Giant Negative Magnetization in a Layered Molecular-Based Magnet

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Outline

- Search for Molecular-Based or Organic Magnets
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Search for Molecular-Based or Organic Magnets

- 1956: Hexacyanometallates reported to order below 50 K

- 1984: Bimetallic magnets with ferrimagnetic order.

- 1991: First room-temperature organic magnet (V[TCNE]$_x$, $T_C = 400$ K)

- 1992: Porphyrin and bimetallic oxalates produced

- 1993: First single-molecule magnet reported (containing Mn$_{12}$)

- 1996: Organic magnet shown to exhibit photomagnetic behavior

- 2000: Bimetallic oxalates with both magnetic and metallic behavior

- 2003: A nanoporous organic magnet with pores that are 3.1 nm wide

This is an emerging field that has grown rapidly in the last 15 years!

[Miller, *Adv. Mat.* **14**, 1105 (2002)]

Despite the advanced state of organic synthesis, the theory of molecular-based magnets is still in its infancy. There are several challenges to understanding these materials:

1. The large separations between the magnetic ions means that previously neglected weak interactions (such as dipolar) may be important.

exchange interaction

dipole interaction

R
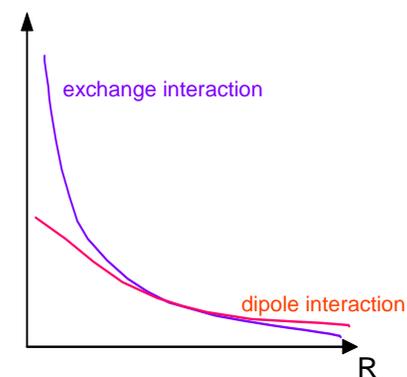
2. The charge carriers must travel through the wide p bands of C and O, challenging the accepted paradigm of magnetism that relies on narrow d bands.

3. Due to symmetry and the sparse electronic densities, the orbital angular momentum **L** of the transition metal ions may not be completely quenched (**J** may not equal **S**).

J **S**

What are the Bimetallic Oxalates?

M'(III) = V, Cr, Fe, Mn, or Ru

M(II) = V, Mn, Fe, Co, Ni, Cu, or Zn

$A[M(II)M'(III)(C_2O_4)_3]$
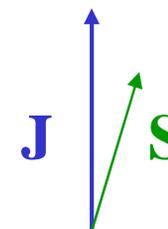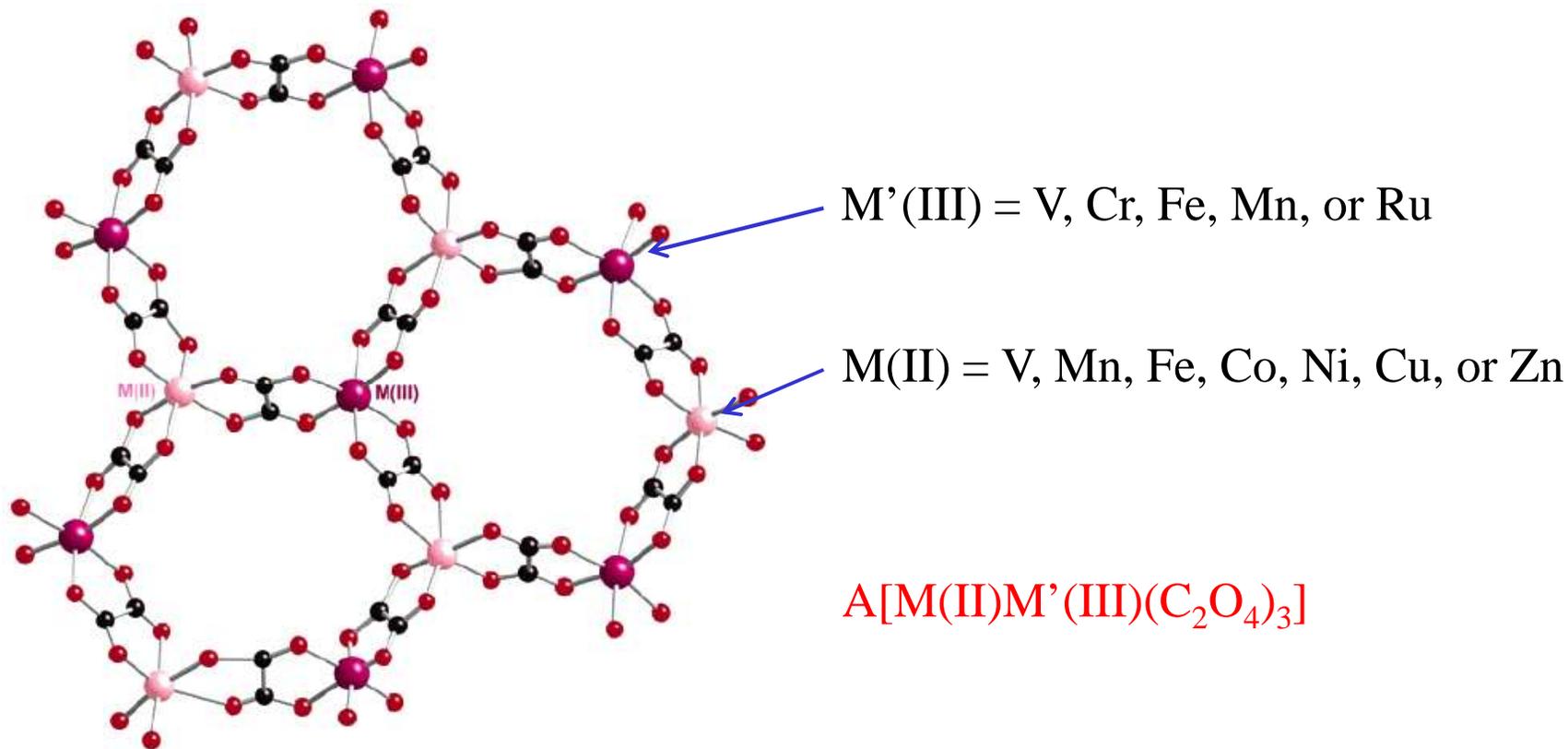
Bimetallic oxalates are a class of layered molecular-based magnets with transition metal ions M(II) and M'(III) coupled in an open honeycomb structure by oxalate ox = C_2O_4 molecules.   [Tamaki *et al.*, *J. Am. Chem. Soc.* **114**, 6974 (1992)]

