Frustrated pairs: magnon BEC in geometrically frustrated spin dimer compounds

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University of Toronto (2008)
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J. Schmalian (Ames)

Numerical simulations:
N. Kawashima (Tokyo)
S. Hass (USC)

Crystallography:
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R. Kiyanagi (IPNS)

Neutron scattering:
C. Ruegg, H. Ronnow,
D. McMorrow (UCL & PSI)
M. Stone, M. Lumsden (ORNL)

EPR:
S. Hill, S.-C. Lee, A. Wilson,
S. Kim (UF)

NMR:
S. Brown (UCLA)
R. Stern (Tallinn, Estonia)
C. Berthier, S. Kraamer,
M. Horvatic (CNRS)

Work at Stanford University is supported by the National Science Foundation, Division of Materials Research under grant DMR-0134613. Crystal growth equipment purchased with support from the Department of Energy, Office of Basic Energy Sciences, under contract DE-AC02-76SF00515.
Research program:

New materials – unconventional magnetic & electronic ground states & phase transitions

(1) Quantum magnetism:

(2) Superconductivity:

(3) Low dimensional materials:

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Crystal growth

- \( \text{Pb}_{1-x} \text{TI}_x \text{Te} \)
- \( \text{BaPb}_{1-x} \text{Bi}_x \text{O}_3 \)
- \( \text{BaFe}_{2} \text{As}_2 \)
- \( \text{RTe}_3 \)
- \( \text{RTe}_2 \)
- \( \text{R}_2 \text{Te}_5 \)

- \( \text{BaCuSi}_2\text{O}_6 \)
- \( \text{Sr}_2\text{Cu(BO}_3)_2 \)
- \( \text{Ba}_2\text{Cu(BO}_3)_2 \)
- \( \text{BaCu}_2\text{Si}_2\text{O}_7 \)
- \( \text{BaCuB}_2\text{O}_5 \)
- \( \text{Ba}_3\text{Mn}_2\text{O}_8 \)

- \( \text{Ba}_2\text{OsNa}_6\text{O}_6 \)
- \( \text{R-Mg-Cd} \)
- \( \text{Al-Pd-Re} \)
- \( \text{R}_6\text{Mo}_4\text{Al}_{43} \)
(1) A short introduction to spin dimer compounds:
   - what they are, and why we should care

(2) “Frustrated pairs”: two neat examples for which frustration plays a crucial role…
   - bct lattice \((\text{BaCuSi}_2\text{O}_6)\)
   - triangular lattice \((\text{Ba}_3\text{Mn}_2\text{O}_8)\)
Properties of an isolated pair

**Low field properties:**
- thermodynamic distribution
- calculate $C_p$, $M$, $\chi$...

$$\chi = \frac{N(g\mu_B)^2}{k_B T (3 + \exp(J/T))}$$

**High field properties:**
- $g\mu_B H_c = J$
- thermal broadening at finite $T$

**Question:**
- what happens for weakly interacting spin dimers?

$$J/k_B = 100K, g = 2.00$$

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\[ J = JS_1 \cdot S_2 \]
Insight from the two leg ladder

\[ H = J \sum_{i=1}^{N} S_{1,i} \cdot S_{2,i} + J' \sum_{\alpha=1}^{2} \sum_{i=1}^{N} S_{\alpha,i} \cdot S_{\alpha,i+1} - h \sum_{\alpha=1}^{2} \sum_{i=1}^{N} S_{\alpha,i}^z, \]

- for \( J > J' \), treat perturbatively

\[ S \equiv \left| \downarrow \right\rangle, \quad T_- \equiv \left| \uparrow \right\rangle \]

\[ H_{\text{eff}} = J' \sum_{i} \left[ \tilde{S}_i^x \tilde{S}_{i+1}^x + \tilde{S}_i^y \tilde{S}_{i+1}^y + \frac{1}{2} \tilde{S}_i^z \tilde{S}_{i+1}^z \right] - \hbar_{\text{eff}} \sum_{i} \tilde{S}_i^z + C \]

