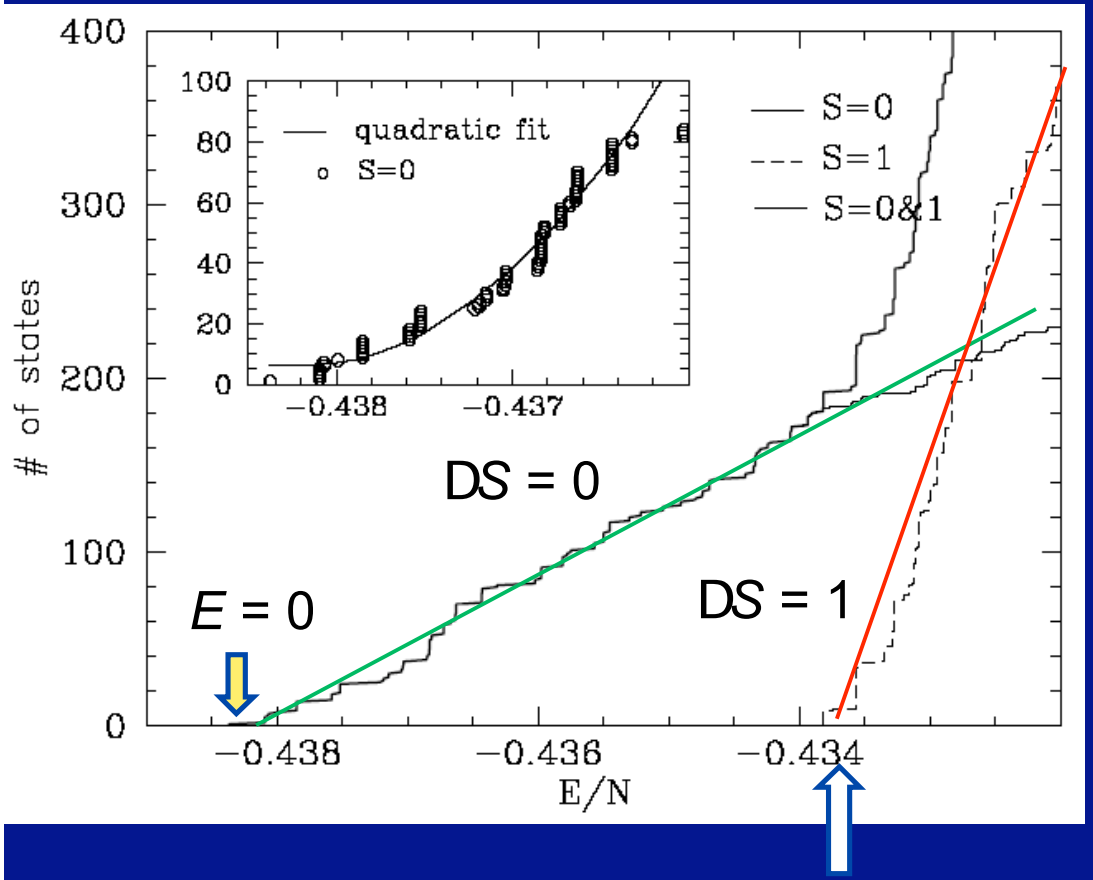
Outline

- General aspects on the kagome AF magnets
- Volborthite vs Herbertsmithite
  common features of the *S*-1/2 kagome
- GS of volborthite: spin glass and liquids
- Magnetization “steps”

Materials: H. Yoshida, Y. Okamoto
NMR: M. Yoshida and M. Takigawa
LT Mag.: T. Tayama and T. Sakakibara
HF Mag.: M. Tokunaga and K. Kindo (ISSP)
ESR: S. Okubo and H. Ohta (Kobe Univ.)
μSR: A. Fukaya and Y.J. Uemura (Columbia Univ.)

GS of the *S*-1/2 kagome: theory

Very small magnetic gap filled up with singlet states?

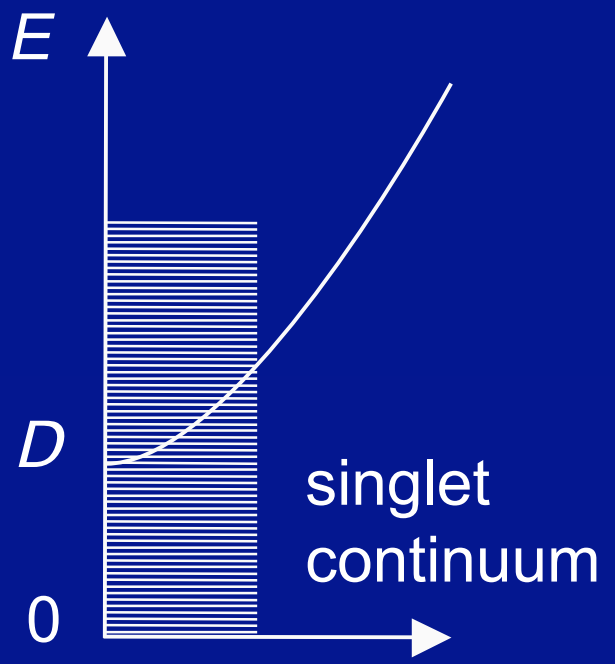


singlet-triplet gap
$D \sim J / 20$

More, S = ½ excitations for odd-number clusters.

Waldtmann, *et al.*, EPB 2, 501 (1998)

One expects a gap in c, but not in C_p.



Classically degenerate states spread over into the singlet continuum!

Materials: can we obtain a perfect frustrated lattice in a real material?

Many obstacles:

- interlayer coupling → 3D long-range order

  Jarosite,...

- disorder

  SCGO, Herbertsmithite, $LiNiO_2$, ...

- distortion

  Volborthite, organics, ...

- long-range interactions
- coupling to the lattice → local singlet state

S-3/2 kagome lattice in $SrCr_8Ga_4O_{19}$ (SCGO)

No LRO, but SG

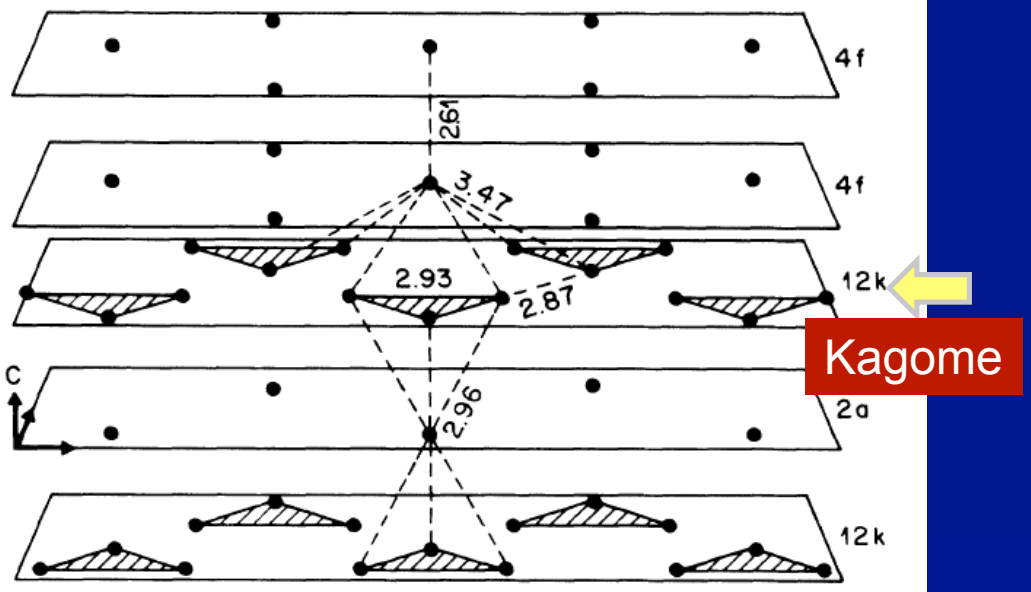
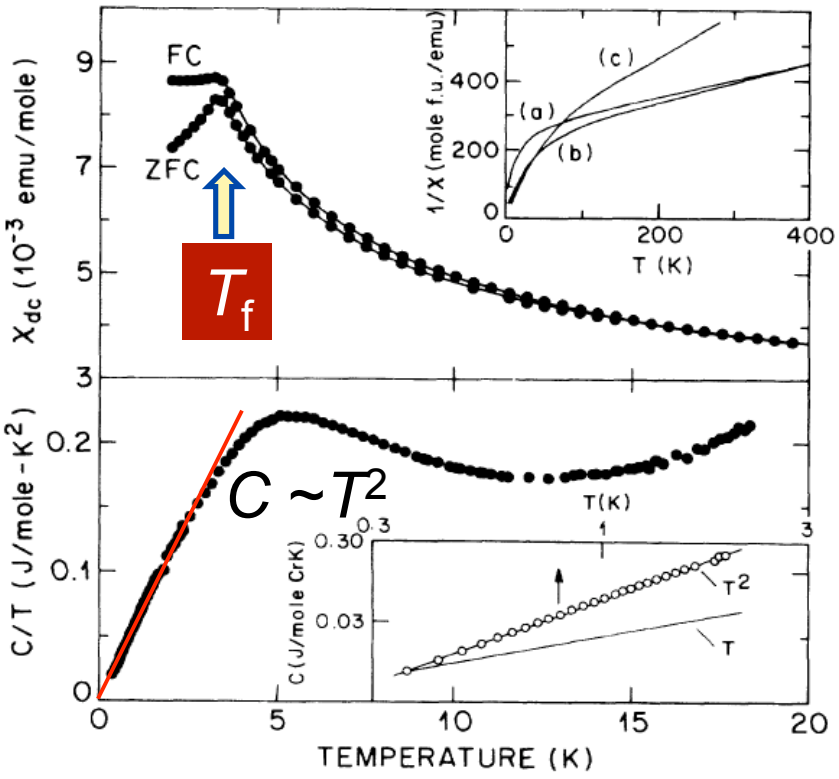


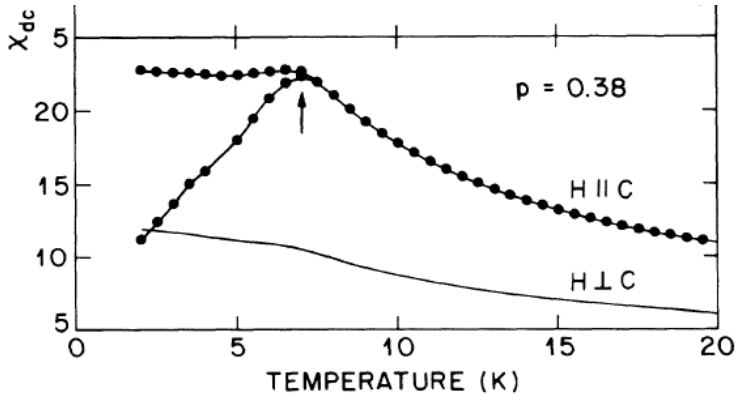
FIG. 1. Structure of $SrCr_9Ga_3O_{19}$ showing only the Cr sites. The 2*a* layer is fully occupied, and the 12*k* and 4*f* layers are only 86% occupied. The relevant nearest-neighbor bond distances are shown in angstroms.

