Quantum `spin-metal' phase in an organic Mott insulator with two-dimensional triangular lattice

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Current projects in Matsuda-Shibauchi group in Kyoto



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Parislec

Acknowledgement:

Kyoto University

N. Kawakami, Yong-Baek Kim, P. A. Lee, T. Senthil, and N. Nagaosa for discussions



Outline

1. Introduction

- 2. A quantum spin liquid state in 2D organic Mott insulator $EtMe_3Sb[Pd(dmit)_2]_2$ with triangular lattice
- 3. Elementary excitations and phase diagram of the quantum spin liquid
- 4. Quantum spin metal: a novel phase in the Mott Insulator
- 5. Summary

M.Yamashita *et al.*, Nature Phys. **5**, 44 (2009).
M. Yamashita *et al.*, Science **328**, 1246 (2010).
D. Watanabe *et al.*, Nature Commun. (2012).



Quantum Liquid

Quantum fluctuation prevents conventional ordering



Quantum spin liquid (QSL)

A state of matter where strong quantum fluctuations melt the longrange magnetic order even at absolute zero temperature.

Spin Liquids are states which do not break any simple symmetry: neither spin-rotational symmetry nor lattice symmetry.

P. W. Anderson, Mater. Res. Bull (1973), Science (1987).

Notion of QSL is firmly established in 1D





Spinon excitation (S=1/2, e=0)

QSL

No LRO

Gapless

□ Algebraic spin correlation (critical phase)

 $\langle S(r)S(0)\rangle \sim r^{-\nu}$

QSLs in two and three dimensions

Geometrical frustrations are required

- Classical A large ground-state degeneracy
- Quantum Quantum fluctuation lifts the degeneracy and a QSL ground state may appear

Only a few candidate materials exist.

Triangular lattice



³He on graphite Organic compounds

Kagome lattice



Pyrochlore lattice



 $Na_4Ir_3O_8$

 $ZnCu_{3}(OH)_{6}CI_{2}$ (Herbertsmithite) BaCu_{3}V_{2}O_{8}(OH)_{2} (Vesigniete)

QSLs in two and three dimensions

Geometrical frustrations are required

- Classical A large ground-state degeneracy
- Quantum Quantum fluctuation lifts the degeneracy and a QSL ground state may appear

Only a few candidate materials exist.

Triangular lattice







Organic compounds bulk

surface

³He on graphite

Organic Mott insulators with trianglar lattice





Strong candidates that host a QSL state

What kind of QSL is realized?

Many types of QSL proposed

- Resonating-valence-bond liquid
 - Chiral spin liquid
 - Quantum dimer liquid
 - Z₂ spin liquid
 - Algebraic spin liquid
 - Spin Bose Metal
 - etc...

Elementary excitations

Spinon with Fermi surface

- Vison
- Majorana fermions
 - etc...

Heisenberg spins on 2D triangular lattice

$$\mathcal{H} = J \sum_{i \in \mathcal{N}} oldsymbol{S}_i \cdot oldsymbol{S}_j$$

(i,j)

Resonating Valence Bond (RVB) Liquid Long-range order

Further fluctuations are required to realize a QSL

Superposition of different of the second spin configurations leads to a liquid-like wavefunction.

P. Fazekas and P. W. Anderson, Philos. Mag. (1974).

3-sublattice Néel order (120° structure)

D. Huse and V. Elser, PRL (1988).

- L. Caprioti, A. E.E. Trumper, S. Sorella, PRL (1999).
- B. Bernu, C. Lhuillier, L. Pierre, PRL (1992).

