Magnetic Dynamics in Orbitally Degenerate Insulators

Motivation:

• insulator-metal transitions in orbitally degenerate systems, comparison to cuprates

• quantitative understanding of magnetic dynamics in insulating progenitors

Examples:

Neutron scattering, analytical and numerical calculations on Mott-Hubbard insulators $YTiO_3$ and YVO_3

Collaborators:

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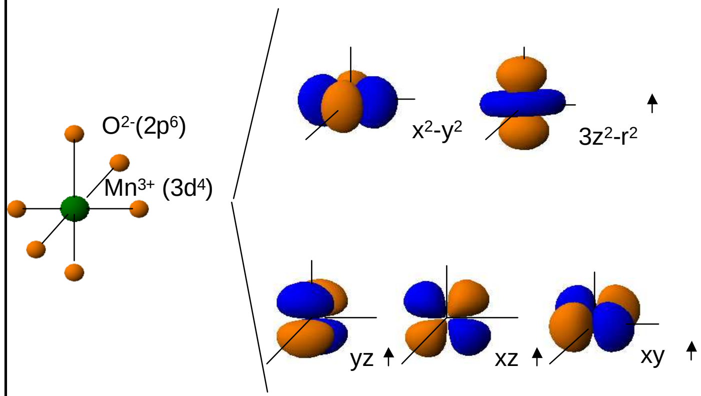
if time permits:

preliminary results on (Sr,La)$FeO_{3\text{-™}}$

Orbital degeneracy

Example: $LaMnO_3$



Mechanisms to lift orbital degeneracy

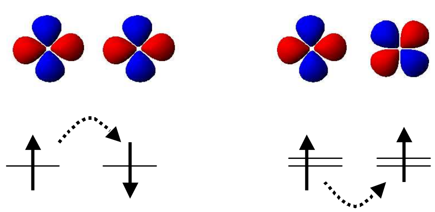
- **Jahn-Teller effect**
- superexchange
- spin orbit coupling

Superexchange Interaction

$$H = \sum_{ij} [J_{ij}(\tau_i, \tau_j) S_i \bullet S_j + K_{ij}(\tau_i, \tau_j)]$$

τ_i, τ_j orbital pseudospin, same commutation relations as S_i, S_j

example:

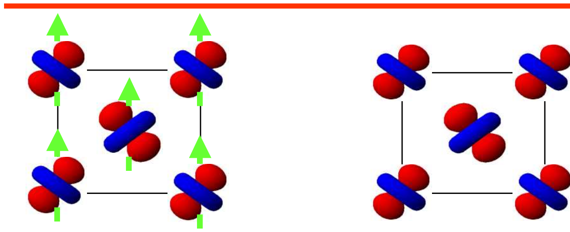


strong, antiferromagnetic

weak, ferromagnetic

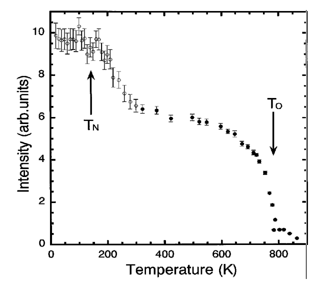
Goodenough-Kanamori Rules

$LaMnO_3$ (S=2, e_g orbitals)

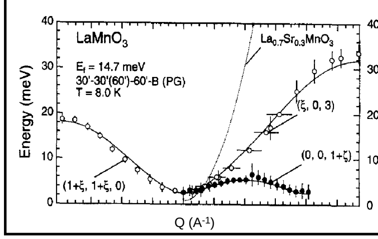


$T<T_N$: magnetic order

$T<T_O$: orbital order locks in exchange interactions



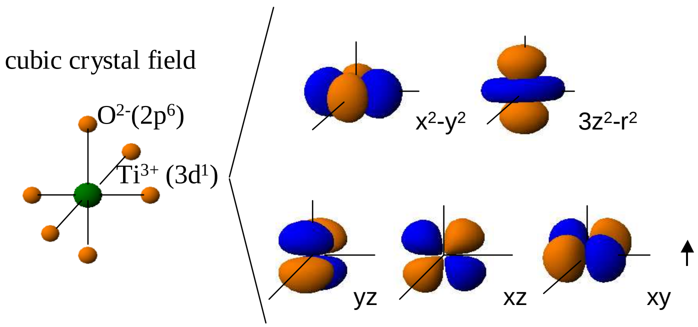
Murakami et al.



