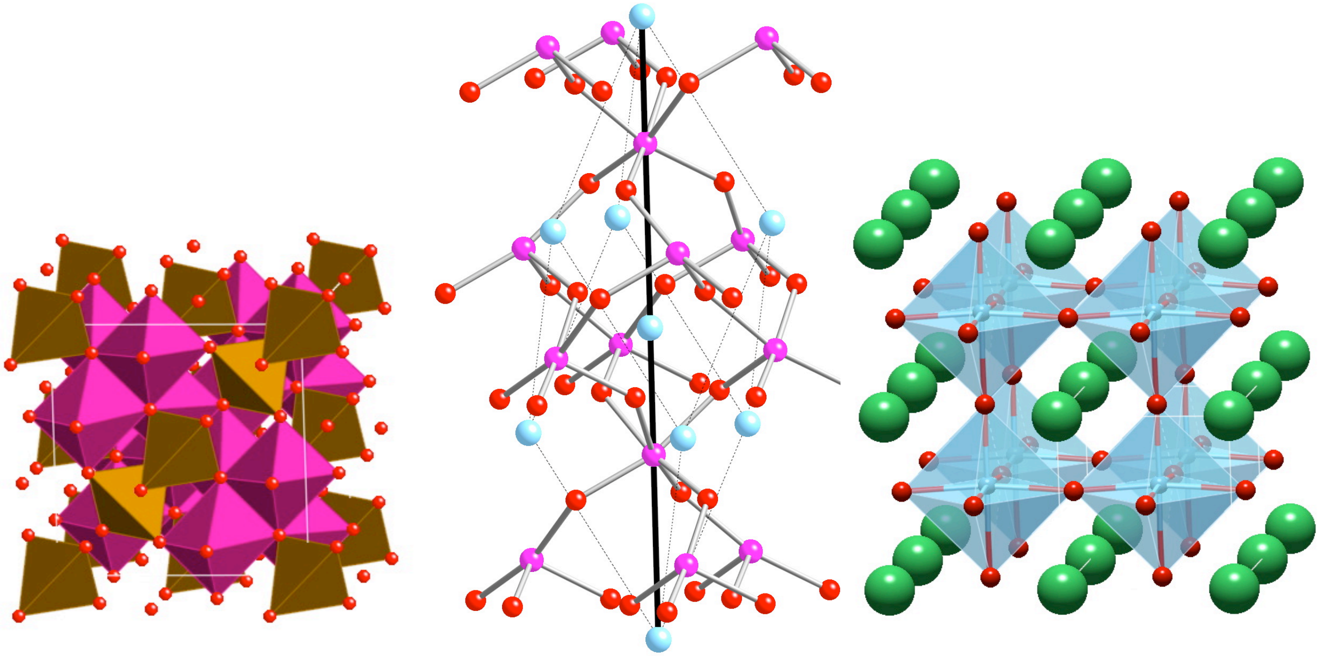
Cornell University

"I would found an institution where any person can find instruction in any study."
− Ezra Cornell, 1868

Competing Ferroic Orders

The magnetoelectric effect

Craig J. Fennie
School of Applied and Engineering Physics
fennie@cornell.edu



Basic Training in Condensed Matter Theory 2009

Module Outline

1. Overview and Background
    - Ferro ordering, the magnetoelectric effect
2. ME revisited, and basic oxide physics
    - ME effect revisited: Toroidal moments
    - Complex oxides basics: Types of insulators (i.e., ZSA classifications), Coordination chemistry

3. Structure and Ferroelectricity
    - Basics of space groups
    - Soft mode theory, lattice dynamics, group theoretic methods
    - Competing lattice instabilities
    - microscopic mechanisms, improper FE
    - Modern theory of polarization (Berry Phase)
4. Magnetism
    - Basics, exchange interactions, superexchange, Dzyaloshinskii-Moria
    - How spins couple to the lattice! Phenomenology and microscopics (spin-phonon, spin-lattice, etc)
    - Competing magnetic orders
    - Systems: $ZnCr_2O_4$, $EuTiO_3$, $SeCuO_4$, $TeCuO_4$

Magnetism and how it couples to the lattice

Isotropic Exchange

- Tuning AFM ⇔FM
  - The Goodenough-Kanamori rules
- Spin-phonon coupling
  - $ZnCr_2O_4$ → spin-induced phonon anisotropy
  - EuTiO3 → magneto-capacitance

Dzyaloshinskii-Moria Exchange

- Spin-lattice coupling
  - Weak ferromagnetism Fe2O3
  - Spin spiral Lifshitz invariant

Magnetic properties of localized systems

Magnetism arises from an incomplete shell

Eu_2O_3

Eu: $4f^7\ 5d^0\ 6s^2$
→ Eu^{3+}: $4f^6\ 5d^0\ 6s^0$

$$\langle 0|\hat{\mu}|0\rangle = g_J \mu_B \langle 0|\hat{J}|0\rangle = 0$$

Question: is Eu_2O_3 magnetic?

What do I mean by magnetic? For now I mean, Does a magnetic field couple to the fairly large $S=3\mu_B$, NO! why? Well magnetic field couples to J=|S-L|

Hund's Rules
1) Max S =3
2) Max L =3
3) J=|S-L| =0 less than half filled (J=|S+L| if more …)

But is it magnetic? Yes!

$$\chi = \frac{N}{V}\left(2\mu_B^2 \underbrace{\sum_n \frac{|\langle 0|L_z + gS_z|0\rangle|^2}{E_n - E_0}}_{\text{Van Vleck Paramagnetism}} - \underbrace{\frac{e^2 m u_0}{6m_e}\sum_{i=1}^{Z}\langle r_i^2\rangle}_{\text{diamagnetism}}\right)$$

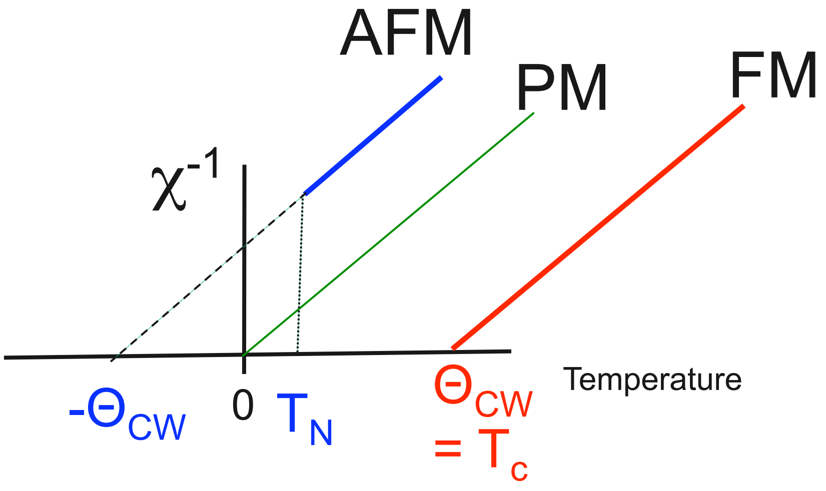
Both terms, small and temperature independent ($\chi_{VV} \sim 1/\Delta$)

Magnetic properties of localized systems

Currie Weiss

Susceptibility

$$\chi \propto \frac{1}{T - \theta_{CW}}$$



$$E = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \sum_i \mathbf{S}_i \cdot \mathbf{H}$$

Magnetic exchange interactions

$$k_B \theta_{CW} = \frac{2}{3} \sum_n J_n z_n S(S+1)$$

Mean-field

Properties of common Antiferromagnets

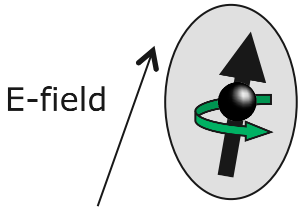
Effect of strong magnetic field (AFM)