magnetoplumbite structure

~90% coverage in the kagome layer
extra Cr ions exist

A. P. Ramirez, *et al*., PRL 64, 2070 (1990)





S-5/2 Kagome lattice in Jarosite

$AFe_3(SO_4)_2(OH)_6$: Fe^{3+}, $3d^5$

A = Na, K → LRO (q = 0)

A = H_2O → spin glass

$(D_3O)Fe_3(SO_4)_2(OD)_6$

97% coverage

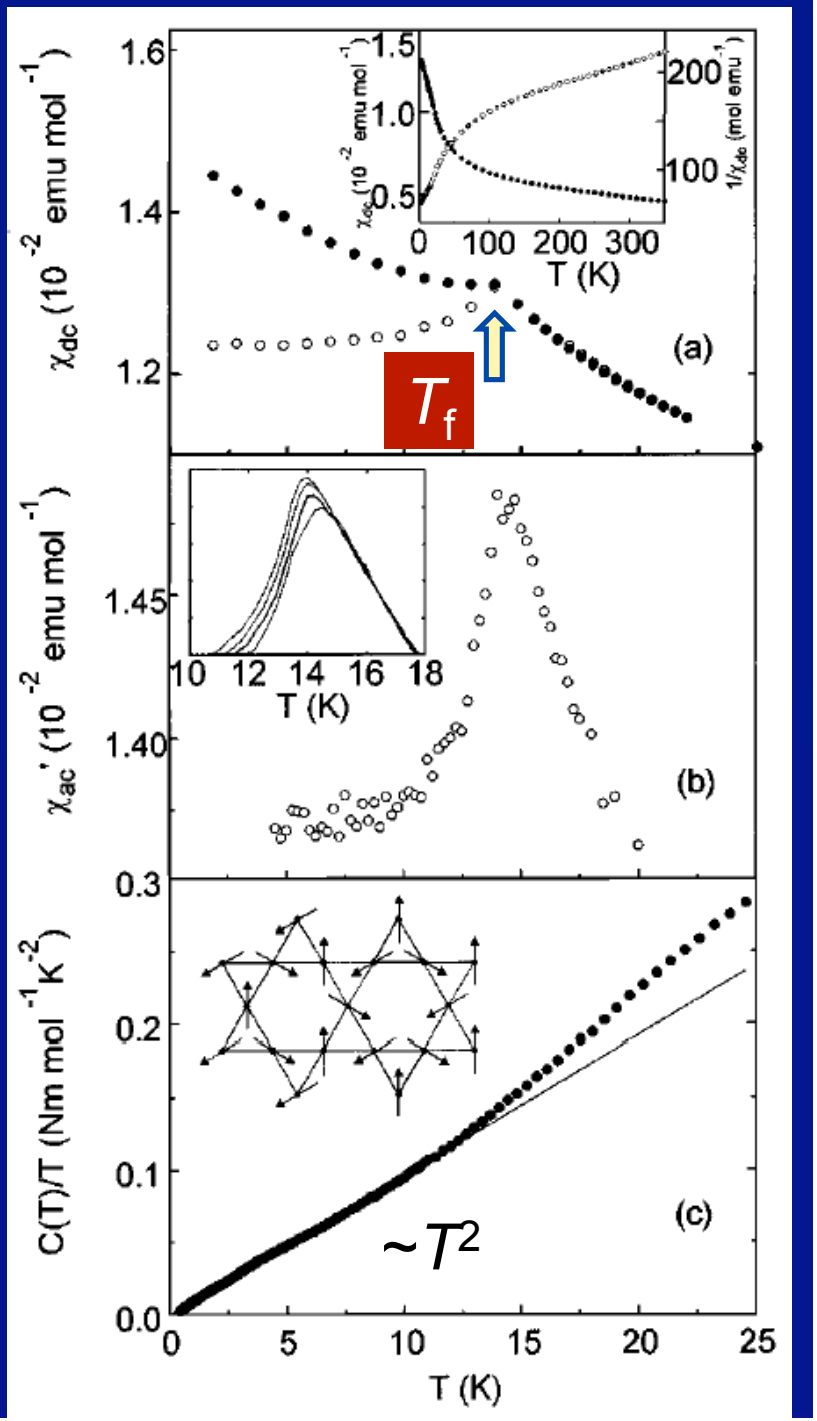
Q_{CW} = -700 K: J = 50 K

T_f = 13.8 K

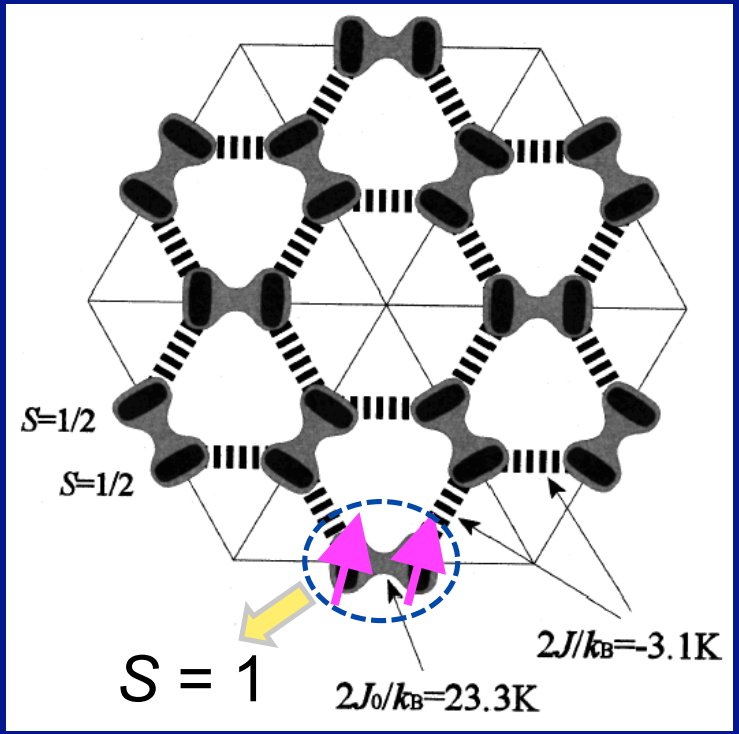
x = 19 A at 2 K

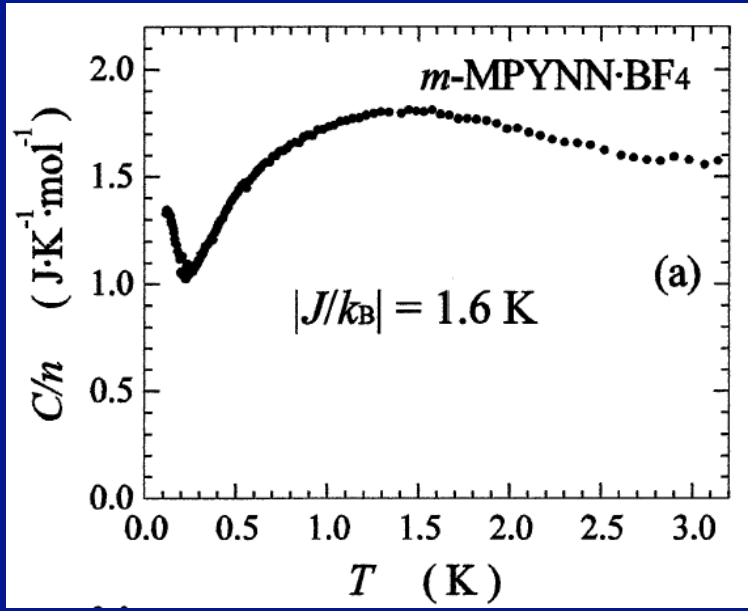
small x, but no gap, why?