- delocalized triplet excitations (triplon)

\[ H_{\text{eff}} \equiv t \sum_{i,\alpha} \left( b_{i+\hat{\alpha}} \cdot b_i + \text{h.c.} \right) + V \sum_{i,\alpha} n_i n_{i+\hat{\alpha}} + \mu \sum_i n_i \quad \text{where} \quad t = V = \frac{J'}{2} \quad \& \quad \mu = h - J \]

- i.e. realization of a lattice gas of hard core bosons, for which \( B \) controls \( \mu \)
Ground states:

- Ordered state is a product of individual dimer terms of form:
  \[ |\psi_i\rangle = \cos \theta_i |s\rangle + \sin \theta_i e^{i\phi_i} |t\rangle \]

- Macroscopic occupancy of minimum of triplet band \((\pi/a, \pi/a)\)
- Triplet density \(\rho = <s_z> = m_z\)
- Amplitude of order parameter = \(m_{xy}\), phase = angle of spins in plane
- Spontaneously broken U(1) symmetry

Example:

- \(\text{SrCu}_2(\text{BO}_3)_2\)
- \(\text{TICuCl}_3\)

No candidate to date
So why study spin dimer compounds?

(1) Can access lattice gas models which would be unphysical for simple AFs: i.e. in the limit of weak spin orbit coupling, can “engineer” Hamiltonian with highly anisotropic effective exchange… … and potentially access to some rather unusual quantum phases of matter

(2) Tunable by magnetic field, so can explore entire quantum phase diagram:

(3) “Protected” against symmetric anisotropies: terms like $D S_z^2$ in effective Hamiltonian can only mix singlet and triplet states in second order $\rightarrow$ terms which break axial symmetry are suppressed relative to a simple AF

(4) Relatively few candidate materials…
This talk: magnon BEC in two neat compounds with geometrically frustrated lattices

(1) BaCuSi$_2$O$_6$

(2) Ba$_3$Mn$_2$O$_8$

more frustrated?
New materials?

Anthropogenic pigments:

- **Egyptian blue** $\text{CaCuSi}_4\text{O}_{10}$
- **Chinese blue** $\text{BaCuSi}_4\text{O}_{10}$
- **Han purple** $\text{BaCuSi}_2\text{O}_6$

Crystal growth

(1) BaCuSi$_2$O$_6$

(a) Evidence for Pb in archeological samples - PbO flux works

(b) but LiBO$_2$ better

(2) Ba$_3$Mn$_2$O$_8$

Mn$^{5+}$ valence unusual
Requires strongly oxidizing flux
NaOH works very well
Case 1: *bct* lattice - BaCuSi$_2$O$_6$

Inelastic neutron scattering (Ch. Ruegg):
- $J \sim 4.5$ meV; $J' \sim 0.5$ meV
- c-axis bandwidth finite but small ($< 0.05$ meV)
- spin gap $\Delta = 3.1$ meV $\Rightarrow H_{c1} = \Delta/g\mu_B \sim 23.5$ T for $H \parallel [001]$
Structural phase transition

(with Z. Islam, APS)

• incommensurate lattice modulation
  • $q_{IC} = 0.129 \, b^*$
  • presumably driven by rigid rotation of SiO$_4$ tetrahedra
  • lack a complete structural model
  • subtle effect, and doesn’t affect subsequent analysis

\[
\frac{b - a}{\frac{1}{2} (b + a)} = 0.2 \%
\]

E. Samulon, Z. Islam et al., PRB 73, 100407(R) (2006).
High field behavior

- does this correspond to BEC of triplons as conceived theoretically?
- address by looking at critical scaling (characteristic of universality class)
- thermal phase transition: \( C_p \sim (T-T_c)^{-\alpha} \)
- quantum phase transition: \( T_c \propto (H - H_{c1})^\nu \)
- BEC universality class: \( \nu = 2/d \)
- 3D Ising: \( \nu = 1/2 \)
Experimental determination of $T_c(H)$ close to the QCP

(a) Magneto-caloric effect: (with Marcelo Jaime, NHMFL)
• jump in $T$ of sample on entering/leaving ordered state

(b) Cantilever torque magnetometry: (with N. Harrison, L. Balicas, NHMFL)
• divergence in 2nd derivative of magnetization

Phase diagram & critical scaling analysis

- Two parameter fit to $T_c \propto (H - H_{c1})^\nu$ with a sliding window
- BEC scaling exponents observed ($\nu = 2/d$)
- Surprise - cross-over to 2D exponent approaching the QCP!