- Susceptibility below T_N and Spin flop
  - Hard vs easy axis

Origin of easy/hard axis

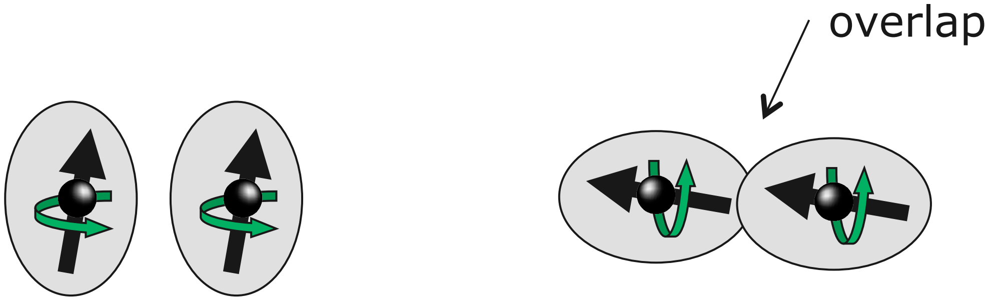
- Spin-orbit interaction $\lambda \vec{\mathbf{L}} \cdot \vec{\mathbf{S}}$

1. Single-ion anisotropy



   1. Crystal field couple to charge density
   2. Charge density couple to spin

2. Anisotropic exchange coupling



Different energy

General form of spin-spin coupling

$$H = \vec{\mathbf{S}}_1 \cdot \tilde{J} \cdot \vec{\mathbf{S}}_2$$

$$H = J\vec{\mathbf{S}}_1 \cdot \vec{\mathbf{S}}_2 + \vec{D} \cdot (\vec{\mathbf{S}}_1 \times \vec{\mathbf{S}}_2)$$

Isotropic symmetric exchange (l=0)

Dzyaloshinskii-Moriya Antisymmetric exchange (l=1)

$$+k_x S_{1x} S_{2x} + k_y S_{1y} S_{2y} + k_z S_{1z} S_{2z}$$

Anisotropic symmetric exchange (l=2)

D and K both spin-orbit effects

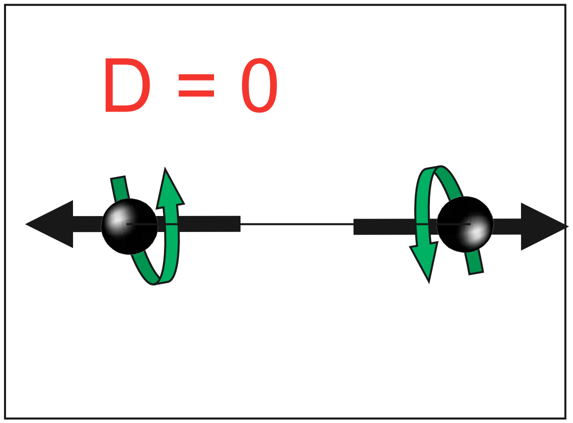
$$D \sim \lambda J \approx (\Delta g/g) J$$

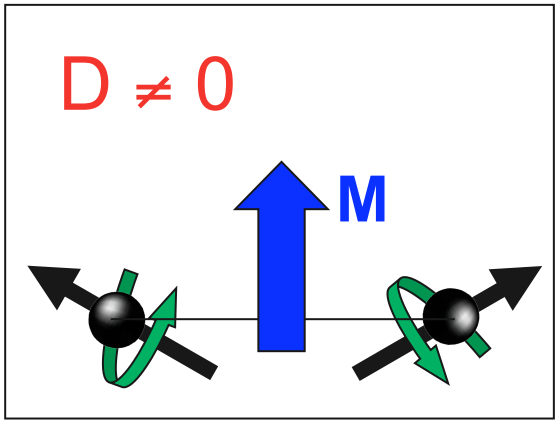
$$k \sim \lambda^2 J \approx (\Delta g/g)^2 J$$

Dzyaloshinskii-Moriya

Relativistic correction to Anderson’s superexchange

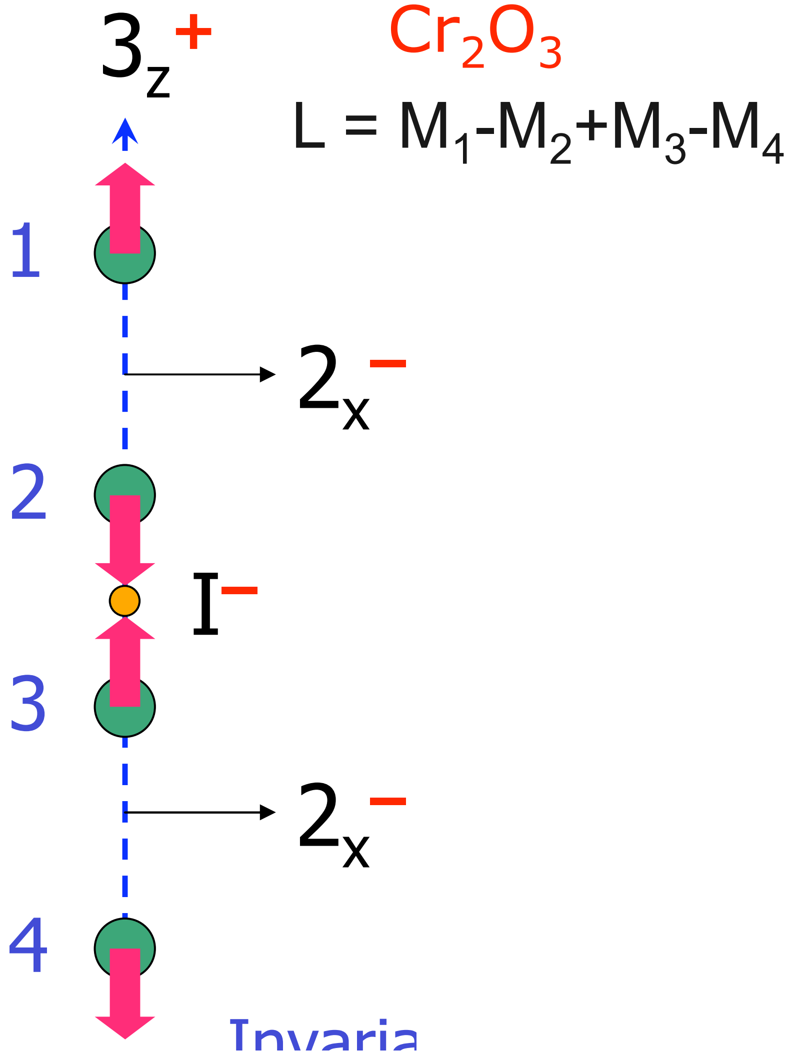
$$E = \underbrace{|J| \langle S_i \cdot S_j \rangle}_{\text{Collinear AFM}} + \underbrace{\sum D_{ij} \cdot \langle S_i \times S_j \rangle}_{\text{Spin canting}}$$