A. Harrison, *et al*., Europhys. Lett. 42, 325 (1998)

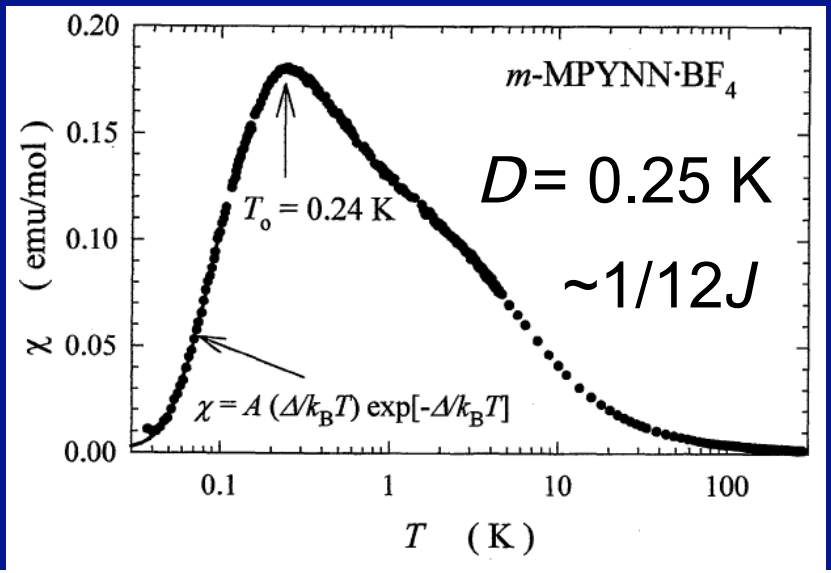


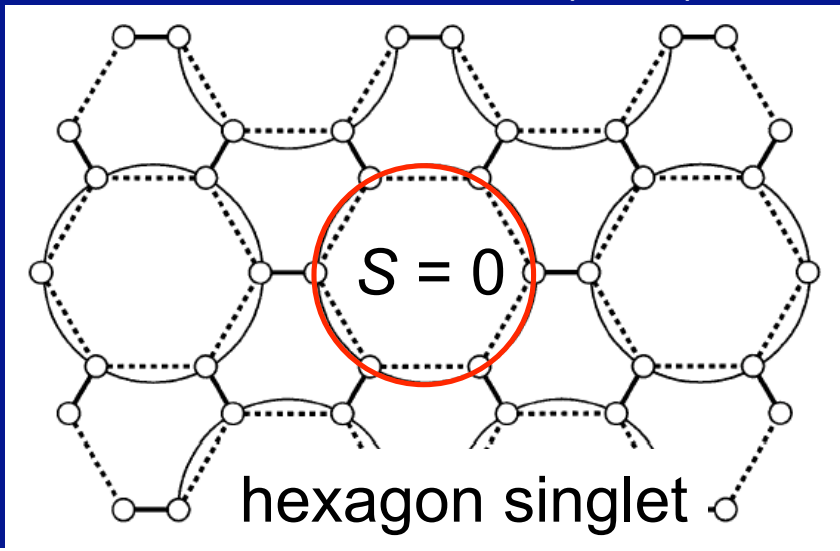
S-1 kagome found in organics



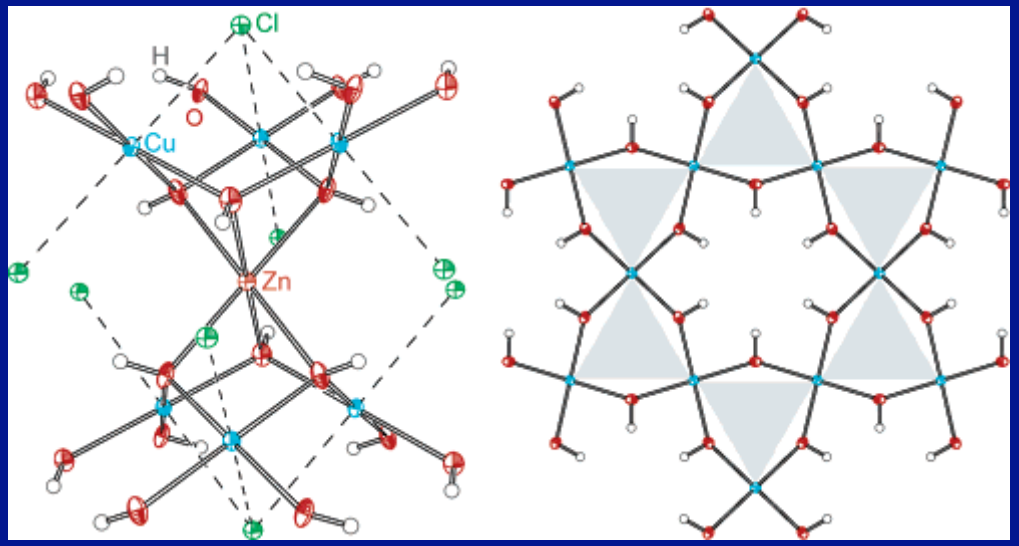


N. Wada, *et al*., JPSJ 66, 961 (1997)
K. Hida, JPSJ 69, 4003 (2000)



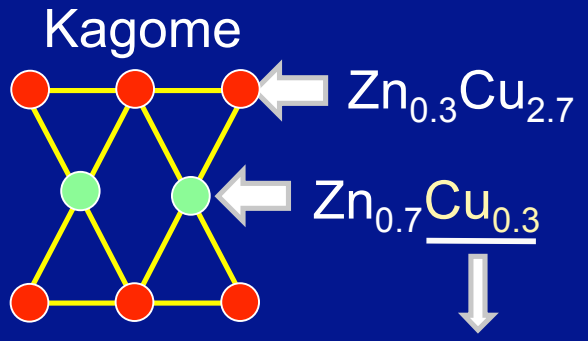


S-1/2 "$_{im}$Perfect" kagome $ZnCu_3(OH)_6Cl_2$



G. Nocera, MIT, JACS 127, 13462 (2005)

ND diffraction by S.-H. Lee & A. Harrison



10% "free" spins!

∠Cu-O-Zn = 96.9°: $J \sim 0$

$Zn_xCu_{3-x}(OH)_6Cl_2$

x = 0: clinoatacamite

$0.33 \leq x < 1$:

Zn-paratacamite

x = 1: herbertsmithite

Absence of

LRO

gaps

spin freezing

down to 50 mK

by NMR, mSR, ac-c, ...

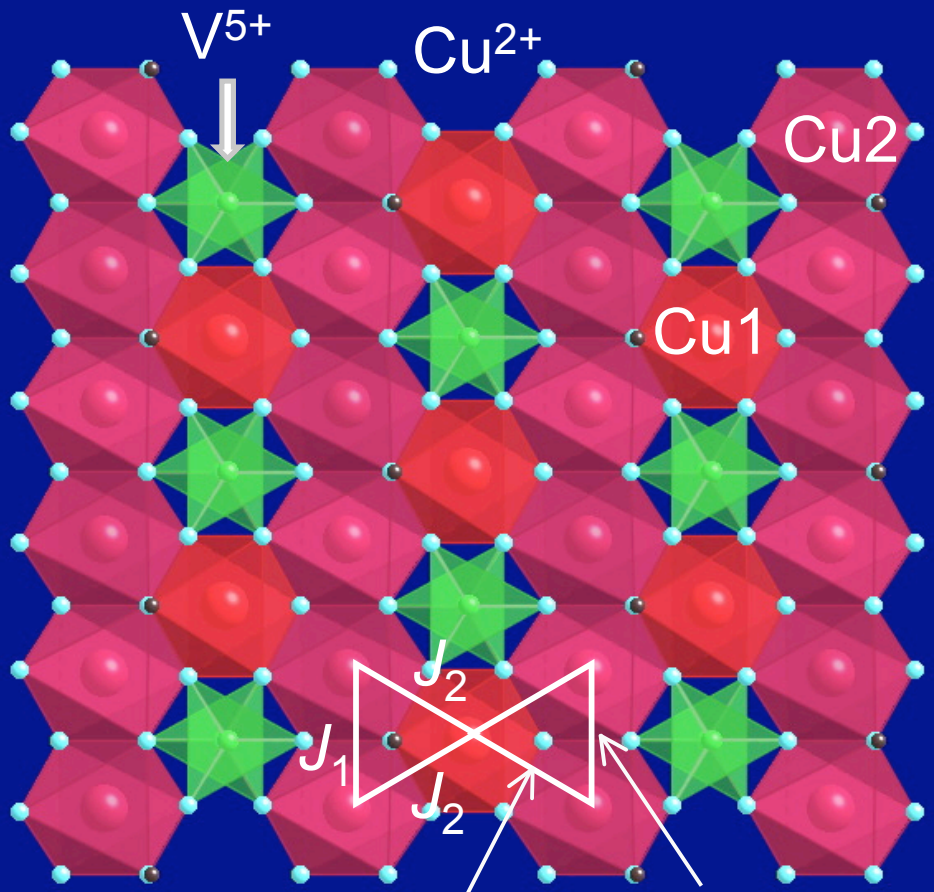
~6% by NMR (Olariu)

~3% in a better sample

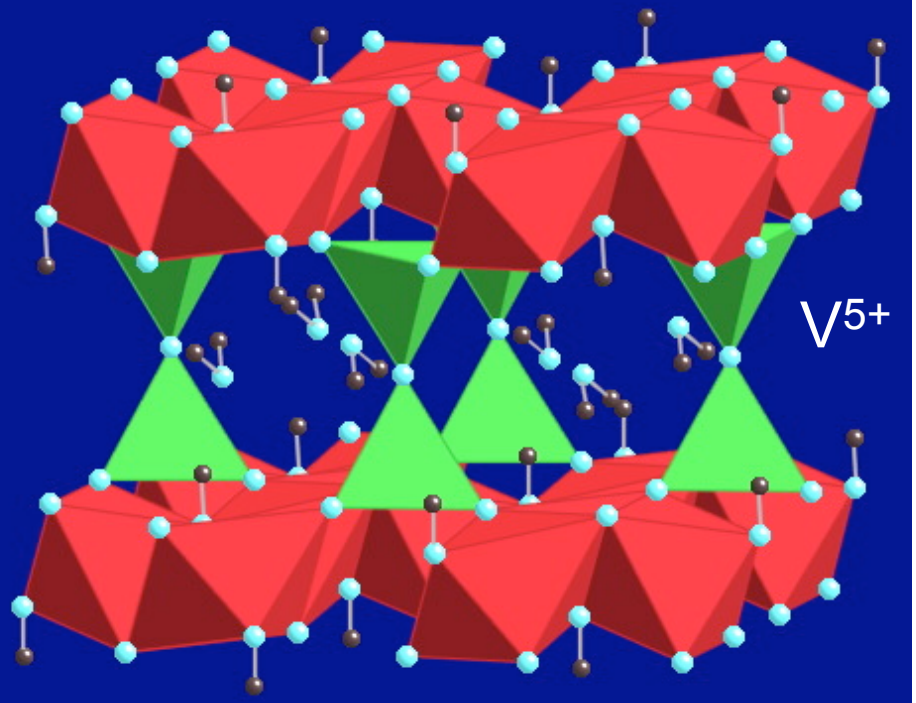
A. Harrison

S-1/2 kagome-like lattice

volborthite: $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$



Monoclinic, *C*2/*m*
a = 10.607Å
b = 5.864Å
c = 7.214Å
b = 94.90°



$J_1 - J_2$ kagome
No exchange, Cu^{2+} / V^{5+}

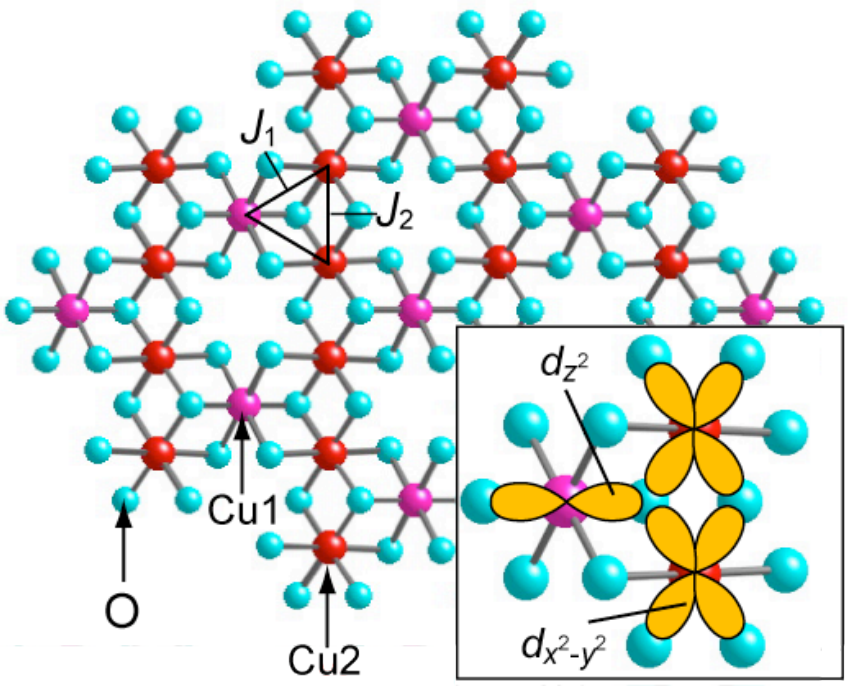
Lafontaine *et al*., J. Solid State Chem. 85, 220 (1990)

ZH *et al*., JPSJ 70, 3377 (2001)