$T<T_N$: anisotropic spin wave spectrum, reflecting orbital ordering pattern

Hirota et al.

3d[1] System: Titanates



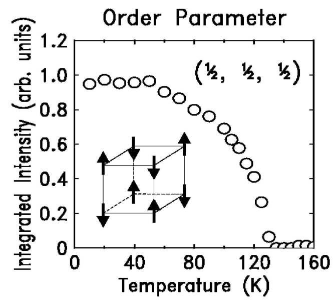
Mechanisms to lift orbital degeneracy

- Jahn-Teller effect
- superexchange
- spin orbit coupling

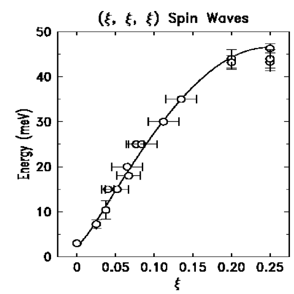
Jahn-Teller distortions in t_{2g}-systems $\Delta d \sim 0.05$ Å
compare to e_g-systems (manganites): $\Delta d \sim 0.25$ Å

Jahn-Teller energy scale] Δd^2
much smaller than in manganites

Neutron scattering from Insulating $LaTiO_3$



- G-type antiferromagnetic order inconsistent with all electronic structure calculations
- small ordered moment ($0.45\mu_B$)



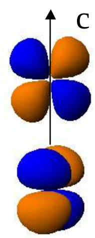
isotropic spin waves

B. Keimer et al, PRL 2000

Theory of $LaTiO_3$

Δd < 0.01 Å 1 negligible Jahn-Teller coupling

Superexchange Hamiltonian:
two active orbitals on every bond



for c-axis bond:

$$H_{SE} = J_{SE} \sum (S_i \cdot S_j + \tfrac{1}{4})(\tau_i \cdot \tau_j + \tfrac{1}{4} n_i n_j)$$

$$J_{SE} = \frac{t^2}{U}$$

$S = \frac{1}{2}$; $\tau = \frac{1}{2}$ in xz, yz subspace

$$\langle n \rangle = \tfrac{2}{3}$$

also need to consider Hund's rule,
spin-orbit interactions

Khaliullin & Maekawa, PRL 2000

Theory of $LaTiO_3$

Orbital liquid model (Khaliullin & Maekawa)

correlated spin-orbital fluctuations:
(spin singlet)×(orbital triplet) ⇔ (spin triplet)×(orbital singlet)
⇒ orbital order obliterated

consequences:
with fixed parameter J = 15.5 meV from neutron scattering

- ordered moment 0.5 μ_B } as observed
- spatially isotropic spin dynamics } as observed
- spin gap 3 meV } as observed
- continuum of fermionic orbital excitations — not yet observed

Conventional orbital order (Imada et al., Khomskii et al.)

special linear combination of orbitals
⇒ subtle crystallographic distortions — not yet observed

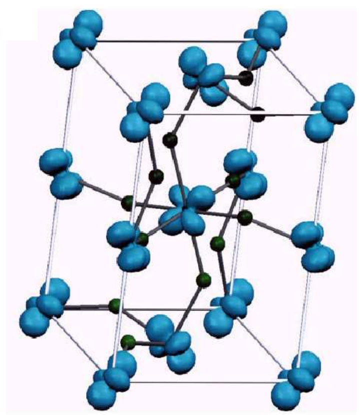
$YTiO_3$

• smaller O-Ti-O bond angle than $LaTiO_3$
weakened superexchange

• spin ferromagnetism as predicted by
electronic structure calculations

Orbital order:

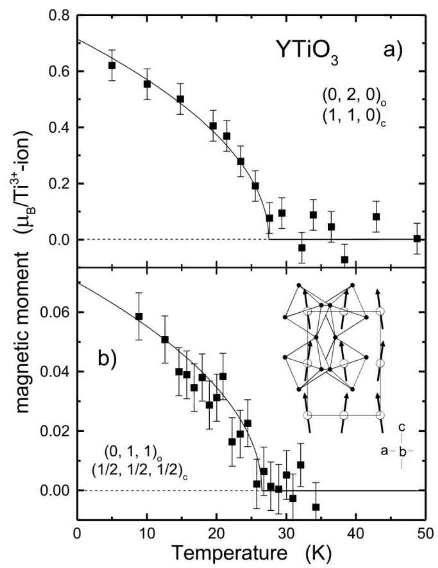
$$|\psi\rangle_{1,3} = c_1|yz\rangle \pm c_2|xy\rangle$$
$$|\psi\rangle_{2,4} = c_1|xz\rangle \pm c_2|xy\rangle$$



Theory:
Sawada & Terakura
Mizokawa et al.
...

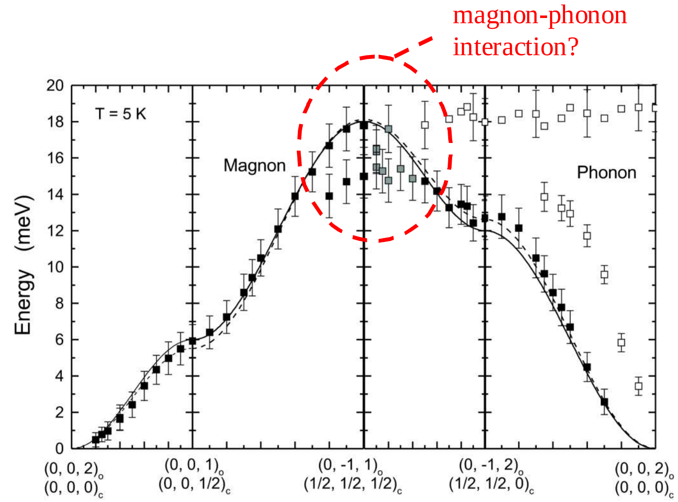
Experiment:
Akimitsu et al. (neutrons)
Itoh et al. (NMR)
...

Elastic Neutron Scattering from $YTiO_3$



ferromagnetism with G-type and A-type
antiferromagnetic canting, canting angle $\phi \sim 5^o$

Inelastic Neutron Scattering from $YTiO_3$



fit to Heisenberg model with **isotropic** ferromagnetic exchange
$E = 6SJ(1 - \gamma_q)$ $J = 3.0$ meV

- $J_c = J_{ab} = J$ identical within ~ 5%
- T_C calculated from J consistent with experiment
- magnon gap = 0.15 meV

C. Ulrich et al., Phys. Rev. Lett. 89, 167202 (2002)

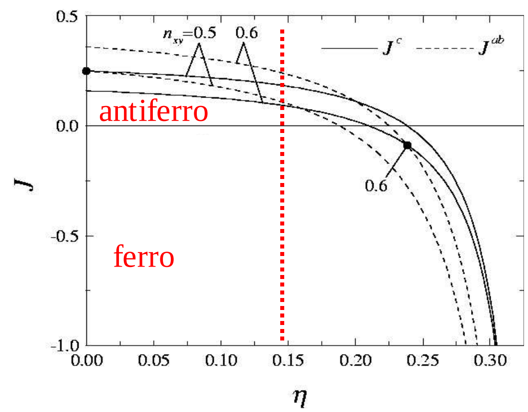
Calculation of Exchange Parameters

orbital state:

$$|\psi\rangle_{1,3} = c_1|yz\rangle \pm c_2|xy\rangle$$

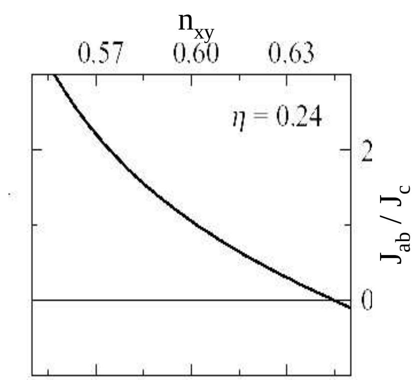
$$|\psi\rangle_{2,4} = c_1|xz\rangle \pm c_2|xy\rangle$$