The magnetic coupling depends primarily on the species of transition metals:

| M(II)M'(III)	orbitals	magnetic order	transition temp.
Mn(II)Cr(III)	$3d^5$, $3d^3$	FM or canted	$T_c = 6$ K
Fe(II)Fe(III)	$3d^6$, $3d^5$	Ferrimagnet	30 K $< T_c <$ 48 K
Mn(II)Fe(III)	$3d^5$, $3d^5$	weak AF	χ peaks at 55 K
Fe(II)Mn(III)	$3d^6$, $3d^4$	AF	$T_c = 21$ K
Ni(II)Mn(III)	$3d^8$, $3d^4$	Ferrimagnet	$T_c = 21$ K
V(II)V(III)	$3d^3$, $3d^2$	Ferrimagnet	$T_c = 11$ K
Co(II)Cr(III)	$3d^7$, $3d^3$	FM	$T_c = 5$ K
V(II)Cr(III)	$3d^3$, $3d^3$	AF coupling	no order
Mn(II)V(III)	$3d^5$, $3d^2$	FM	$T_c < 2$ K

For a single cation A = NBu$_4$ = N(n-C$_4$H$_9$)$_4$, the transition temperatures are shown below:
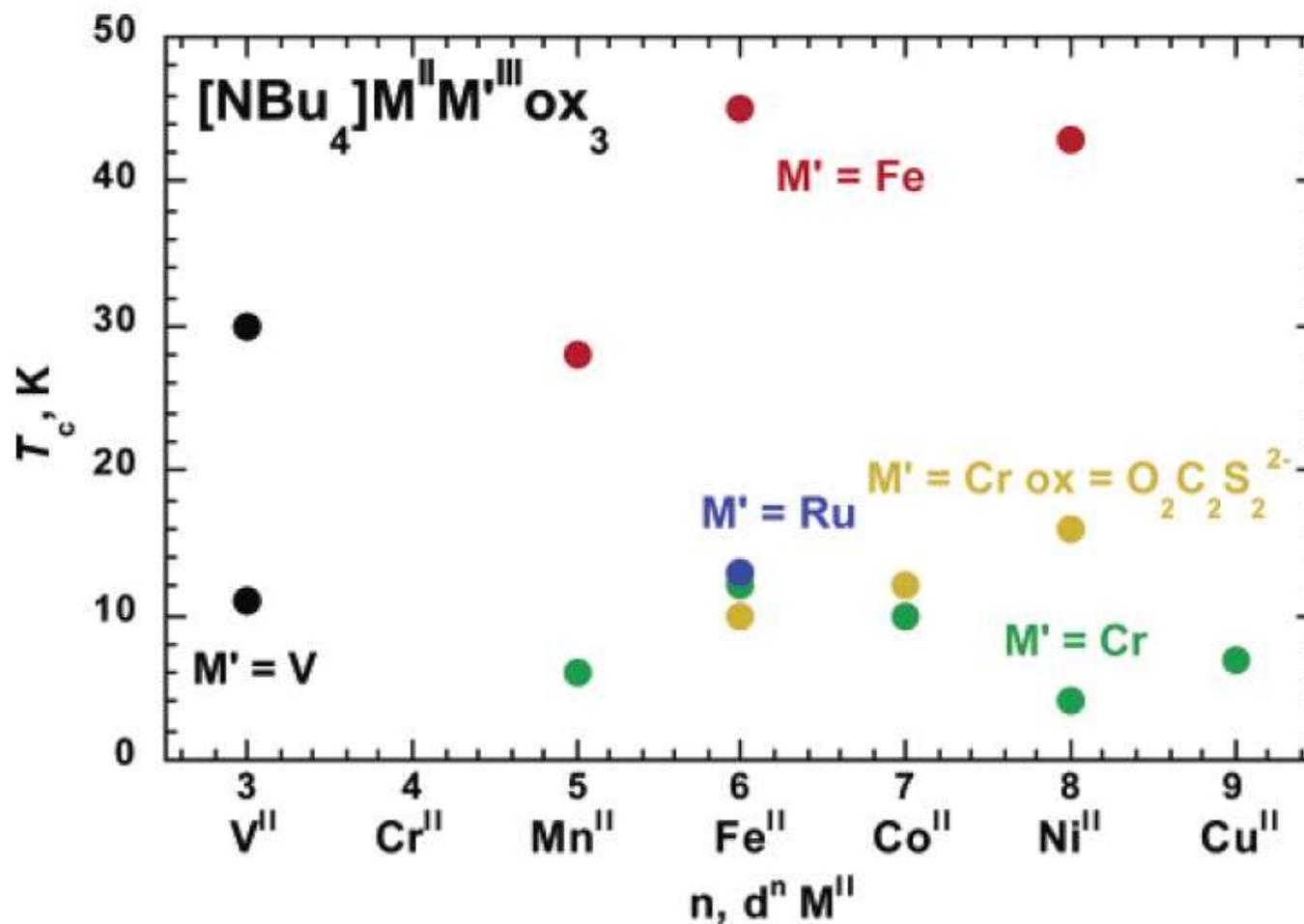
[Min, Rhinegold, and Miller, *Inorg. Chem.* **44**, 8443 (2005)]