Volborthite vs Herbertsmithite

Anisotropic kagome

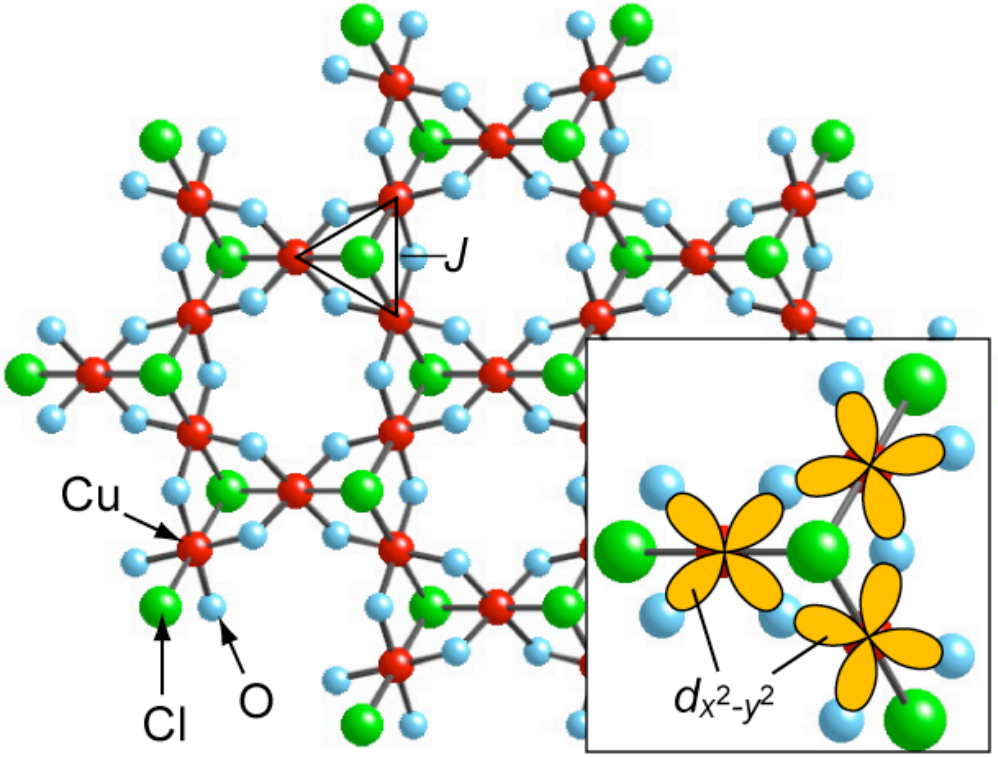
Volborthite $Cu_3V_2O_7(OH)_2 \cdot 2H_2O$



Monoclinic, *C*2/*m*
d(Cu1-Cu2) = 3.031 Å
d(Cu2-Cu2) = 2.937 Å
∠Cu1-O-Cu2 = 105.6° (82.7°): J_1
∠Cu2-O-Cu2 = 101.1° (91.5°): J_2
$J_{av} = (2J_1 + J_2) / 3$

Isotropic kagome

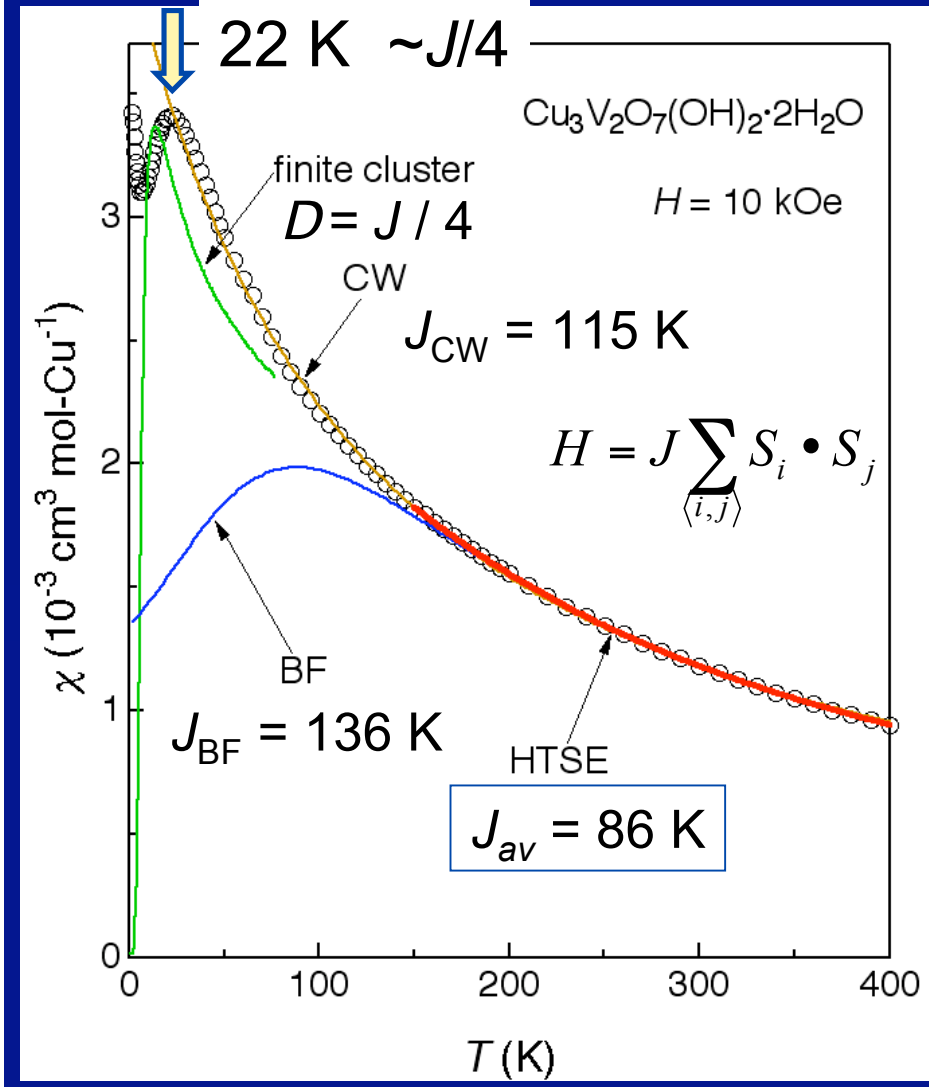
Herbertsmithite $ZnCu_3(OH)_6Cl_2$

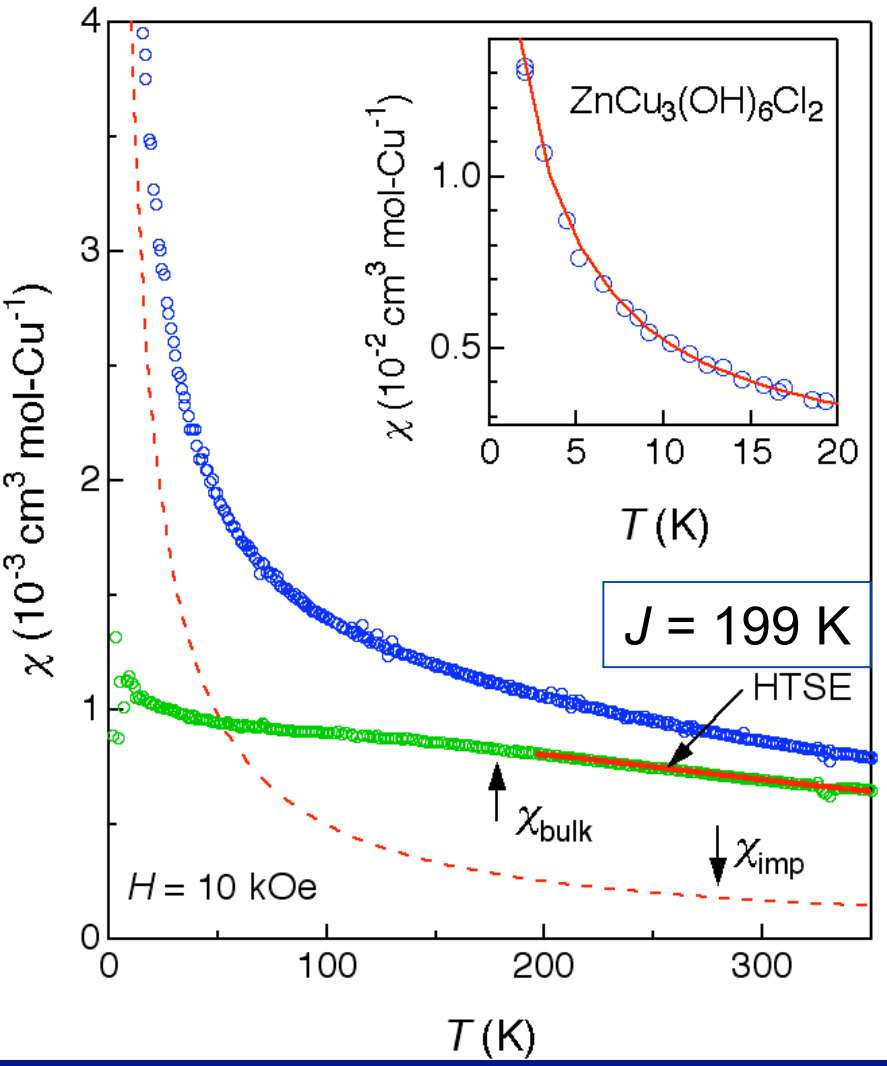


Rhombohedral, *R*-3*m*
d(Cu-Cu) = 3.414 Å
∠Cu-O-Cu = 119°: J
∠Cu-O-Zn = 96.9°: $J \sim 0$

$\Delta J \lesssim 20\%$? cf. Sindzingre

Volborthite vs Herbertsmithite: c_{bulk}





crystalline defects?