$n_{xy} = c_2^2 \sim 0.5$, $\eta = J_H/U \sim 0.15$ } from experiment



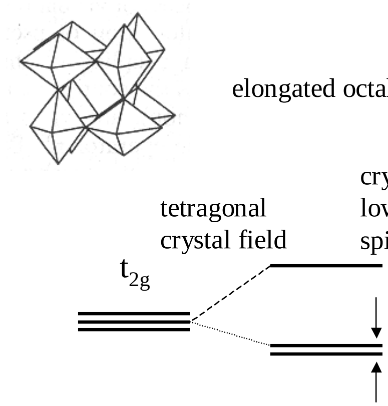
isotropic ferromagnetism only for $\eta > \eta_{exp}$

Calculation of Exchange Parameters



spin Hamiltonian highly sensitive to orbital state
spatially isotropic ferromagnetism requires coincidence

Estimate of magnon gap Δ



$$\Delta = J_{SE}\left(\frac{\lambda}{D}\right)^2, \quad J_{SE} \sim 0.1J$$

$$\text{canting angle } \phi = \frac{J_{SE}}{3J}\frac{\lambda}{D}$$

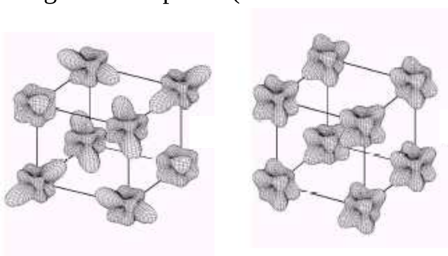
} D > 200 meV

Large orbital splitting of unknown origin required to explain small magnon gap

1 fine tuning on several levels required to reconcile orbitally ordered state with measured magnetic dynamics

New Orbitally Ordered States

derived from superexchange model with spin ferromagnetism imposed (Okamoto & Khaliullin)



G. Khaliullin and S. Okamoto, Phys. Rev. Lett. 89, 167201 (2002)

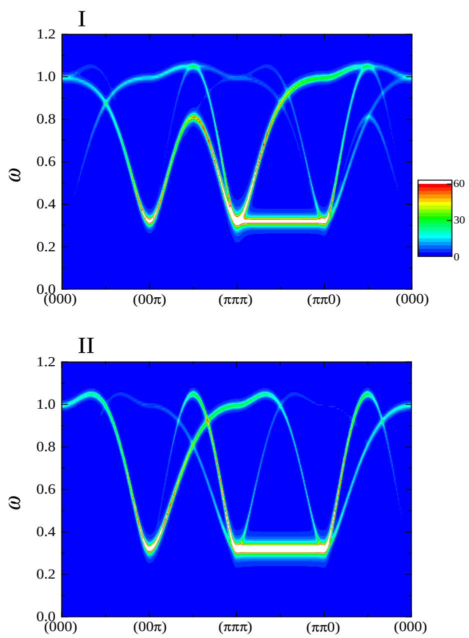
- reduced anisotropy due to strong orbital quantum fluctuations
- naturally explains spatially isotropic magnon dispersions, small magnon gap
- need to check compatibility with neutron and NMR form factors
- ordering pattern cannot explain observed lattice distortions, but magnetic dynamics not strongly altered when experimental lattice distortion is included

Octahedral Distortions in Non-JT Systems

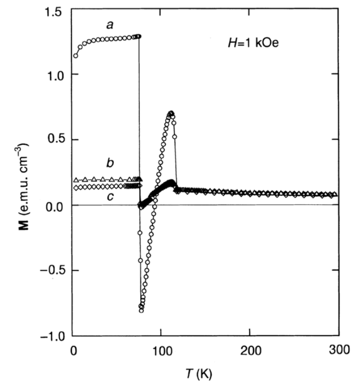
	θc	θab	ΔL=l−s	ΔL/L (%)
$SmAlO_3$*	159	161	0.003	0.16
$GdAlO_3$	157	157	0.008	0.43
$HoAlO_3$	153	152	0.022	1.14
$YAlO_3$	152	152	0.026	1.36
$YAlO_3$#			0.020	1.05
$YTiO_3$	144	140	0.060	2.94
$YFeO_3$$	144	145	0.033	1.64