Quantum spin liquid on a 2D triangular lattice

Heisenberg model for a triangular lattice

4 spin ring exchange model

$$\hat{H}_{\text{ring}} = J_2 \sum_{\bullet \bullet} P_{12} + J_4 \sum_{\bullet \bullet} \left(P_{1234} + P_{1234}^{\dagger} \right)$$

$$P_{1234} = (\mathbf{s}_1 \cdot \mathbf{s}_2)(\mathbf{s}_3 \cdot \mathbf{s}_4) + (\mathbf{s}_1 \cdot \mathbf{s}_4)(\mathbf{s}_3 \cdot \mathbf{s}_2)$$

$$-(\mathbf{s}_1 \cdot \mathbf{s}_3)(\mathbf{s}_2 \cdot \mathbf{s}_4)$$
When $J_4 > 0$

$$\theta_1 - \theta_2 + \theta_3 - \theta_4 = \pi$$

4-spin ring exchange yields a strong frustration

G. Misguich et al., PRB (1999).

W. LiMing, G. Misguish, P. Sindzingre, C. Luhuiller, PRB (2000).

QSL with gapped excitations



Quantum spin liquid on a 2D triangular lattice



Yoshioka-Koga-Kawakami, PRL (2010).

Energy resolutions of these calculations are not enough to discuss low energy excitations ($E \sim J/100$)

κ -(BEDT-TTF)₂Cu₂(CN)₃



Mott insulator : *t*~54.5 meV, *t*~57.5 meV and *U*~448 meV (*U*/*t*~8.2)

κ -(BEDT-TTF)₂Cu₂(CN)₃





μSR F. L. Pratt *et al.*, Nature (2011).

κ -(ET)₂Cu₂(CN)₃ : inhomogeneity or phase separation



$$-M(t)/M(\infty) = \exp[-(t/T_1)^{\alpha}]$$

Y. Shimizu *et al.* PRB **73**, 140407 (2006). NMR recovery curve shows stretched exponential α <0.5 below 1K (n



Relaxation curve below 300 mK

two components

S. Nakajima *et al.* ArXiv 1204.1785

Microscopic phase separation between gapped and gapless regions

singlet region _____(non-magnetic gapped)

The genuine feature of the QSL may be masked by inhomogeneity or phase separation. More homogeneous system is required.

β' - EtMe₃Sb[Pd(<u>dmit)</u>₂]₂





✓Very clean single crystals are available✓Many material variants are available

t'/t = 0.93



R. Kato's group at RIKEN

Quantum spin liquid state in β' - EtMe₃Sb[Pd(d<u>mit)₂]₂</u>

Two-dimensional Mott system with a quasi-triangular lattice Clean system with small defects



New QSL system EtMe₃Sb[Pd(<u>dmit</u>)₂]₂



K. Kanoda and R. Kato Annu. Rev. Condens. Matter Phys. (2011).



No magnetic order down to $\sim J/10,000$

 $\chi(T)$: 2D triangular

No muon spin rotation





Itou et al., Nature Phys. (2010).

New QSL system EtMe₃Sb[Pd(<u>dmit</u>)₂]₂



K. Kanoda and R. Kato Annu. Rev. Condens. Matter Phys. (2011).



β' -(Cation)[Pd(dmit)₂]₂



What kind of a QSL in $EtMe_3Sb[Pd(dmit)_2]_2$?

Two key questions

Elementary excitations

Gapped or gapless?

Magnetic or nonmagnetic?

Spin-spin correlation function

Phase diagram

How the nature of the QSL varies when tuned by non-thermal parameters, such as frustration?

Quantum critical nature of the QSL







Contaminated by large Schottky contribution at low temperatures



M. Yamashita et al., Science 328, 1246 (2010).

Thermal conductivity

 $\kappa = C \cdot \upsilon_s \cdot \ell$

Clear residual of κ/T $\kappa/T(T\rightarrow 0) = 0.19 \text{ W/K}^2\text{m}$ Evidence for a *gapless excitation*, like electrons in normal metals.

Estimation of mean free path $C/T \sim 20 \text{mJ}/\text{K}^2 \text{mol}$

 $largent \ell = 1.2 \ \mu m >> a \sim 1 \ nm$

More than 1000 times longer than the interspin distance!!

Itinerant excitation

Homogeneous Extremely long correlation length



M. Yamashita et al., Science 328, 1246 (2010).

Thermal conductivity



M. Yamashita et al., Science 328, 1246 (2010).

 $\Delta 7$

What kind of QSL state in $EtMe_3Sb[Pd(dmit)_2]_2$?

