Frustration in the diamond lattice and a spin-orbital liquid state

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INSTITUTE FOR **QUANTUM MATTER**

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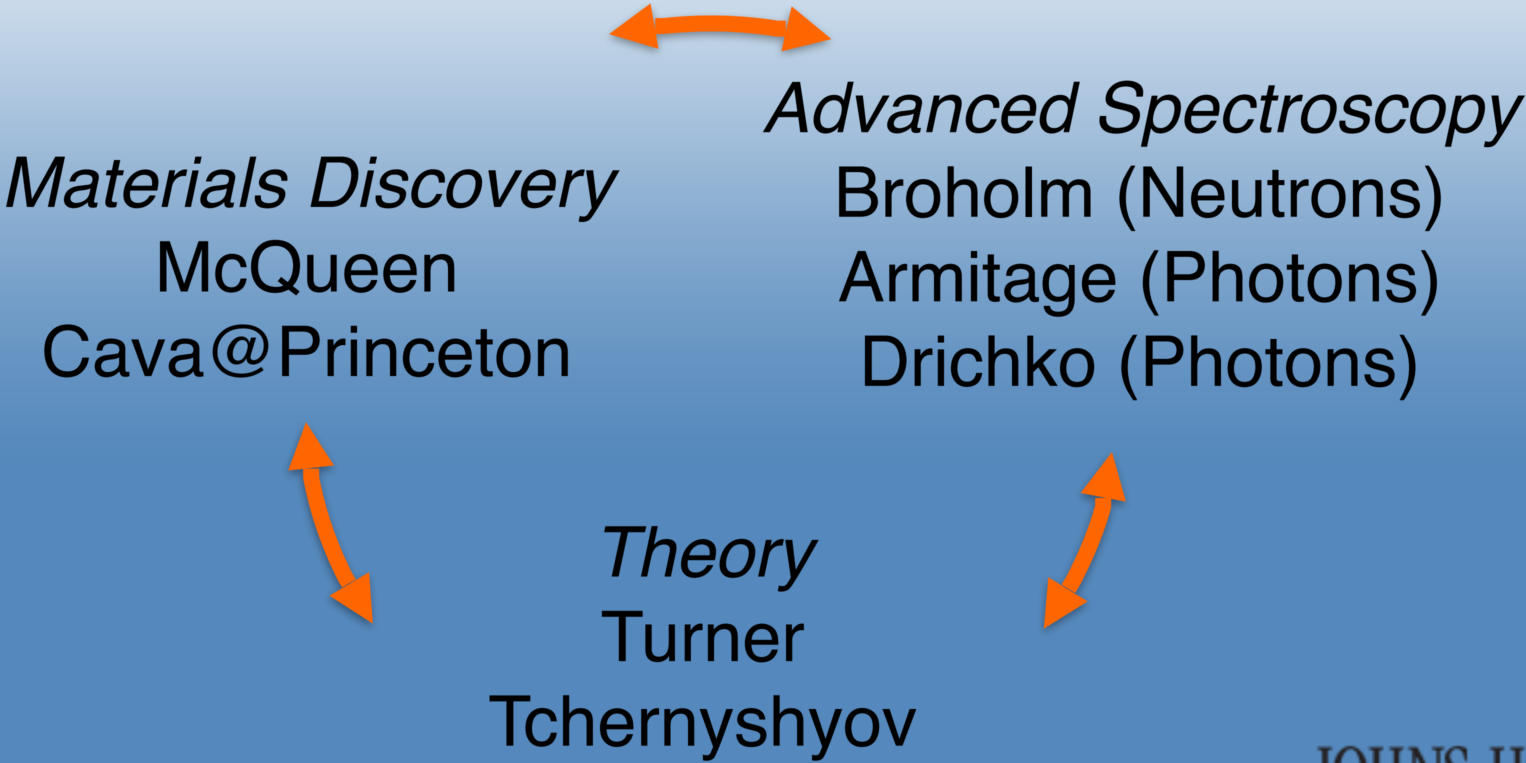
Understanding quantum correlations in the solid-state



Materials Discovery
McQueen
Cava@Princeton

Advanced Spectroscopy
Broholm (Neutrons)
Armitage (Photons)
Drichko (Photons)

Theory
Turner
Tchernyshyov

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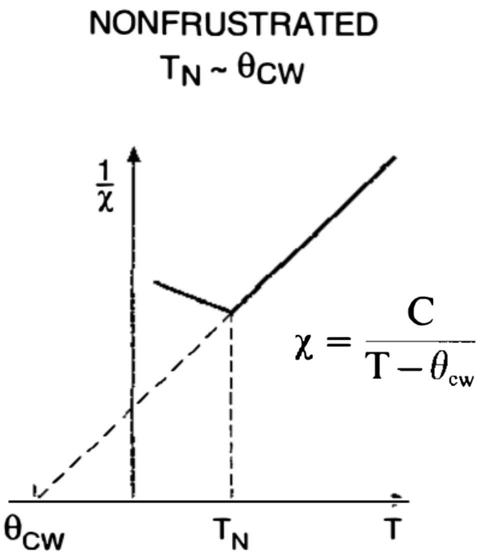
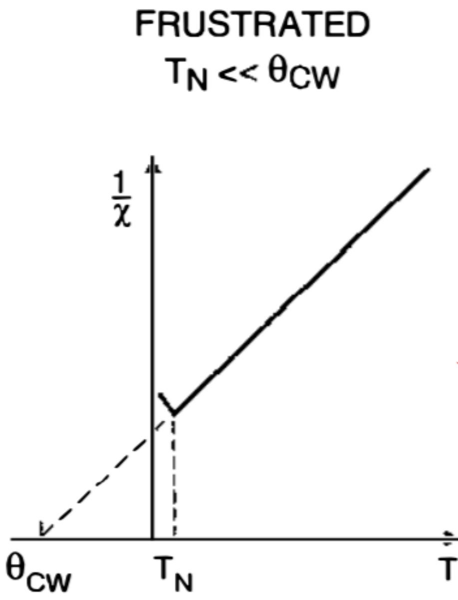
Novel magnetic ground states and excitations

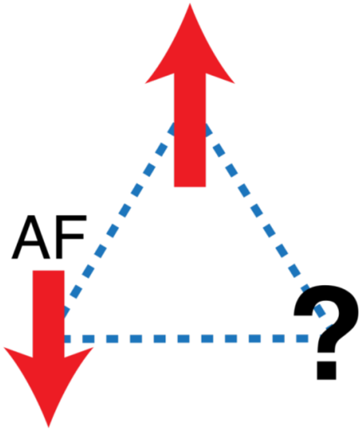


$$H = -\frac{1}{2}\sum_{ij} J_{ij}\mathbf{S}_i \bullet \mathbf{S}_j$$

Interacting spins on a lattice

At large dimension on conventional lattices → broken symmetries and “classical” ground states.





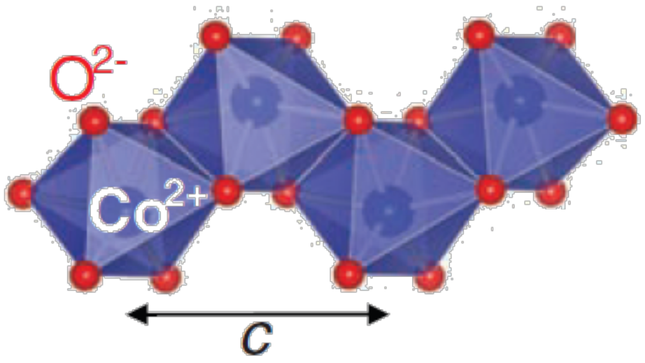
Want to study magnetic states with unconventional ground and excited states.

Frustration, low-dimensionality, or “competing interactions” give non-classical ground states → Macroscopic quantum entangled wave functions

Different routes to novel ground states and excitations in insulating spin systems

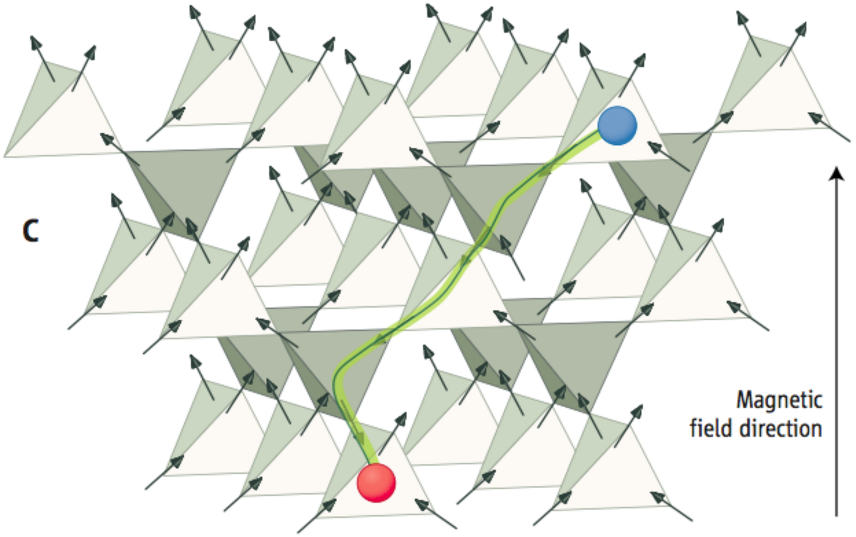
1D Ising systems

(Low dimensionality)



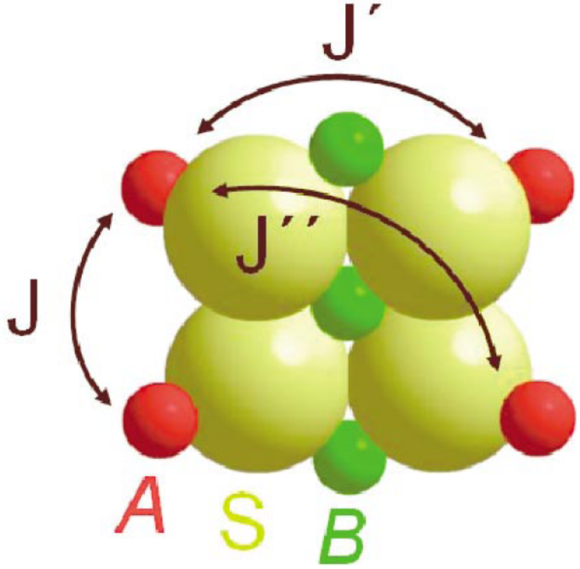
Quantum spin ice

(Frustration)

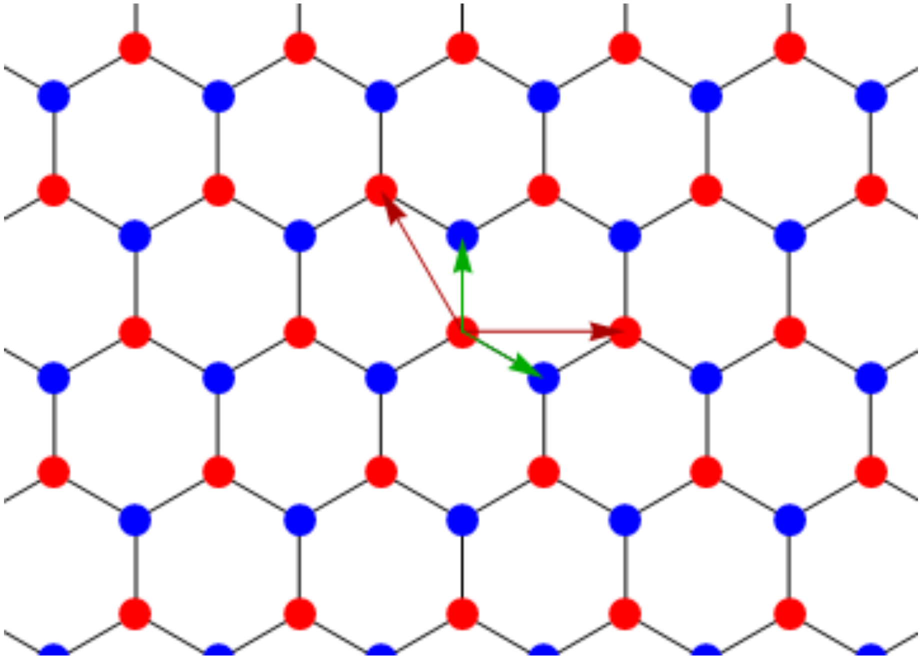


Spin-orbital liquid

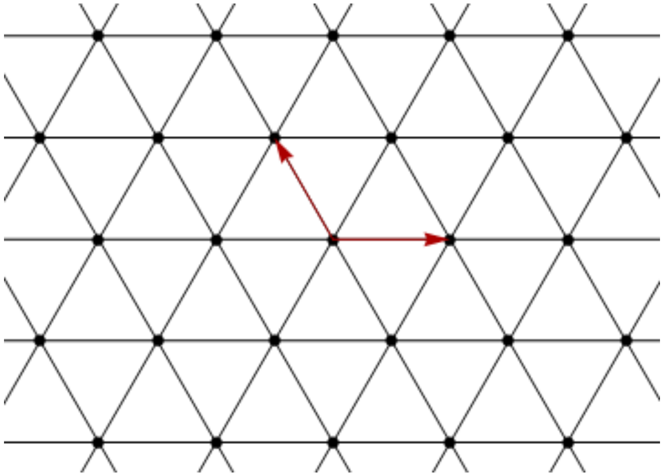
(Competing Interactions)