J_{av} = 86 K
x_{imp} = 0.5%

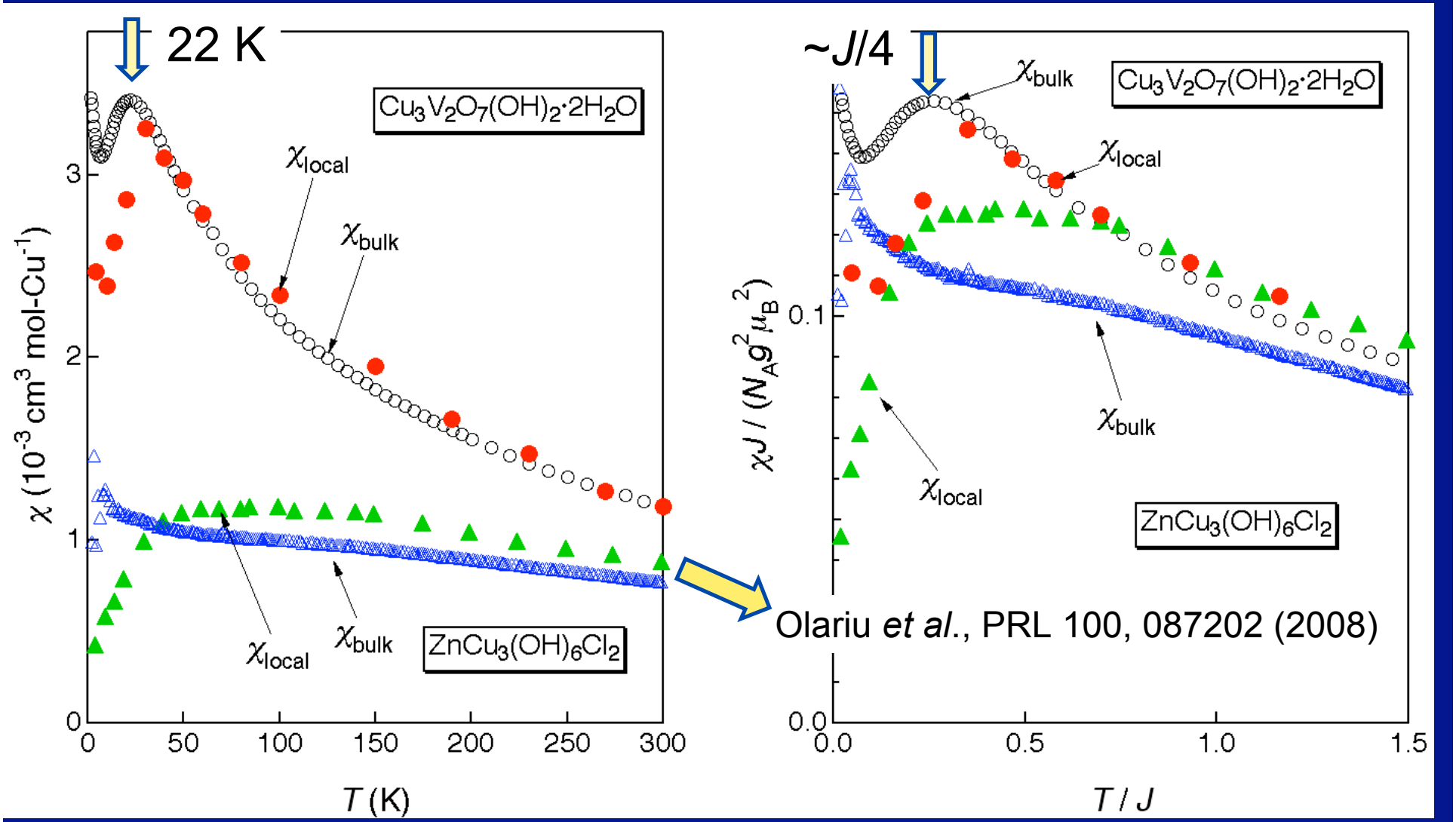
⟺

J = 199 K
x_{imp} = 10%

cf. J = 170 ~ 190 K from Cu spins at the Zn site

Volborthite vs Herbertsmithite: c_{loc}

c_{loc} from NMR Knight shift K: $K = A c_{loc} / N_A$



A = 6.6 kOe / m_B for volborthite and 35 kOe / m_B for herbertsmithite

Volborthite vs Herbertsmithite: defects

Volborthite

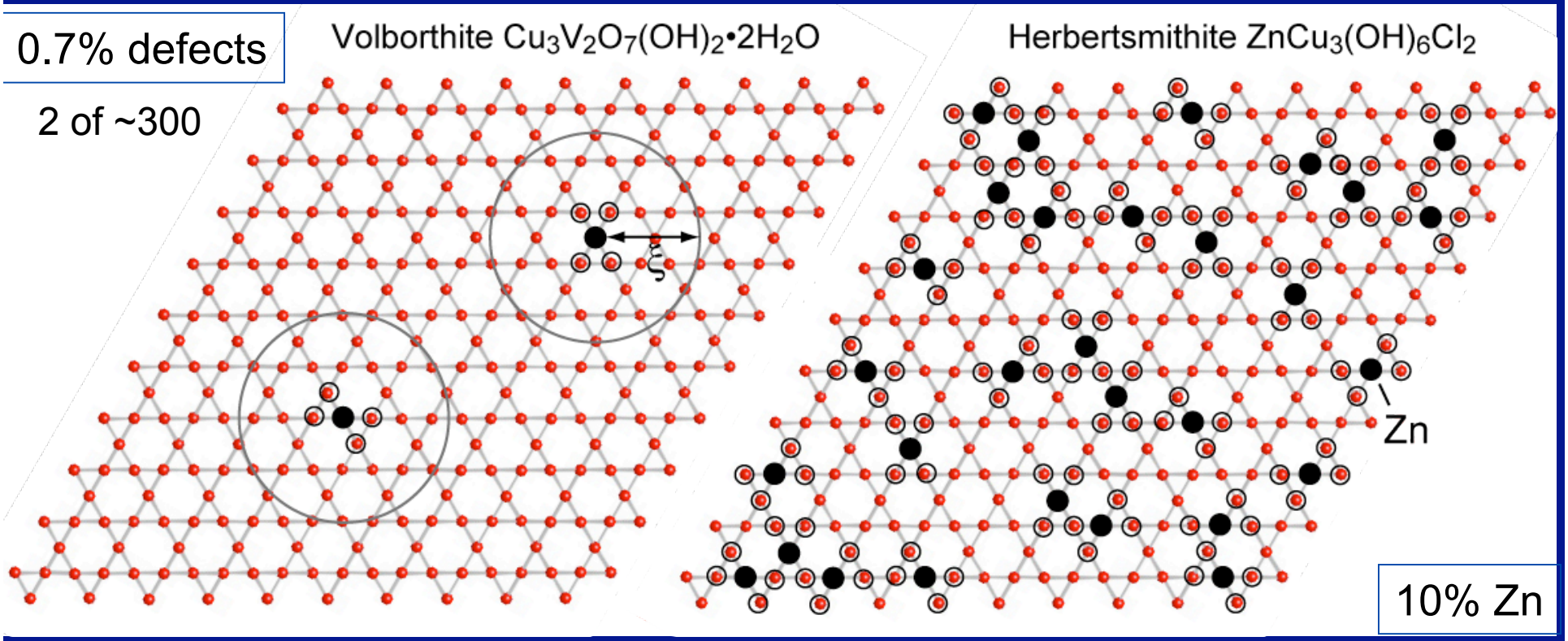
Herbertsmithite

crystalline defects near surfaces?

3 – 10% Zn

0.7% defects

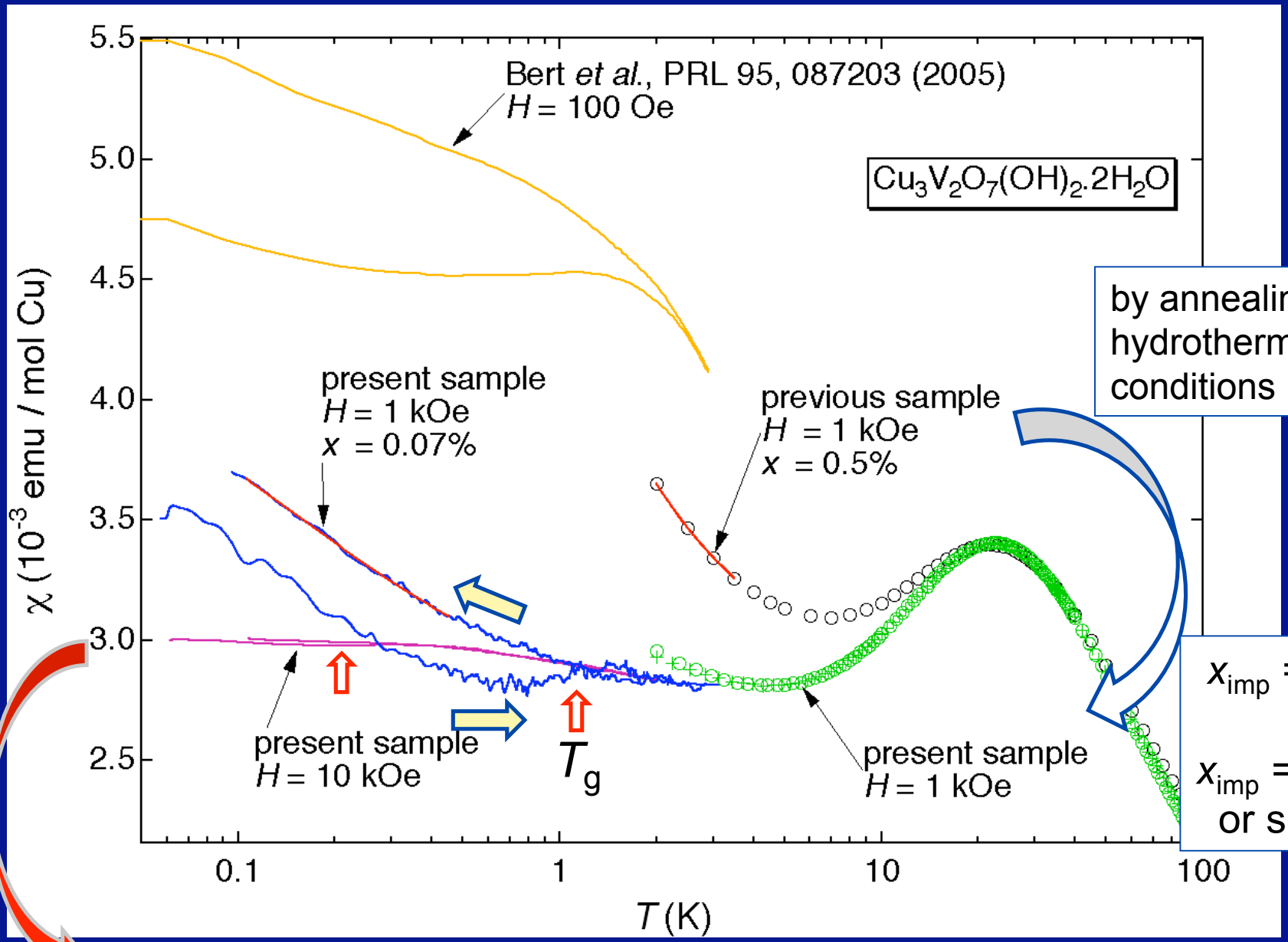
2 of ~300



x_0 can be limited by 1 / x_{imp} in the dirty milit.

- The number of intact spins decreases rapidly with x_{imp}.
- Even for small x_{imp}, a defect may influence the surroundings.