Douglas du Boulay, PhD Thesis (The Univ. of Western Australia, 1996)
*Marezio et al. J. Sol. Stat. Chem., 4, 11 (1972)
#Diehl & Brandt, Mat. Res. Bull., 10, 85 (1975)
$Marezio et al. J. Sol. Stat. Chem., 6, 23 (1971)

Prediction: **Orbiton Dispersions**



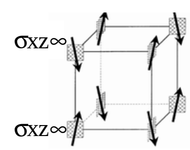
YVO_3 Phenomenology



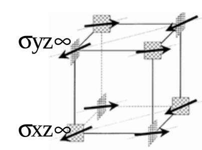
magnetization reversals
memory effects

Y. Ren et al.,
Nature 396, 441 (1998)

- |xy⟩ orbital fully occupied on every site
  |xz⟩, |yz⟩ occupation alternates:



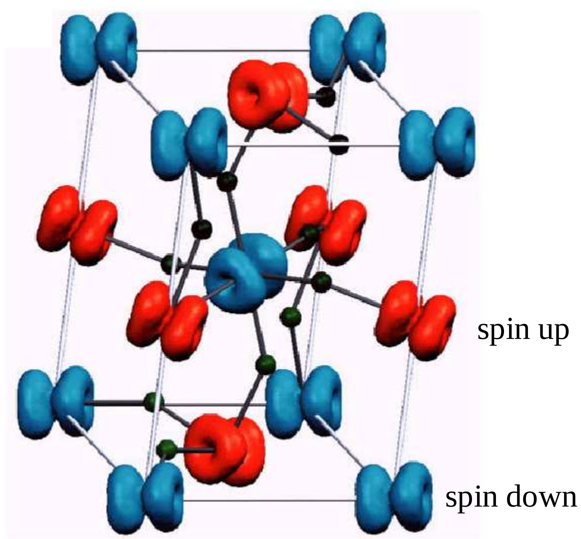
T < 77K



77K < T < 118K

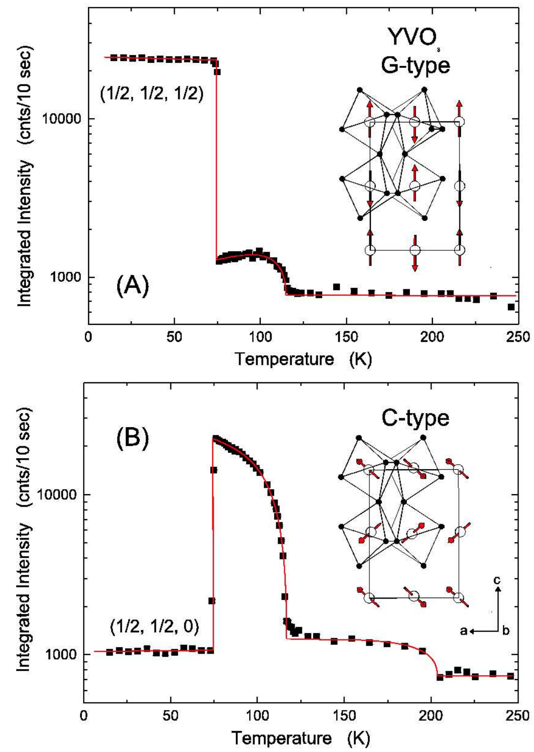
- interplay between single-ion and superexchange anisotropies responsible for magnetization reversals, large single-ion anisotropy ~ J required in conventional picture