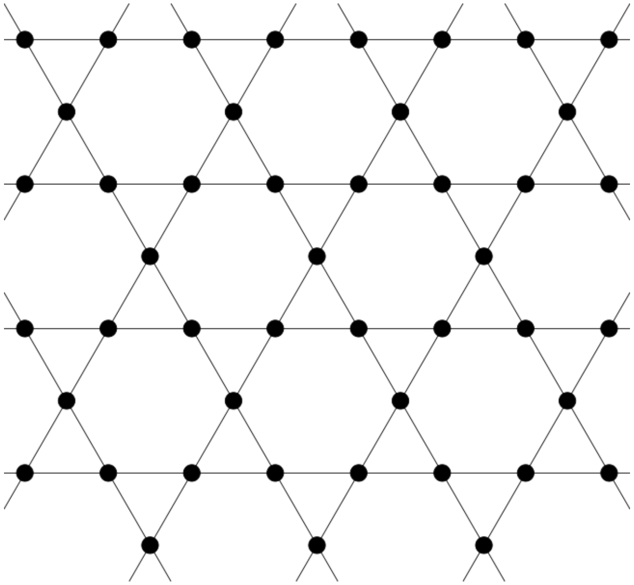


Bipartite

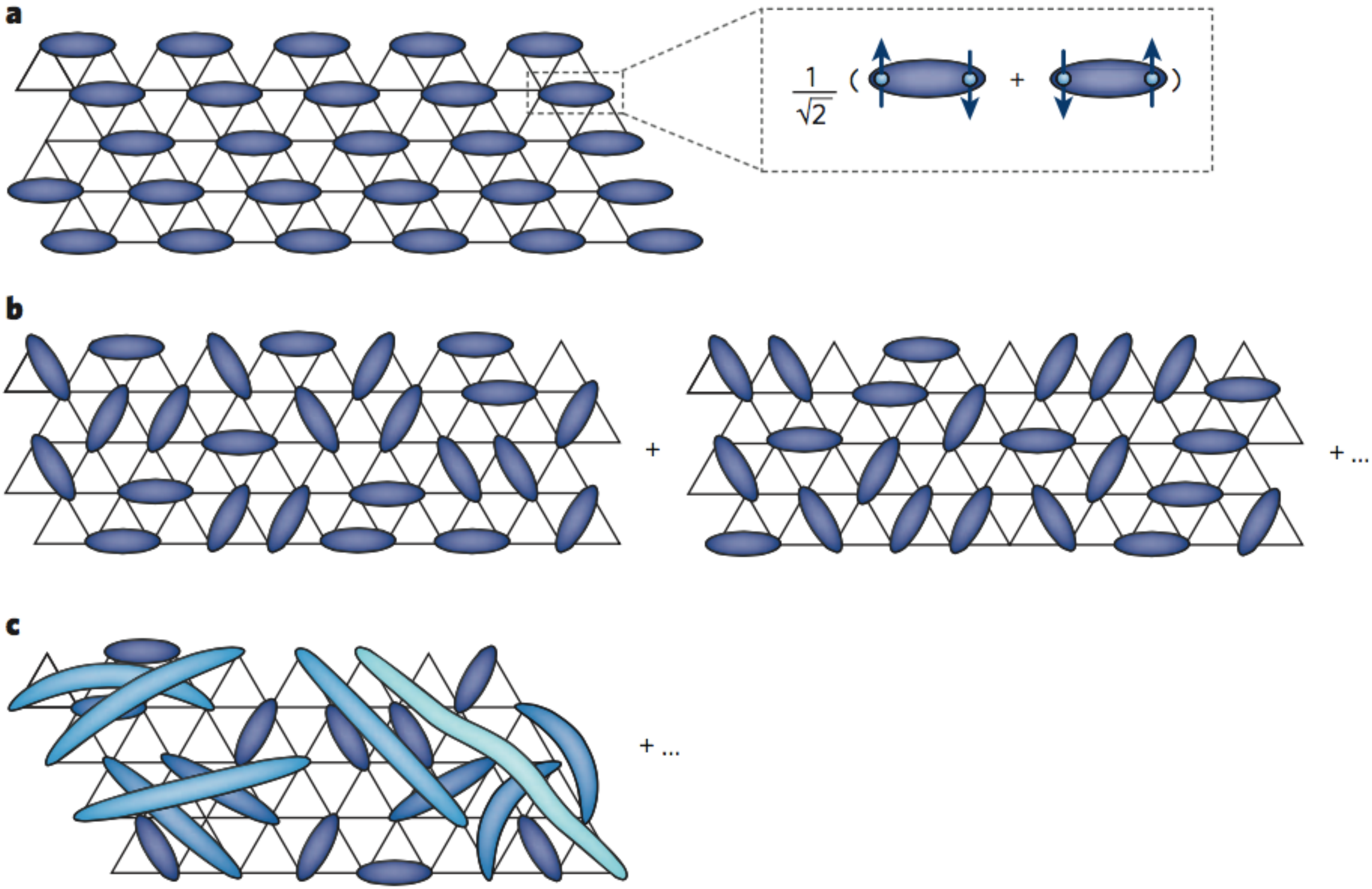


non-Bipartite



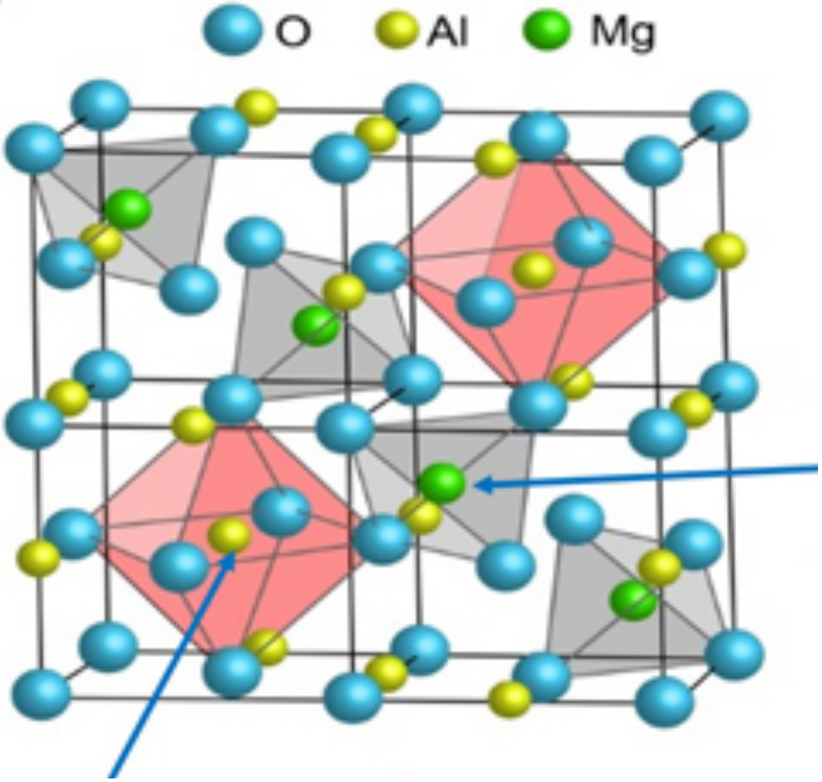


Spin singlet formation on a lattice



Slide courtesy of L. Balents

Spinel AB_2O_4



A site - metal with four NN oxygens.

Tetrahedral site

B site - metal with six NN oxygens

Octahedral site

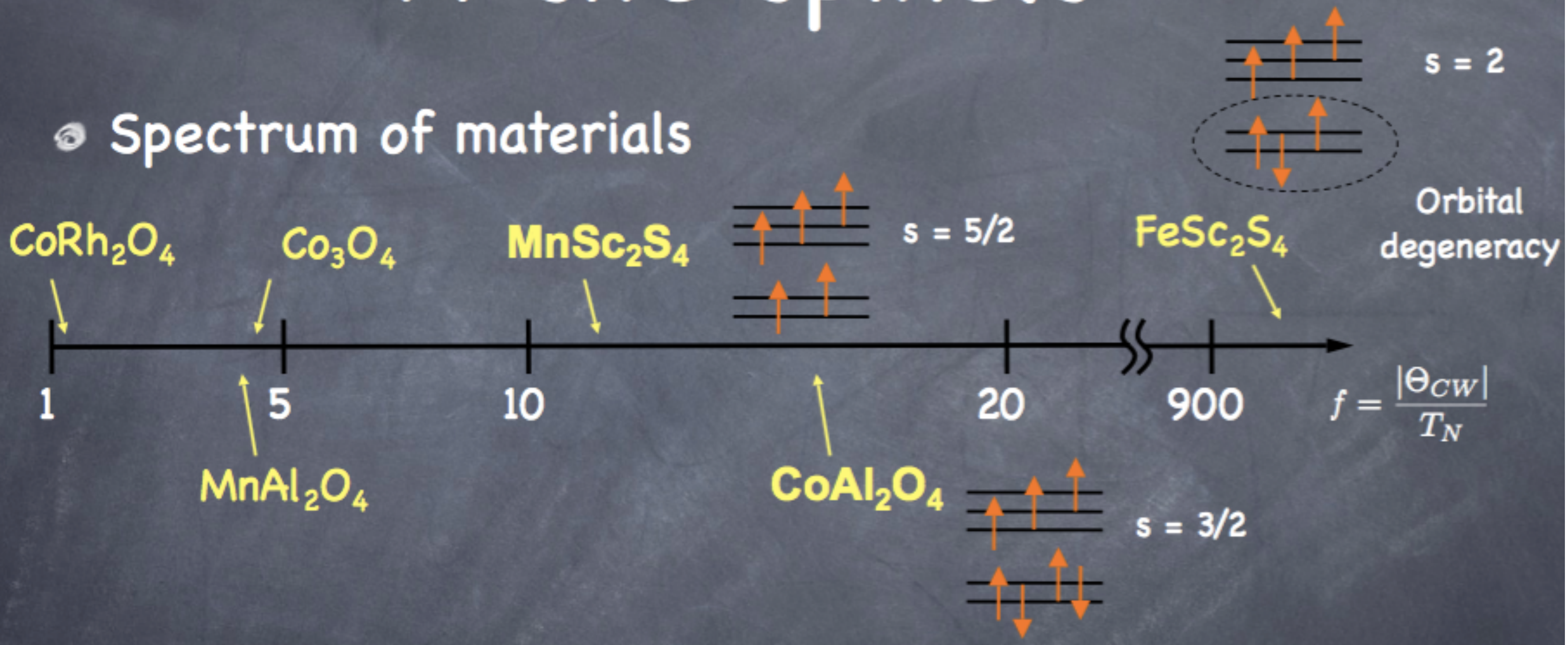
Bipartite Lattice

not geometrically frustrated

non-magnetic $MgAl_2O_4$ (true spinel) is a common gem

A-site spinels

- Spectrum of materials



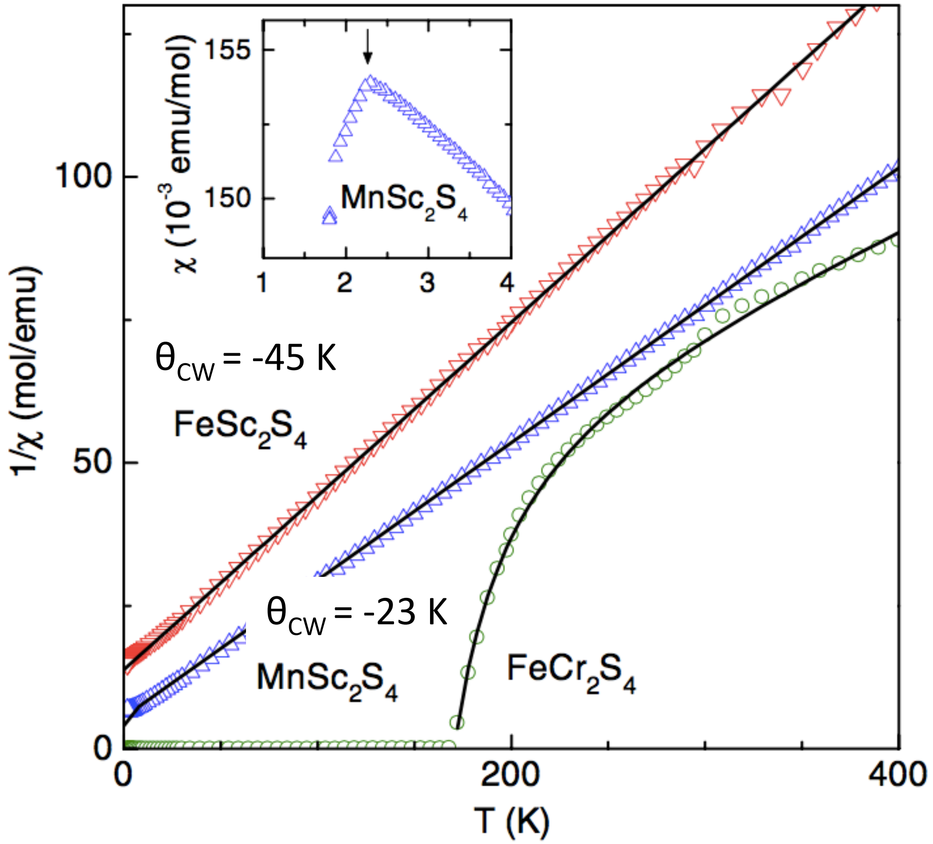
V. Fritsch et al. PRL **92**, 116401 (2004); N. Tristan et al. PRB **72**, 174404 (2005); T. Suzuki *et al.* (2006)

Slide courtesy of L. Balents

VOLUME 92, NUMBER 11 PHYSICAL REVIEW LETTERS week ending 19 MARCH 2004

Spin and Orbital Frustration in $MnSc_2S_4$ and $FeSc_2S_4$

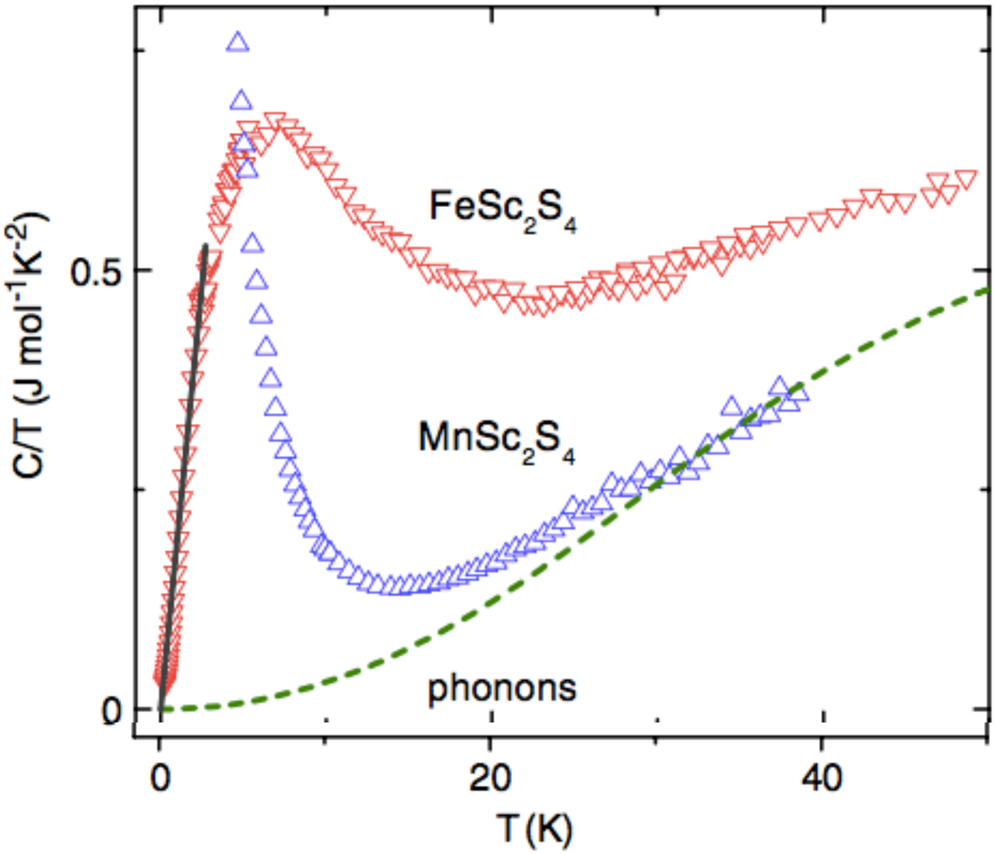
V. Fritsch,[1,*] J. Hemberger,[1] N. Büttgen,[1] E.-W. Scheidt,[2] H.-A. Krug von Nidda,[1] A. Loidl,[1] and V. Tsurkan[1,3]
[1]*Experimentalphysik V, Center for Electronic Correlations and Magnetism, Institut für Physik, Universität Augsburg, D-86159 Augsburg, Germany*



For $FeSc_2S_4$,
T_N not visible down to 50 mK

$f = |\Theta_{CW}|/T_N$

$f > 1000!$



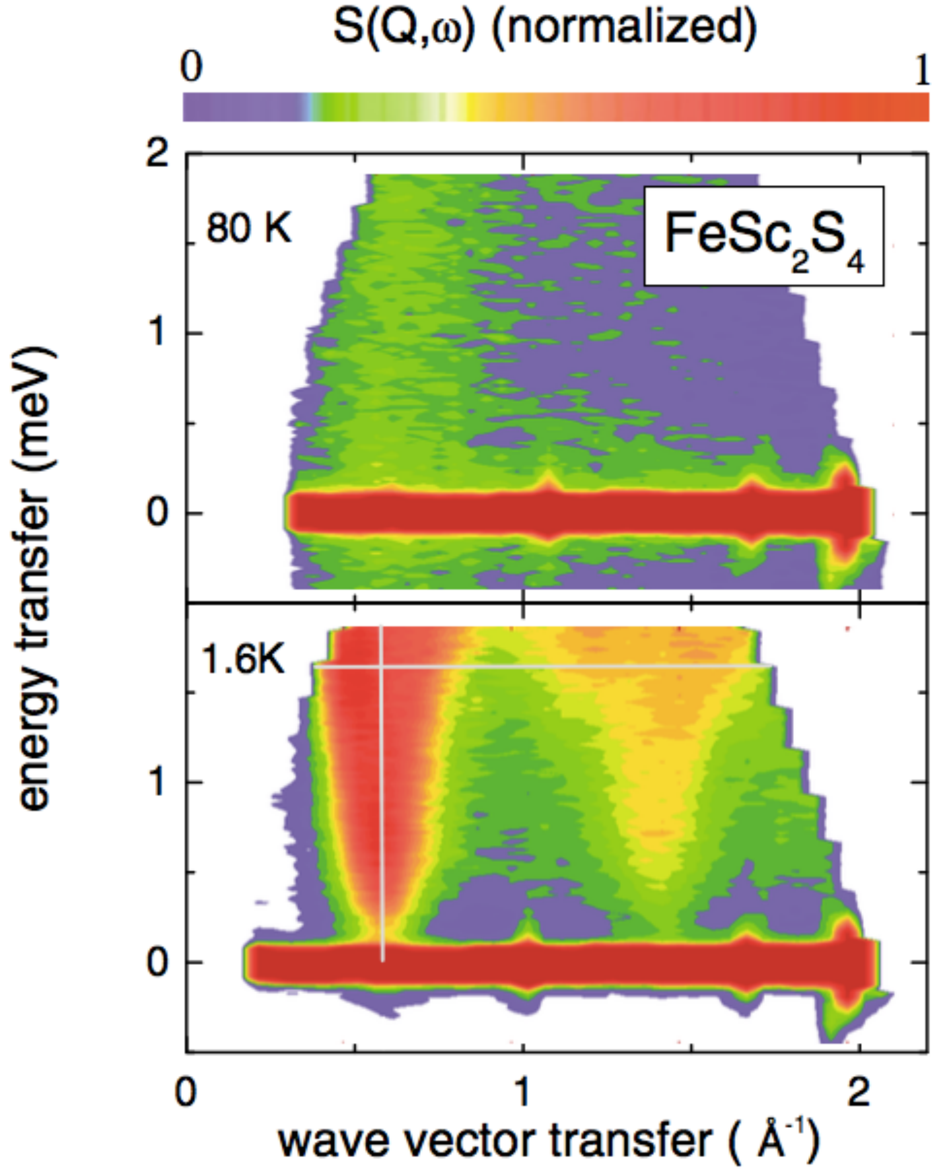
$$\chi \sim \frac{C}{T - \Theta_{CW}}$$

$$C = \frac{\mu_B^2}{3k_B} N g^2 J(J+1),$$

$\mu_{eff} \sim 5.1\ \mu_B$

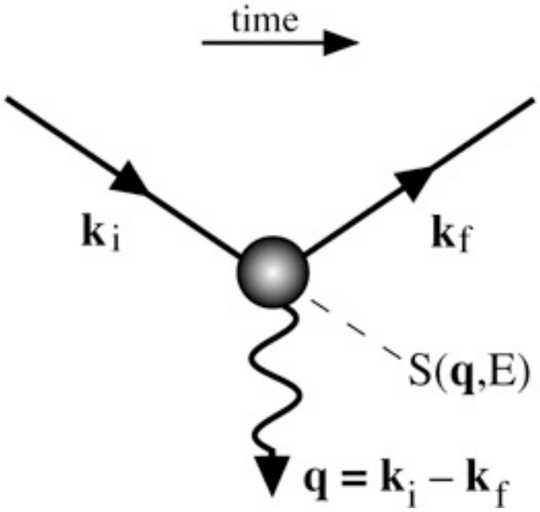
$\mu_{pred} \sim 4.9\ \mu_B$ for J,S=2

Neutron scattering in $FeSc_2S_4$

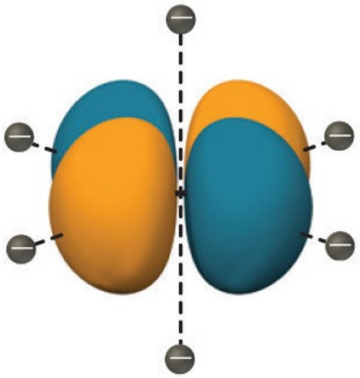


Neutron scattering shows no magnetic Bragg peaks

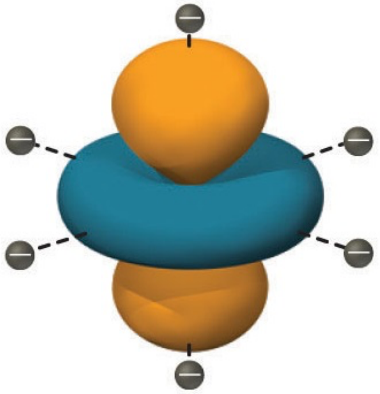
- soft mode at zone edge; Krimmel et al. (2005)



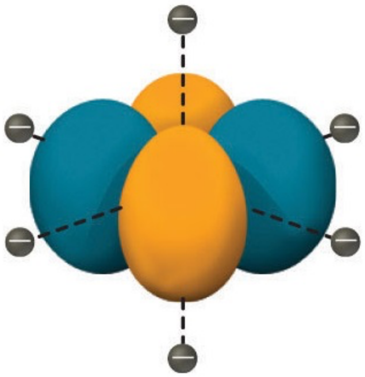
what about local interactions?