Higher-quality sample: *c* down to 60 mK



by annealing in hydrothermal conditions

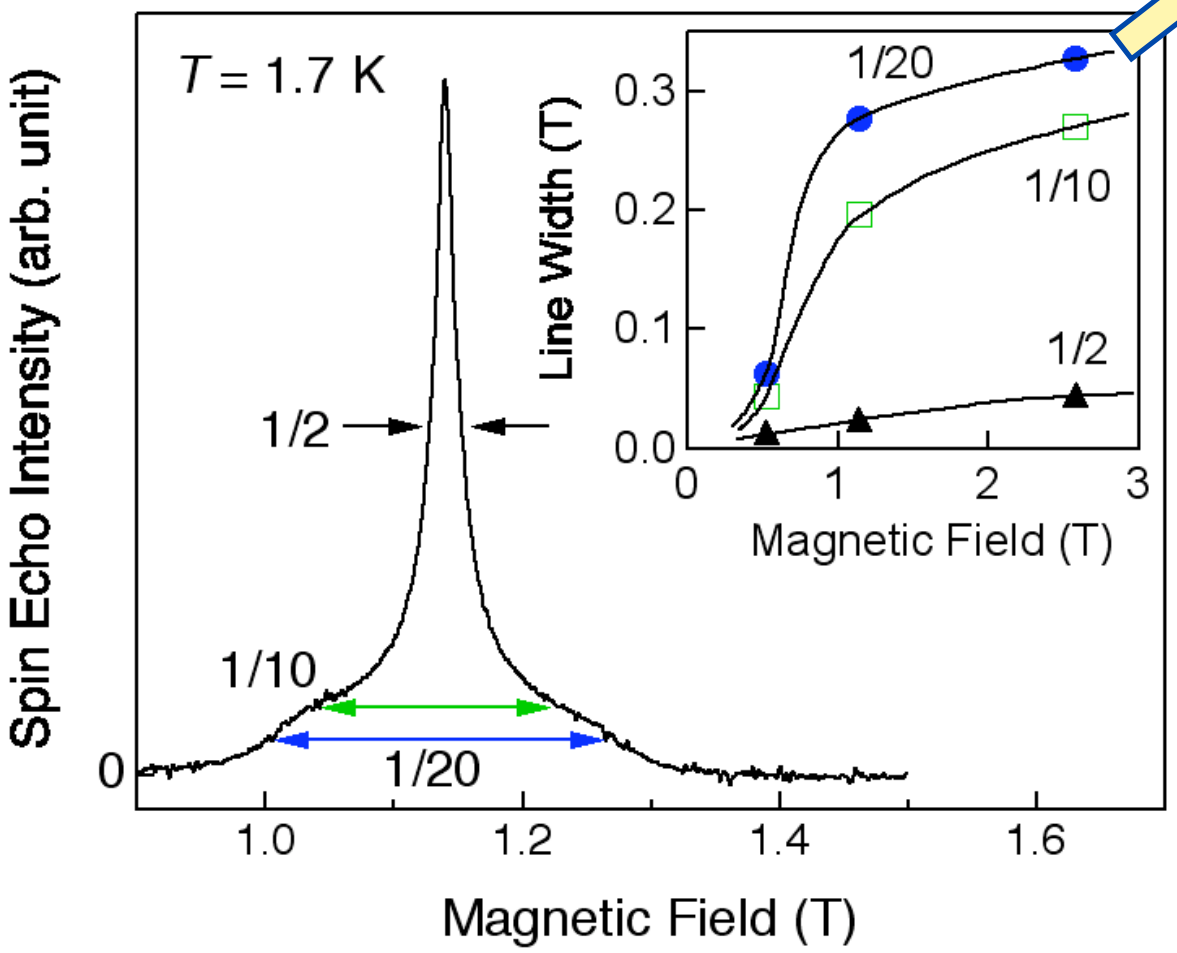
x_{imp} = 0.5%
↓
x_{imp} = 0.07% or smaller

Gapless, or $D < J / 1500$

T. Tayama & T. Sakakibara

Field-induced moments near a defect

Previous V NMR spectrum at 1.7 K

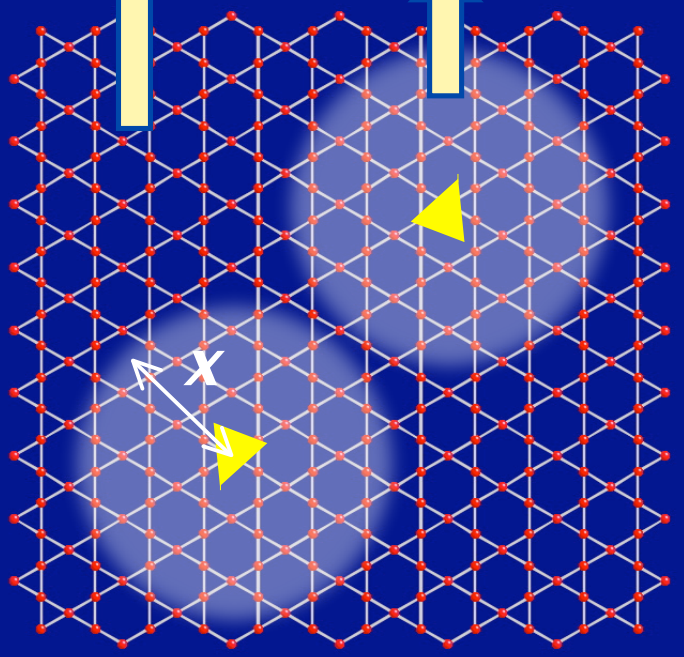


The line width increases with *H*.

cf. HAF chains in Sr_2CuO_3
chain ends or defects
induce staggered moments.

Sharp peak

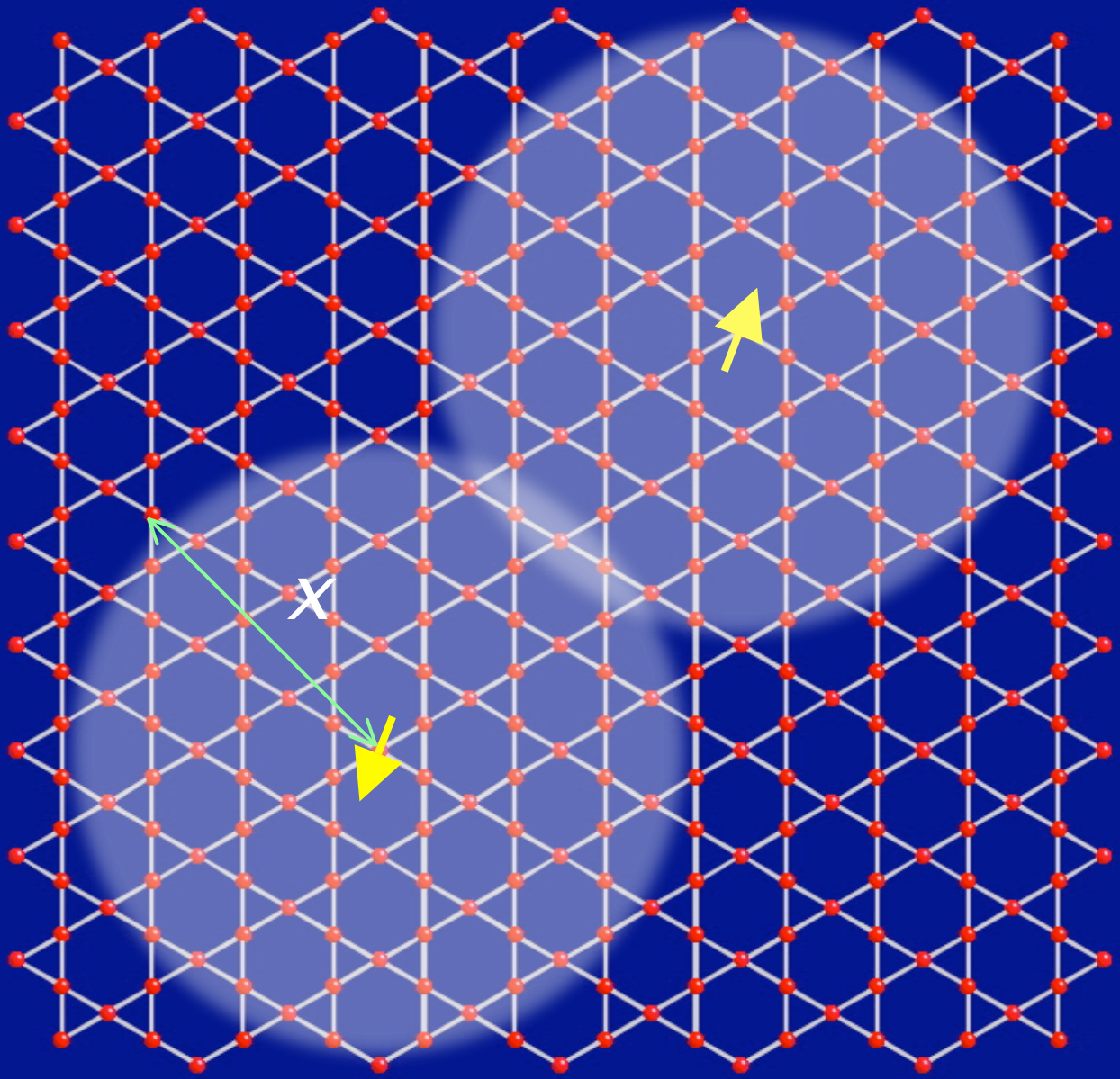
Broad hump



ZH *et al*., JPSJ 70, 3377 (2001)

No more broad component in a clean sample.