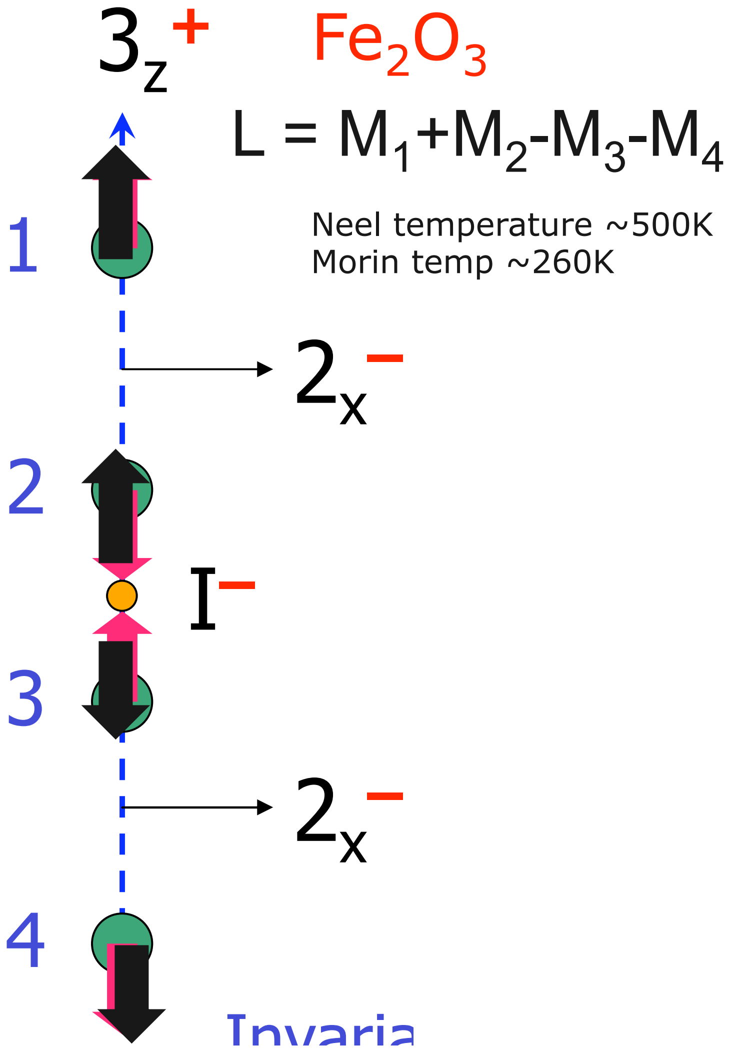
- Direction of canting determined by the sign of D

Weak ferromagnetism vs ME effect



Cr_2O_3

$L = M_1-M_2+M_3-M_4$

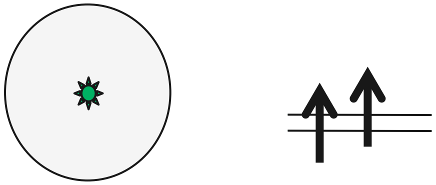


Fe_2O_3

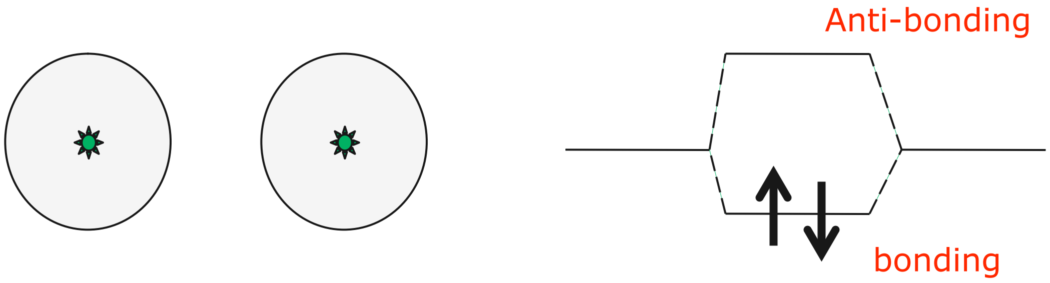
$L = M_1+M_2-M_3-M_4$

Neel temperature ~500K
Morin temp ~260K

Exchange: Background



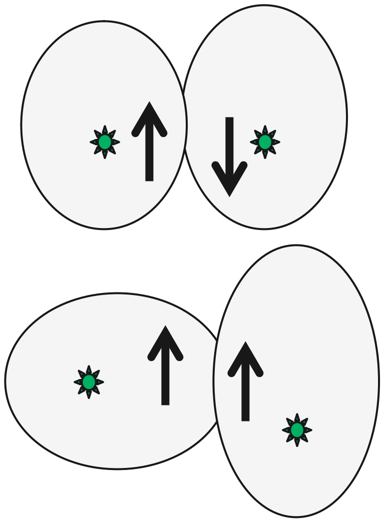
Hund’s rule ➠ like FM



Covalent bond
➠ like AFM

Exchange: Background

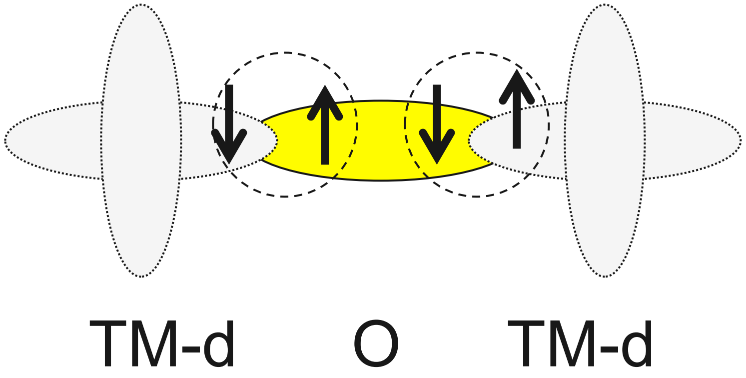
Direct exchange



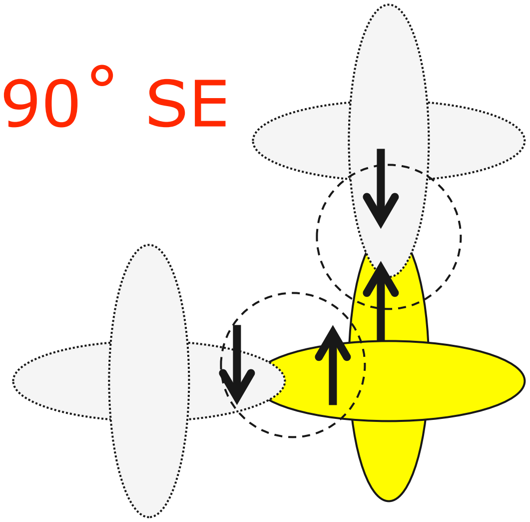
If they are the same orbital ➠ AFM

If they are the different orbital ➠ FM

Superexchange



90° SE



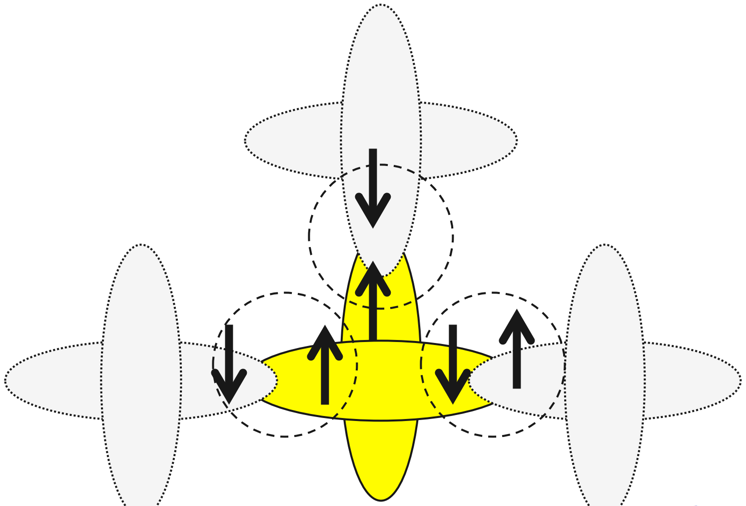
90° Hund's rule J_H coupling on the anion