**Question:** Individual triplets can move in 3D, so why is the collective behavior at the QCP in just 2D?

Dispersion relation for perfect $bct$ lattice

$$E = J' \left( \cos k_x + \cos k_y \right) + 2J_f \cos \frac{k_x}{2} \cos \frac{k_y}{2} \cos k_z$$

Case of non-interacting triplets:
- At $T = 0$ all particles will be in the condensate at $k = (\pi, \pi)$
- But there is no interlayer hopping for $k = (\pi, \pi)$!
- $\rightarrow$ independent $2d$ condensates
Origin of vanishing dispersion: geometric frustration

- In-plane ordering wave-vector = \((\pi, \pi)\)

- Body centered tetragonal lattice
- Geometric frustration
- Adjacent planes decoupled!
Order from disorder?

- Must consider the effect of phase fluctuations on this delicate frustration…

leads to an effective unfrustrated biquadratic interlayer hopping / coupling \( K \sim \rho^2 \)
- restores 3D phase coherence for finite triplet concentrations \( \rho \)

- but at the QCP, \( \rho \to 0 \) so \( K \to 0 \)
- 2D fixed point determines universal scaling

Theory: C. Batista, LANL & J. Schmalian, Ames

Batista, Schmalian et al., PRL 98, 257201 (2007).
• BEC implies a spontaneously broken axial symmetry
• What effects might break this apparently delicate symmetry?

For BaCuSi$_2$O$_6$, it turns out that the largest effect is from dipolar interactions…

• Dipolar energy $\sim 1/r^3$, so consider first the intradimer dipolar coupling…
U(1) symmetry?

- Intradimer dipolar coupling causes zfs of the triplet...

\[ H \parallel c: \]

\[ zfs = D = \frac{\mu_0}{16\pi r^3} \left( 2g_{\|}^2 + g_{\perp}^2 \right) \mu_B^2 \approx 0.11K \]

\[ H_{dip} = DS_z^2 \quad D_{obs} = 0.10(1) K \]

- For \( H \perp \) dimer axis \( \rightarrow \) effective anisotropy energy (gap to “Goldstone” mode)

\[ \approx \frac{DJ'}{J} \approx 10 mK \]

- i.e. the axial symmetry required for BEC is remarkably robust (“protected”)
Case 2: triangular lattice

(1) BaCuSi$_2$O$_6$

(2) Ba$_3$Mn$_2$O$_8$

\[ \chi (10^{-3} \text{ emu/molOe}) \]

\[ T (\text{K}) \]

\[ H = 5000 \text{ Oe} \]

\[ H \parallel [001] \]

\[ H \parallel [100] \]

more frustrated?
Ba$_3$Mn$_2$O$_8$

- R$3m$
- Mn$^{5+}$, 3d$^2$, s=1 dimers

3 twists:
- in-plane frustration
- single ion anisotropy
- triplet and quintuplet condensation

3 twists:
• in-plane frustration
• single ion anisotropy
• triplet and quintuplet condensation

Spin-orbit coupling for 3d ions:

L is quenched, but “residual” SO interaction leads to…

• g anisotropy: $g \rightarrow g_{\mu\nu}$
• anisotropy energy: $D S_z^2$

no effect for $s=1/2$
but significant for $s=1$
Triplon dispersion (M. Stone & M. Lumsden, ORNL)

spin gap: $\Delta = 1.081$ meV
intradimer: $J_0 = 1.642$ meV
in-plane interdimer: $J_2 = 0.256$ meV ($& J_3 = 0.142$ meV)
out-of-plane interdimer: $J_1 = -0.118$ meV ($& J_4 = -0.037$ meV)
single ion anisotropy: $D = -0.032$ meV (from EPR)

• i.e. quasi-2D material in which planes of vertical dimers arranged on triangular layers interact weakly in the perpendicular direction
High field behavior: triplet ordered states

Heat capacity:

(a) $H \parallel c$

(b) $H \parallel \alpha$

MCE (with M. Jaime, NHMFL):

(a) $H \parallel c$

(b) $H \perp c$
High field behavior: triplet ordered states

Torque (with L. Balicas & Y.-J Jo, NHMFL):

Magnetic structure?