Gapless elementary excitations

Remaining key question

Are they magnetic?

Spin-spin correlation function

1D S=1/2 Heisenberg



Haldane system (S = 1)



What kind of QSL state in EtMe₃Sb[Pd(dmit)₂]₂?

Gapless elementary excitations Are they magnetic? Remaining key question Uniform susceptibility and magnetization at low temperatures Magnetic torque+ESR (down to 30 mK up to 32 T) SQUID (Only down to ~4 K due to Curie contribution) 2.10 C* g_{c*-b} M 2.05 Forque (arb. unit) g-value Н 1.95 0.3 K a or b 1.8 K 1.90 90 135 180 225 θ (dea) Isotropic contribution from impurities is cancelled. Torque picks up only anisotropic components.

•High sensitivity.

yoto University

Measurements on a tiny single crystal are possible.



Magnetic torque measurements in EtMe₃Sb[Pd(dmit)₂]₂





T-independent and remains finite at $T \rightarrow 0K$

increases linearly with H

 $\begin{array}{c} & \bigoplus \\ \Delta \propto \xi^{-1} \end{array} \begin{array}{c} \text{Gapless magnetic excitations (absence of spin gap)} \\ & \Delta \propto \xi^{-1} \end{array} \begin{array}{c} (\xi: \text{ magnetic correlation length, } \Delta: \text{ spin gap }) \\ & \bigoplus \\ \end{array} \begin{array}{c} \text{Divergence of } \xi \text{, i.e. QSL is in a critical state} \\ & \left\langle S^{z}(r)S^{z}(0)\right\rangle \propto r^{-\eta} \end{array} \begin{array}{c} \text{Algebraic spin liquid} \end{array}$

How the QSL changes when the degree of frustration varies?

Deuteration





Deuteration changes the degrees of geometrical frustration.



Deuteration changes the degrees of geometrical frustration.

Both h_9 - and d_9 -dmit systems exhibit essentially the same paramagnetic behavior with gapless magnetic excitations.

Both systems are in a critical state down to $k_B T \sim J/10,000$



Both h_9 -dmit and d_9 -dmit with different degrees of frustration exhibit essentially the same paramagnetic behavior with gapless magnetic excitations.

An extended quantum critical phase, rather than a QCP.

What kind of spin liquid is realized in dmit?

f t

Resonating-Valence-Bond theory

RESONATING VALENCE BONDS: A NEW KIND OF INSULATOR ?*

P. W. Anderson Bell Laboratories, Murray Hill, New Jersey 07974 and Cavendish Laboratory, Cambridge, England

(Perceived December 5 1972; Invited**)

Algebraic spin liquid

'HYSICAL REVIEW B, VOLUME 65, 165113 Quantum orders and symmetric spin liquids

Xiao-Gang Wen*

Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (Received 3 June 2001; revised manuscript received 21 December 2001; published 10 April 2002)

A concept-quantum order-is introduced to describe a new kind of orders that generally appear in quantum states at zero temperature. Quantum orders that characterize the universality classes of quantum states (described by complex ground-state wave functions) are much richer than classical orders that characterize the universality classes of finite-temperature classical states (described by positive probability distribution functions). Landau's theory for orders and phase transitions does not apply to quantum orders since they cannot be



of symmetric spin liquids, which have SU(2), U(1), or Z_2 gauge

VOLUME 86, NUMBER 9

PHYSICAL REVIEW LETTERS

Resonating Valence Bond Phase in the Triangular Lattice Quantum Dimer Model

R. Moessner and S.L. Sondhi Department of Physics, Princeton University, Princeton, New Jersey 08544 (Received 3 August 2000)

We study the quantum dimer model on the triangular lattice, which is expected to describe the singlet dynamics of frustrated Heisenberg models in phases where valence bond configurations dominate their rast to the square lattice, that there is a truly short ranged resonating valence ess excitations and with deconfined, gapped, spinons for a finite range of pash the presence of crystalline dimer phases.