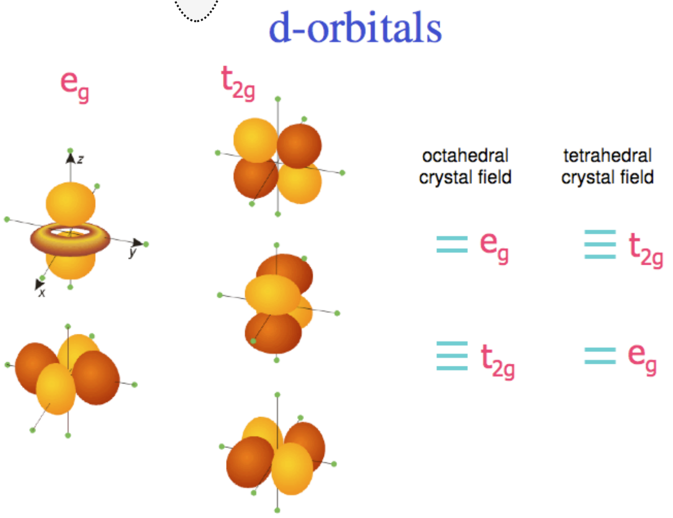
Exchange: Background

NiO

Competing interactions

1. Strong AFM Ni-O-Ni 180°
2. Weaker FM 90° SE

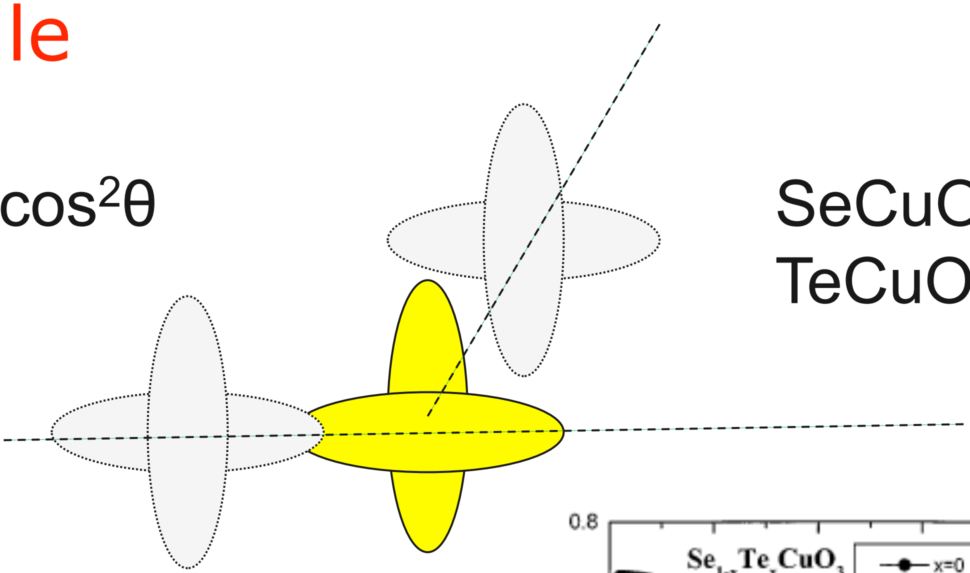




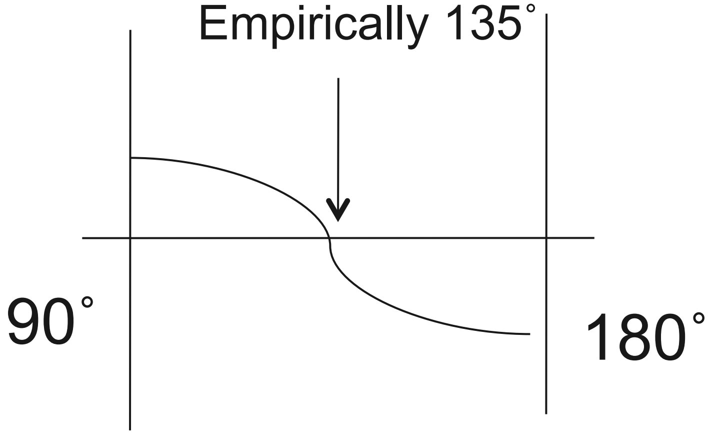
Exchange: Background

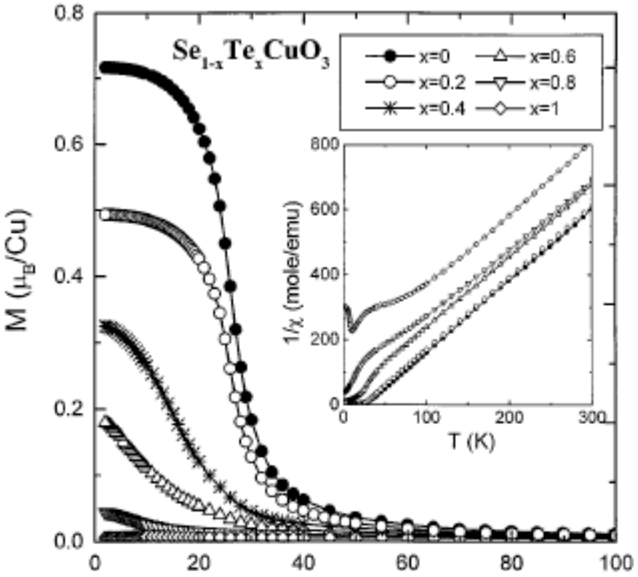
Arbitrary angle

$$J = J_{90} \sin^2\theta + J_{180} \cos^2\theta$$



SeCuO3 FM
TeCuO3 AFM





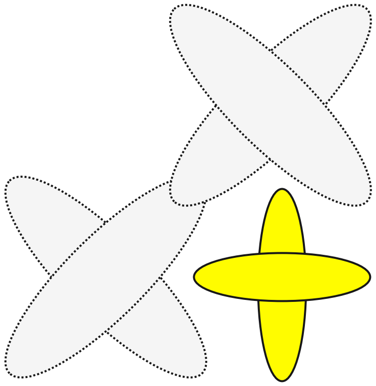
Structural Tuning of Ferromagnetism in a 3D Cuprate Perovskite

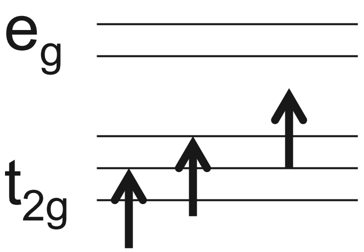
M. A. Subramanian,[1] A. P. Ramirez,[2] and W. J. Marshall[1]
[1] *DuPont Central Research and Development, Experimental Station, Wilmington, Delaware 19880-0328*
[2] *Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, New Jersey 07974-0636*
(Received 13 October 1998)