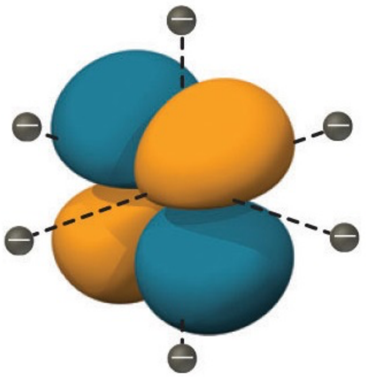
$d_{x^2-y^2}$



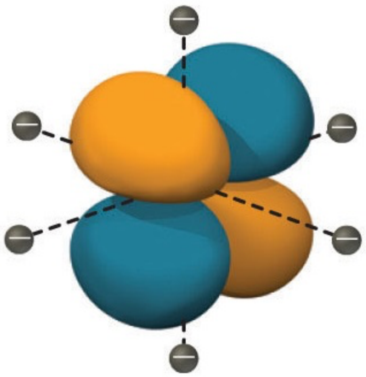
d_{z^2}



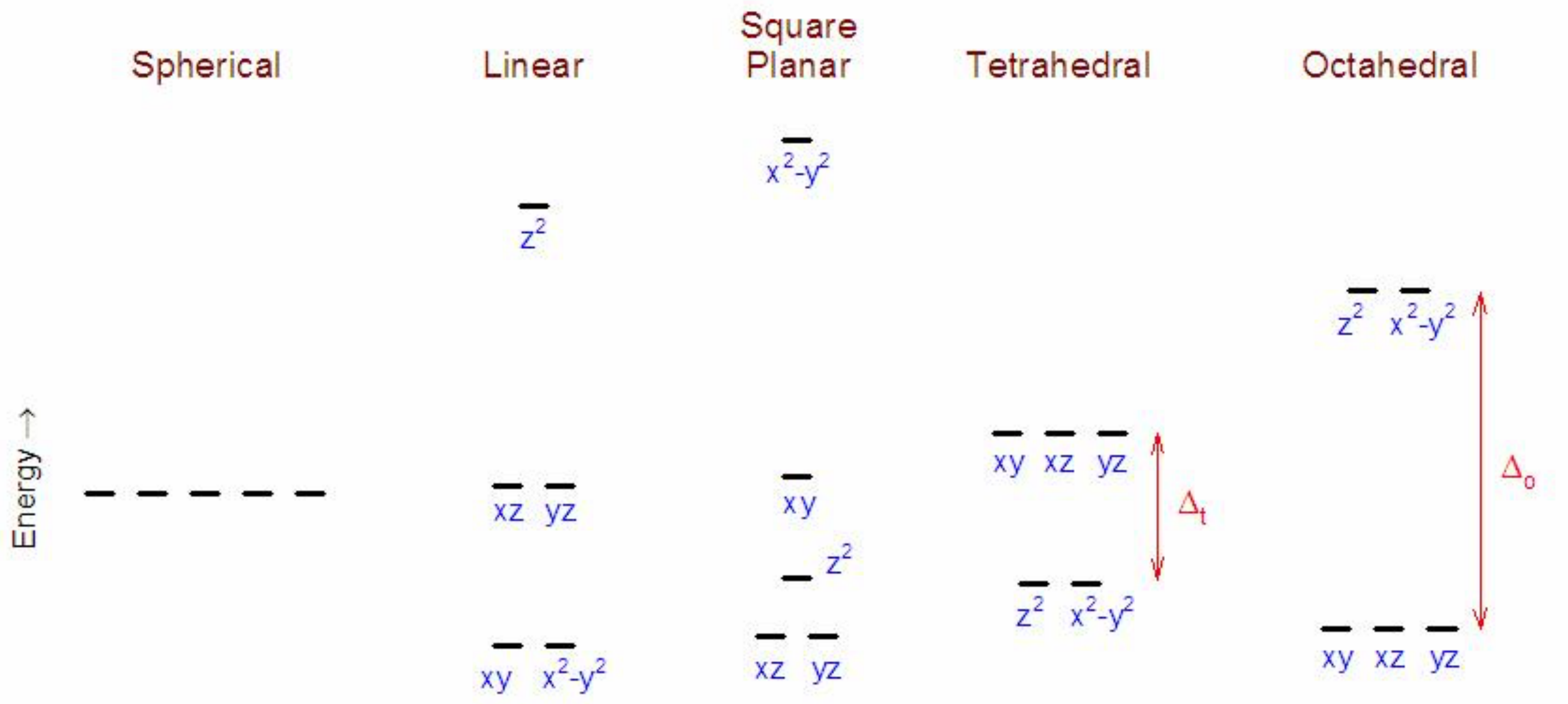
d_{xy}

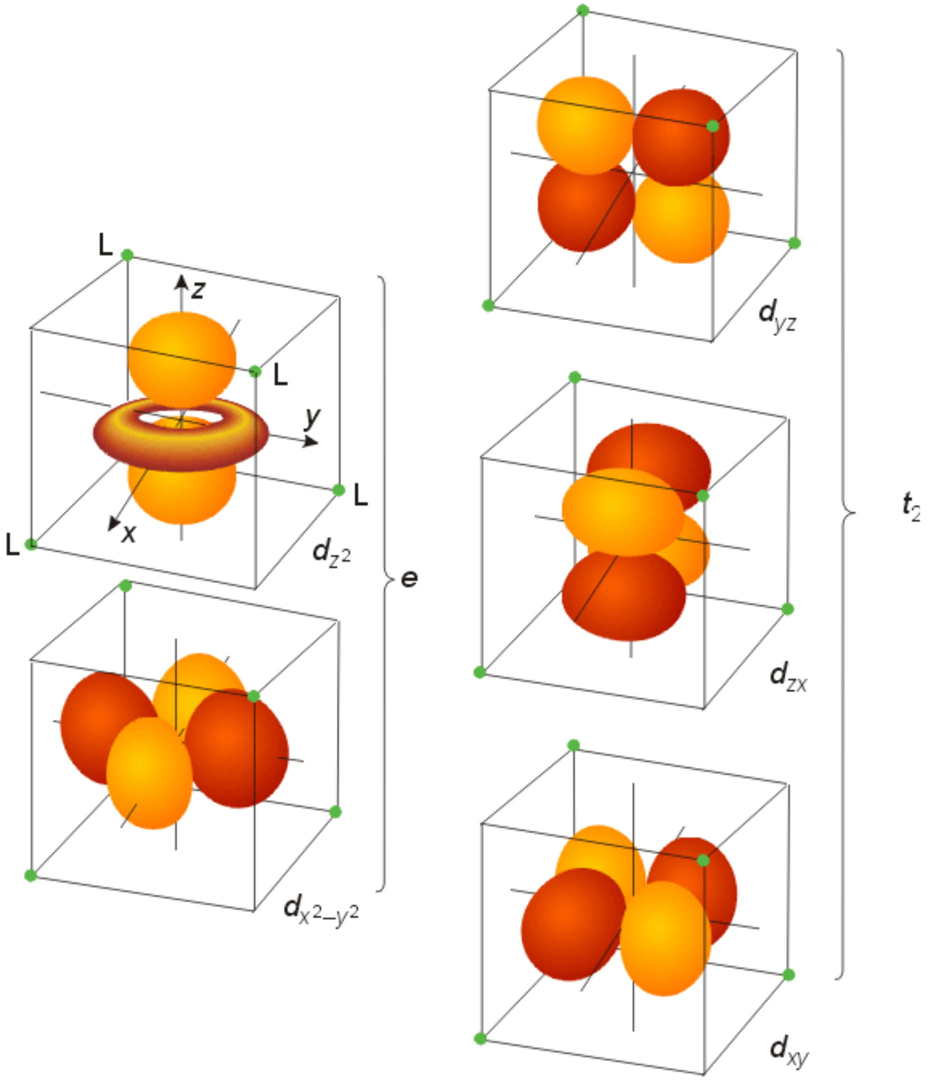


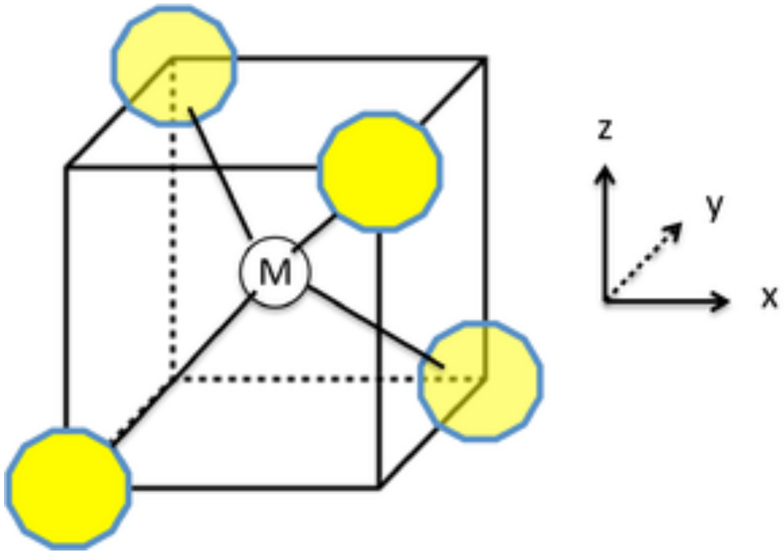
d_{xz}



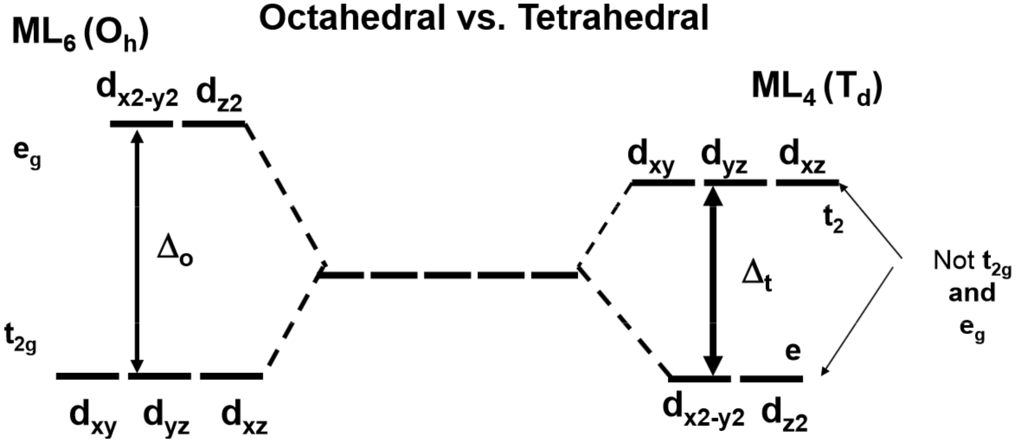
d_{yz}







Octahedral vs. Tetrahedral



ML_6 (O_h)

d_{x2-y2} d_{z2}

e_g

Δ_o

t_{2g}

d_{xy} d_{yz} d_{xz}

ML_4 (T_d)