Material properties can be *designed* by choosing the cation that lies between the layers!


$[BETS]_3[MnCr(C_2O_4)_3]$
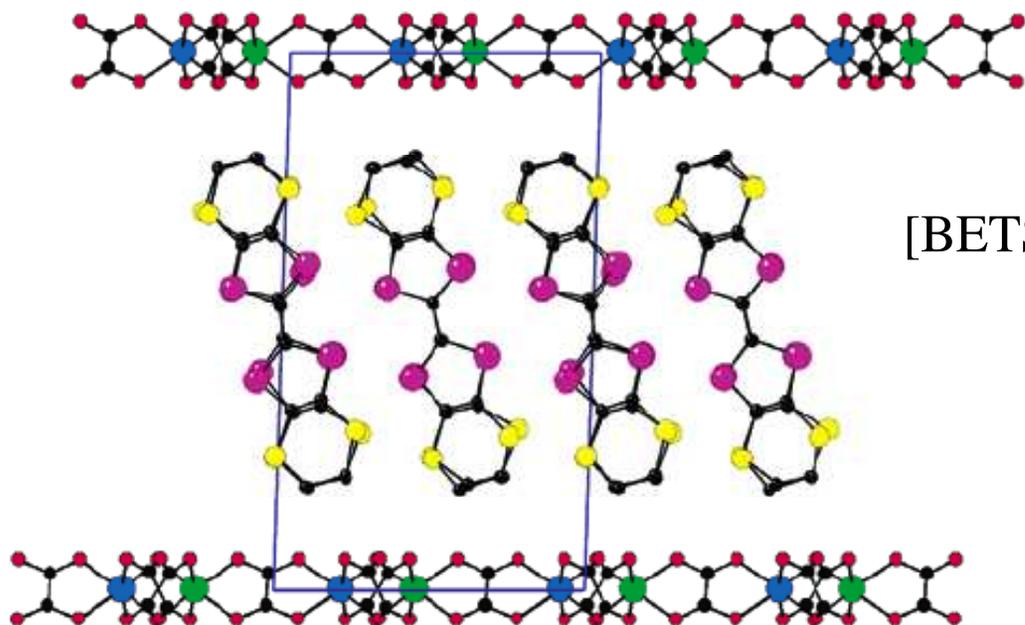
[Alberola, Coronado, Galán-Mascaros, Giménez-Saiz, and Gómez-Garcia, *J. Am. Chem. Soc.* **125**, 10774 (2003)]

For different cations, a bimetallic oxalate can be:

- optically active

- metallic

- disordered

With a *photochromic cation*, the magnetic hardness increases
dramatically upon application of ultraviolet light:

yellow closed form (CF)   red open form (OF)

soft

hard
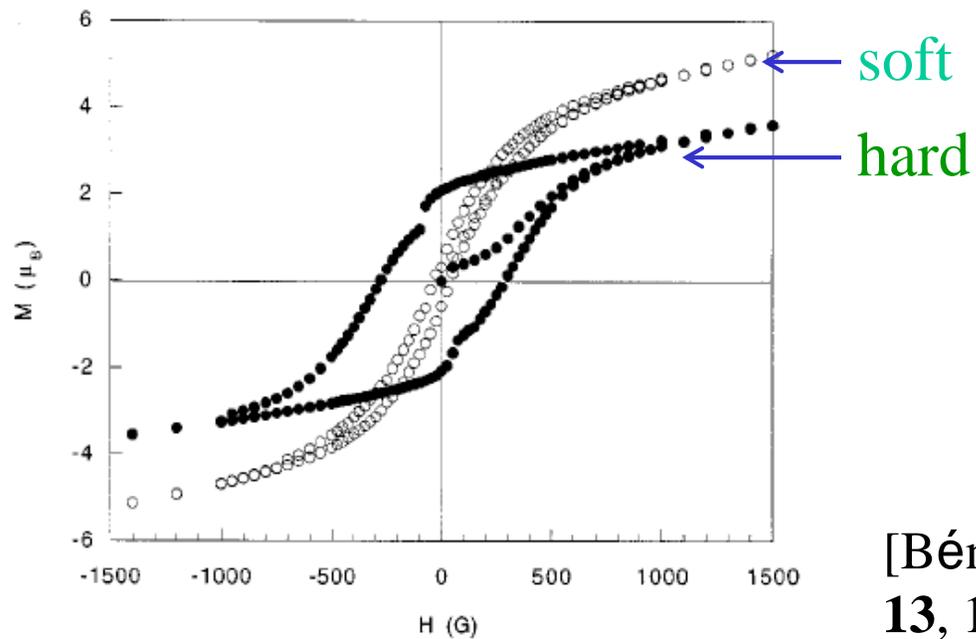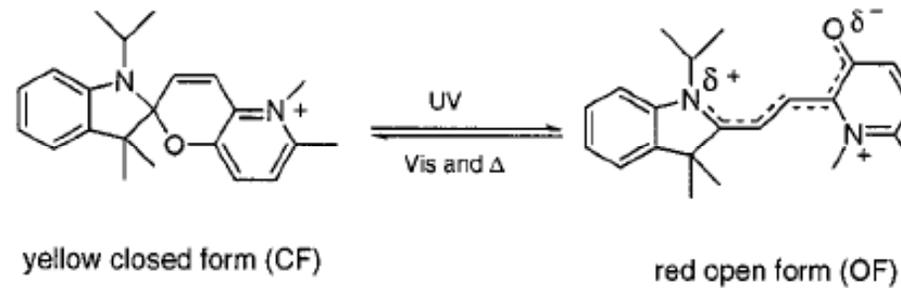
[Bénard *et al.*, *Chem. Mater.*
13, 159 (2001)]

