Frustracija v antiferomagnetnih sistemih – laboratorij za nova stanja snovi
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Electron correlations and phase diagrams

Wilson’s rule 1931:
partially filled energy band → metal
otherwise → insulator

Chu et al.,
Nat. Phys. 5, 787 (2009)

Mott state, in addition to be insulating, can also accompanied by spontaneously broken symmetry (AFI) or gapped or gapless low energy neutral particle excitations
Antiferromagnets

\[ H = \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \]

exchange is short-range: local

Ground state has long-range magnetic Néel order, or “collinear magnetic (CM) order”

Néel order parameter:
\[ \phi = (-1)^{i_x + i_y} \mathbf{S}_i \]

\[ \langle \phi \rangle \neq 0 ; \quad \langle \mathbf{S}_i \rangle \neq 0 \]

Sublattice magnetization

Detection with local probes, such as NMR or with neutron scattering

Localized excitation has discrete spectrum with nonzero gap, and plane wave forms sharp band

Example: \( \beta\text{-TeVO}_4 \) (Pregelj et al., unpublished)
Frustrated magnets are materials in which localized magnetic moments, or spins, interact through competing exchange interactions that cannot be simultaneously satisfied, giving rise to a large degeneracy of the system ground state.

**Frustrated lattices:**
non-bipartite lattice (triangular, kagomé, pyrochlore, ...)

**How nature solves frustration problems?**

On 2D and 3D lattices, such degeneracies can persist. When they do, fluctuations are enhanced and ordering is suppressed.

**Frustration in 1D**

Frustration parameter $f = J/T_N$
How nature solves frustration problems?

Suppression of $T_N$, but the system still orders!

By breaking translational symmetry on a nano- or mesoscale

By forming novel intricate states of matter, such as quantum spin liquids
Spin stripes in frustrated AF systems

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OPEN

Spin-stripe phase in a frustrated zigzag spin-1/2 chain


\( \beta\)-TeVO\(_4\)
**β-TeVO$_4$ : the structure and exchange interactions**

V$^{4+}$ located inside corner-sharing square pyramids forming zig-zag chains separated by large Te$^{4+}$ ions

Monoclinic structure: Meunier, 1973

$J_{AF} = 21.4$ K

<table>
<thead>
<tr>
<th>Field direction</th>
<th>Curie-Weiss temp $\theta$ (K)</th>
<th>$g$-value for the V$^{4+}$ ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H</td>
<td></td>
<td>b$</td>
</tr>
<tr>
<td>$H</td>
<td></td>
<td>a$ ((H\perp b))</td>
</tr>
<tr>
<td>$H</td>
<td></td>
<td>c$ ((H\perp b))</td>
</tr>
</tbody>
</table>

Savina et al. PRB 84, 104447 (2011).

$J = -21.4$ K?? Frustration?
**β-TeVO$_4$**: the structure & exchange interactions : DFT study

NN interactions are ferromagnetic.

NNN are antiferromagnetic.

GEOMETRICAL FRUSTRATION in a ZIG-ZAG chain

Interchain interactions are not entirely negligible.

**TABLE I.** Magnetic couplings up to the eighth nearest neighbor calculated using Eq. (1) with $U = 4$ eV, $J = 1$ eV, on-site energies, and hopping integrals from MLWF calculations. According to the convention used in Eq. (1), positive couplings correspond to AFM interactions.

<table>
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<th>distance (Å)</th>
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<tr>
<td>$J_1$</td>
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<tr>
<td>$J_6$</td>
<td>5.633</td>
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<td>-1</td>
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<tr>
<td>$J_7$</td>
<td>5.758</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$J_8$</td>
<td>5.935</td>
<td>0</td>
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**FM**

**AFM**
**β-TeVO₄**: the structure & exchange interactions: fitting $\chi$

- **B** $\parallel$ **a**

![Graph showing $\chi$ vs. $T$](image)

Fit:

- $J_1$/

$J_4 = -1.25$
- $J_1 = -38.3$ K
- $zJ'' = -4.5$ K
- $\theta = \frac{1}{2}(2(J_1+J_4)+zJ'') = 5.4$ K

**Table I.** Magnetic couplings up to the eighth nearest neighbor calculated using Eq. (1) with $U = 4$ eV, $J = 1$ eV, on-site energies, and hopping integrals from MLWF calculations. According to the convention used in Eq. (1), positive couplings correspond to AFM interactions.