Orbital Order in G-type Phase of YVO_3

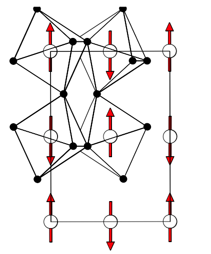


Sawada & Terakura 1994

YVO_3: Elastic Neutron Scattering

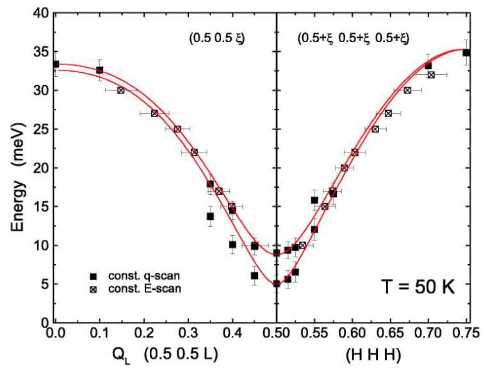


YVO_3: Low Temperature Phase



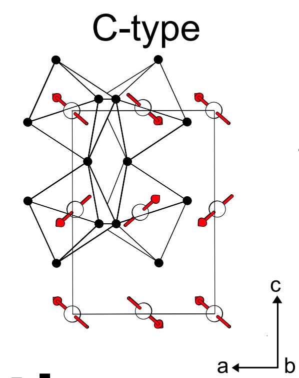
G-type $\mu_z = 1.72\ \mu_B$

agrees with
Kawano, Yoshizawa & Ueda
J. Phys. Soc. Jpn. 1994



J_{ab} = 5.5 meV, J_c = 5.8 meV

YVO_3: High Temperature Phase



C-type:
$\mu_x = 0.49\ \mu_B$
$\mu_y = 0.89\ \mu_B$

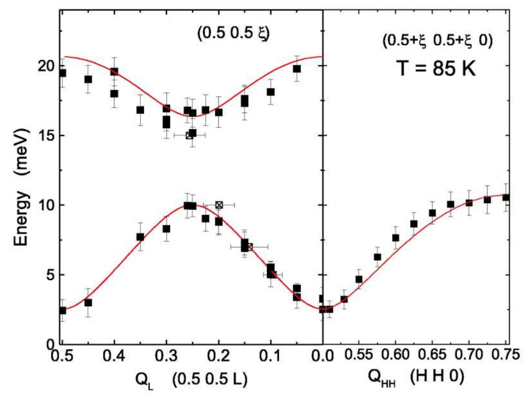
G-type:
$\mu_z = 0.30\ \mu_B$

total:
$\mu = 1.05\ \mu_B$

- total ordered moment
  $<< 2\ \mu_B$ (free ion moment)
  $< 1.72\ \mu_B$ (ordered moment of G-phase at same temperature)

- canting angle = 16°
  much larger than expected from ordinary Dzyaloshinskii-Moriya and/or single-ion exchange anisotropy

YVO_3: High Temperature Phase



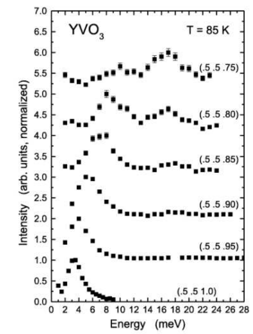
- spin gap at (½,½,½) same as at (½,½,0) but different from G-phase at same temperature

  1 two-phase coexistence ruled out

- overall collapse of magnon band width (20 meV in C-phase vs. 35 meV in G-phase)

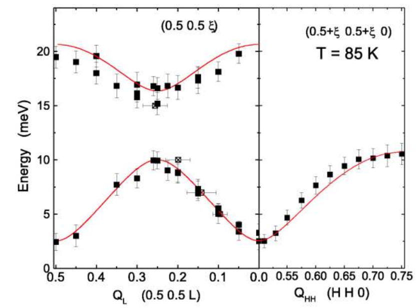
- band width larger in ferromagnetic c-direction than in antiferromagnetic ab-plane (would expect opposite based on Goodenough-Kanamori rules)