The role of a *single layer* at determining the magnetic properties is demonstrated by two sets of experiments:

1. In the $N(n\text{-}C_nH_{2n+1})_4[Fe(II)Fe(III)ox_3]$ compounds, the interlayer spacing grows from 8.2 to 10.2 Å as n increases from 3 to 5.   But the ferrimagnetic transition temperature then *increases* from 35 to 48 K. [Mathonière *et al.*, *Inorg. Chem.* **35**, 1201 (1996)]

2. The insertion of a magnetic s = 1/2 $Fe(Cp^*)_2$ cation has almost no effect on the magnetic properties. [Clemente-León, Coronado, Galán-Mascaros, and Gómez-Garcia, *Chem. Commun.* 1727 (1997)]

According to the *Mermin-Wagner theorem*, gapless spin excitations would destroy long-range magnetic order for a single isolated layer. We argue that spin-orbit coupling within each layer is responsible for the magnetic ordering.

Giant Negative Magnetization

In the Fe(II)Fe(III) bimetallic oxalates the magnetization changes sign in a small field below about 30 K.

H = 100 G

compensation temperature
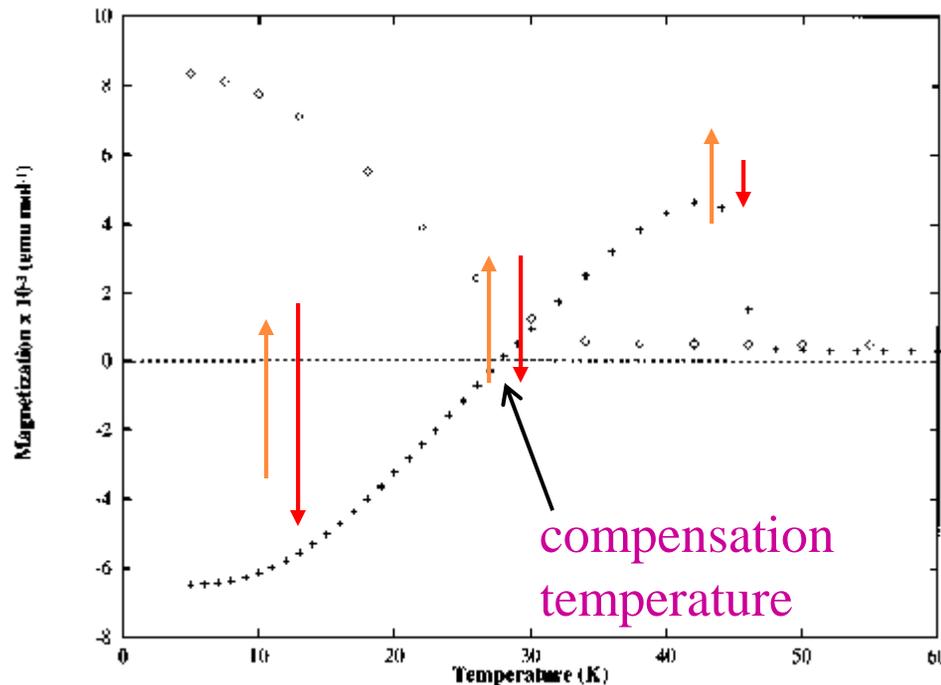
[Mathonière *et al.*, *Inorg. Chem.* **35**, 1201 (1996)]

This behavior has been observed and understood in ferrites (due to next-nearest neighbor coupling) but is not understood in a system where both magnetic ions have the same crystal symmetry.

Some Fe(II)Fe(III) compounds exhibit GNM, others do not!