Impurity-induced spin-glass on frustrated lattices

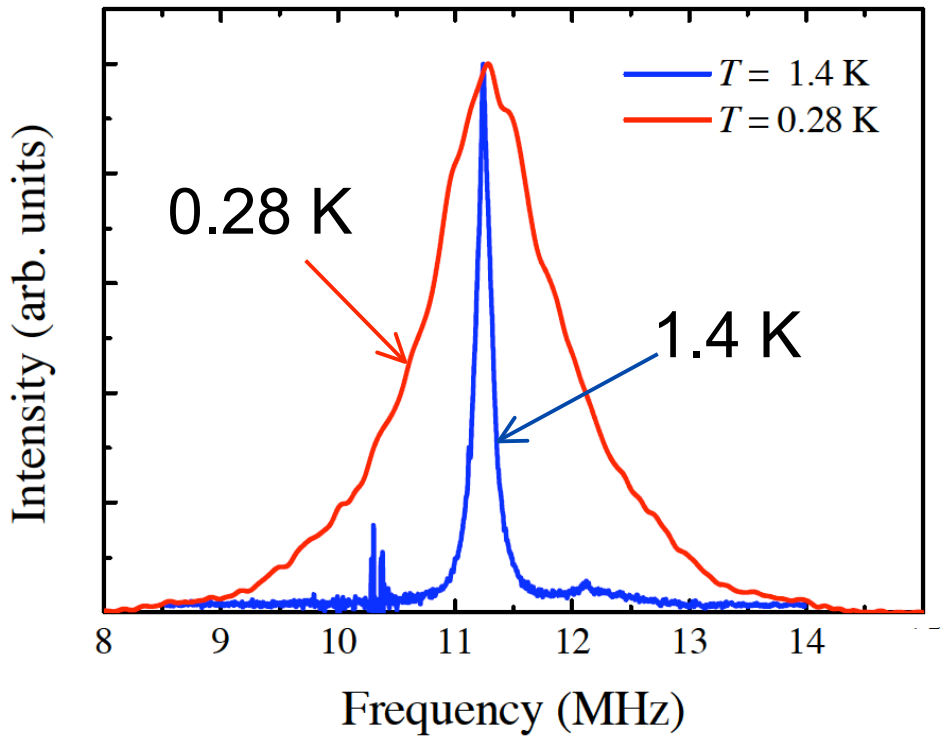


Gapless or
a very tiny gap
means large *x!*

Maybe,
x becomes very
large as $T \rightarrow 0$,
close to the
quantum critical

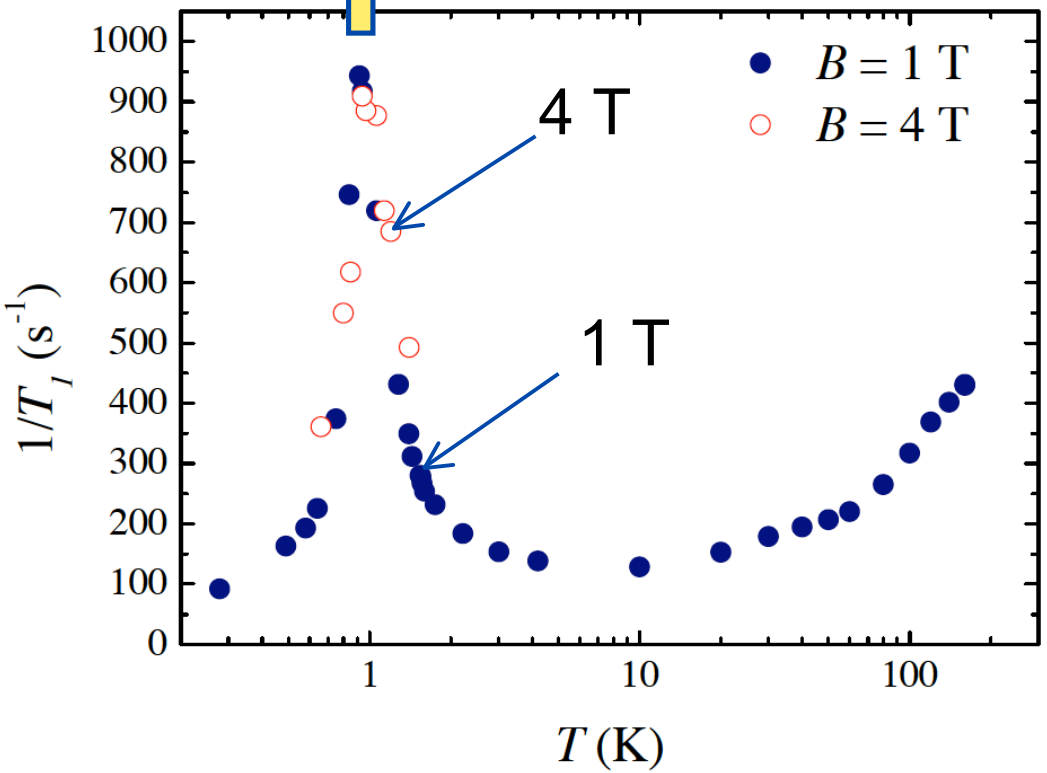
Even a small x_{imp}
can cause SG.

A spin glass transition may occur, when domains with staggered moments induced by defects overlap with each other.



Recent ^{51}V NMR results on a sample with x_{imp} < 0.1%

LRO at T ~ 0.9 K?



No hump, but only a sharp peak at 1.4 K.

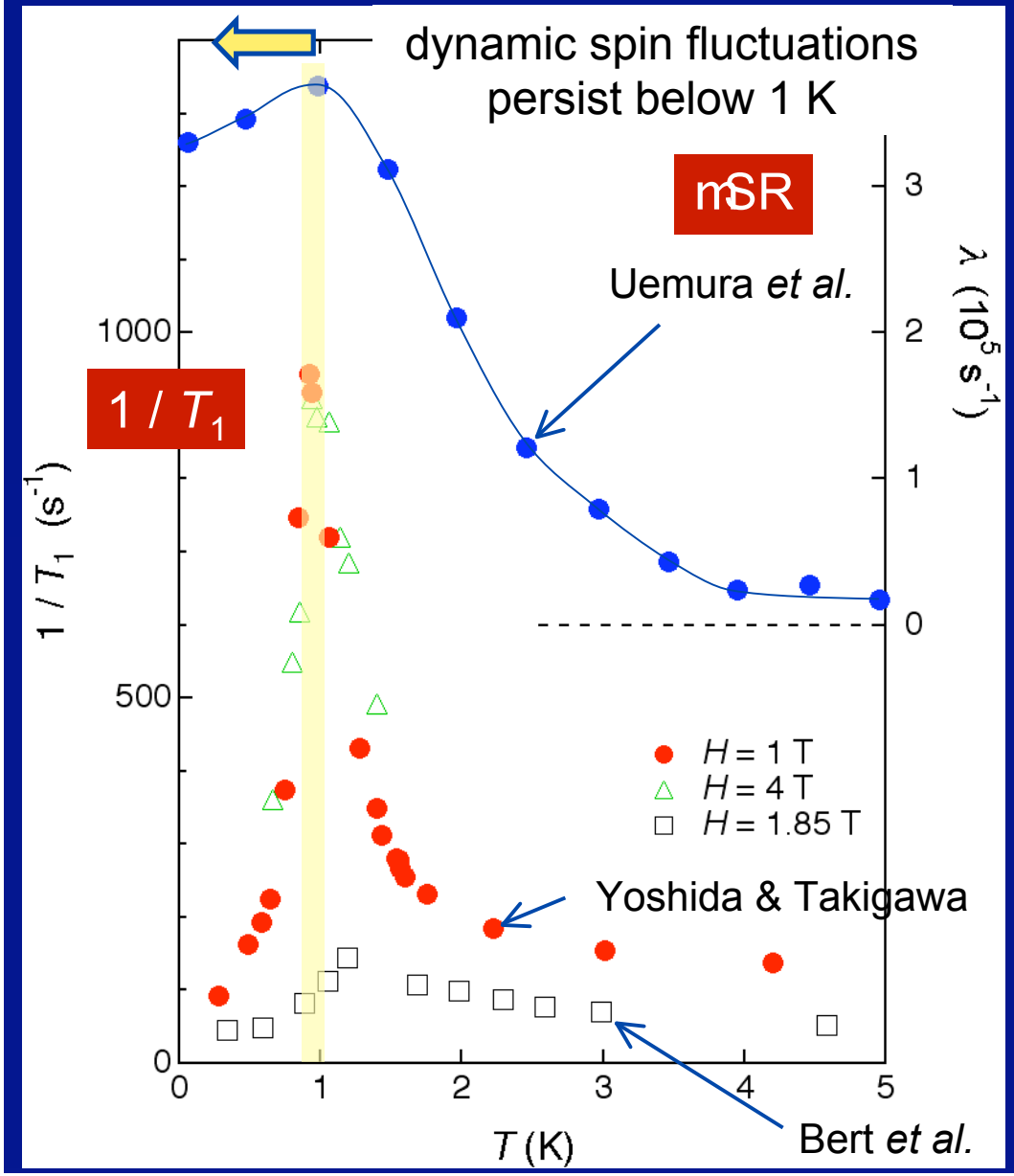
$1/T_1$ seems to diverge at T ~ 0.9 K!