ACr2X4: Cubic Spinel Structure

Cr^{3+}: $3d^3$ $4s^0$

Superexchange pathways

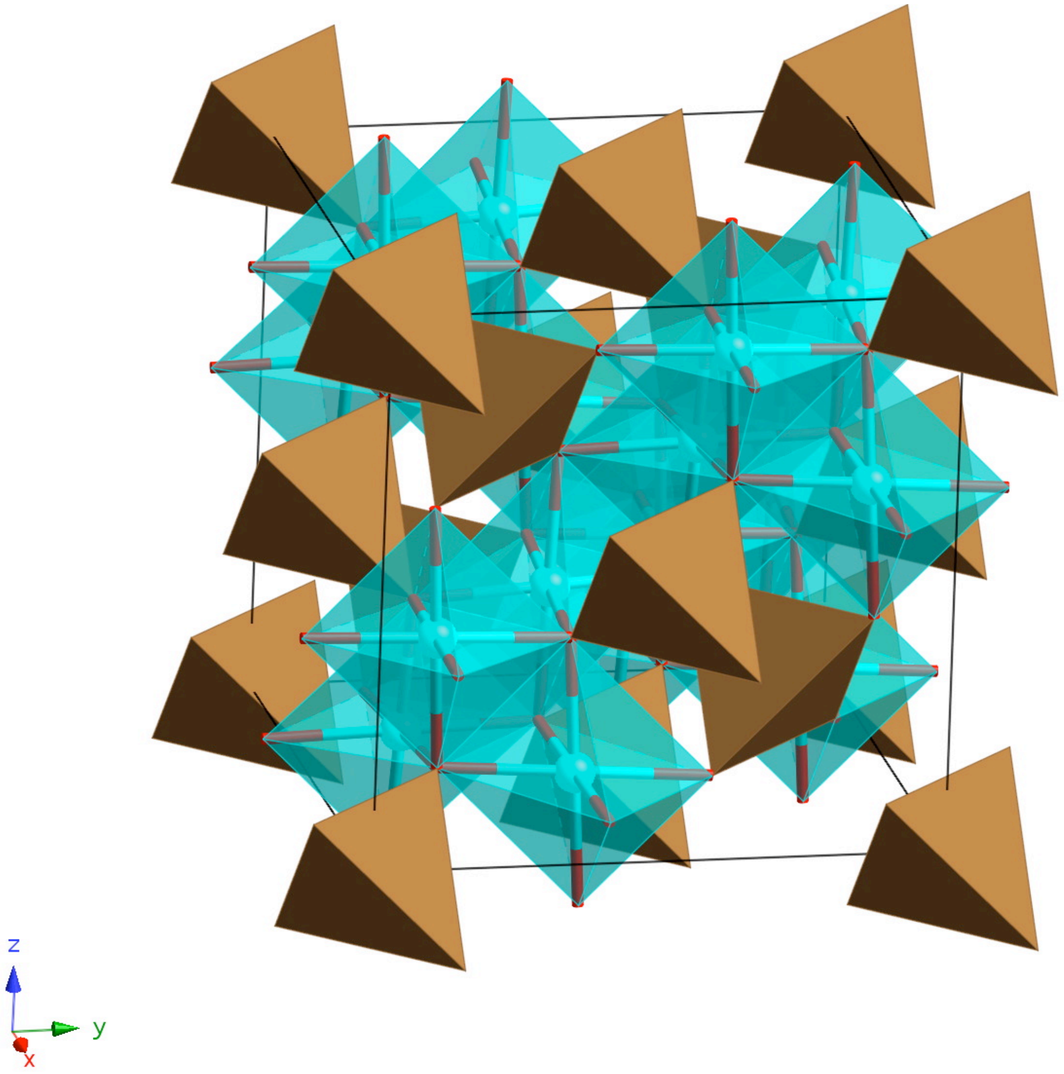




⇒ S=3/2

What is Moment?
μ ~ S =3/2
Why -> orbital dof quenched

ACr2X4: Cubic Spinel Structure



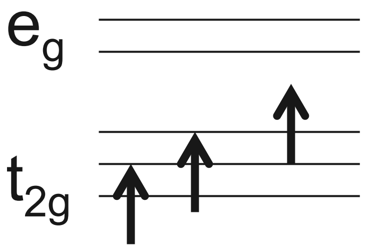
- Network of edge sharing octahedra

Background: Spinels

ACr_2X_4

- A= Zn, Cd, Hg
- X= O, S, Se

Cr^{3+}: $3d^3\ 4s^0$



⇒ S=3/2

	a (Å)	
	Theory	Exp.
$CdCr_2S_4$	10.12	10.24
$CdCr_2Se_4$	10.63	10.74
$HgCr_2Se_4$	10.65	10.74
$ZnCr_2O_4$	8.26	8.31
$CdCr_2O_4$	8.54	8.59

Ferromagnetic Insulators

T_c ~100K,

T_Θ ~200K

Anti-ferromagnetic Insulators

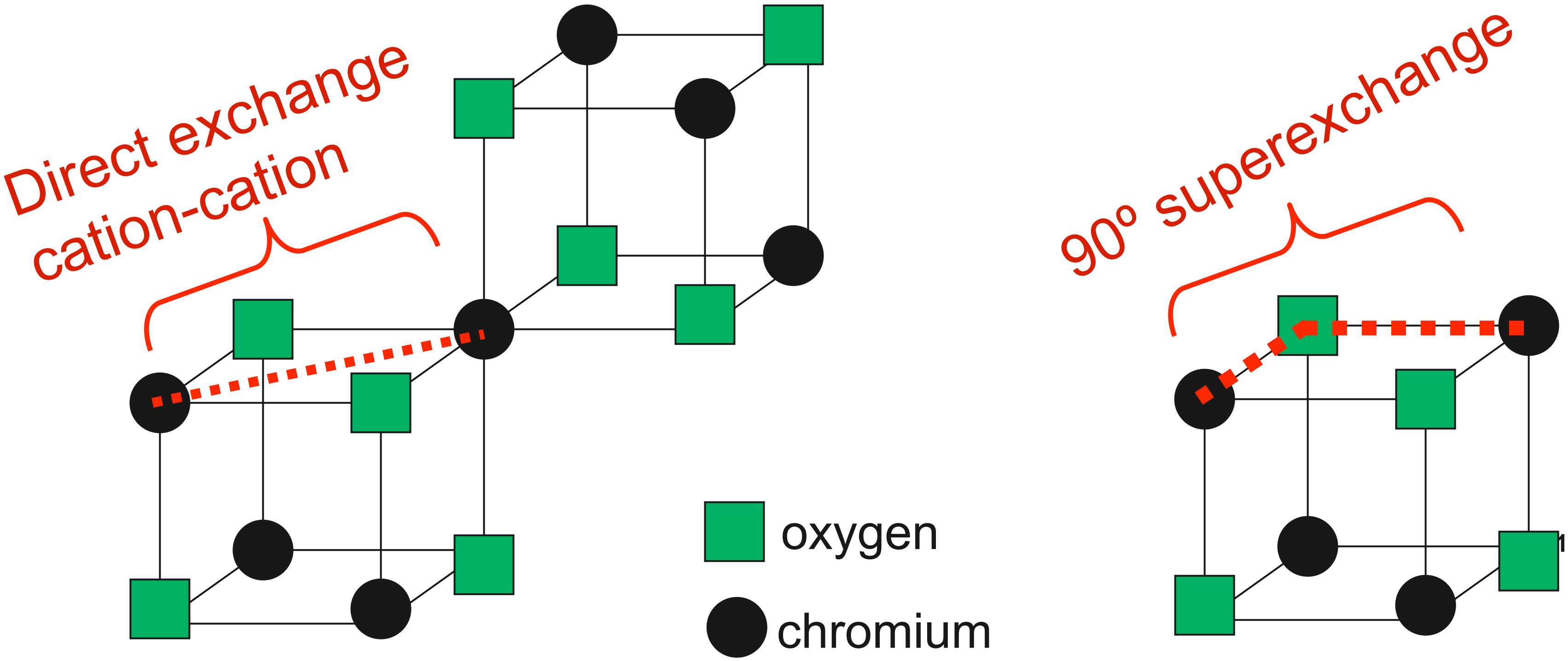
T_N ~10K,

T_Θ ~ 100K

Exchange interactions

- Direct Cr-Cr exchange → AFM
- 90° Cr-O-Cr SE → FM

AFM → FM a) as lattice constant increases
b) as electronegativity of anion decreases