A	T_c	GNM?
$N(n\text{-}C_nH_{2n+1})_4$ $(n = 3)$	35 K	no
$P(C_6H_5)_4$	37 K	no
$As(C_6H_5)_4$	35 K	no
$N(n\text{-}C_nH_{2n+1})_4$ $(n = 4 \text{ or } 5)$	45, 48 K	yes
$N(C_6H_5CH_2)(n\text{-}C_4H_9)_3$	44 K	yes
$(C_6H_5)_3PNP(C_6H_5)_3$	45 K	$T_{comp} = 28$ K
$P(n\text{-}C_4H_9)_4$	45 K	$T_{comp} = 30$ K

Open questions about the Fe(II) Fe(III) bimetallic oxalates:

1. How does the spin-orbit coupling stabilize magnetic order even for well-separated bimetallic planes?

2. What produces the GNM? Why in some compounds and not in others?

3. Why do GNM compounds have higher T_c's?

4. Can the magnetic compensation be controlled?

5. How large is the spin-wave gap?

Crystal Field Potential and Spin-Orbit Energy

We will assume that there is a heirarchy of energies:

I. Hund's coupling

By *Hund's first* and *second laws*, the ground states of Fe(II) and Fe(III) are given by

Fe(II) ($3d^6$): $S = 2, L = 2$

Fe(III) ($3d^5$): $S' = 5/2, L' = 0$

II. Crystal-field potential V with C_3 symmetry about each Fe(II)

III. AF exchange $J_c \mathbf{S} \cdot \mathbf{S'}$, spin-orbit coupling $\lambda \mathbf{S} \cdot \mathbf{L}$ ($\lambda < 0$, on the Fe(II) site only), and distortions of the crystal-field potential that violate C_3 symmetry

The dominant crystal-field potential V at the Fe(II) site has C_3 symmetry.
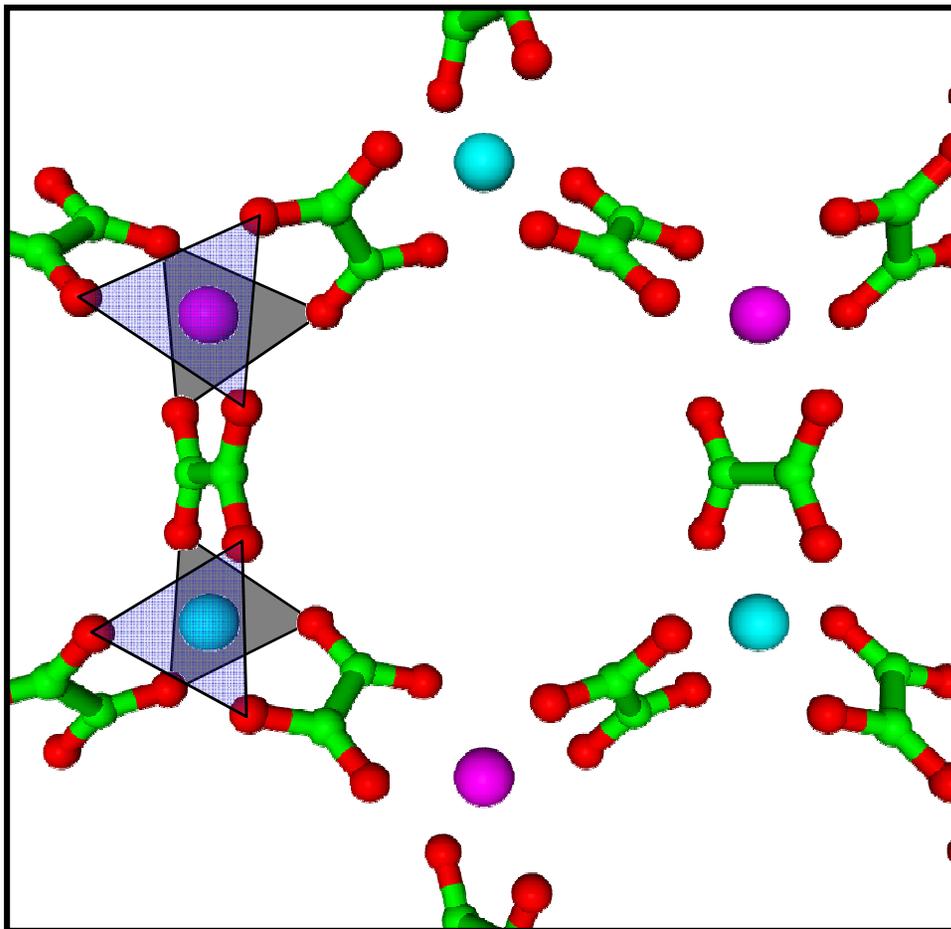
There are two oxygen triangles above and below each Fe(II) ion, one larger than the other and rotated by 48º.

The C_3 symmetric crystal-field potential V can be written as:

$$V(\rho,\theta,\phi) = \sum_{n\geq 0,\, n'\geq 0,\, n+3n'>1} A_{n,n'}\, \rho^{n+3n'}\, P_n(\cos\theta)\cos(3n'\phi + \mu_{n,n'})$$

After integrating over the $3d^6$ orbitals, we can parameterize the crystal-field Hamiltonian $H^{cf} = <m_1|V|m_2>$ of the $L = 2$ state.