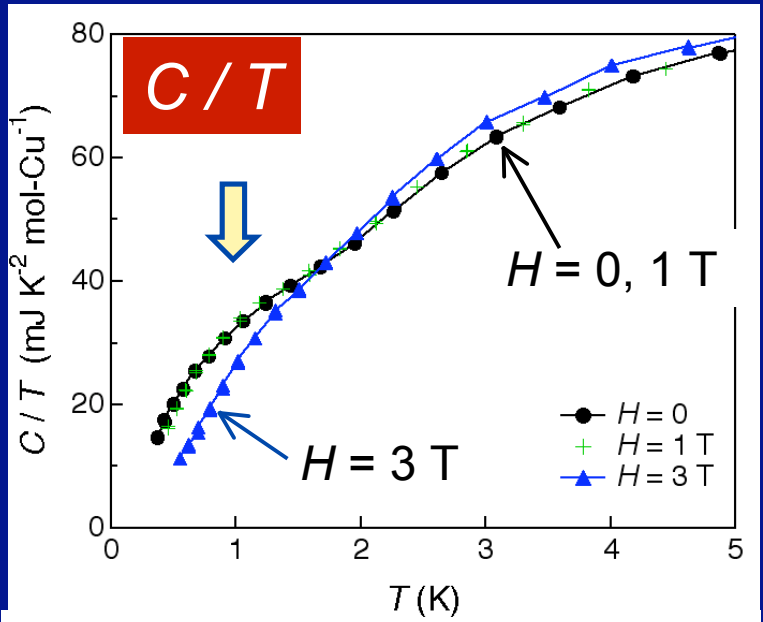
M. Yoshida & M. Takigawa

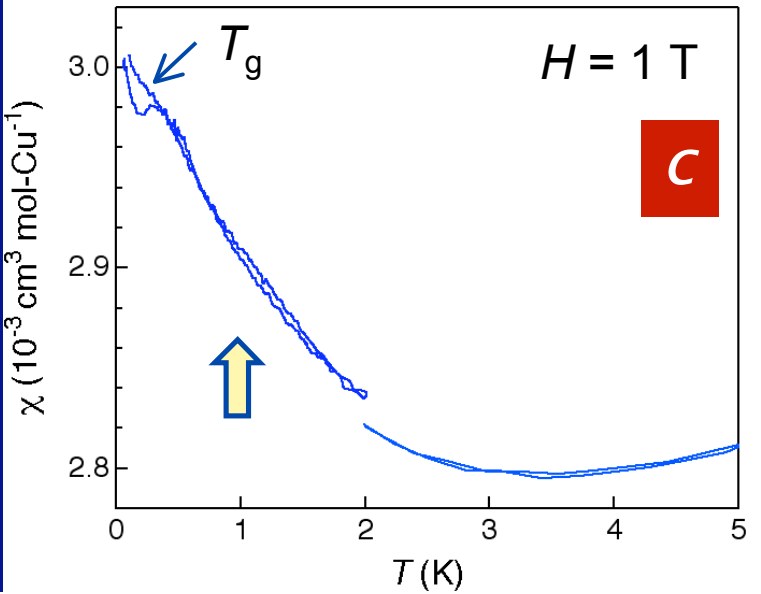
Slow spin dynamics

No anomalies in *c* and *C*

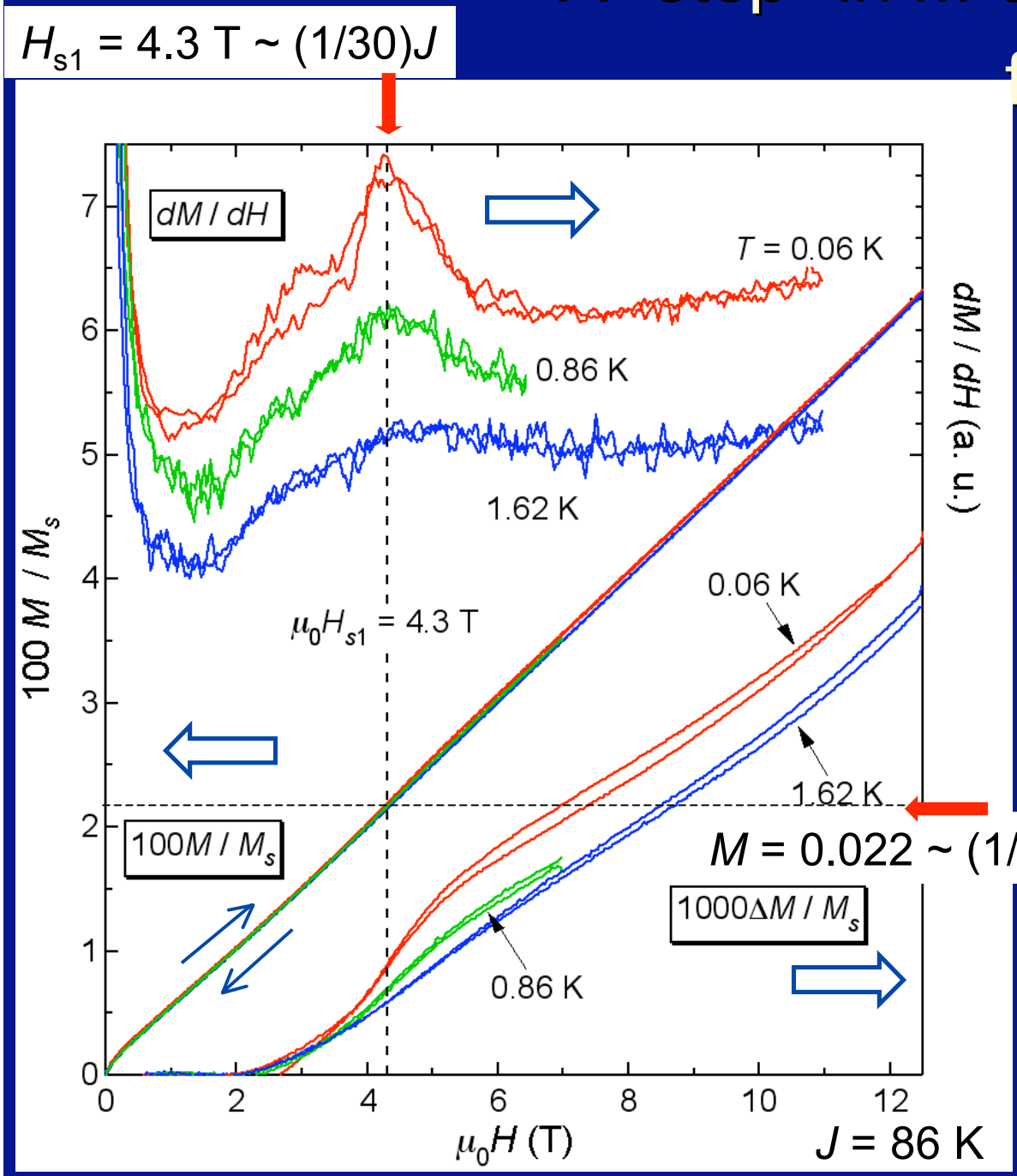
Slowing down toward $T \sim 0.9$ K, but may not go to LRO!







A "step" in M under a magnetic field



M = 0.022 ~ (1/45)M_s

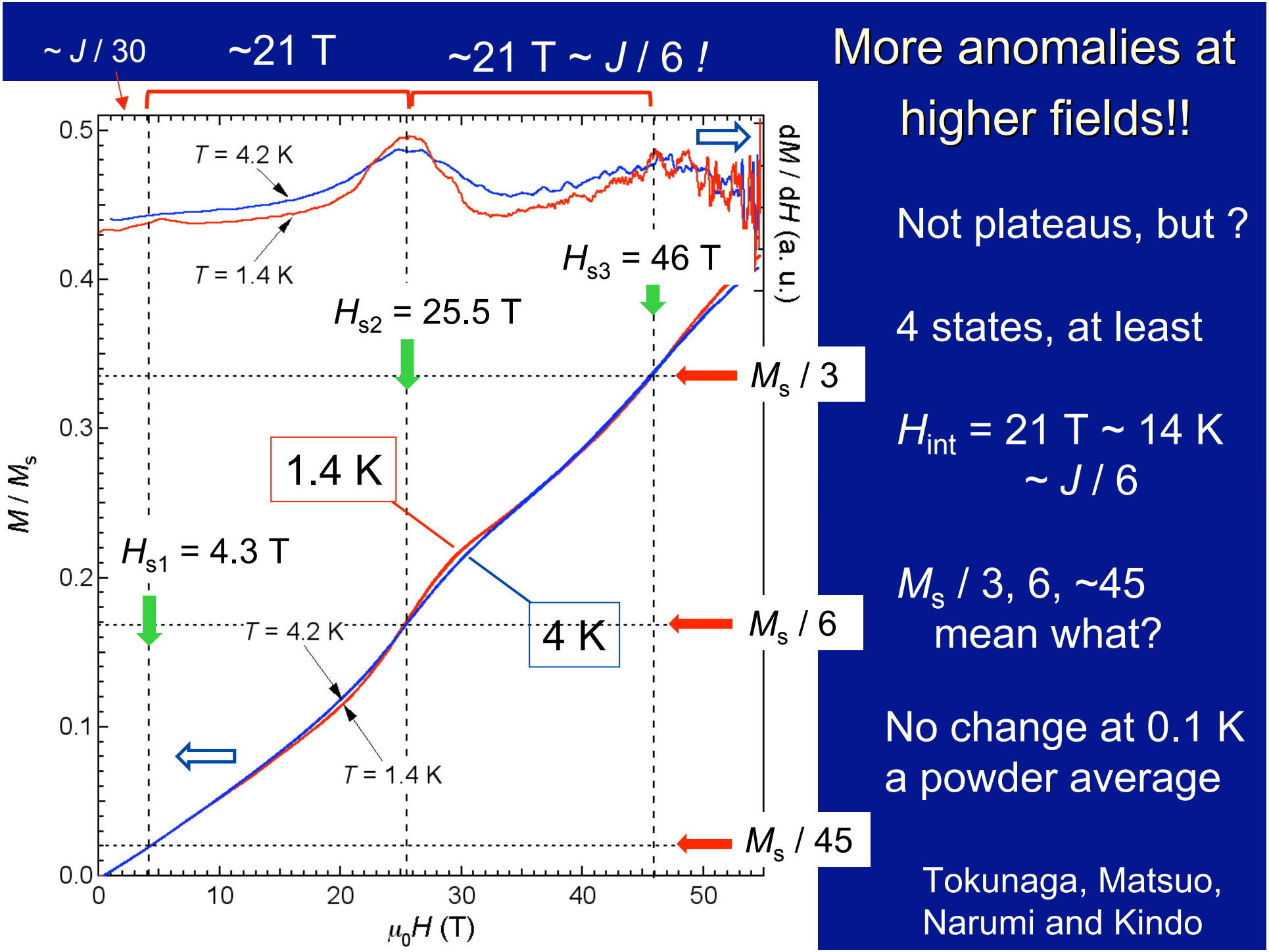
Nothing before;
free spins masked.

with less x_{imp},
after SG,

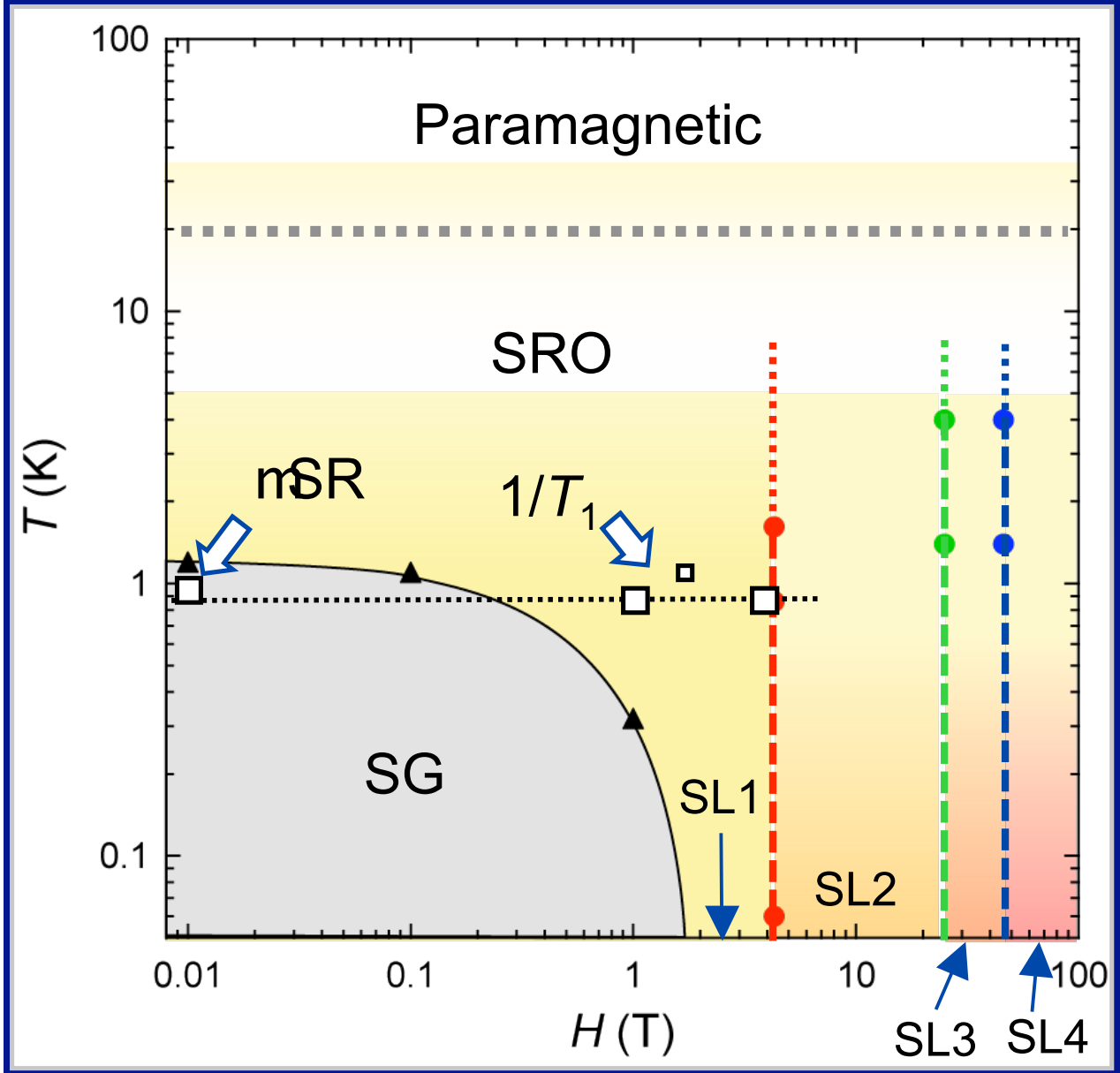
Anomaly at
H_{s1} = 4.3 T,
M = 0.022M_s

Spin flop?
Metamagnetic?
but no LRO.

Tayama & Sakakibara


~ J / 30
~21 T
~21 T ~ J / 6 !
More anomalies at higher fields!!
Not plateaus, but ?
4 states, at least
H_int = 21 T ~ 14 K ~ J / 6
M_s / 3, 6, ~45 mean what?
No change at 0.1 K a powder average
Tokunaga, Matsuo, Narumi and Kindo
T = 4.2 K
T = 1.4 K
H_s3 = 46 T
H_s2 = 25.5 T
H_s1 = 4.3 T
1.4 K
4 K
M_s / 3
M_s / 6
M_s / 45
M / M_s
dM / dH (a. u.)
μ_0H (T)
0.0
0.1
0.2
0.3
0.4
0.5
0
10
20
30
40
50

Phase diagram of volborthite: Summary



Spin liquids
- $D < J / 1500$
- large x
- extremely slow spin dynamics?

Impurity effects
- SG due to large x
- suppressed by H

Mag. steps
???
a lot of mysteries remain for future!