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Interchain interactions are not entirely negligible.

**Geometrical frustration** in a ZIG-ZAG chain.
Frustrated \((J_1-J_2)\) spin-1/2 chain

**Magnetic modulation \(\theta\) in zero-field**

Classical expression:
\[
\theta = \arccos \left( \frac{-J_1}{4J_2} \right)
\]

\(\beta\)-TeVO\(_4\)
\[\arccos \left( \frac{-J_1}{4J_2} \right) \sim k_z = 0.42.\]

Collinear AFM

Collinear FM

Majumdar-Ghosh (MG) Hamiltonian at which the ground state consists of dimerized singlets with a gap to the excited states.

\[\omega_{MF} = \tan^{-1} (-1/4) = 3.3865\]

Magnetic transitions

- At low temperatures several magnetic transitions exist:
  - \( T_{N1} = 4.65 \text{ K} \)
  - \( T_{N2} = 3.28 \text{ K} \)
  - \( T_{N3} = 2.26 \text{ K} \)
- This indicates the existence of several energetically almost equivalent magnetic states.
Magnetic structures – neutron diffraction study

- Neutron diffraction experiments on the TriCS diffractometer at the Paul Scherrer Institute
- Spherical-neutron-polarimetry experiments were performed at the Institute Laue Langevin, Grenoble

**T-evolution of the main**

\[ \mathbf{k} = (-0.195 \ 0 \ 0.413) \]

@ \( T_{N1} = 4.5 \text{ K} \)

\[ \mathbf{k} = (-0.208 \ 0 \ 0.423) \]

@ \( T_{N3} = 2.2 \text{ K} \)

**Magnetic reflection**

\( T_{N1} = 4.5 \text{ K} \)

\( T_{N2} = 3.1 \text{ K} \)

\( T_{N3} = 2.2 \text{ K} \)

\( \beta\text{-TeVO}_4 \)

\[ \arccos(-J_1/4J_2) \sim k_z = 0.42 \]

Vector chiral phase \( T < T_{N3} \)

\( \sigma_{\text{max}} \approx 0.9 \mu_B \)

Spiral spin structure with magnetic moments on the two chains lying in two different crystallographic planes (\(bc\) and \(ab\))

Two order parameters (two irreducible representations)

M. Pregelj et al., PHYSICAL REVIEW B 94, 081114(R) (2016)
Magnetic structures – neutron diffraction study

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M. Pregelj et al., PHYSICAL REVIEW B 94, 081114(R) (2016)

Collinear SDW phase

\[ T_{N1} < T < T_{N2} \]

Maximal magnetic moment \( \sigma_{\text{max}} \approx 0.7 \mu_B \)

Magnetic moments on the two chains have orthogonal orientations (along \( a \) and \( c \))

One order parameter (one irreducible representation)
Magnetic structures – phase diagram

Theoretical phase diagram for the frustrated $J_1$-$J_2$ chain

\[ T_{N1} < T < T_{N2} \]

\[ T < T_{N3} \]

$\beta$-TeVO$_4$

Magnetic structures – $T$-$B$ phase diagram

**Collinear SDW phase**, $T_{N1} < T < T_{N2}$

**Vector chiral phase**, $T < T_{N3}$

Magnetization study

Magnetic-field dependence ($B \parallel a$) of the (0.208 2 0.577) reflection
Magnetic structures – $T$-$B$ phase diagram

- Collinear SDW phase, $T_{N1} < T < T_{N2}$
- Vector chiral phase, $T < T_{N3}$
Magnetic structures – $T$-$B$ phase diagram

Collinear SDW phase, $T_{N1} < T < T_{N2}$

Vector chiral phase, $T < T_{N3}$


M. Pregelj et al., NATURE COMMUNICATIONS 6, 7255 (2015)
Magnetic structures – intermediate phase

\[ \mathbf{k} = (h, 0, l) \]

\[ \mathbf{k} + \Delta \mathbf{k} = (h + \Delta h, 0, l + \Delta l) \]
The $\Delta k/k$ and the main incommensurate modulation $k/k$ are not parallel.