The eigenstates of H^{cf} consist of two doublets and a singlet.

$$H^{cf} = \begin{pmatrix} \gamma & 0 & 0 & \alpha & 0 \\ 0 & \gamma' & 0 & 0 & -\alpha \\ 0 & 0 & 0 & 0 & 0 \\ \alpha^* & 0 & 0 & \gamma' & 0 \\ 0 & -\alpha^* & 0 & 0 & \gamma \end{pmatrix}$$

$|\varepsilon^{(0)}|$
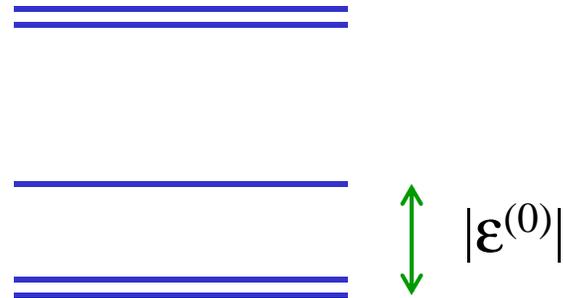
The low-energy doublet is given by:

$$|\psi_1\rangle \propto -2\alpha|2\rangle + (\gamma - \gamma' + r)|-1\rangle$$

$$|\psi_2\rangle \propto 2\alpha|1\rangle + (-\gamma + \gamma' + r)|-2\rangle$$

with energy

$$\epsilon_1 = \epsilon_2 = \epsilon^{(0)} \equiv (\gamma + \gamma')/2 - r/2$$

$$r = \sqrt{(\gamma - \gamma')^2 + 4|\alpha|^2}$$

and orbital angular momentum

$$\langle\psi_1|L_z|\psi_1\rangle = -\langle\psi_2|L_z|\psi_2\rangle = \frac{2|\alpha|^2 - (\gamma - \gamma')^2 - (\gamma - \gamma')r}{4|\alpha|^2 + (\gamma - \gamma')^2 + (\gamma - \gamma')r}$$

which depends only on $(\gamma-\gamma')/|\alpha|$. $L_z^{cf} = |\langle\psi_i|L_z|\psi_i\rangle|$ can vary from 0 to 2.

Below the curve $\gamma\gamma' = |\alpha|^2$, the doublet is lower in energy than the singlet.

The red dot is an estimate that uses the atomic positions of the oxygen atoms from a Mn(II)Cr(III) compound, the d-orbitals from density-functional theory, and assumes that each of the oxygens has the same charge.
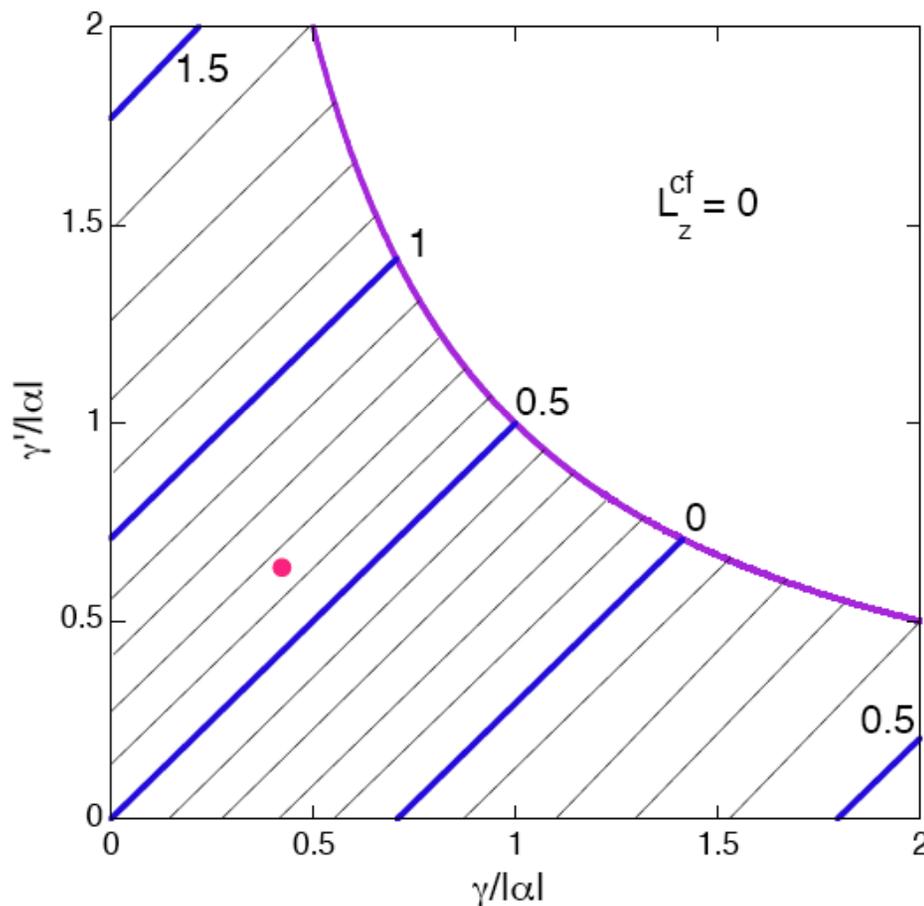
Reduced Hamiltonian

The transition temperature and magnetic moments are solved using mean-field theory. Then the reduced Hamiltonians on the Fe(II) and Fe(III) sites, *restricted to the low-energy doublet*, are:

$$H_{II} = \lambda \mathbf{L} \cdot \mathbf{S} + 3J_c \langle S_z' \rangle S_z \qquad H_{III} = 3J_c \langle S_z \rangle S_z'$$

The average magnetization is $M^{\mathrm{avg}} = (M'+M)/2 = (|M'|-|M|)/2$, where (set $\mu_B = 1$)

$$M = \langle 2S_z + L_z \rangle \qquad\qquad M' = 2\langle S_z' \rangle$$

In zero field, we adopt the convention that $M < 0$ and $M' > 0$.