Huge spin-phonon coupling

AFM-$ZnCr_2O_4$

PRL **94,** 137202 (2005) PHYSICAL REVIEW LETTERS week ending 8 APRIL 2005

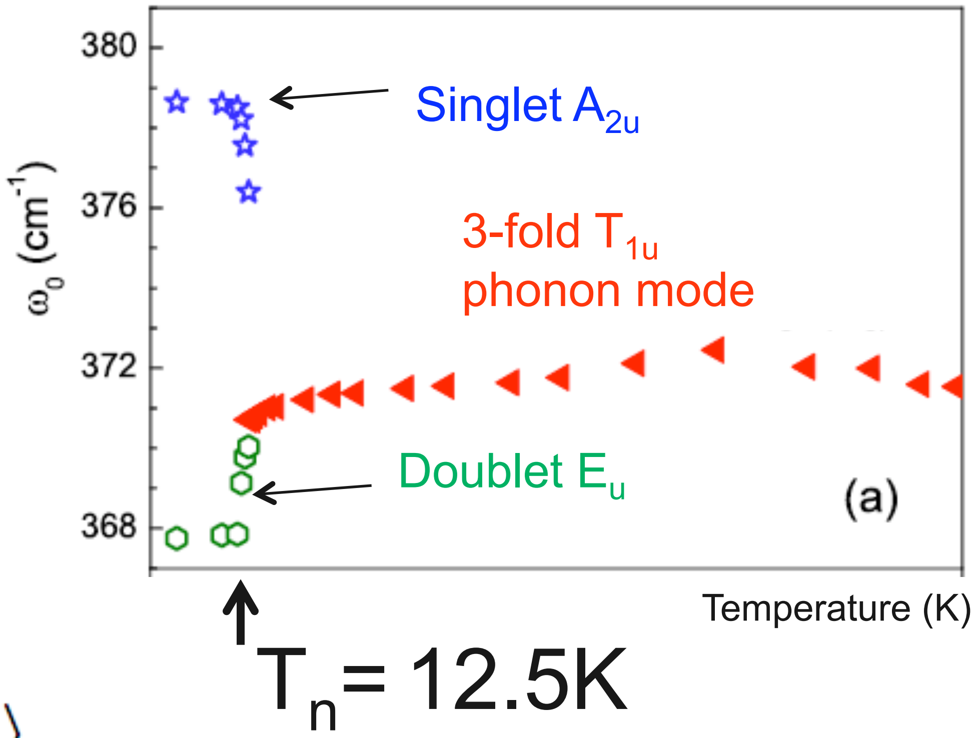
Probing Spin Correlations with Phonons in the Strongly Frustrated Magnet $ZnCr_2O_4$

A. B. Sushkov,[1] O. Tchernyshyov,[2] W. Ratcliff II,[3] S. W. Cheong,[3] and H. D. Drew[1]

Symmetry lowering at Tn

$O_h \rightarrow D_{4h}$

Cubic to tetragonal



Phonon splitting at Tn

$T1u \rightarrow A2u \oplus Eu$

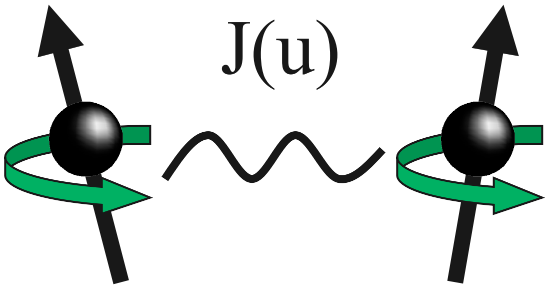
$$\omega_{AFM} = \omega_{PM} + \lambda\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$

Exp: λ =6-10 cm^{-1}

Spin-phonon coupling

Phonon modulated exchange interaction

Baltensperger and Helman, Helvetica physica acta 1968.

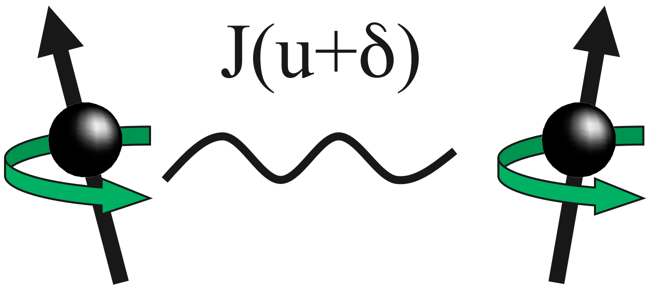


$$\mathcal{E} = \mathcal{E}_0 + \mathcal{E}_{\text{phonon}} + \mathcal{E}_{\text{spin}}$$

$$\mathcal{E}_{\text{ph}} = 1/2\ \omega_0^2 u^2$$

$$\mathcal{E}_{\text{sp}} = -\sum J_{ij} \langle S_i \cdot S_j \rangle$$

$$\boxed{J(u) \approx J(0) + 1/2\ \partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle\ u^2}$$



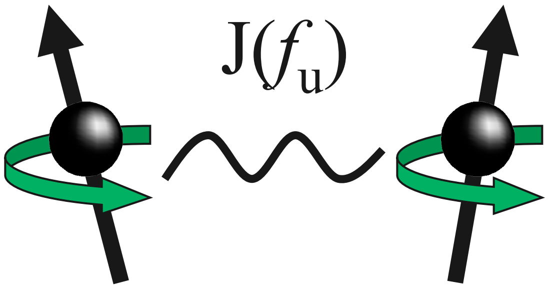
$$\Rightarrow \quad \underbrace{\omega^2}_{\text{renormalized phonon}} \propto \underbrace{\omega_0^2}_{\text{bare phonon}} - \underbrace{\partial^2 J/\partial u^2 \langle S_i \cdot S_j \rangle}_{\text{magnetic contribution}}$$

e.g. can understand large spin-phonon coupling in $ZnCr_2O_4$
Fennie and Rabe, Phys. Rev Lett. May 2006

Spin-phonon coupling

Phonon modulated exchange interaction

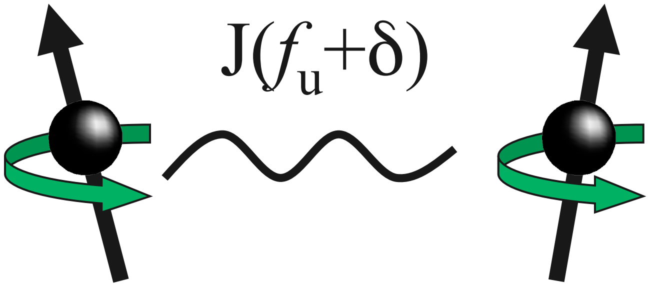
Baltensperger and Helman, Helvetica physica acta 1968.



$$E = E_0 + E_{phonons} + E_{spin}$$

$$E_{ph} = \frac{1}{2} \sum_{\eta\eta'} C_{\eta,\eta'} f_\eta f_{\eta'}$$

$$E_{spin} = -\sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$$



$$J(f_\eta)_{ij} \approx J(0)_{ij} + \frac{\partial J_{ij}}{\partial f_\eta} f_\eta + \frac{1}{2} \frac{\partial^2 J_{ij}}{\partial f_\eta \partial f_{\eta'}} f_\eta f_{\eta'}$$

$$\tilde{C}_{\eta,\eta'} = C_{\eta,\eta'} - \sum_{ij} \frac{\partial^2 J_{ij}}{\partial f_\eta \partial f_{\eta'}} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$