d_{xy} d_{yz} d_{xz}

t_2

Δ_t

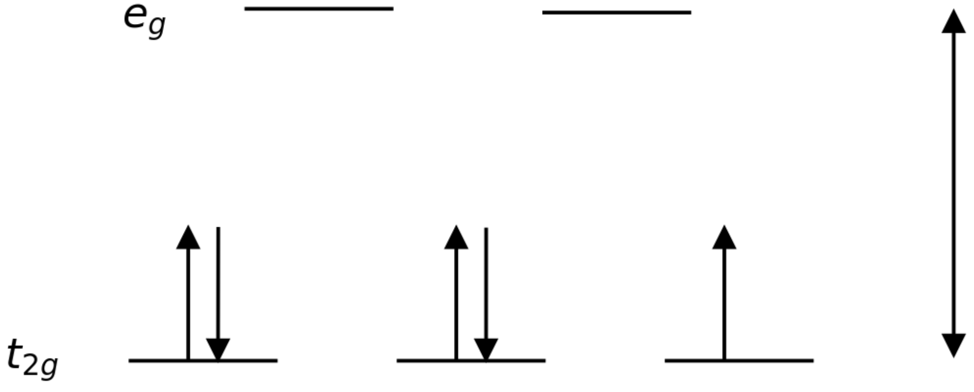
e

d_{x2-y2} d_{z2}

Not t_{2g} and e_g

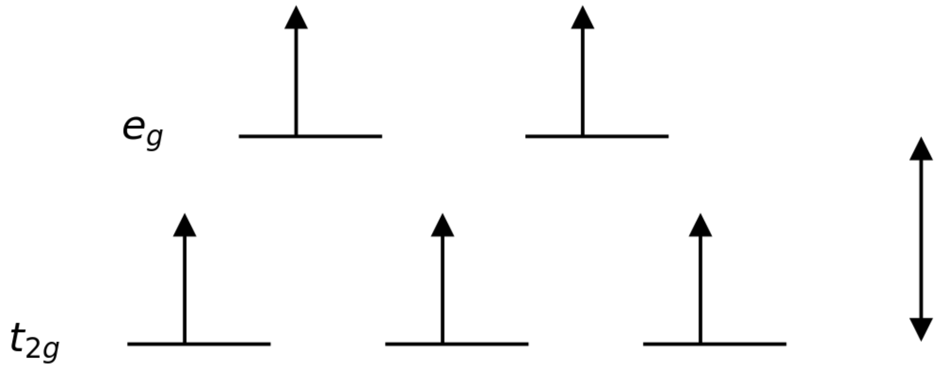
Low spin vs. High spin configurations

Hund's coupling U ⇄ crystal field spitting Δ



Low Spin
$[FeBr_6]^{3-}$

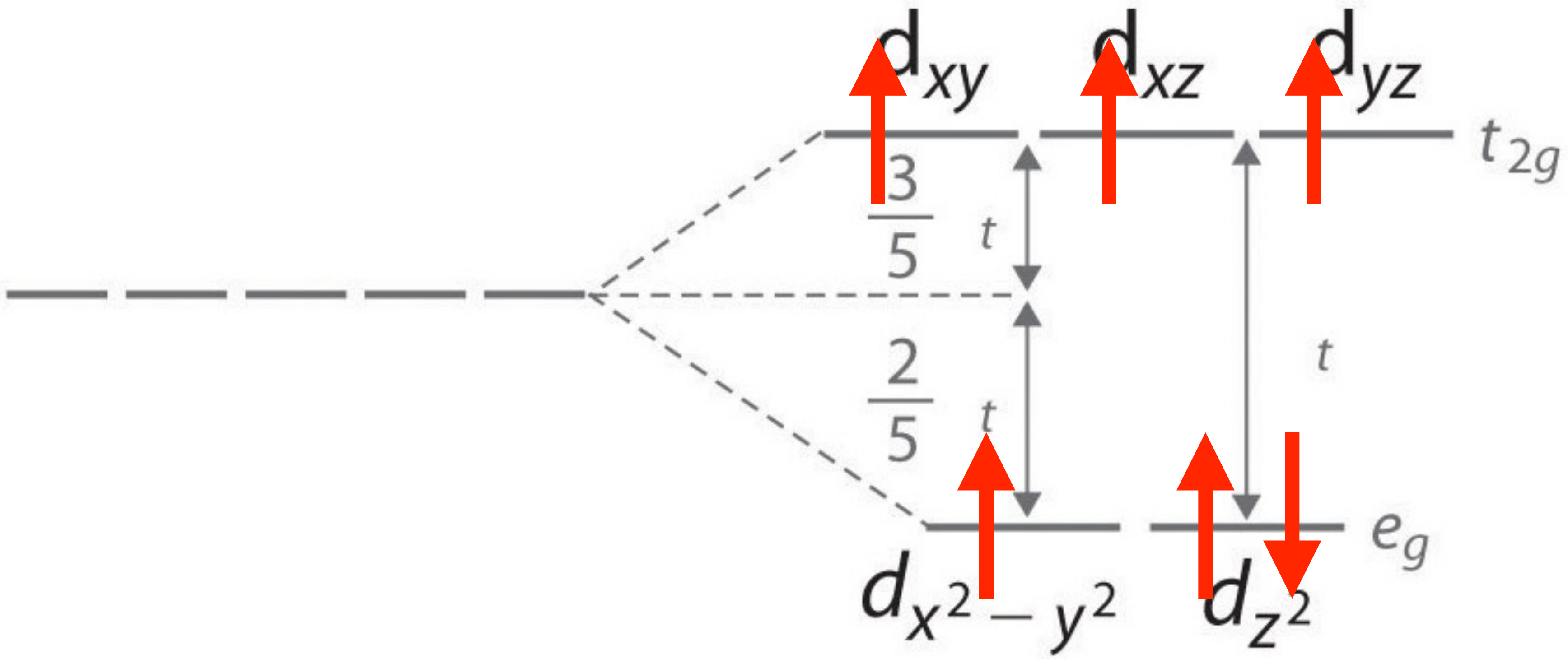
Δ_o Large



High Spin
$[Fe(NO_2)_6]^{3-}$

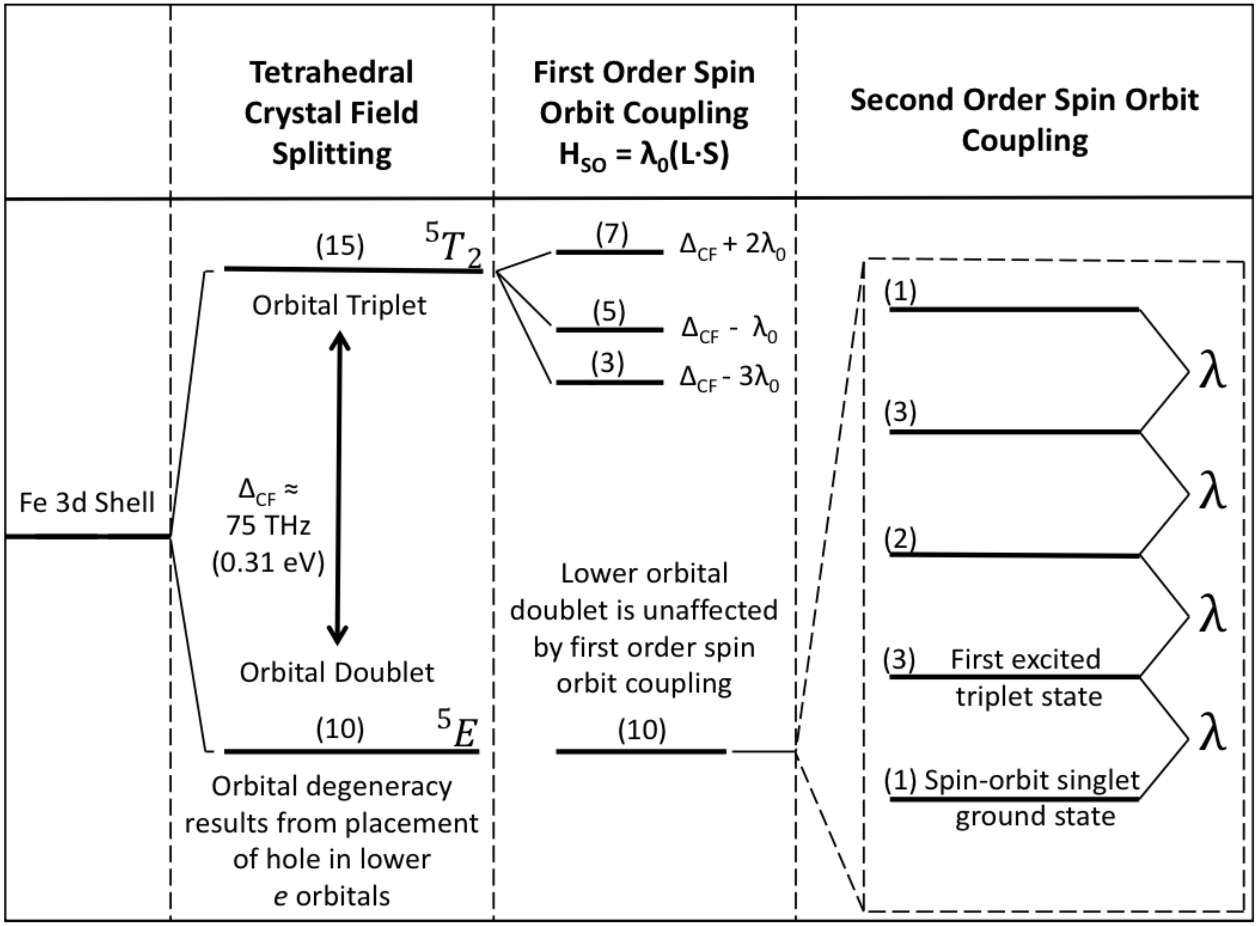
Δ_o Small

Tetrahedral complex have small Δ so usually high spin



Tetrahedral

Fe^{2+} → 6 e- in tetrahedral CF with S=2 high spin configuration



Tetrahedral Crystal Field Splitting

First Order Spin Orbit Coupling $H_{SO} = \lambda_0(L\cdot S)$

Second Order Spin Orbit Coupling

Fe 3d Shell

(15) $^5T_2$

Orbital Triplet

$\Delta_{CF} \approx$ 75 THz (0.31 eV)

Orbital Doublet

(10) ^5E

Orbital degeneracy results from placement of hole in lower *e* orbitals

(7) $\Delta_{CF} + 2\lambda_0$

(5) $\Delta_{CF} - \lambda_0$

(3) $\Delta_{CF} - 3\lambda_0$

Lower orbital doublet is unaffected by first order spin orbit coupling

(10)

(1)

(3)

(2)

(3) First excited triplet state

(1) Spin-orbit singlet ground state

λ

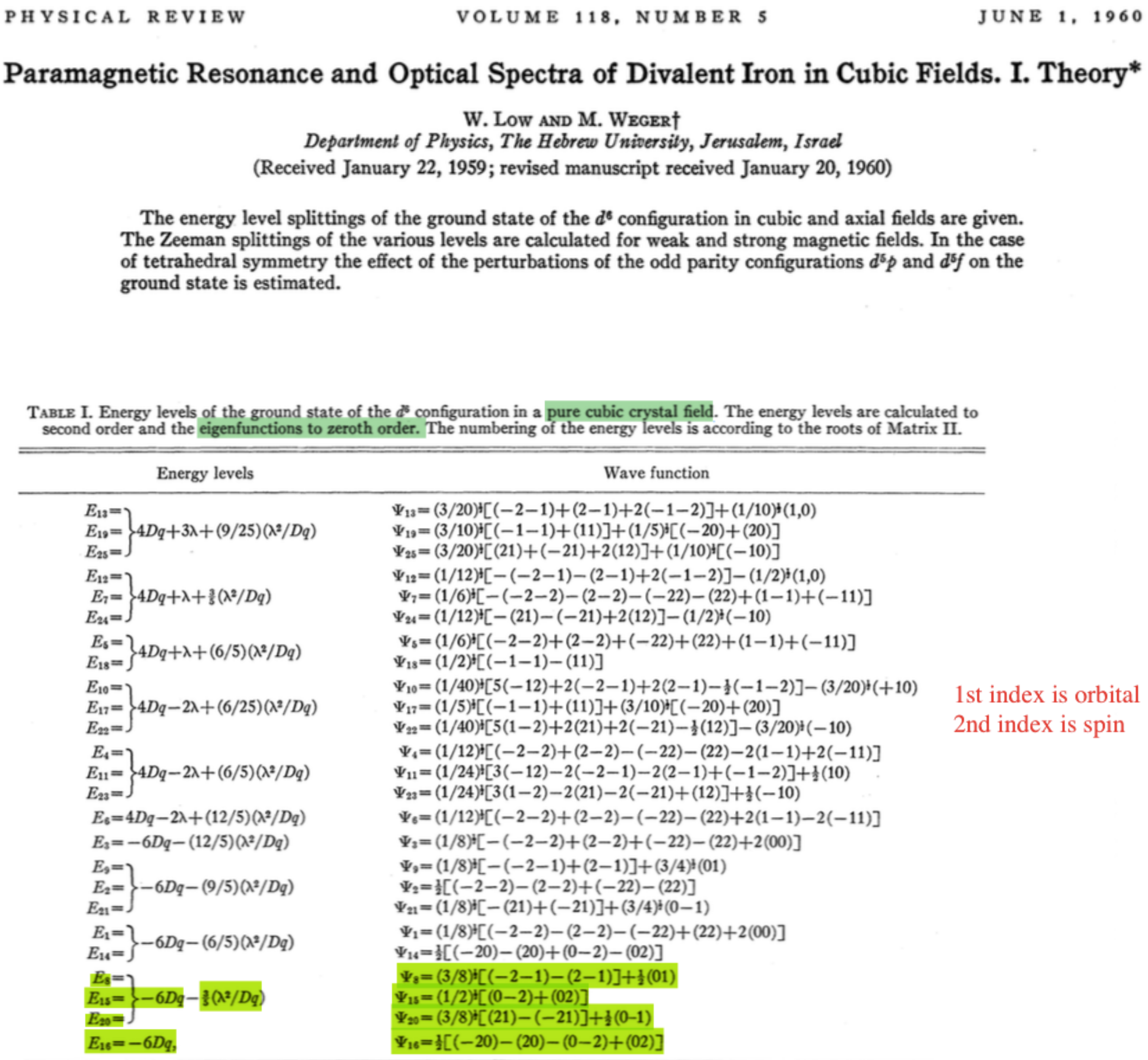
λ

λ

λ

At single ion level ground state is a highly entangled "Spin-Orbit singlet"

$$\Psi_g = \frac{1}{\sqrt{2}}|x^2-y^2\rangle|S^z=0\rangle+\frac{1}{2}|3z^2-r^2\rangle[|S^z=+2\rangle+|S^z=-2\rangle]$$



PHYSICAL REVIEW VOLUME 118, NUMBER 5 JUNE 1, 1960

Paramagnetic Resonance and Optical Spectra of Divalent Iron in Cubic Fields. I. Theory*

W. Low and M. Weger†
Department of Physics, The Hebrew University, Jerusalem, Israel

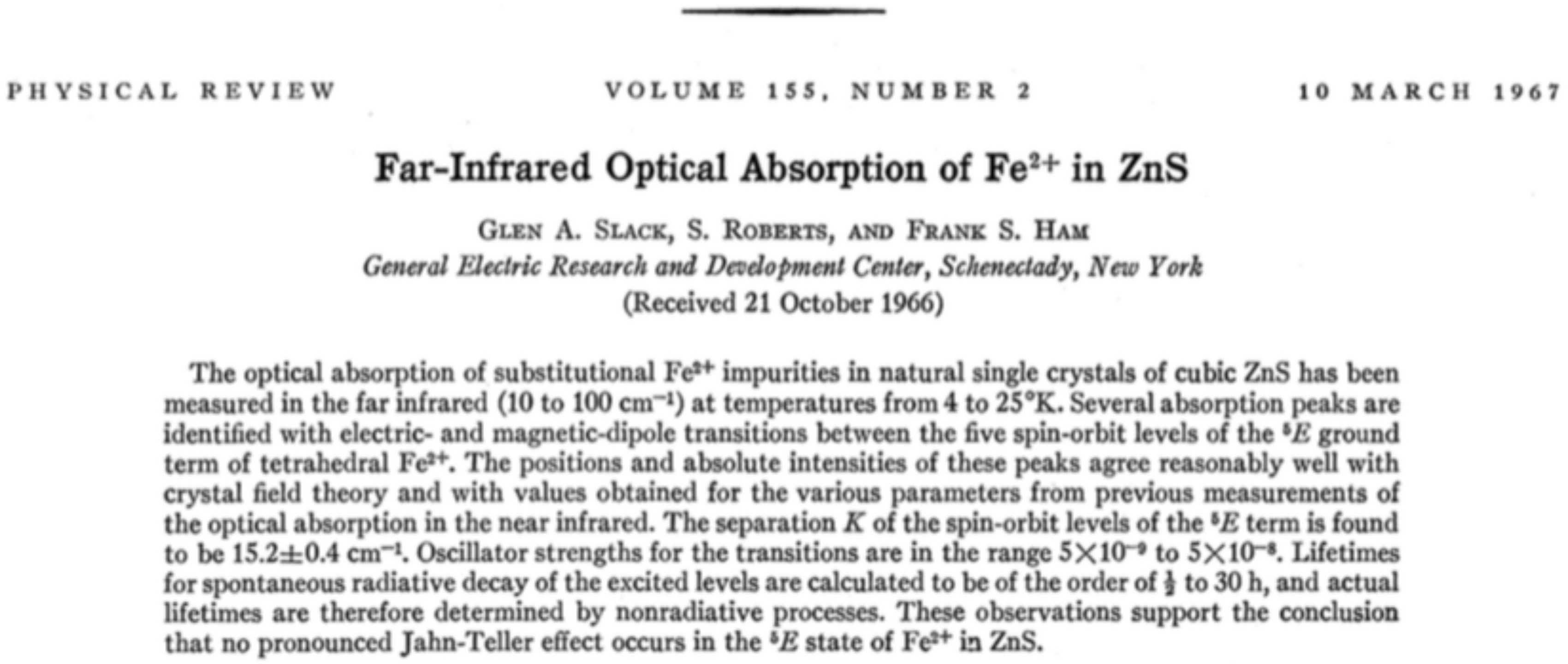
(Received January 22, 1959; revised manuscript received January 20, 1960)

The energy level splittings of the ground state of the d^6 configuration in cubic and axial fields are given. The Zeeman splittings of the various levels are calculated for weak and strong magnetic fields. In the case of tetrahedral symmetry the effect of the perturbations of the odd parity configurations d^5p and d^5f on the ground state is estimated.

TABLE I. Energy levels of the ground state of the d^6 configuration in a pure cubic crystal field. The energy levels are calculated to second order and the eigenfunctions to zeroth order. The numbering of the energy levels is according to the roots of Matrix II.

Energy levels	Wave function
$E_{13}=$ $4Dq+3\lambda+(9/25)(\lambda^2/Dq)$	$\Psi_{13}=(3/20)^{1/2}[(-2-1)+(2-1)+2(-1-2)]+(1/10)^{1/2}(1,0)$
$E_{19}=$	$\Psi_{19}=(3/10)^{1/2}[(-1-1)+(11)]+(1/5)^{1/2}[(-20)+(20)]$
$E_{25}=$	$\Psi_{25}=(3/20)^{1/2}[(21)+(-21)+2(12)]+(1/10)^{1/2}[(-10)]$
$E_{12}=$ $4Dq+\lambda+\frac{3}{5}(\lambda^2/Dq)$	$\Psi_{12}=(1/12)^{1/2}[-(-2-1)-(2-1)+2(-1-2)]-(1/2)^{1/2}(1,0)$
$E_7=$	$\Psi_7=(1/6)^{1/2}[-(-2-2)-(2-2)-(-22)-(22)+(1-1)+(-11)]$
$E_{24}=$	$\Psi_{24}=(1/12)^{1/2}[-(21)-(-21)+2(12)]-(1/2)^{1/2}(-10)$
$E_5=$ $4Dq+\lambda+(6/5)(\lambda^2/Dq)$	$\Psi_5=(1/6)^{1/2}[(-2-2)+(2-2)+(-22)+(22)+(1-1)+(-11)]$
$E_{18}=$	$\Psi_{18}=(1/2)^{1/2}[(-1-1)-(11)]$
$E_{10}=$ $4Dq-2\lambda+(6/25)(\lambda^2/Dq)$	$\Psi_{10}=(1/40)^{1/2}[5(-12)+2(-2-1)+2(2-1)-\frac{1}{2}(-1-2)]-(3/20)^{1/2}(+10)$
$E_{17}=$	$\Psi_{17}=(1/5)^{1/2}[(-1-1)+(11)]+(3/10)^{1/2}[(-20)+(20)]$
$E_{22}=$	$\Psi_{22}=(1/40)^{1/2}[5(1-2)+2(21)+2(-21)-\frac{1}{2}(12)]-(3/20)^{1/2}(-10)$
$E_4=$ $4Dq-2\lambda+(6/5)(\lambda^2/Dq)$	$\Psi_4=(1/12)^{1/2}[(-2-2)+(2-2)-(-22)-(22)-2(1-1)+2(-11)]$
$E_{11}=$	$\Psi_{11}=(1/24)^{1/2}[3(-12)-2(-2-1)-2(2-1)+(-1-2)]+\frac{1}{2}(10)$
$E_{23}=$	$\Psi_{23}=(1/24)^{1/2}[3(1-2)-2(21)-2(-21)+(12)]+\frac{1}{2}(-10)$
$E_6=4Dq-2\lambda+(12/5)(\lambda^2/Dq)$	$\Psi_6=(1/12)^{1/2}[(-2-2)+(2-2)-(-22)-(22)+2(1-1)-2(-11)]$
$E_3=-6Dq-(12/5)(\lambda^2/Dq)$	$\Psi_3=(1/8)^{1/2}[-(-2-2)+(2-2)+(-22)-(22)+2(00)]$
$E_9=$ $-6Dq-(9/5)(\lambda^2/Dq)$	$\Psi_9=(1/8)^{1/2}[-(-2-1)+(2-1)]+(3/4)^{1/2}(01)$
$E_2=$	$\Psi_2=\frac{1}{2}[(-2-2)-(2-2)+(-22)-(22)]$
$E_{21}=$	$\Psi_{21}=(1/8)^{1/2}[-(21)+(-21)]+(3/4)^{1/2}(0-1)$
$E_1=$ $-6Dq-(6/5)(\lambda^2/Dq)$	$\Psi_1=(1/8)^{1/2}[(-2-2)-(2-2)-(-22)+(22)+2(00)]$
$E_{14}=$	$\Psi_{14}=\frac{1}{2}[(-20)-(20)+(0-2)-(02)]$
$E_8=$ $-6Dq-\frac{3}{5}(\lambda^2/Dq)$	$\Psi_8=(3/8)^{1/2}[(-2-1)-(2-1)]+\frac{1}{2}(01)$
$E_{15}=$	$\Psi_{15}=(1/2)^{1/2}[(0-2)+(02)]$
$E_{20}=$	$\Psi_{20}=(3/8)^{1/2}[(21)-(-21)]+\frac{1}{2}(0-1)$
$E_{16}=-6Dq,$	$\Psi_{16}=\frac{1}{2}[(-20)-(20)-(0-2)+(02)]$