YVO_3: High Temperature Phase



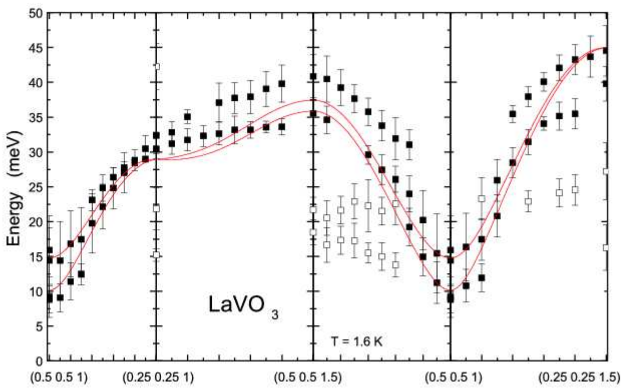
anticrossing of spin wave branches along (½, ½, L)

would expect crossing due to staggered canting alone



excellent fit obtained by three exchange parameters:
J_{ab} = 2.6 meV, J_{c1} = – 2.2 meV, J_{c2} = – 4.0 meV
1 dimerization of exchange bonds along the c-axis

Contrast: $LaVO_3$



- C-type spin structure, no canting
- J_{ab} = 6.5 meV > σJ_cσ = 4.0 meV
- no optical/acoustic splitting
- large magnon gaps

Spin-Orbital Hamiltonian

spin S=1
σxy∞ orbital fully occupied, at least for T < 200K
⇒ controls AF interactions in plane

orbital pseudospin τ= ½, acting in σxz∞, σyz∞ subspace
Hamiltonian along c-axis:

$$H = J_{SE}\sum_i [\frac{1}{2}(S_i S_{i+1} + 1)\tilde{J}_{i,i+1} + \tilde{K}_{i,i+1}]$$

$$\tilde{J}_{i,i+1} = (1 + 2\frac{\eta}{1-3\eta})(\tau_i\tau_j + \frac{1}{4}) - \frac{\eta}{1+2\eta}(\tau_i^z\tau_j^z + \frac{1}{4})$$

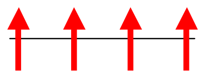
$$\tilde{K}_{i,i+1} = \frac{\eta}{1-3\eta}(\tau_i\tau_j + \frac{1}{4}) + \frac{\eta}{1+2\eta}(\tau_i^z\tau_j^z + \frac{1}{4})$$

$$\eta = J_H / U$$

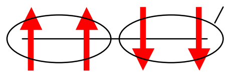
Khaliullin et al., PRL 86, 3879 (2001)

(intra-atomic spin-orbit interaction λ discussed later)

competing ground states:
large η: uniform ferromagnet



small η: orbital Peierls state, 4-site periodicity



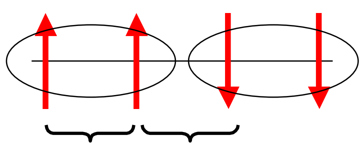
limiting case: $\eta = 0$

$$H = \frac{J_{SE}}{2}\sum_i (S_i S_{i+1} + 1)(\tau_i \tau_{i+1} + \tfrac{1}{4})$$

single bond:

$E = -J_{SE}/2$

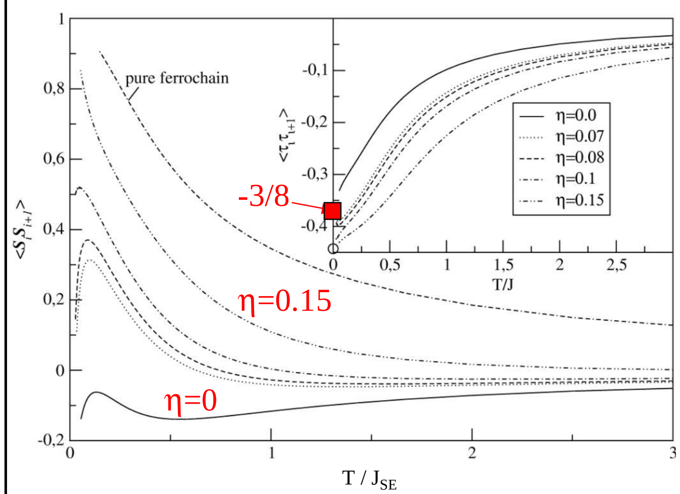
$\langle \tau_i \tau_{i+1} \rangle = -3/4 \qquad \langle S_i S_{i+1} \rangle = 1$