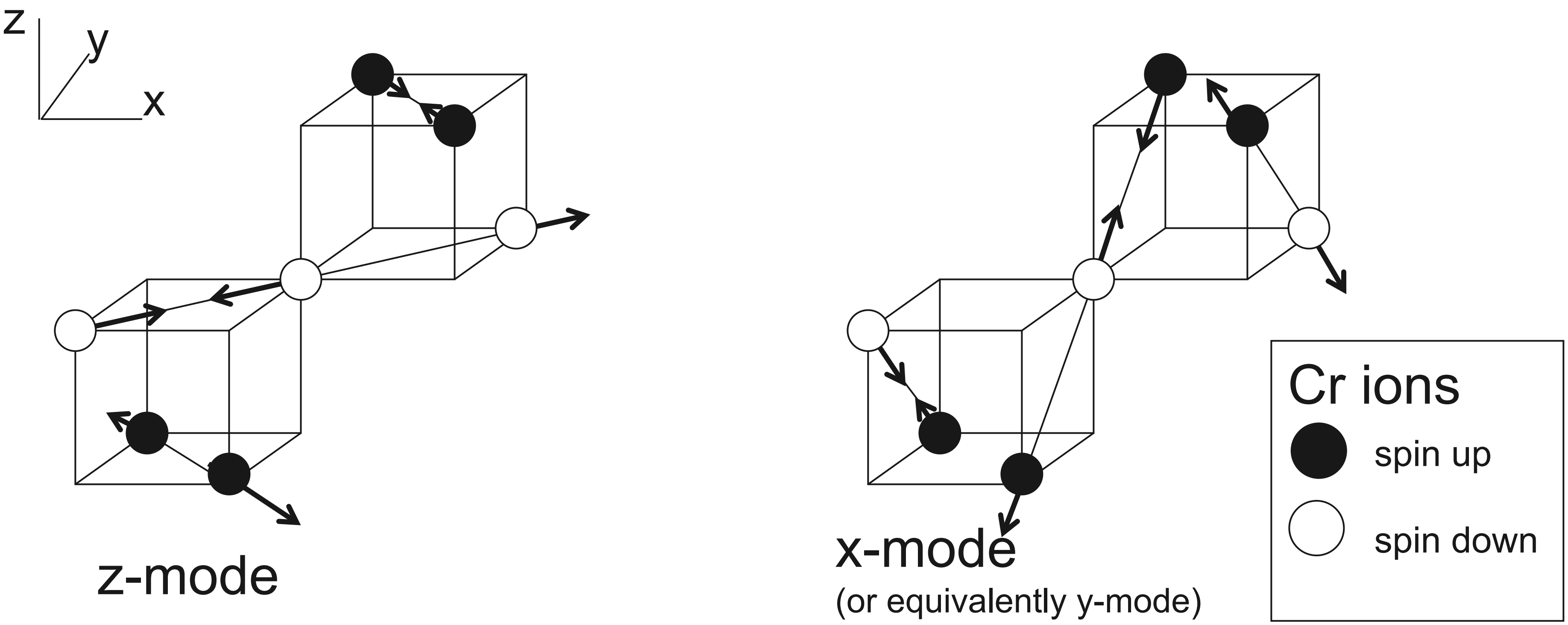
e.g. can understand large spin-phonon coupling in $ZnCr_2O_4$
Fennie and Rabe, Phys. Rev Lett. May 2006

to lowest order in $S_i S_j$

Origin of large anisotropy

f_3 has significant anisotropy in force constant matrix

f3: One set of T1u Partner functions



z-mode

x-mode
(or equivalently y-mode)