1st index is orbital
2nd index is spin



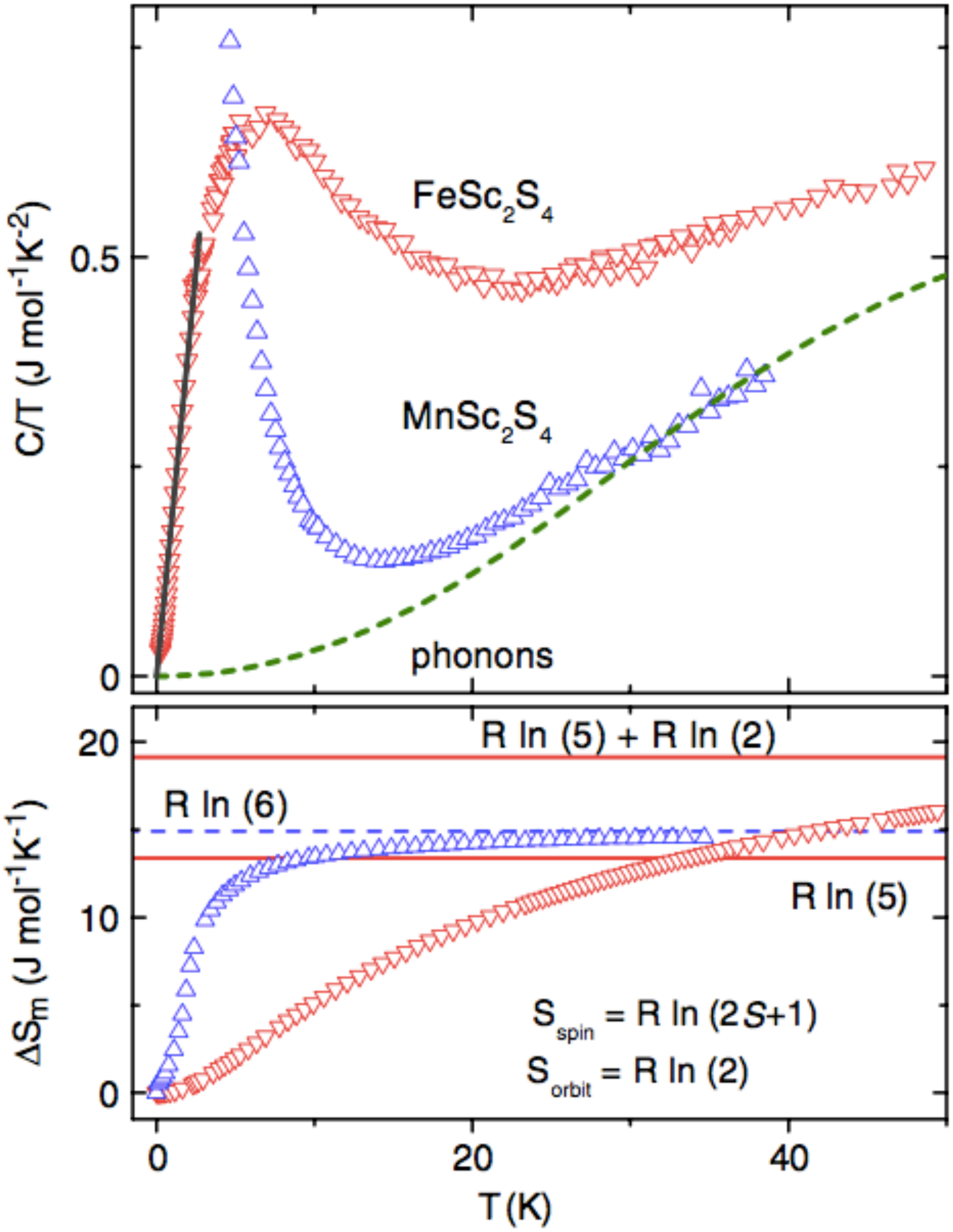
PHYSICAL REVIEW VOLUME 155, NUMBER 2 10 MARCH 1967

Far-Infrared Optical Absorption of Fe^{2+} in ZnS

Glen A. Slack, S. Roberts, and Frank S. Ham
General Electric Research and Development Center, Schenectady, New York

(Received 21 October 1966)

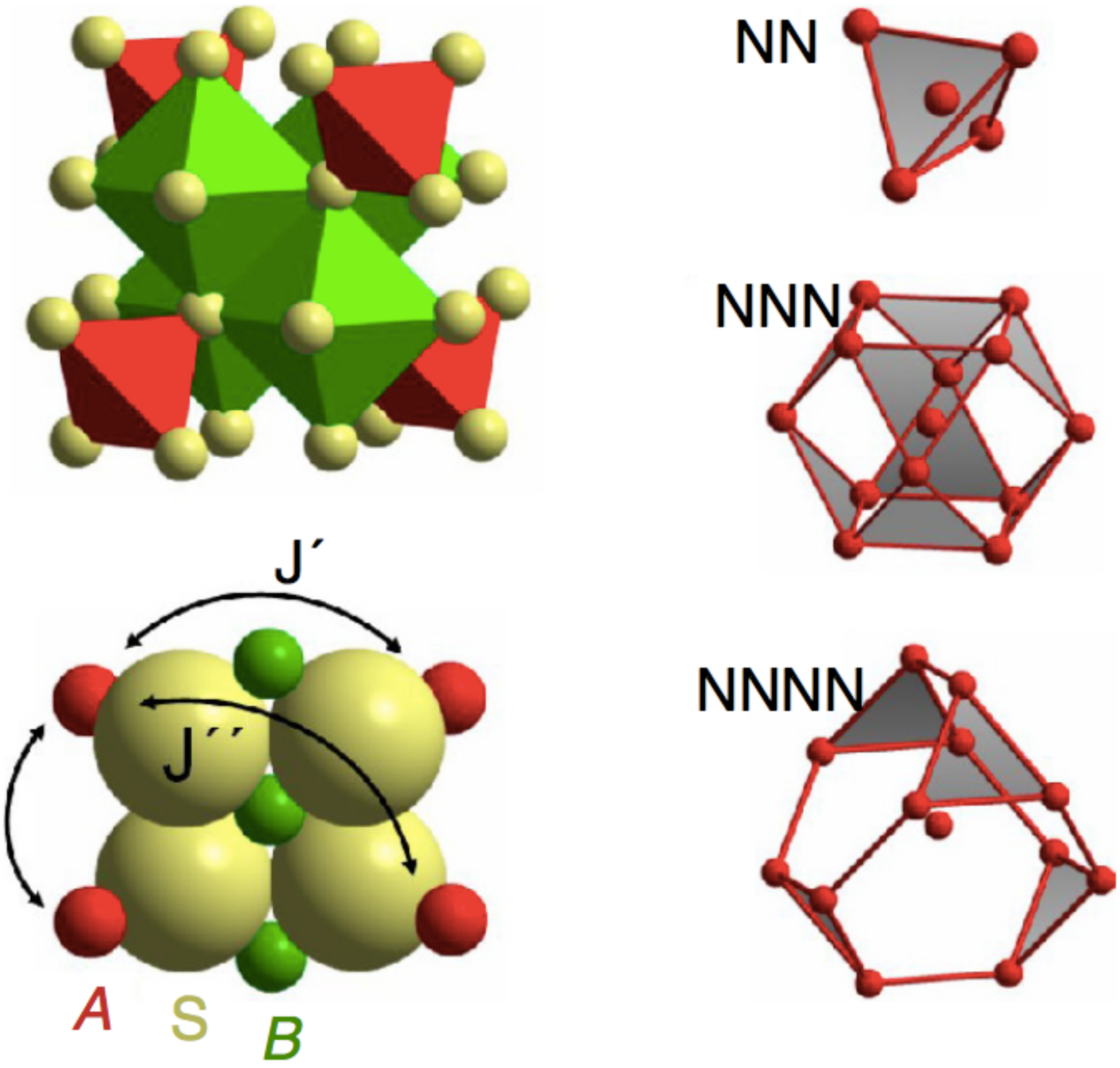
The optical absorption of substitutional Fe^{2+} impurities in natural single crystals of cubic ZnS has been measured in the far infrared (10 to 100 cm^{-1}) at temperatures from 4 to 25°K. Several absorption peaks are identified with electric- and magnetic-dipole transitions between the five spin-orbit levels of the ^5E ground term of tetrahedral Fe^{2+}. The positions and absolute intensities of these peaks agree reasonably well with crystal field theory and with values obtained for the various parameters from previous measurements of the optical absorption in the near infrared. The separation K of the spin-orbit levels of the ^5E term is found to be 15.2 ± 0.4 cm^{-1}. Oscillator strengths for the transitions are in the range 5×10^{-9} to 5×10^{-8}. Lifetimes for spontaneous radiative decay of the excited levels are calculated to be of the order of $\frac{1}{2}$ to 30 h, and actual lifetimes are therefore determined by nonradiative processes. These observations support the conclusion that no pronounced Jahn-Teller effect occurs in the ^5E state of Fe^{2+} in ZnS.



Entropy release indicates correct number of low T degrees of freedom, when counting orbits and spins

From Fritsch et al. Phys. Rev. Lett. 2004

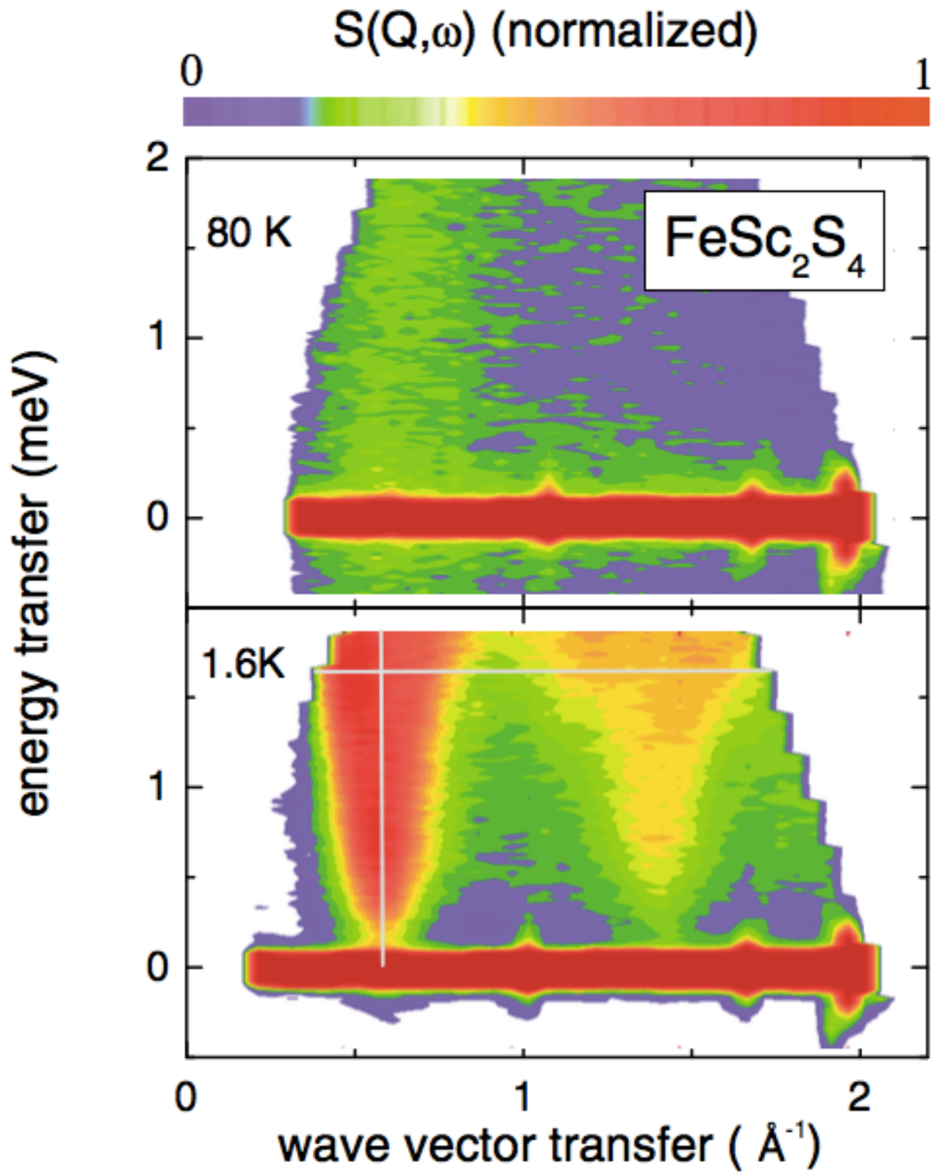
what about exchange?



Three different types of A-S-B-S-A interaction paths in spinel structure. NN and NNNN both have a S-B-S bond angle of 90 degrees

DFT predicts J’/J ~ 37

Neutron scattering in $FeSc_2S_4$



Soft mode at zone edge;
Krimmel et al. (2005)

$$Q = 0.6\ \text{Å}^{-1}$$

A forbidden reflection for the fcc Fd3m space group —>

Dominant AF ordering on the fcc lattice

Indicates dominance of J' coupling

Gives route to frustration because fcc lattice is NOT bipartite!