(a) NMR (H∥c): (S. Brown, UCLA):

(b) Neutron scattering (H∥a): (M. Stone & M. Lumsden, ORNL)

- in-plane wave vectors are both very close to \((2\pi/3a, 2\pi/3a)\)

- in absence of other information, resort to an analysis of the spin Hamiltonian for a qualitative understanding of the ground states…
Spin Hamiltonian for \( \text{Ba}_3\text{Mn}_2\text{O}_8 \)  

Theory: Cristian Batista (LANL)

For \( \text{Ba}_3\text{Mn}_2\text{O}_8 \) the minimal spin Hamiltonian is:

\[
H = \sum_{i,j,\mu,\nu} \frac{J_{i\mu j\nu}}{2} S_{i\mu} \cdot S_{j\nu} + D \sum_{i,\nu} \left( S^\eta_{i\mu} \right)^2 - g_{\alpha\alpha} \mu_B H \sum_{i \mu} S^z_{i\mu}
\]

The resulting effective Hamiltonian is:

\[
H = \frac{4J_1}{3} \sum_{l\langle\langle i,j\rangle\rangle} \left[ s_{i,l} \cdot s_{j,l+1} - \frac{13}{16} s_{i,l}^z s_{j,l+1}^z \right] + \frac{8J_2}{3} \sum_{l\langle\langle i,j\rangle\rangle} \left[ s_{i,l} \cdot s_{j,l} - \frac{13}{16} s_{i,l}^z s_{j,l}^z \right] + J_1 \alpha(\eta) \sum_{l\langle\langle i,j\rangle\rangle} \left( s_i^x s_j^x - s_i^y s_j^y \right) + 2J_2 \alpha(\eta) \sum_{l\langle\langle i,j\rangle\rangle} \left( s_i^x s_j^x - s_i^y s_j^y \right) - B \sum_{l,i} s_{i,l}^z
\]

i.e. anticipate canted AF, with xy components similar to triangular Heisenberg AF

Form approximate eigenstates from linear combination of singlet and triplet:

\[
|\psi_{i,l}\rangle = \cos \theta_{i,l} |00\rangle + \sin \theta_{i,l} e^{i\phi_{i,l}} |11\rangle \quad \rightarrow \quad |\psi_{\tilde{r}}\rangle = \frac{\sqrt{1 \pm \xi(\tilde{r})}}{2} |00\rangle + \frac{\sqrt{1 \pm \xi(\tilde{r})}}{2} e^{i\tilde{\phi}} |11\rangle
\]

Where \( \xi(\tilde{r}) = \sqrt{\cos^2 \theta + \sin^2 \theta \sin^2 \gamma \sin^2 \tilde{q} \tilde{r}} \) & \( \tan \phi_{\tilde{r}} = \cos \gamma \tan \tilde{q} \tilde{r} \)

Determine the ground states by minimizing \( E \) with respect to each parameter
Spin Hamiltonian for $\text{Ba}_3\text{Mn}_2\text{O}_8$  

Theory: Cristian Batista (LANL)

For $\text{Ba}_3\text{Mn}_2\text{O}_8$ the minimal spin Hamiltonian is:

$$H = \sum_{i,j,k} \left( -J \vec{S}_i \cdot \vec{S}_j + J_1 \vec{S}_i \cdot \vec{S}_j \right) + \sum_{i} \left( -B \vec{s}_i + \mu_B H \vec{s}_i \right)$$

The resulting effective Hamiltonian is:

$$H = \frac{4J}{3} + J_1 \alpha(n) + \sum_{l,i} \left( -B \vec{s}_i + \mu_B H \vec{s}_i \right)$$

Aside: Classical ground state for a Heisenberg AF on a triangular lattice

For a single triangular plaquette:

$$E = J \left( \vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3 + \vec{S}_3 \cdot \vec{S}_1 \right) = \frac{J}{2} \left( \vec{S}_1 + \vec{S}_2 + \vec{S}_3 \right)^2 - \frac{3}{2} JS^2$$

From which the energy is minimized when...

$$\vec{S}_1 + \vec{S}_2 + \vec{S}_3 = 0$$

... corresponding to a 120° structure:

$$q = (2\pi/3, 2\pi/3)$$

Determine the ground states by minimizing $E$ with respect to each parameter
Classical groundstates: $H \parallel c$