Hence, the stripe modulation does not steam from intrachain interactions alone.

- Initial SDW$^{(ac)}$ order is accompanied by additional SDW$^{(b)}$ order.
- The two SDW orders have different wave vectors, i.e., $k$ and $k + \Delta k$.
- The VC phase is formed, when modulations match ($\Delta k \to 0$).
Summary

\( \beta\text{-TeVO}_4 \) = frustrated zigzag spin chain system

On the \( T\text{-}B \) phase diagram, SDW, VC, STRIPE and probably also spin quadrupolar phase

STRIPE phase = nanometric texturing of the magnetic order parameter

STRIPE phase is in fact dynamic

Peculiar excitations: two coupled orthogonal phason modes
Frustrated magnetism and quantum spin liquids

- Usually: all systems should order at low $T$ (Landau theory, symmetry breaking)
- But frustration can suppress order, even to $\sim 0$ K (degenerate ground state and/or quantum fluctuations) $\Rightarrow$ Exotic phases of matter!
- **Quantum spin liquids**

When valence bonds undergo quantum mechanical fluctuations $\Rightarrow$ valence bond liquid
Resonating valence bond (RVB) state

$\Psi = \frac{1}{\sqrt{2}} (\text{Valence bond solid}) + \ldots$
Fractional excitations in quantum spin liquids

Spinons

1D spin chains:

- A domain wall between the two AF ground states
- Flipping two spins on each side of the central spin produces a state with the same energy, so the spinons can move independently within the chain

Continuum, no gap (Bethe, 1931)

\[ \varepsilon(q) > \frac{\pi}{2} J \sin(q) \]
\[ \varepsilon(q) < \pi J \sin(q/2) \]

2D Quasi 1D spin chains:

- Creating a spinon requires the flipping of a semi-infinite line of spins along a chain. The spinon cannot hop between chains.

- In a 2D QSL, a spinon is created simply as an unpaired spin, which can then move by locally adjusting the valence bonds.
Fractional excitations in quantum spin liquids

Spinons

Fractional quantum number: excitation with $\Delta S = \frac{1}{2}$
Magnon is not an elementary excitation: it decays into two spinons

Spinons can have varied character:
- Gapped (require a non-zero energy to excite)
- Gappless

Dirac QSLs

Spinon Fermi surface

non-Fermi liquid “spin metal”
Experimental evidences for quantum spin liquids

Long range order, yes or no?

Nature of excitations?

Magnetic resonance techniques:
- Nuclear magnetic resonance
- Muon spin relaxation

\[ \mathcal{H} = \mathcal{H}_Z + \mathcal{H}_{CS} + \mathcal{H}_Q + \mathcal{H}_{e-n} + \mathcal{H}_c \]

Spin-lattice relaxation time:

\[ \frac{1}{T_1} = \gamma^2 N k_B T \sum_{q, \alpha} A_{\alpha}(q)^2 \frac{\chi_{\alpha}^\prime(q, \omega_N)}{\omega_N} \]
Experimental evidences for quantum spin liquids

Long range order, yes or no?

Herbertsmithite is the end-compound of the Zn-paratacamite family $\text{Zn}_x\text{Cu}_{4-x}(\text{OH})_6\text{Cl}_2$

The oscillations due to the existence of well defined static fields progressively disappear and, for $x > 0.5$, the frozen magnetism disappears.