PRL **102,** 096406 (2009) PHYSICAL REVIEW LETTERS week ending 6 MARCH 2009

Spin-Orbital Singlet and Quantum Critical Point on the Diamond Lattice: $\mathbf{FeSc_2S_4}$

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[1]*Physics Department, University of California, Santa Barbara, California 93106, USA*
[2]*Kavli Institute for Theoretical Physics, University of California, Santa Barbara, California 93106, USA*

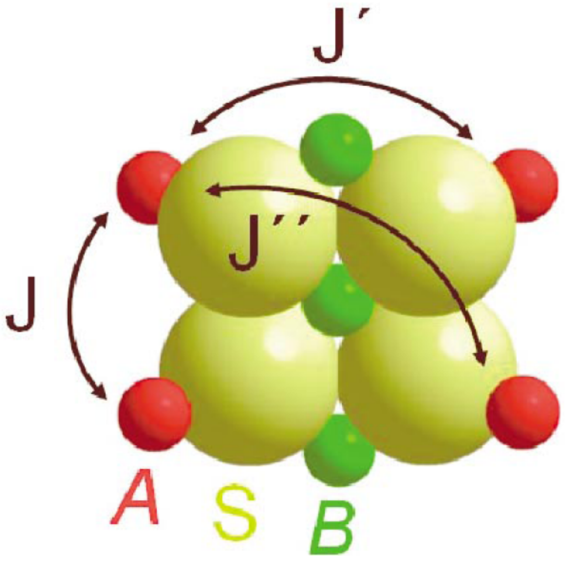
(Received 3 October 2008; published 5 March 2009)

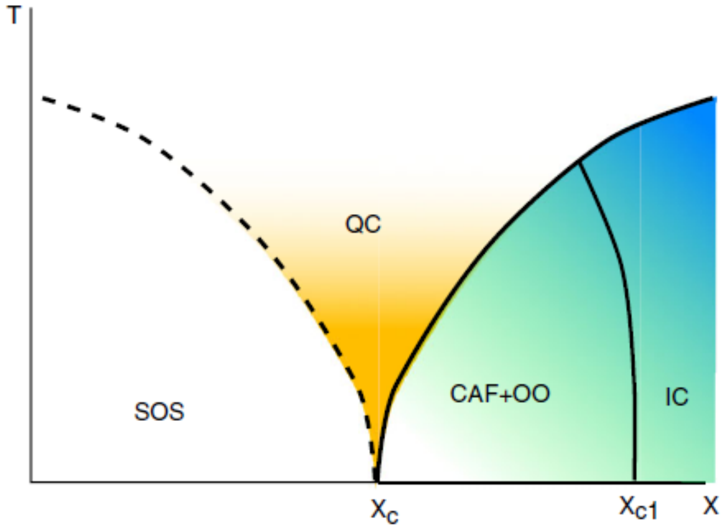
“J_2 / λ” Kugel Khomskii Model

$$\mathcal{H} = \sum_i \mathcal{H}_0^i + \mathcal{H}_{\rm ex}.$$

$$\mathcal{H}_0^i = -\frac{\lambda}{3}\{\sqrt{3}T_i^x[(S_i^x)^2-(S_i^y)^2]+T_i^z[3(S_i^z)^2-\mathbf{S}_i^2]\}.$$

$$\mathcal{H}_{\rm ex} = \frac{1}{2}\sum_{ij}[J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j + 8K_{ij}\mathbf{T}_i\cdot\mathbf{T}_j + \tilde{K}_{ij}\mathbf{T}_i^y\mathbf{T}_j^y + (L_{ij}\mathbf{T}_i\cdot\mathbf{T}_j+\tilde{L}_{ij}\mathbf{T}_i^y\mathbf{T}_j^y)\mathbf{S}_i\cdot\mathbf{S}_j],$$





The spin-orbital liquid

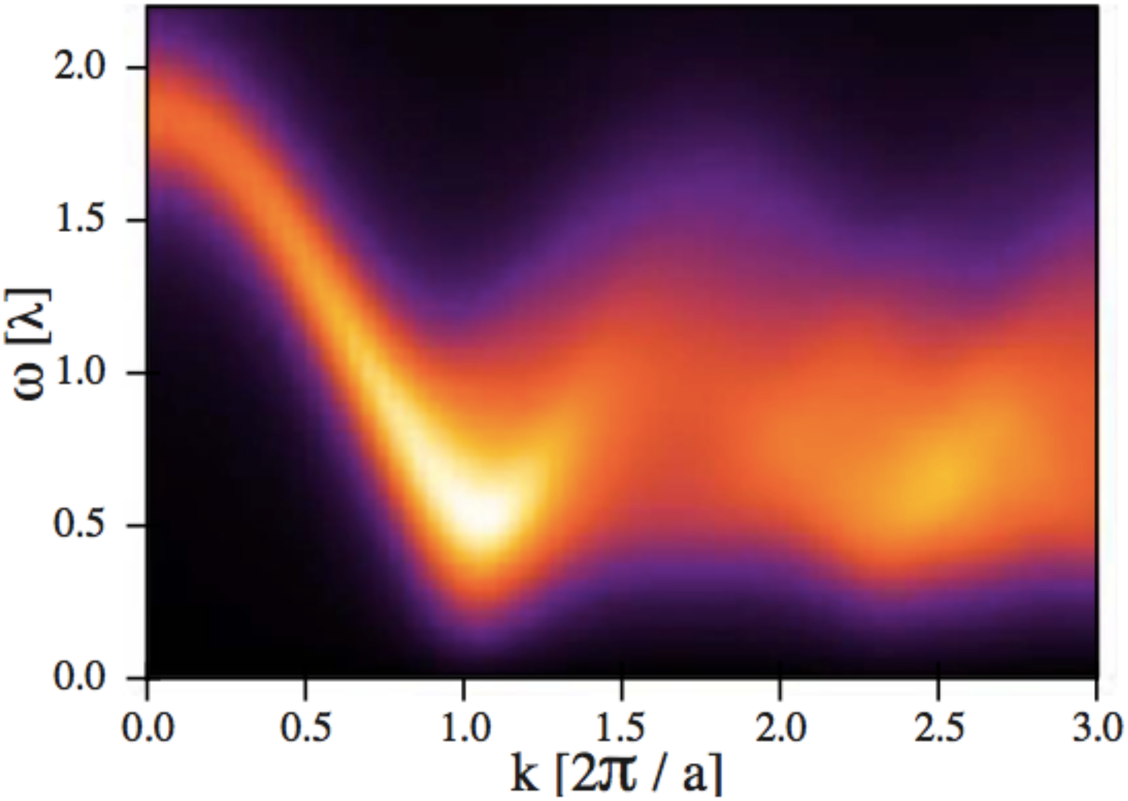
Since quantum disordered phase breaks no symmetries other than crystal, SOL is built out of objects similar to ionic singlet with similar excited state structure

$$\Psi_g = \frac{1}{\sqrt{2}}|x^2-y^2\rangle|S^z=0\rangle+\frac{1}{2}|3z^2-r^2\rangle[|S^z=+2\rangle+|S^z=-2\rangle]$$

$$E(q) = \lambda + 2J_2\sum_{A}\cos(\mathbf{q}\cdot\mathbf{a}),$$

← Expansion in exchange

Random phase approximation →



PRL **114,** 207201 (2015) PHYSICAL REVIEW LETTERS week ending 22 MAY 2015

Singlet-Triplet Excitations and Long-Range Entanglement in the Spin-Orbital Liquid Candidate $\mathrm{FeSc_2S_4}$

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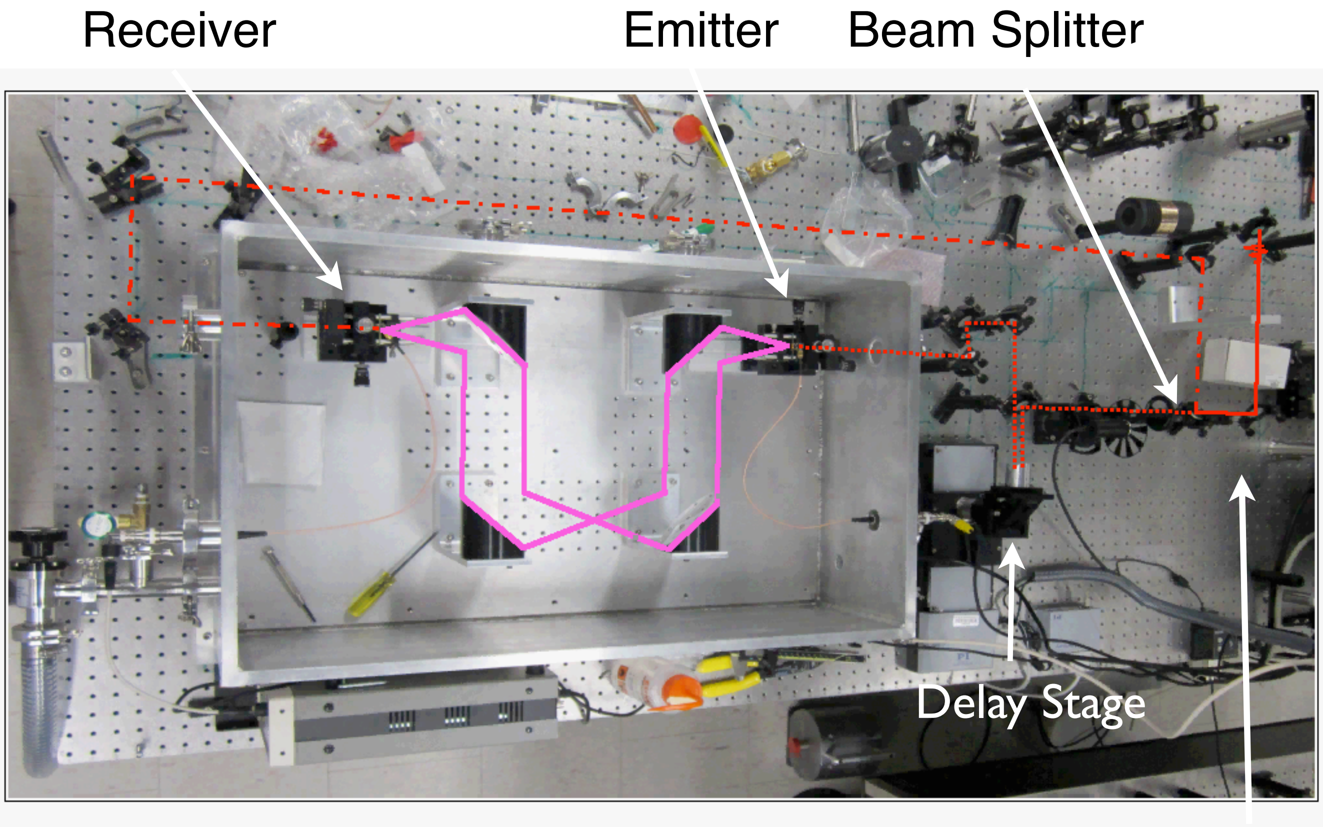
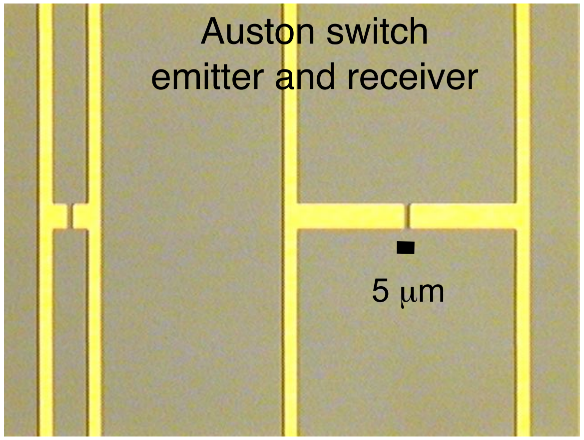
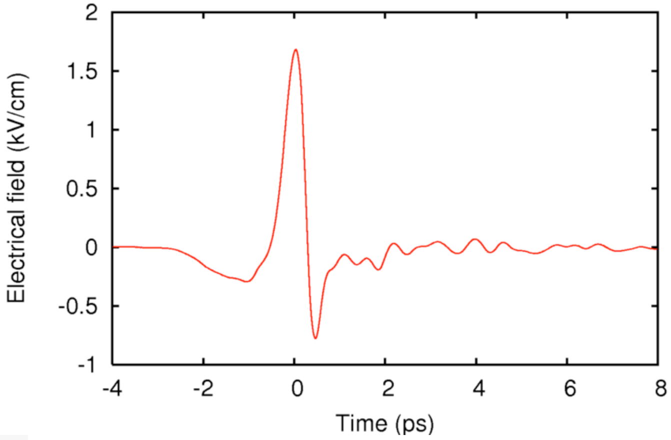
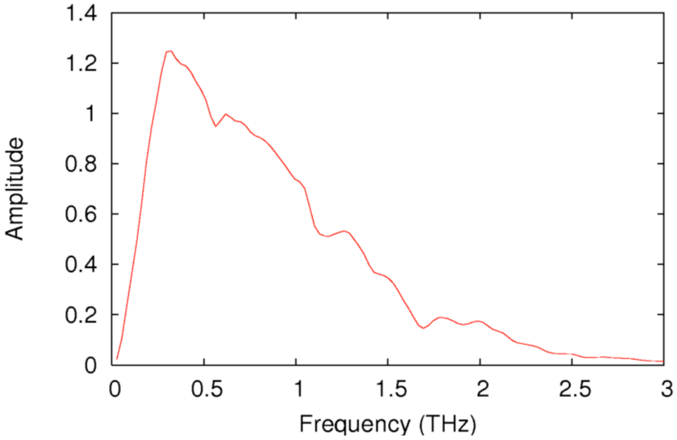
Time Domain THz Spectroscopy





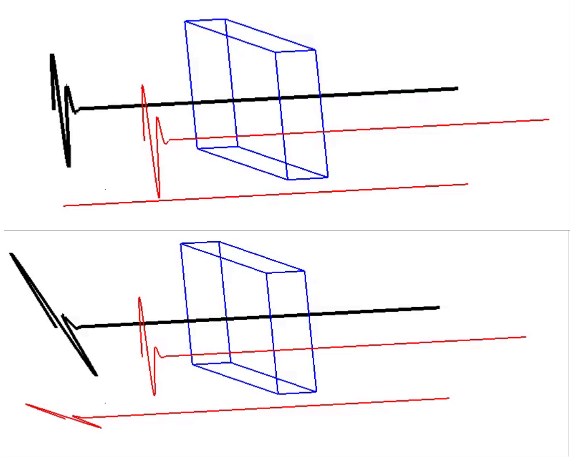


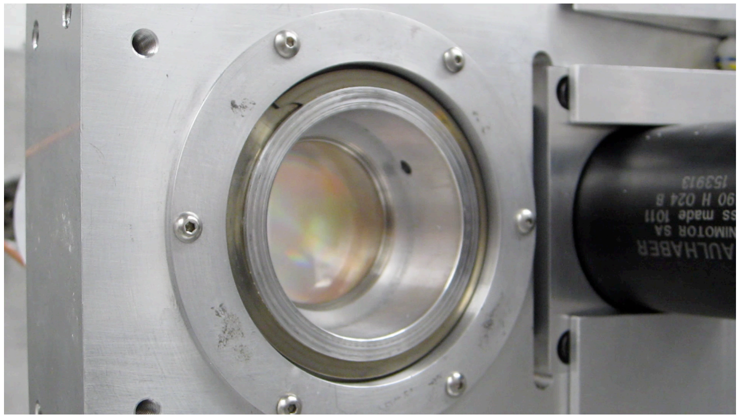
- fs laser excites photoconductive emitter and receiver. Coherent detection of field allows **complex** optical response functions to be measured: 100 GHz - 3 THz (0.8 meV - 12 meV), @ 1.4K - 300K.
- Usually light couples to charge, but can excite **magnetic** dipoles with THz B field
- Broad band THz electron spin resonance (ESR)
- Transmission —> $\ln(T(\omega)) \sim -\omega\chi(q\sim0,\omega)$

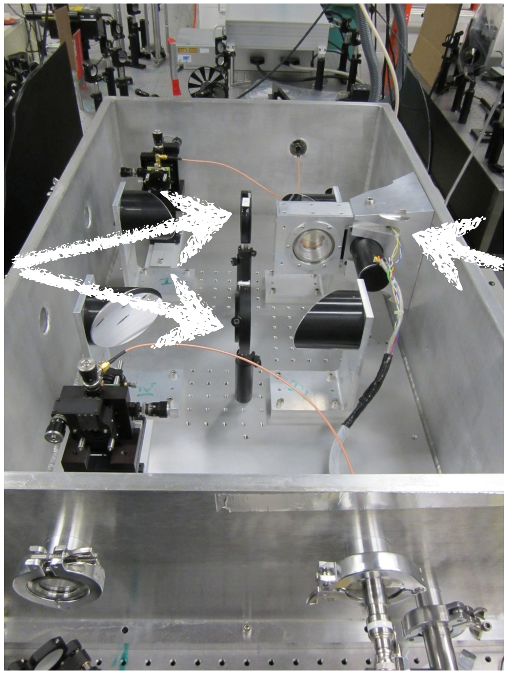


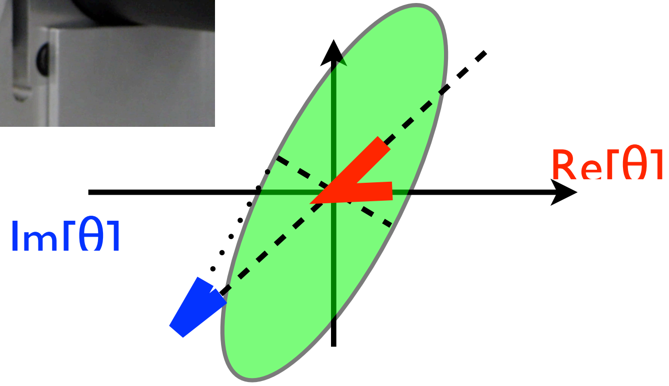
“The Fast Rotator”

C. M. Morris *et al.* Optics Express, Vol. 20, Issue 11 (2012)









Polarizer spun at 5000 rpm, Lockin @ 2ω.

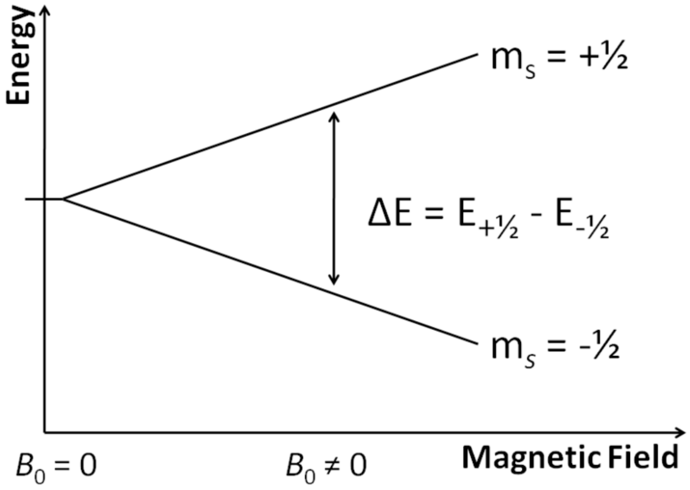
In- and out-of-phase lockin response ∝ to E_x and E_y.