(a) no interlayer coupling ($J_1 = 0$):

(b) finite interlayer coupling ($J_1 > 0$):

$\Delta E$ due to deviation from $120^\circ$:
- in-plane coupling: even (quadratic)
- out-of-plane coupling: odd (linear)

$$\alpha = \cos^{-1}\left(-\frac{1}{2} + \frac{J_1}{4J_2}\right) \approx 117^\circ$$
Classical groundstates: $H \parallel c$

(a) no interlayer coupling ($J_1 = 0$):
- In-plane coupling: even (quadratic)
- Out-of-plane coupling: odd (linear)

(b) finite interlayer coupling ($J_1 > 0$):
- Ferromagnetic interlayer coupling
- In-plane spiral structure:

\[
\begin{pmatrix}
1 & -1 & 0 \\
-1 & 1 & 1 \\
0 & 1 & 1
\end{pmatrix}
\approx 117^\circ
\]

\[
\frac{1}{J_1} - \frac{1}{J_2} \approx 117^\circ
\]

\[
\alpha \approx \frac{\pi}{3} \approx 120^\circ
\]
Classical groundstates: $H \perp c$

(a) $D = 0, J_1 = 0$:
- Easy axis in x-y plane
- Sum of xy components $\sim 0$
- $\Rightarrow$ modulated structure
- But modulation costs energy…

(b) $D < 0, J_1 > 0$:
- Easy axis in x-y plane
- Sum of xy components $\sim 0$
- $\Rightarrow$ modulated structure
- But modulation costs energy…

\[
\frac{8J_2}{3} \sum_{l<i,j} \left[ s_{i,l} \cdot s_{j,l} - \frac{13}{16} s_i^z s_j^z \right]
\]
What about dimensional reduction?

(1) \( \text{BaCuSi}_2\text{O}_6 \)

- \( q = (\pi/a, \pi/a) \)
- frustrates interlayer coupling

(2) \( \text{Ba}_3\text{Mn}_2\text{O}_8 \)

- if \( q = (2\pi/3a, 2\pi/3a) \), then interlayer coupling is also perfectly frustrated
- but \( q \neq (2\pi/3a, 2\pi/3a) \)…

more frustrated
BaCuSi$_2$O$_6$ vs Ba$_3$Mn$_2$O$_8$: symmetry

- Planar inversion symmetry about $Q = (\pi/a, \pi/a)$
- Interlayer coupling can only introduce terms quadratic in $k$

$$E(Q + k) \approx J'(k_x^2 + k_y^2) + 2J_f k_x k_y$$

- No inversion symmetry about $Q = (2\pi/3a, 2\pi/3a)$
- Interlayer coupling introduces terms linear in $k$

$$E(Q + k) \propto J_2 \left(-3 + k_x^2 + k_y^2 + k_x k_y\right) + \frac{\sqrt{3}}{2} J_1 \left(k_x + k_y\right)$$

$Q \neq (2\pi/3a, 2\pi/3a) \Rightarrow 3D$ spiral
So which lattice is more frustrated?

(1) BaCuSi$_2$O$_6$

- robust interlayer frustration
- dimensional reduction at T = 0

(2) Ba$_3$Mn$_2$O$_8$

- perfect frustration is not protected
- 3d incommensurate spiral

less frustrated!
What about the quintuplet states of Ba$_3$Mn$_2$O$_8$?

**Magnetization:**
(with R. McDonald, NHMFL)

**C$_p$ & MCE:**
(with M. Jaime, NHMFL)
What about the quintuplet states of $\text{Ba}_3\text{Mn}_2\text{O}_8$?

- Second region of LRMO
- Can be understood following a similar treatment of the effective Hamiltonian
Summary

Spin dimer compounds provide access to some exciting physics and some beautiful magnetic structures...

S. Sebastian et al., PRB. 72, 100404(R) (2005).
E. Samulon et al., PRB 73, 100407(R) (2006).
S. E. Sebastian et al., PRB 74, 180401(R) (2006).
Ch. Ruegg et al., PRL 98, 017202 (2007).
S. Kramer et al., PRB 76, 100406(R) (2007).


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