Muon spin relaxation

Static magnetic order

Quantum spin liquids may be considered "quantum disordered" ground states of spin systems, in which zero point fluctuations are so strong that they prevent conventional magnetic long range order. Non-local fractional excitations (spinons) $\text{EtMe}_2\text{Sb}[\text{Pd(dmit)}_2]_2$

No $^1\text{H}$ line broadening down to 32 mK $\Rightarrow$ absence of AF LRO

Not really a perfect triangular lattice

Itou et al., NATURE PHYSICS 6, 673 (2010)
Quantum spin liquids may be considered as „quantum disordered“ ground states of spin systems, in which zero point fluctuations are so strong that they prevent conventional magnetic long range order.

Non-local fractional excitations (spinons)

\[
\frac{1}{T_1} = \frac{2\gamma_n^2 kT}{(\gamma_e\hbar)^2} \sum_q A_q A_{-q} \chi''(\bar{q}, \omega) \omega
\]

No broadening of NMR lines $\rightarrow$ no AF LRO

fully gapless spin liquid with a spinon Fermi surface, where the imaginary part of the susceptibility remains constant (Fermi-liquid case)

Itou et al., NATURE PHYSICS 6, 673 (2010)
Bulk $1T$-$\text{TaS}_2$

- Simple crystal structure, composed of planes of Ta atoms, surrounded in an octahedral arrangement by S atoms.
- Within the plane, Ta atoms arranged in a triangular lattice

$1T$-$\text{TaS}_2$ famous for showing a sequence of CDW phases with some kind of ordering close to a $\sqrt{13} \times \sqrt{13}$ superstructure

<table>
<thead>
<tr>
<th>State</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal metal</td>
<td>550 K</td>
</tr>
<tr>
<td>ICCDW</td>
<td>350 K</td>
</tr>
<tr>
<td>NCCDW</td>
<td>180 K</td>
</tr>
<tr>
<td>CCDW</td>
<td></td>
</tr>
</tbody>
</table>
Commensurate CDW in 1T-TaS$_2$

CCDW phase
The displacement of Ta atoms leads to the formation of David-star clusters where twelve Ta atoms within the layer move inwards towards a thirteenth central Ta atom.

Resistivity abruptly increases (decreases) by over an order of magnitude on entering the C (NC) phase. The hysteresis loop between cooling and warming defines the temperature region of metastability between the two phases.

Commensurate superstructure that is rotated by 13.9° with respect to the atomic lattice.

Ordering vector directions

$\phi_c \approx 13.9^\circ$  $\phi_{NC} = 11.6^\circ \sim 13.1^\circ$
Commensurate CDW in $1\text{T-TaS}_2$

The reconstructed band structure collapses into submanifolds separated by distinct energy gaps. The lattice deformation does not fully gap the electronic system, with only twelve out of the thirteen electrons of the new unit cell occupying the electronic states below the energy gap. The ‘thirteenth’ electron presides above the deformation-induced gap.

Fazekas and Tosatti (1974): a small width ($\sim 80$ meV), it is susceptible to a Mott–Hubbard transition.

CCDW – Mott insulating state
The insulating ground state of $1\text{T-TaS}_2$ is, however, unique as it resides inside a CCDW state.
The localization centres in $1\text{T-TaS}_2$ are CDW superlattices, instead of atomic sites found in conventional MIs.
Commensurate CDW in $1T$-TaS$_2$

CCDW – Mott insulating state
The localization centres in $1T$-TaS$_2$ are CDW superlattices, instead of atomic sites found in conventional MIs.

Magnetism?
1T-TaS$_2$ – lack of AF LRO

Muon spin relaxation experiment

ZF μSR: no oscillations of the μSR signal
no frozen local magnetic fields

wTF μSR:
• $\nu = \gamma_\mu B_{wTF}$
• the wTF μSR signal corresponds to the full muon asymmetry
no frozen local magnetic fields

Static magnetic order

$P_z(t) = \frac{1}{3} + \frac{2}{3} \cos(\gamma B_\mu t)$
1T-TaS$_2$ – lack of AF LRO

Muon spin relaxation experiment

LF $\mu$SR: a weak relaxation process due to the dynamics of the local fields of electronic origin