Very precise measurements possible because common mode noise cancels in ratio $\theta = E_y/E_x$

Invented for “axion regime” in topological insulators and point group symmetry breaking in cuprates

Using time-domain THz to measure magnetic excitations

Usually light couples to charge, but can excite **magnetic** dipoles with THz B field
Broad band THz electron spin resonance (ESR)

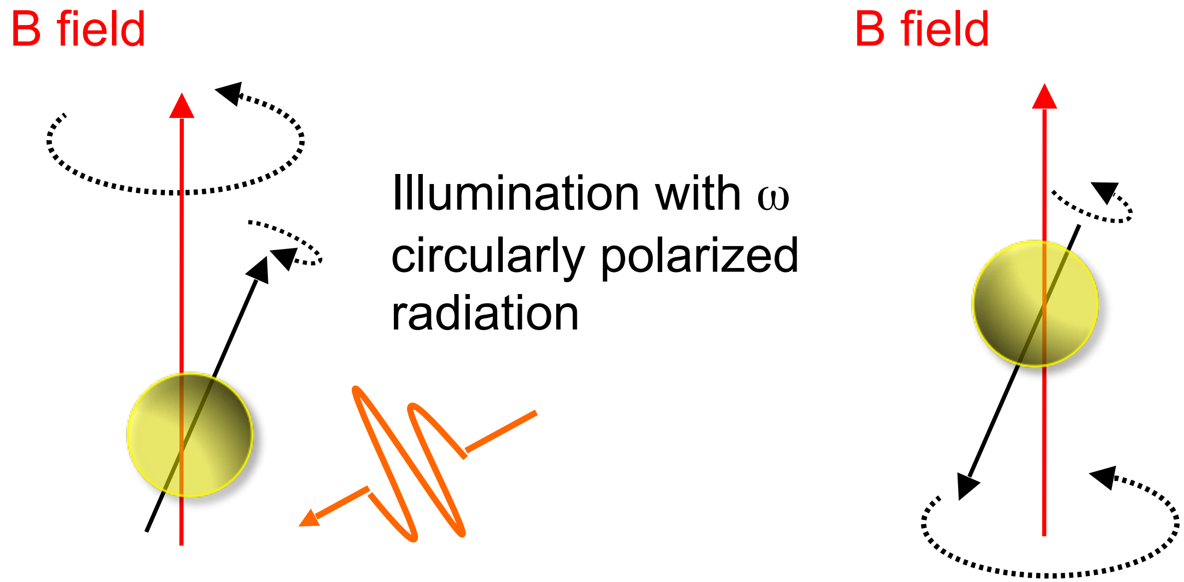


In transmission $T(\omega)$
$\ln(T(\omega)) \sim -\omega\chi(q\sim0,\omega)$

Can measure complex $\chi(\omega) = \chi' + i\chi''$
$M = \chi H$

High resolution (10 μeV)
High signal to noise; Smaller samples

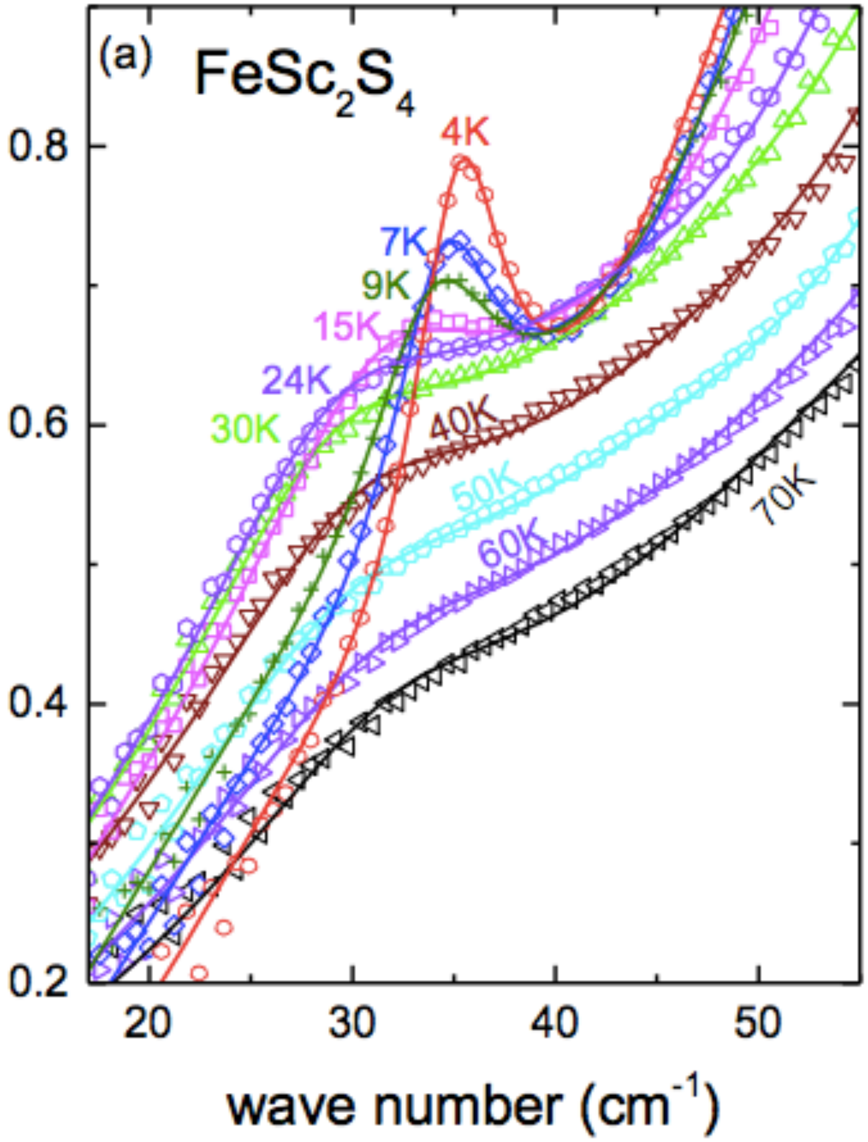
Not just a “poor man’s” neutron scattering
unique information



Precession
with $\omega = \gamma B$

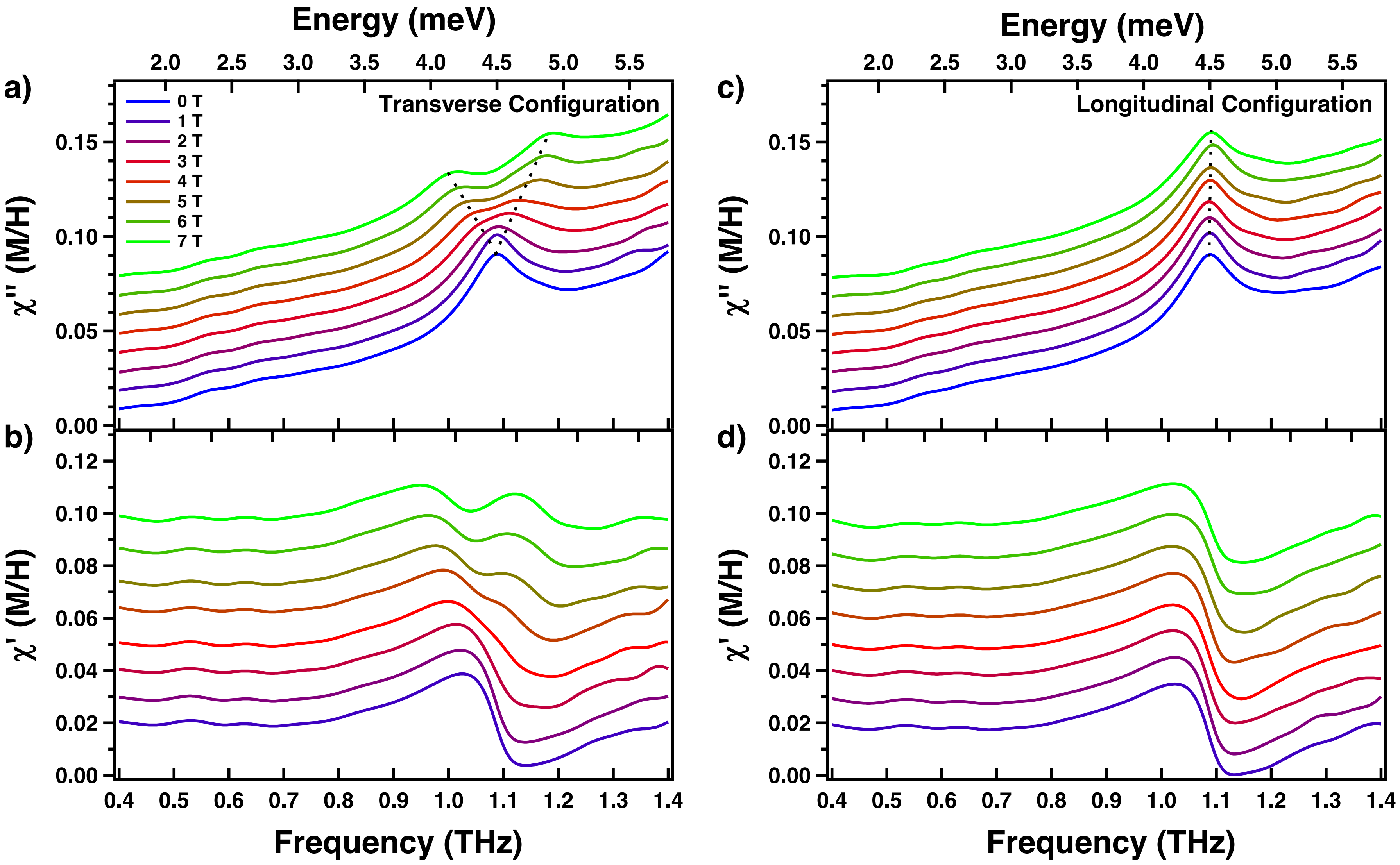
Illumination with ω
circularly polarized
radiation

THz time domain spectroscopy on $FeSc_2S_4$

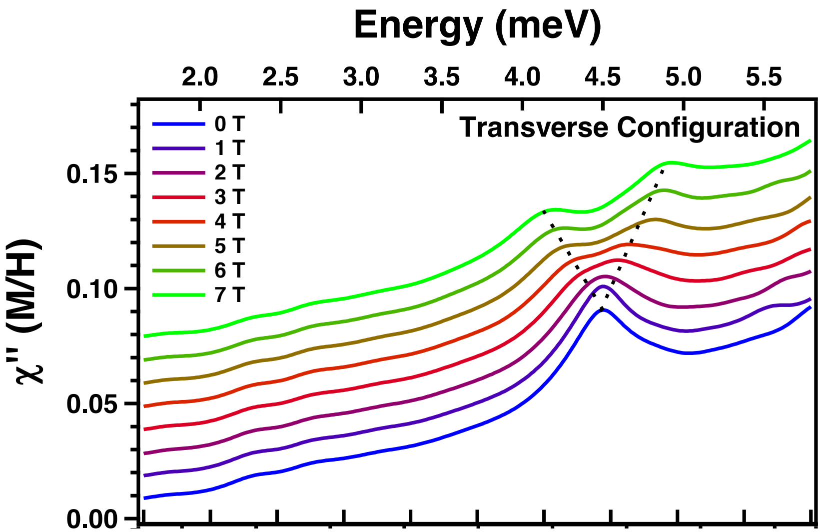


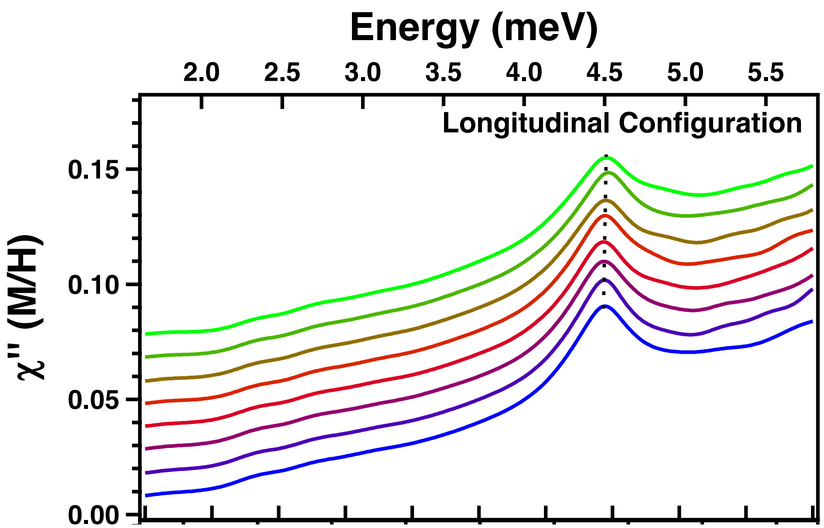
Prominent peak develops below 10K on broad background

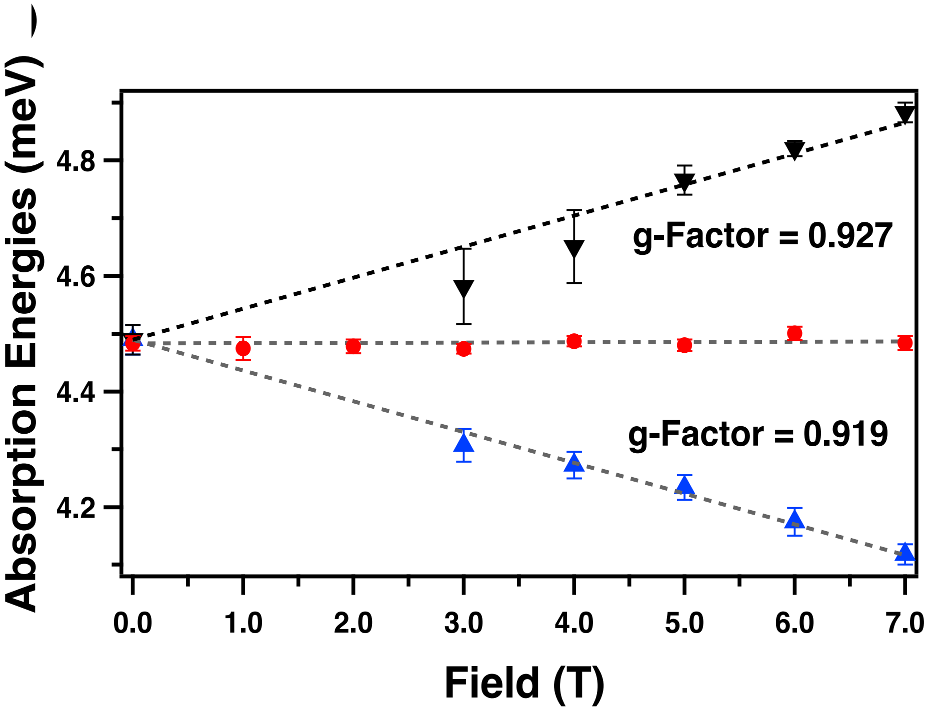
THz time domain spectroscopy on $FeSc_2S_4$



THz time domain spectroscopy on $FeSc_2S_4$



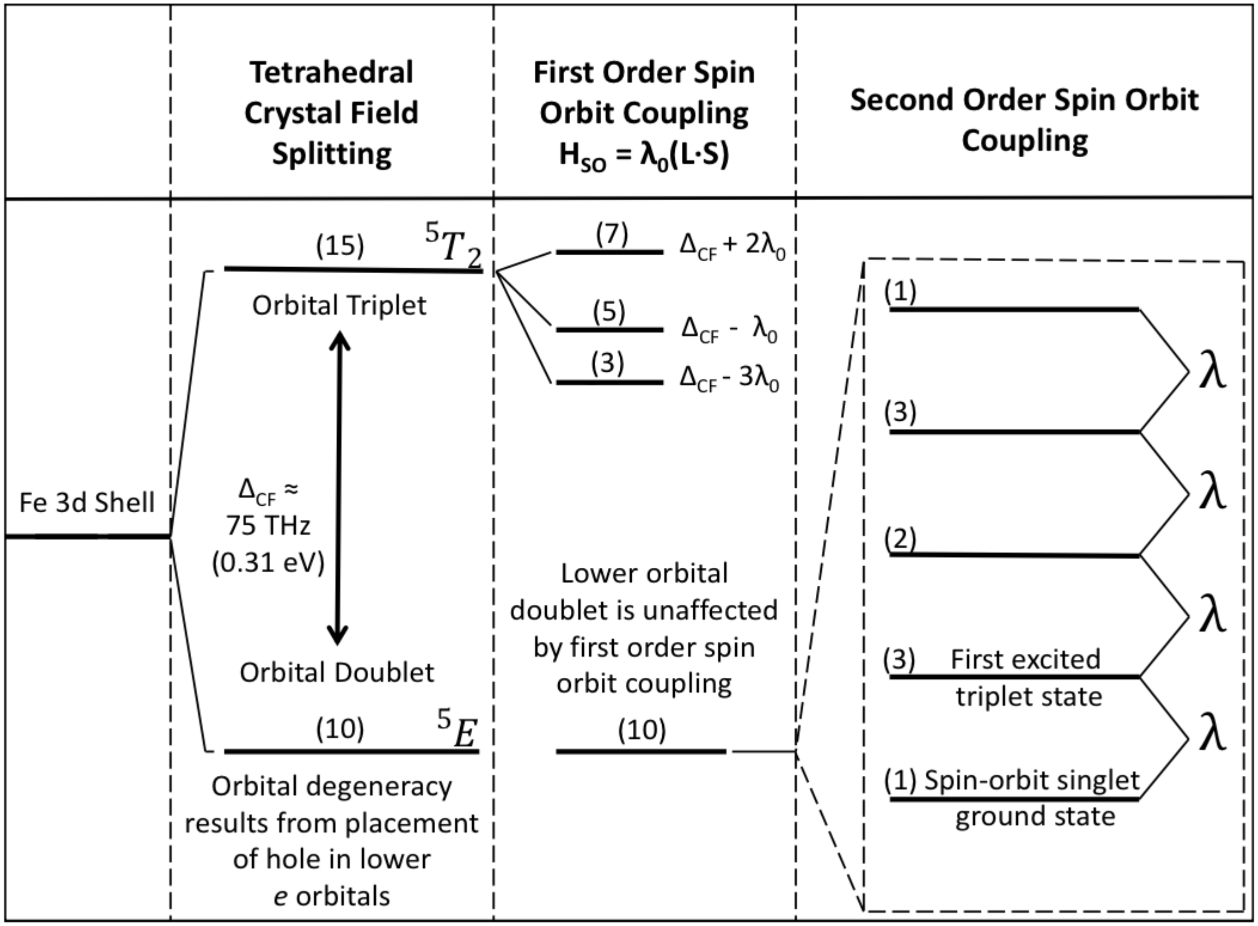




$$E(q) = \lambda + 2J_2 \sum_{A} \cos(\mathbf{q} \cdot \mathbf{a}),$$

$$E = \lambda(1 + 24x) \qquad x = J_2/\lambda$$

Fe^{2+} → 6 e- in tetrahedral CF with S=2 high spin configuration



Tetrahedral Crystal Field Splitting

First Order Spin Orbit Coupling $H_{SO} = \lambda_0(L\cdot S)$

Second Order Spin Orbit Coupling

Fe 3d Shell

(15) $^5T_2$

Orbital Triplet

$\Delta_{CF} \approx$ 75 THz (0.31 eV)