The ferrimagnetic transition T_c and compensation temperatures T_{comp} are shown on the right. T_c/J_c depends only on $-\lambda L_z^{cf}/J_c$.

For large $-\lambda/J_c$, magnetic compensation occurs when $L_z^{cf} < 1$. The Fe(II) moment then dominates just below T_c and the Fe(III) moment dominates below T_{comp}.
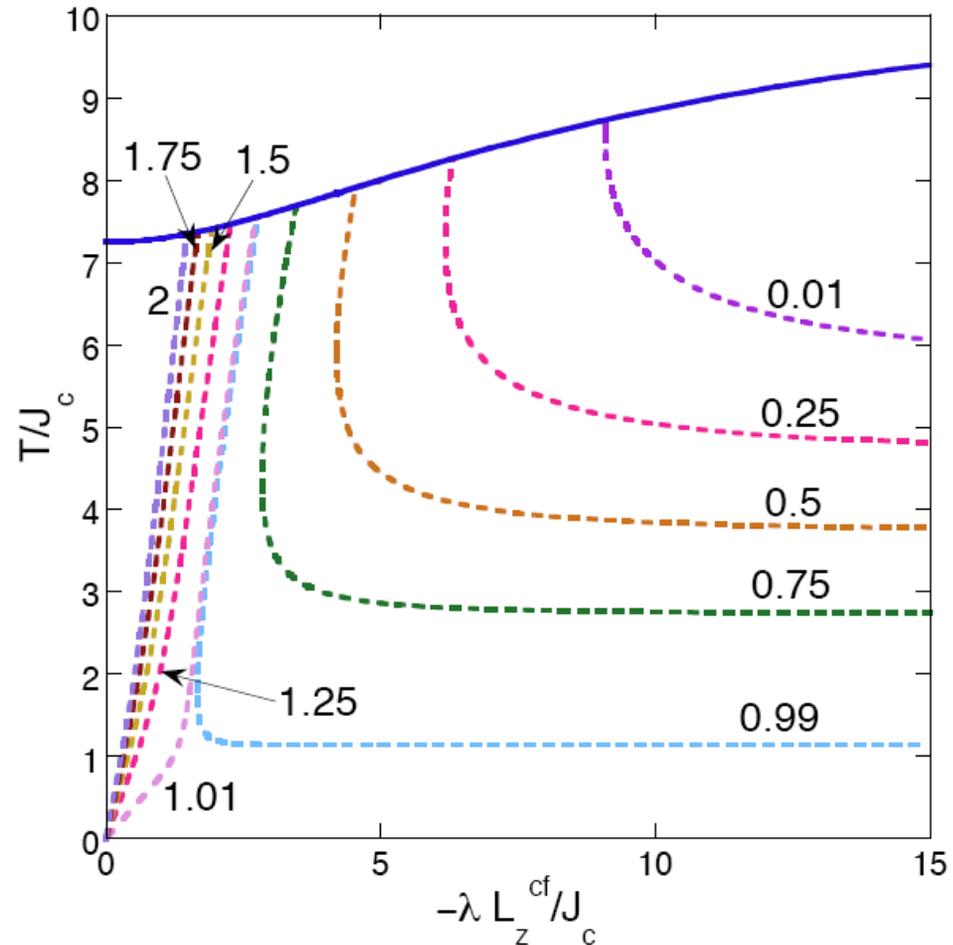

Bear in mind that mean-field theory will overestimate T_c for small $-\lambda/J_c$.

The average magnetization is plotted for $\lambda/J_c = -8$.
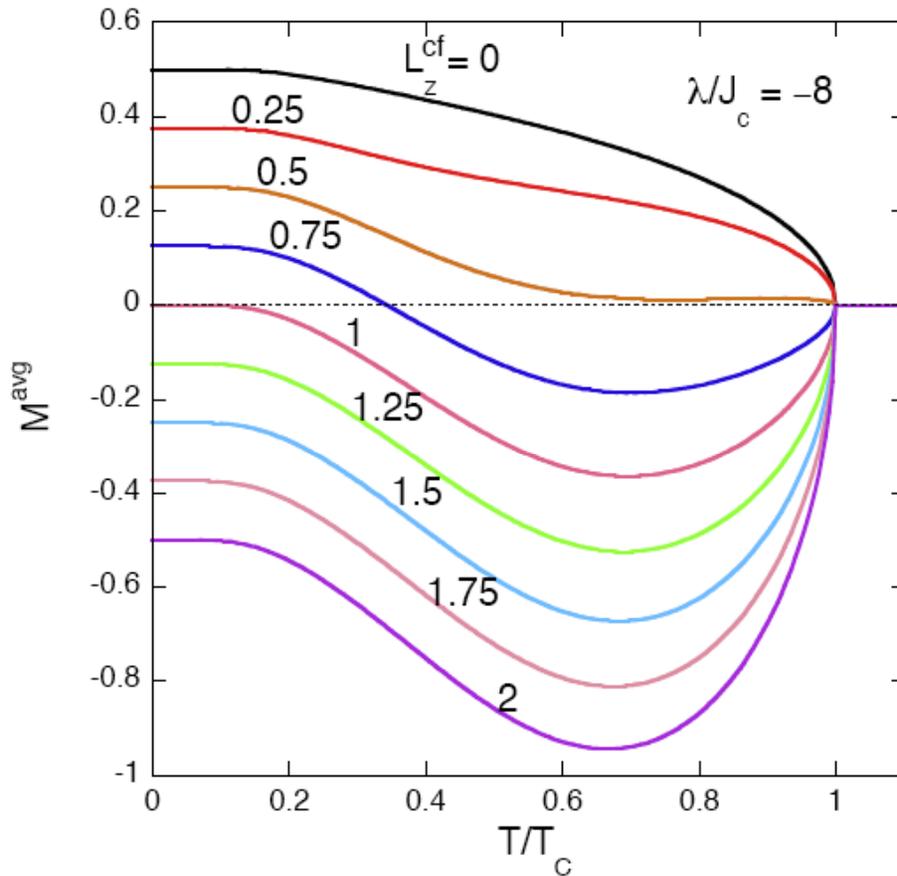
The number of compensation points n_{comp} where M^{avg} goes through 0 is given by