PRL 102, 176401 (2009)

PHYSICAL REVIEW LETTERS

Dynamics and Transport of the Z_2 Spin Liquid: Application to κ -(ET)₂Cu₂(CN)₃

Yang Qi, Cenke Xu, and Subir Sachdev Department of Physics, Harvard University, Cambridge Massachusetts 02138, USA (Received 6 September 2008; published 29 April 2009; publisher error corrected 30 April 2009)

We describe neutron scattering, NMR relaxation, and thermal transport properties of Z_2 spin liquids in two dimensions. Comparison to recent experiments on the spin S = 1/2 triangular lattice antiferromagnet in κ -(ET)₂Cu₂(CN)₃ shows that this compound may realize a Z₂ spin liquid. We argue that the topological "vison" excitations dominate thermal transport, and that recent thermal conductivity experiments by M. Yamashita et al. have observed the vison gap.

Spin liquid with spinon Fermi surface

PHYSICAL REVIEW LETTERS week ending 15 JULY 2005 PRL 95, 036403 (2005)

> U(1) Gauge Theory of the Hubbard Model: Spin Liquid States PHYSICAL REVIEW B 72, 045105 (2005)

Variational study of triangular lattice spin-1/2 model with ring exchanges and spin liquid state De in κ -(ET)₂Cu₂(CN)₃

v		Olexei I. Motrunich	
forr tria	PRL 98, 067006 (2007)	PHYSICAL REVIEW LETTERS	week ending 9 FEBRUARY 2007
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Amperean Pairing Instability in the U(1) Spin Liquid State with Fermi Surface and Application to ĸ-(BEDT-TTF)2Cu2(CN)3

Sung-Sik Lee,¹ Patrick A. Lee,¹ and T. Senthil^{1,2}

¹Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA ²Center for Condensed Matter Theory, Department of Physics, Indian Institute of Science, Bangalore 560 012, India (Received 12 July 2006; published 8 February 2007)

Recent experiments on the organic compound ~-(BEDT-TTF)2Cu2(CN)3 raise the possibility that the system may be described as a quantum spin liquid. Here we propose a pairing state caused by the "Amperean" attractive interaction between spinons on a Fermi surface mediated by the U(1) gauge field. We show that this state can explain many of the observed low temperature phenomena and discuss testable

Spin Bose Metal

PHYSICAL REVIEW B 79, 205112 (2009)

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Spin Bose-metal phase in a spin- $\frac{1}{2}$ model with ring exchange on a two-leg triangular strip

D. N. Sheng,¹ Olexei I. Motrunich,² and Matthew P. A. Fisher³

¹Department of Physics and Astronomy, California State University, Northridge, California 91330, USA ²Department of Physics, California Institute of Technology, Pasadena, California 91125, USA ³Microsoft Research, Station Q, University of California, Santa Barbara, California 93106, USA (Received 4 March 2009; published 20 May 2009)

Recent experiments on triangular lattice organic Mott insulators have found evidence for a two-dimensional (2D) spin liquid in close proximity to the metal-insulator transition. A Gutzwiller wave function study of the triangular lattice Heisenberg model with a four-spin ring exchange term appropriate in this regime has found that the projected spinon Fermi sea state has a low variational energy. This wave function, together with a slave particle-gauge theory analysis, suggests that this putative spin liquid possesses spin correlations that are singular along surfaces in momentum space, i.e., "Bose surfaces." Signatures of this state, which we will refer to as a "enin Rose metal" (SBM), are expected to manifest in quasi-one-dimensional (quasi-1D) ladder sys-



VOLUME 59, NUMBER 18

PHYSICAL REVIEW LETTERS

2 NOVEMBER 1987

Equivalence of the Resonating-Valence-Bond and Fractional Quantum Hall States

V. Kalmeyer Department of Physics, Stanford University, Stanford, California 94305

and

R. B. Laughlin

Department of Physics, Stanford University, Stanford, California 94305, and University of California, Lawrence Livermore National Laboratory, Livermore, California 94550 (Received 24 July 1987)