$-J_{SE}/4 \quad +J_{SE}/8$

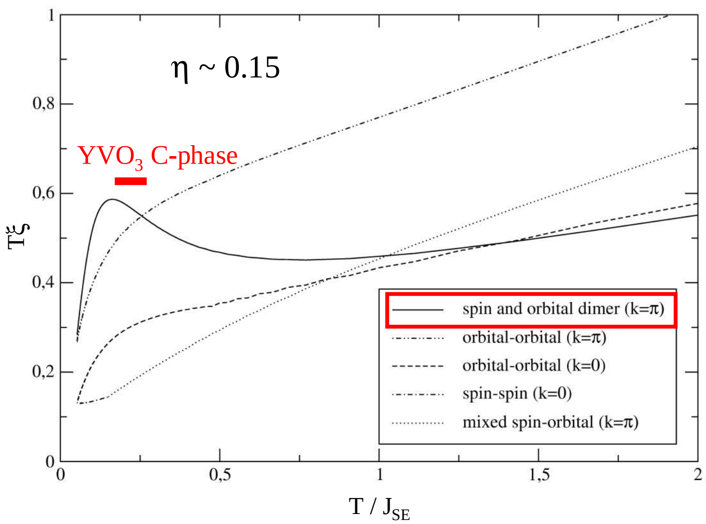
weak exchange bounds
1 large entropy

TMRG Results



- Critical η ~ 0.11 for zero-temperature phase transition between dimerized and ferromagnetic states close to experimental η ~ 0.15
- for T > 0, spin correlations strongly reduced compared to model without orbital dynamics

TMRG Results



ferromagnetism is ground state at T = 0

due to large entropy, dimer phase is leading instability in relevant temperature range

Spin-Orbit Coupling

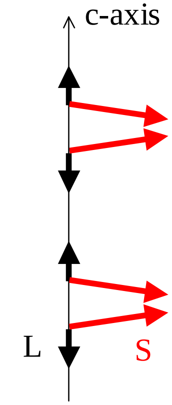
λ ~ 15-20 meV for V^{3+}

- anti-aligns orbital and spin moments at every site
- incompatible with superexchange (which prefers orbital antiferromagnetism, spin ferromagnetism along c)

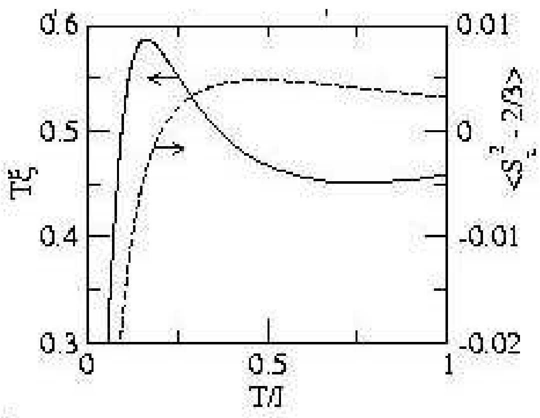
orbital magnetization c (from σxz∞, σyz∞ orbitals)

induces spin-flop transition

1 large G-type canting as observed



Spin-Orbit Coupling



- spin direction in xy plane
- mixed correlator $\langle S_i \cdot \tau_i \rangle$ yields canting angle of order 10°

Conclusions

- magnetic order & dynamics measured by neutron scattering exquisitely sensitive to orbital state
- static Goodenough-Kanamori picture inadequate
- models incorporating orbital quantum dynamics provide quantitative description of many aspects of the neutron data
- understanding of magnetization reversals and memory effects in YVO_3 in terms of T-dependent superexchange parameters
- realization of spin-orbital chains in 3D insulator
- entropy driven orbital Peierls state

Unresolved issues

- experimental detection of orbital order, orbiton dispersions in $YTiO_3$
- influence of charge carriers