ZF $\mu$SR: no oscillations of the $\mu$SR signal

LF $\mu$SR: no frozen local magnetic fields

wTF $\mu$SR:
- $\nu = \gamma_\mu B_{wTF}$
- the wTF $\mu$SR signal corresponds to the full muon asymmetry

no frozen local magnetic fields
$^{181}$Ta Nuclear Quadrupole Resonance: another local probe

$^{181}$Ta: $I = 7/2$

$$E_m = \frac{e^2 q Q}{4I(2I-1)} \left(3m^2 - I(I+1)\right)$$

ZERO MAGNETIC FIELD

- $\pm 7/2$
- $\pm 5/2$
- $\pm 3/2$
- $\pm 1/2$

![Graph showing NMR frequency (units of $\gamma$) vs. $\eta$ with peaks at different frequencies.](A) T = 25 K

- $\alpha$
- $\beta, \gamma$

intensity (arb. u.)

frequency (MHz)
\textbf{\textsuperscript{181}Ta NQR: another local probe}

\begin{itemize}
  \item \textbf{c}_0 \text{ stacking: 3 lines in ratio } \alpha: \beta: \gamma = 1:6:6
  \item \textbf{c}_0 + a_0 \text{ stacking (breaks trigonal symmetry)}
    \begin{itemize}
      \item 7 lines in ratio
      \item \alpha: \beta_1: \beta_2: \beta_3: \gamma_1: \gamma_2: \gamma_3 = 1:2:2:2:2:2:2
    \end{itemize}
  \item \textbf{c}_0 + 2a_0 \text{ stacking}
    \begin{itemize}
      \item every \( \beta \) and \( \gamma \) line split (13 lines)
    \end{itemize}
\end{itemize}
$^{181}$Ta NQR: No long-range AF order

No broadening of $\alpha$-line

No static internal fields due to AF LRO
Probing the spin state
Probing the spin state

\[ T_1 \propto T^2 \] Evidence for quantum spin liquid

\[ T < 50 \text{ K} \]

Additional local inhomogeneities

\[ T_{\text{C}} \]

\[ T_f \]

Temperature (K)
Probing the spin state

$T < 50 \text{ K}$

- a broad distribution of $1/T_1$ values where the stretching exponent $p=0.5$ implies a highly inhomogeneous magnetic phase at all Ta sites;
- a slowing down of the spin fluctuations leading to an unusually high power-law exponent $n=4$ of the $^{181}\text{Ta}$ relaxation, which implies a suppression of spinon density of states;
- symmetry breaking of the homogeneous spin structure of the Star-of-David Ta-atom clusters, in which the central site Ta atom shows very different relaxation than the surrounding 12 atoms.

Evidence for quantum spin liquid

$1/T_1 \propto T^2$
Low-temperature inhomogeneities

Random Heisenberg Chain
Bond randomness in $\text{BaCu}_2(\text{Si}_{1-x}\text{Ge}_x)_2\text{O}_7$
Conclusions

1. atomic-cluster spins on the triangular lattice of a charge-density wave state of 1T-TaS$_2$ establish a QSL
2. nuclear quadrupole resonance and muon-spin-relaxation experiments reveal that the spins show gapless QSL dynamics and no long-range magnetic order at least down to 70 mK. Canonical $T^2$ power-law temperature dependence of the spin relaxation dynamics characteristic of a QSL is observed from 200 K to ~55 K.
3. T < 55 K: a new gapless state with reduced density of spin excitations and high degree of local disorder

1T-TaS$_2$ as a quantum spin liquid

K. T. Law$^a$ and Patrick A. Lee$^{b,1}$

A high-temperature polaron spins

Martin Klanšek$^3$, Andrej Zorko
Pabitra Kumar Biswas$^4$, Peter Prelovšek$^*$,Dragan Miljković$^{*}$, and Urska Alagon

Contributed by Patrick A. Lee, May 26, 2017 (sent for review April 24, 2017; reviewed by Steven A. Kivelson and N. Phuan Ong)
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