26 FEBRUARY 2001

ssociated order parameters. We introduced a mathematical object-

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week ending 1 MAY 2009

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Gapless Spin Liquid

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Resonating-Valence-Bond theory

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Xiao-Gang Wen* Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139 (Received 3 June 2001; revised manuscript received 21 December 2001; published 10 April 2002)

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26 February 2001

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We study the quantum dimer model on the triangular lattice, which is expected to describe the singlet dynamics of frustrated Heisenberg models in phases where valence bond configurations dominate their physics. We find, in contrast to the square lattice, that there is a truly short ranged resonating valence bond phase with no gapless excitations and with deconfined, gapped, spinons for a *finite* range of parameters. We also establish the presence of crystalline dimer phases.

PRL 102, 176401 (2009)

PHYSICAL REVIEW LETTERS

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two dimensions. Comparison to recent experiments on the spin S = 1/2 triangular lattice antiferromagnet in κ -(ET)₂Cu₂(CN)₃ shows that this compound may realize a Z_2 spin liquid. We argue that the topological "vision" excitations dominate thermal transport, and that recent thermal conductivity experiments by M. Yamashita *et al.* have observed the vison gap.

Gapless Fermionic spinon or spin Bose metal



Gapped Bosonic spinon



Spin liquid with spinon Fermi surface?



A simple thermodynamic test assuming 2D Fermion with Fermi surface

Pauli susceptibility $\chi_{\perp} = \frac{1}{4}g_{c^{*}}^{2}\mu_{B}^{2}D(\varepsilon_{F})$ $\chi_{\perp} = 8.0(5) \times 10^{-4} \text{ emu/mol}$ $D(\varepsilon_{F}) = n/\varepsilon_{F}$ Specific heat coefficient C/T $\gamma = \frac{1}{3}\pi^{2}k_{B}^{2}D(\varepsilon_{F}) = \frac{1}{3}\pi^{2}k_{B}^{2}\frac{4\chi_{\perp}}{g_{c^{*}}^{2}\mu_{B}^{2}} \sim 56 \text{ mJ/K}^{2} \text{ mol}$ $\gamma \sim 20 \text{mJ/K}^{2} \text{ mol (experimental value)}$ Fermi temperature $T_{F} = \varepsilon_{F}/k_{B} = \frac{g_{c^{*}}^{2}\mu_{B}^{2}}{4\chi_{\perp}k_{B}} \sim 480 \text{ K} \quad J/k_{B} \sim 250 \text{ K (exp. value)}$

These values are (semi-)quantitatively consistent with the theory of the QSL that possesses a spinon Fermi surface.

A new phase in a Mott insulator



D. F. Mross and T. Senthil, PRB (2011).

Spin excitation behave as in Pauli paramagnetic metals with Fermi surface, even though the charge degrees of freedom are frozen.

Spin liquid with spinon Fermi surface?

More direct methods to detect the spinon Fermi surface

Thermal Hall effect

H. Katsura, N. Nagaosa and P. A. Lee, PRL (2010).



Quantum oscillation

O. I. Mitrunich, PRB (2006).



No discernible oscillation

The coupling between the magnetic field and the gauge flux may be weak. Z_2 spin liquid with pseudo-Fermi surfaces? Barkeshli, Yao, Kivelson (2012).

Summary

Ground state and phase diagram of the QSL in 2D organic Mott insulator $EtMe_3Sb[Pd(dmit)_2]_2$ with triangular lattice

Distinct residual thermal conductivity and paramagnetic susceptibility in the zero temperature limit.

The QSL is an algebraic spin liquid with a magnetically gapless ground state, *i.e.* a critical state with infinite magnetic correlation length.

Essentially the same results in the deuterated sample with a different degree of geometrical frustration

The emergence of an extended `quantum spin-metal phase' in the Mott insulator, in which the low-energy spin excitations behave as in Pauli paramagnetic metals with Fermi surface.

> M.Yamashita *et al.*, Nature Phys. **5**, 44 (2009). M. Yamashita *et al.*, Science **328**, 1246 (2010). D. Watanabe *et al.*, Nature Commun. **3**, 1090 (2012).