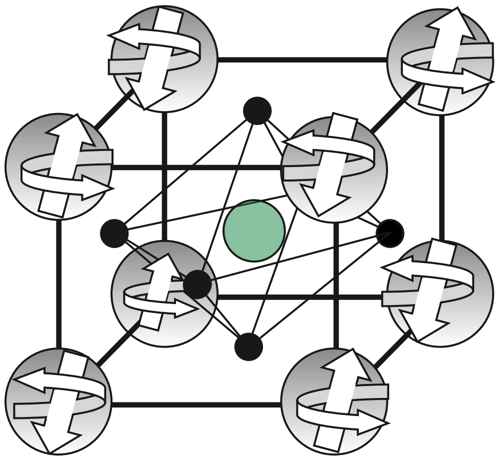
Direct-exchange length scale, α^{-1}

Exp: α=8.9 Å^{-1}

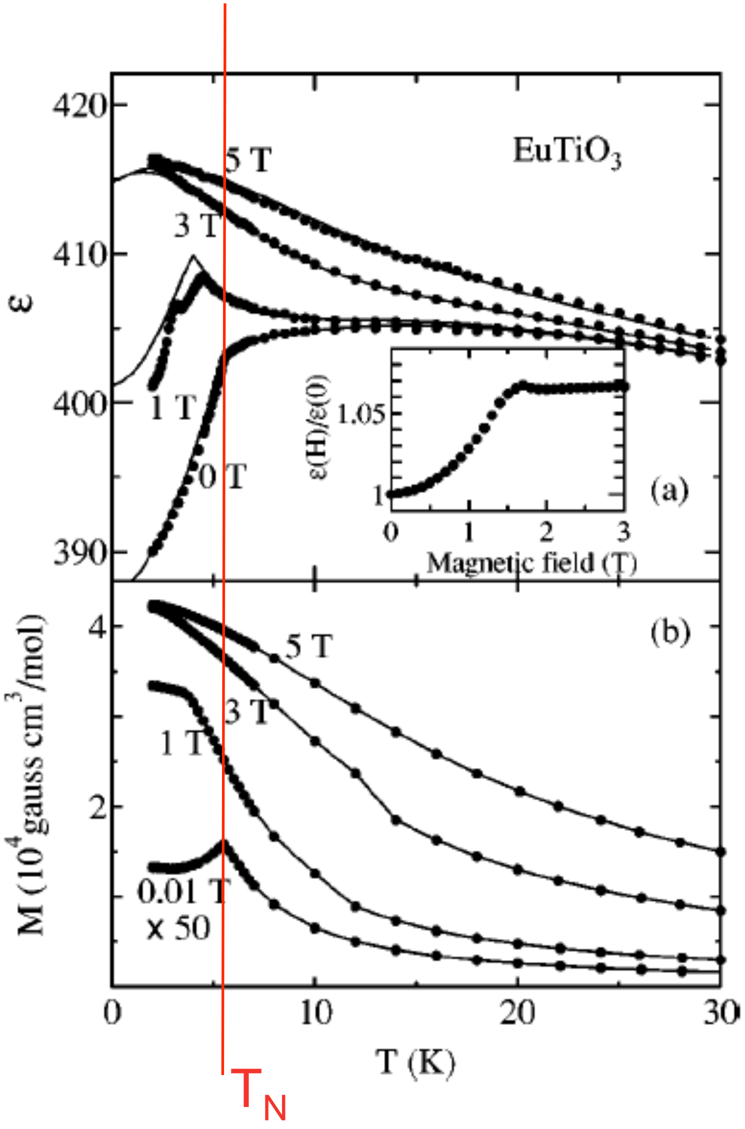
Theory: α=9.05 Å^{-1}

$$J_d(R_c)\approx J_d e^{-\alpha\Delta R_c}$$

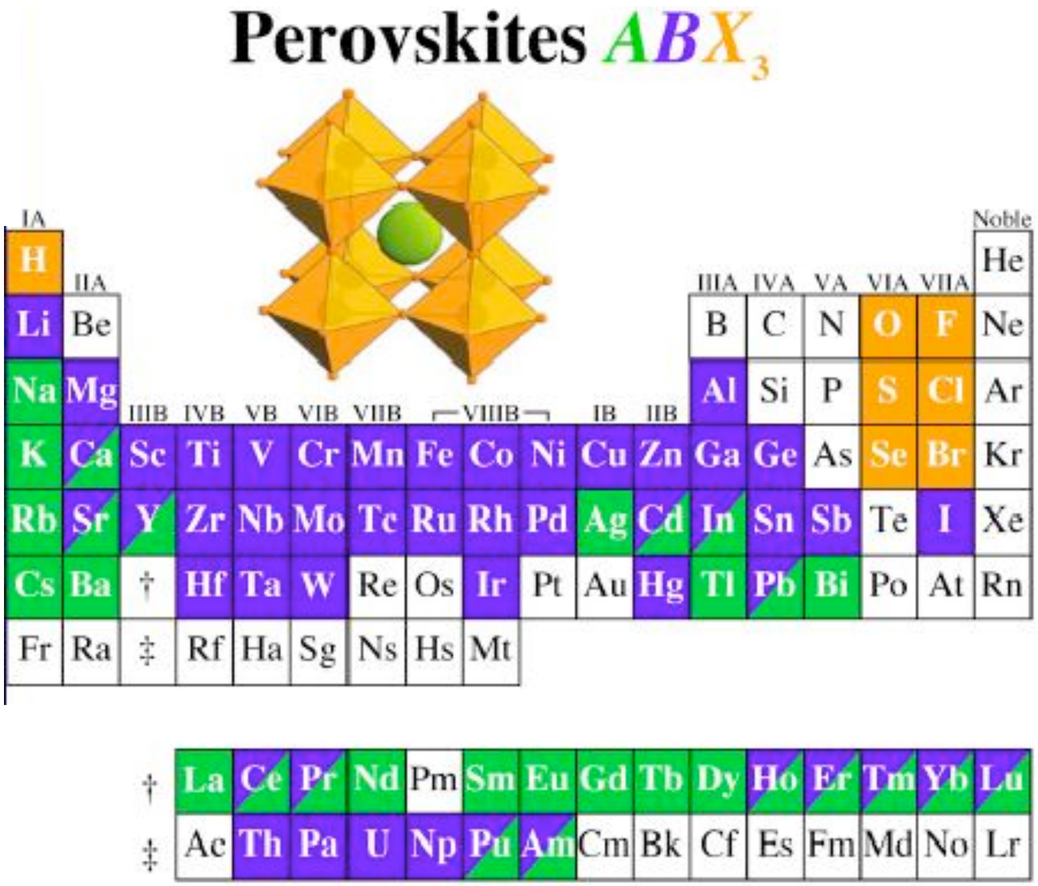
Bulk $Eu^{2+}Ti^{4+}O_3$: Ground state antiferromagnetic paraelectric



- $r(Eu^{2+}) \sim r(Sr^{2+})$; Cubic perovskite
- $Eu^{2+} \rightarrow J=S=7/2$; $T_n \sim 5.5K$, G-type AFM



Perovskites and the Period Table



IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	Noble
🟧 H																	He
🟪 Li	Be											B	C	N	🟧 O	🟧 F	Ne
🟩 Na	🟪 Mg											🟪 Al	Si	P	🟧 S	🟧 Cl	Ar
🟩 K	🟪🟩 Ca	🟪 Sc	🟪 Ti	🟪 V	🟪 Cr	🟪 Mn	🟪 Fe	🟪 Co	🟪 Ni	🟪 Cu	🟪 Zn	🟪 Ga	🟪 Ge	As	🟧 Se	🟧 Br	Kr
🟩 Rb	🟪🟩 Sr	🟪🟩 Y	🟪 Zr	🟪 Nb	🟪 Mo	🟪 Tc	🟪 Ru	🟪 Rh	🟪 Pd	🟩 Ag	🟪🟩 Cd	🟪🟩 In	🟪 Sn	🟪 Sb	Te	🟪 I	Xe
🟩 Cs	🟩 Ba	†	🟪 Hf	🟪 Ta	🟪 W	Re	Os	🟪 Ir	Pt	Au	🟪 Hg	🟩 Tl	🟪🟩 Pb	🟩 Bi	Po	At	Rn
Fr	Ra	‡	Rf	Ha	Sg	Ns	Hs	Mt									

†	🟩 La	🟪🟩 Ce	🟪🟩 Pr	🟩 Nd	Pm	🟩 Sm	🟩 Eu	🟩 Gd	🟩 Tb	🟩 Dy	🟪🟩 Ho	🟪🟩 Er	🟪🟩 Tm	🟪🟩 Yb	🟪🟩 Lu
‡	Ac	🟪 Th	🟪 Pa	🟪 U	🟪 Np	🟪🟩 Pu	🟪🟩 Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Substitutions on A, B or both

$(A_{1-x}A'_x)(B_{1-y}B'_y)O_3$

Random distribution or ordered

Phonon anomaly at Tc

FM- $CdCr_2S_4$

Symmetry lowering at Tc

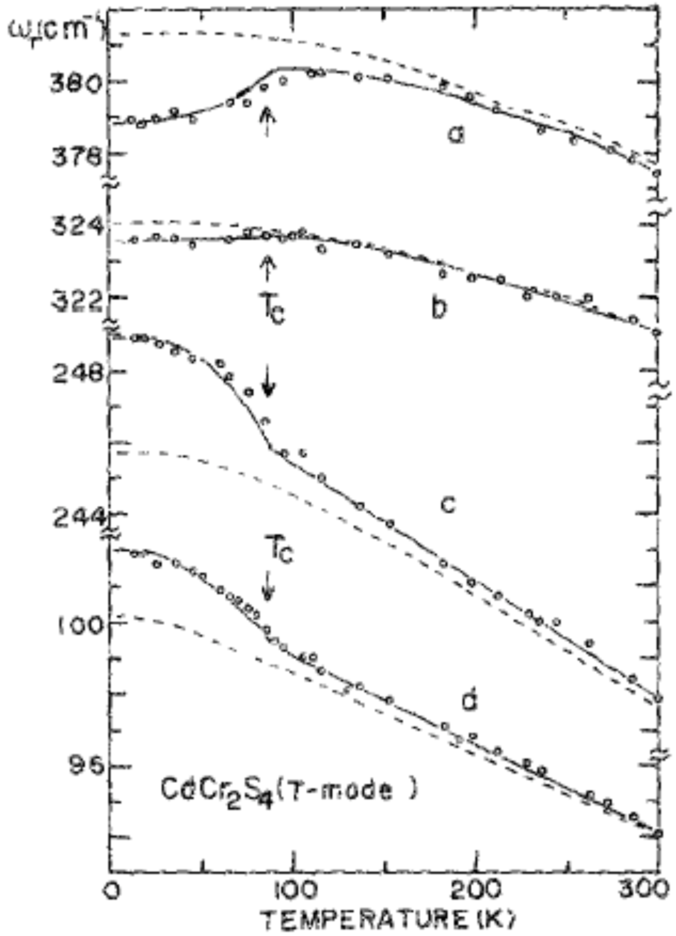
$O_h \rightarrow O_h$

Cubic to cubic (ignoring LS)

No phonon splitting at Tc

$T_{1u} \rightarrow T_{1u}$

$$\omega_{FM} = \omega_{PM} + \lambda \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$$



Effect of magnetic ordering on phonon parameters for infrared active modes in ferromagnetic spinel $CdCr_2S_4$

Kunio Wakamura
Department of Natural Science, Okayama University of Science, 1-1 Ridai-cho, Okayama-city, Okayama 700, Japan

Toshihiro Arai
Institute of Applied Physics, University of Tsukuba, Sakura-mura, Niihari-gun, Ibaragi 305, Japan

J. Appl. Phys. 63 (12), 15 June 1988