Orbital Doublet

(10) ^5E

Orbital degeneracy results from placement of hole in lower *e* orbitals

(7) $\Delta_{CF} + 2\lambda_0$

(5) $\Delta_{CF} - \lambda_0$

(3) $\Delta_{CF} - 3\lambda_0$

Lower orbital doublet is unaffected by first order spin orbit coupling

(10)

(1)

(3)

(2)

(3) First excited triplet state

(1) Spin-orbit singlet ground state

λ

λ

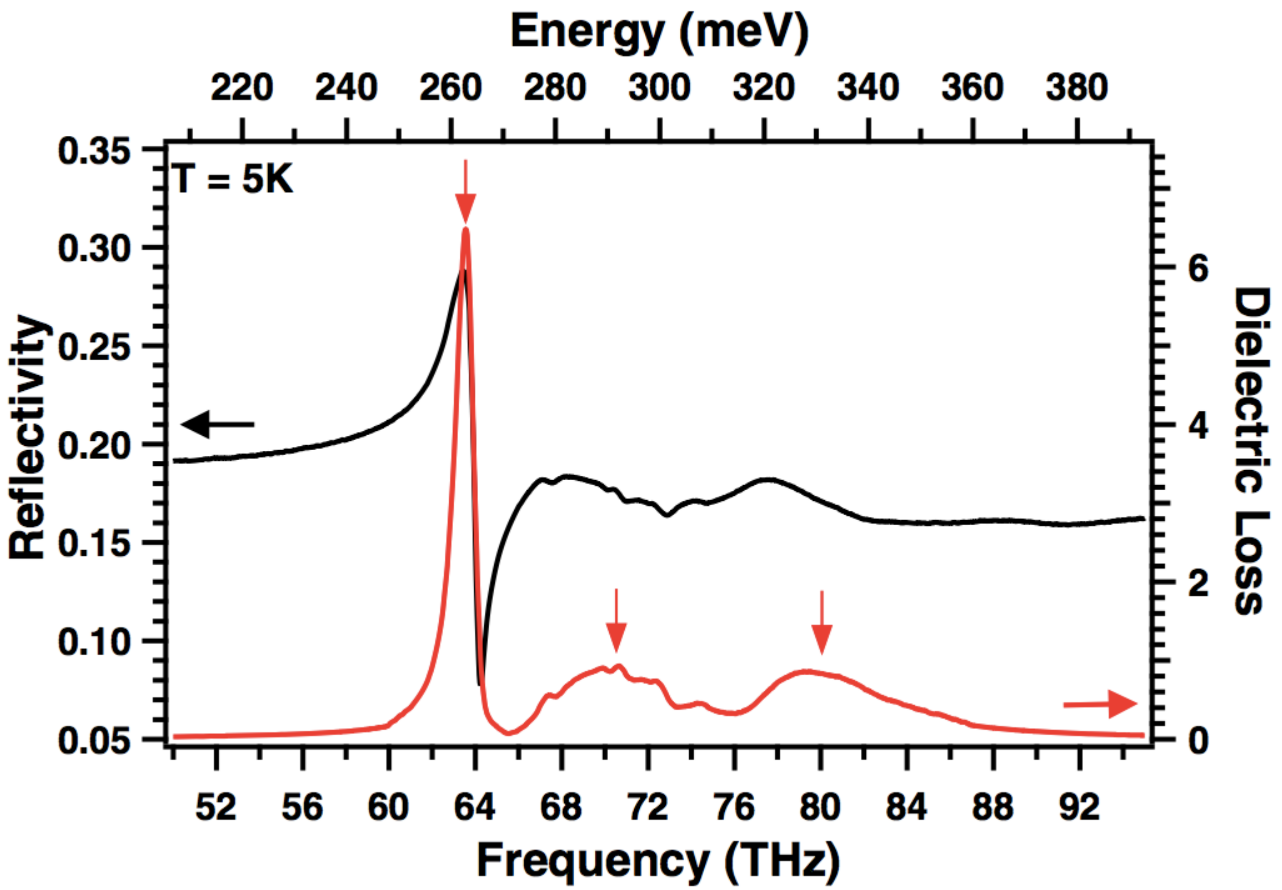
λ

λ

At single ion level ground state is a highly entangled “Spin-Orbit singlet”

$$\Psi_g = \frac{1}{\sqrt{2}}|x^2-y^2\rangle|S^z = 0\rangle+\frac{1}{2}|3z^2-r^2\rangle[|S^z = +2\rangle+|S^z = -2\rangle]$$

Spin-orbit coupling strength in $FeSc_2S_4$



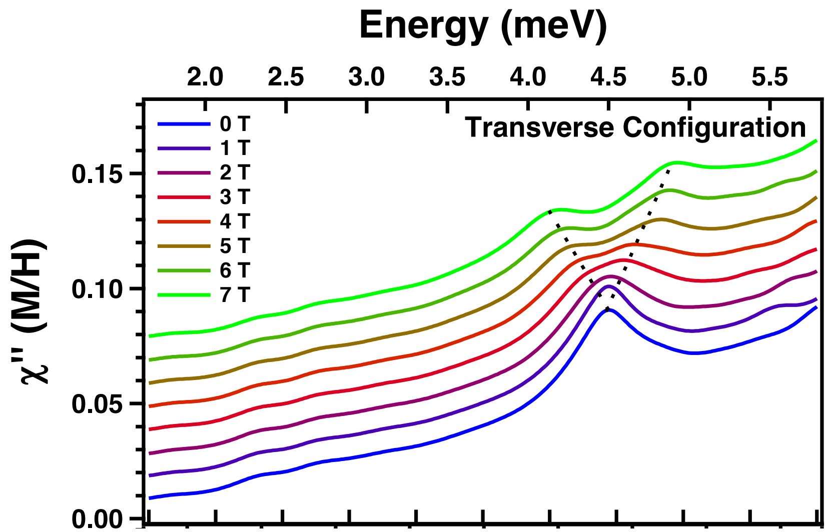
One expects only two optically active excitations from ^5E to $^5T_2$ states, but additional and shifted absorptions are expected due to strong coupling of the $^5T_2$ levels to vibrational modes

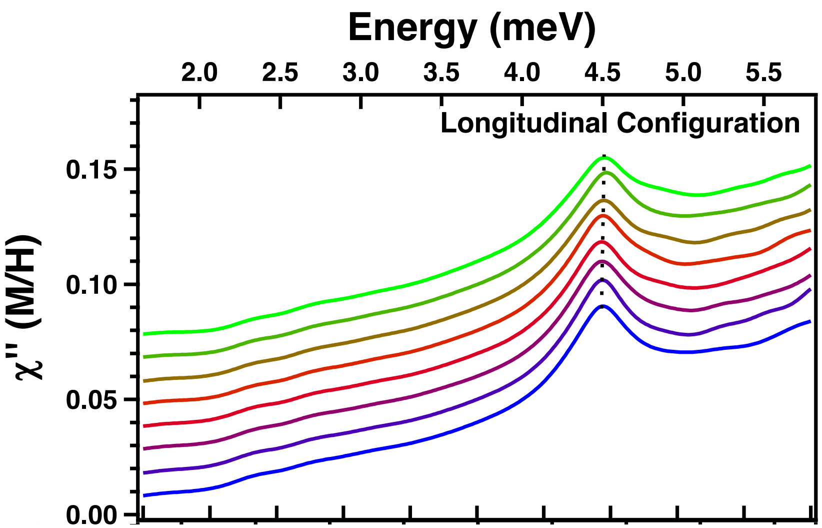
Following Wittekoek, et al, the crystal field splitting, SOC constant, Jahn-Teller coupling mode energies (E_{JT}), and coupling constants ($\hbar\omega_{JT}$) can be extracted from the mode energies and intensities.

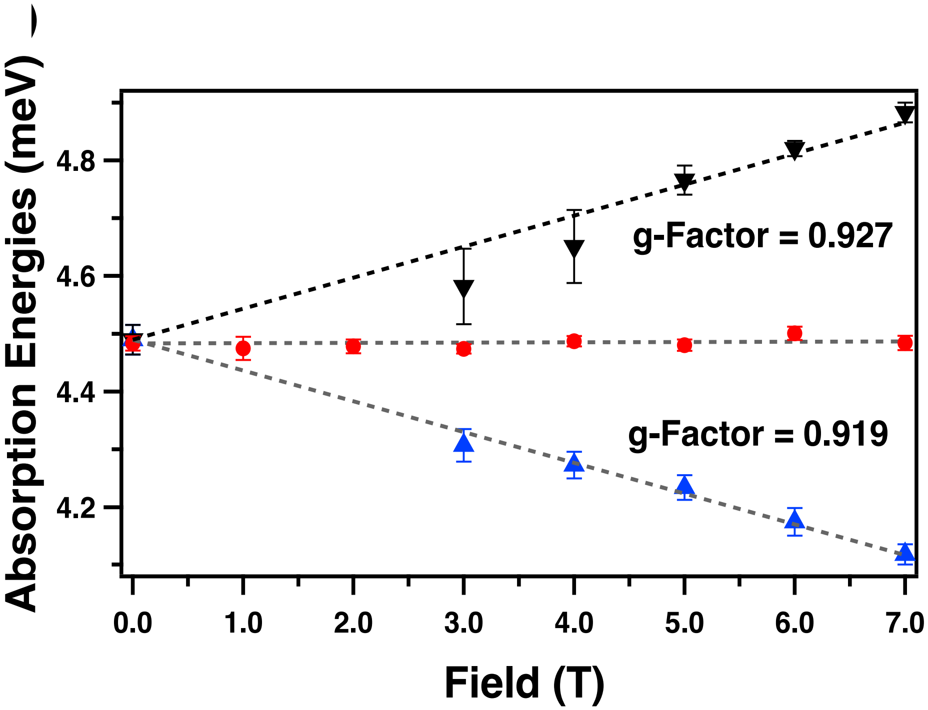
Determine values of Δ_{CF} ~296 meV, λ_0 ~8.8 meV and E_{JT}/λ~ 1.6, and $\hbar\omega_{JT}/\lambda$ ~ 4. From these $\lambda = 6\lambda^2_0/\Delta_{CF}$ ~1.57 meV.

Values correspond closely to values found in other Fe^{+2} tetrahedral compounds

THz time domain spectroscopy on $FeSc_2S_4$







$$E(q) = \lambda + 2J_2 \sum_A \cos(\mathbf{q} \cdot \mathbf{a}),$$

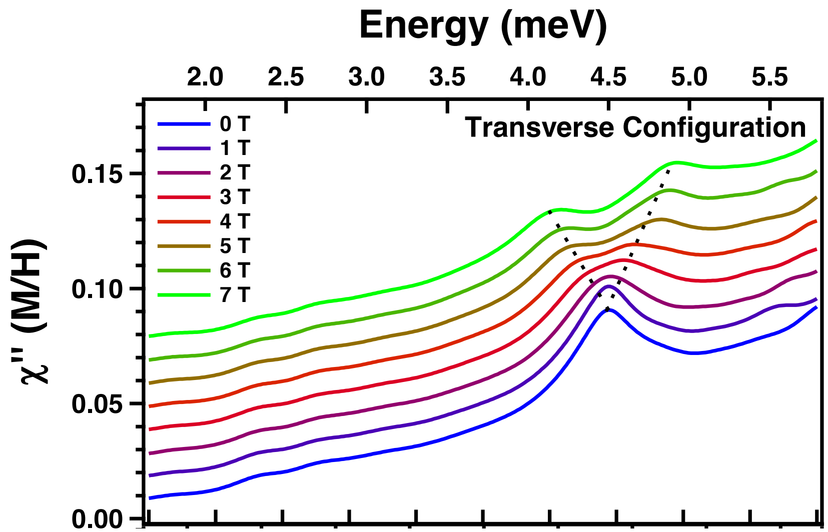
$$E = \lambda(1 + 24x) \qquad x = J_2/\lambda$$

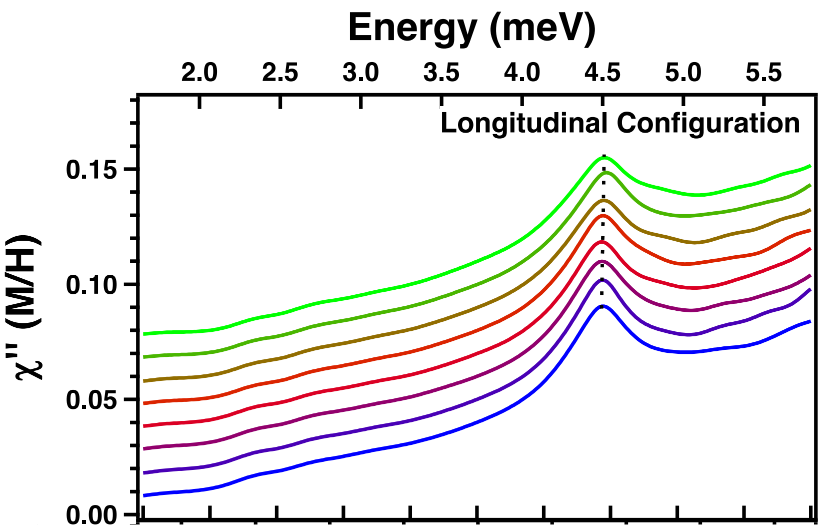
Using J_2 from Curie Weiss, one predicts E~5.4 meV

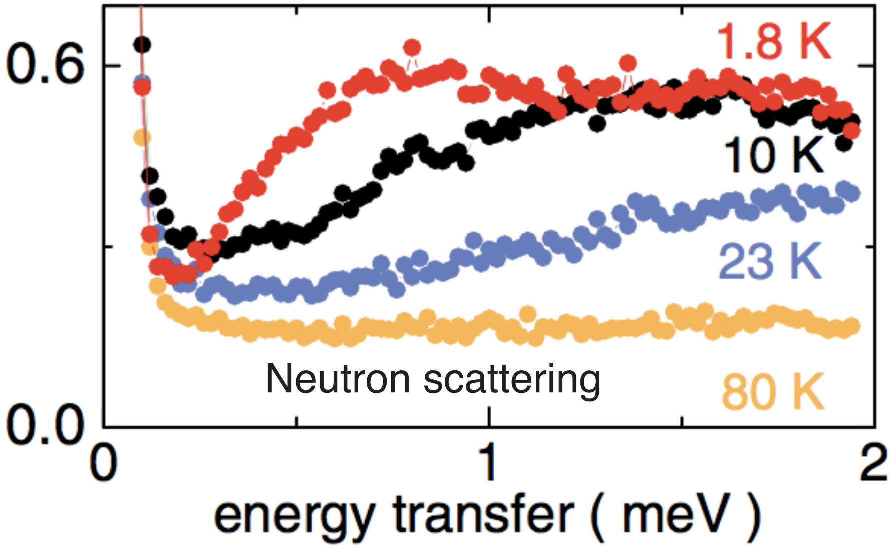
$$g = \pm[1 - 2(\lambda_0/\Delta_{CF})]$$

$g_2 \sim \pm 0.94$

THz time domain spectroscopy on $FeSc_2S_4$







"Euclidean multicomponent Φ^4 scalar field theory in 4 space-time dimensions."
- Chen and Balents, 2009

$$\xi = \frac{hv}{E} \rightarrow v = \frac{a}{8h}\sqrt{\frac{\lambda^3}{J_2}} \rightarrow \xi = \frac{\lambda a}{8E}\sqrt{\frac{1}{x}}$$

$$x = J_2/\lambda \approx 0.08$$

$\xi/(a/2) \approx 8.2$ Long range entangled

Review

Different routes to non-classical magnetic ground states

A-site spinels show “hidden” frustration

Frustration enhanced by competition with SO effect

Existence of novel spin-orbital liquid state