$$0 \le L_z^{cf} < 0.51: \qquad n_{comp} = 0$$

$$0.51 < L_z^{cf} < 0.54: \quad n_{comp} = 2$$

$$0.54 < L_z^{cf} < 1: \qquad n_{comp} = 1$$

$$1 < L_z^{cf} \le 2: \qquad n_{comp} = 0$$

These results are summarized in the "phase diagram:"
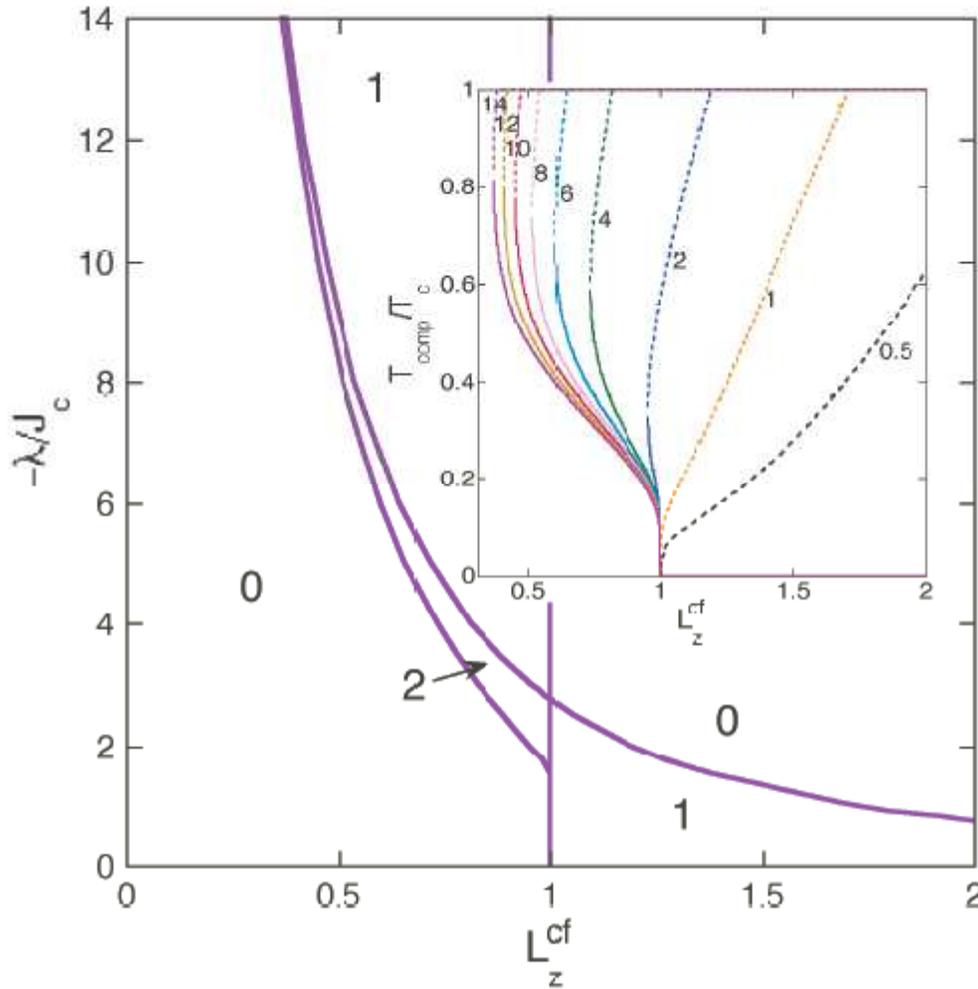
There are two regions with $n_{comp}=1$:

(i) strong spin-orbit coupling and $L_z^{cf} < 1$

(ii) weak spin-orbit coupling and $L_z^{cf} > 1$.

Where do the GNM compounds fall on this phase diagram?

Paramagnetic resonance measurements on Fe(II) compounds give

$$\lambda = -102 \text{ cm}^{-1} = -12.65 \text{ meV}$$

Using $T_c = 45$ K and $T_{comp}/T_c = 0.62$, we then estimate

$$J_c = 0.45 \text{ meV}, \quad L_z^{cf} = 0.274$$

The critical value of L_z^{cf} below which $n_{comp} = 0$ is about 0.23. So the GNM compounds are just inside the region with $n_{comp} = 1$.

While GNM materials lie above this dividing line, "normal" materials lie below.
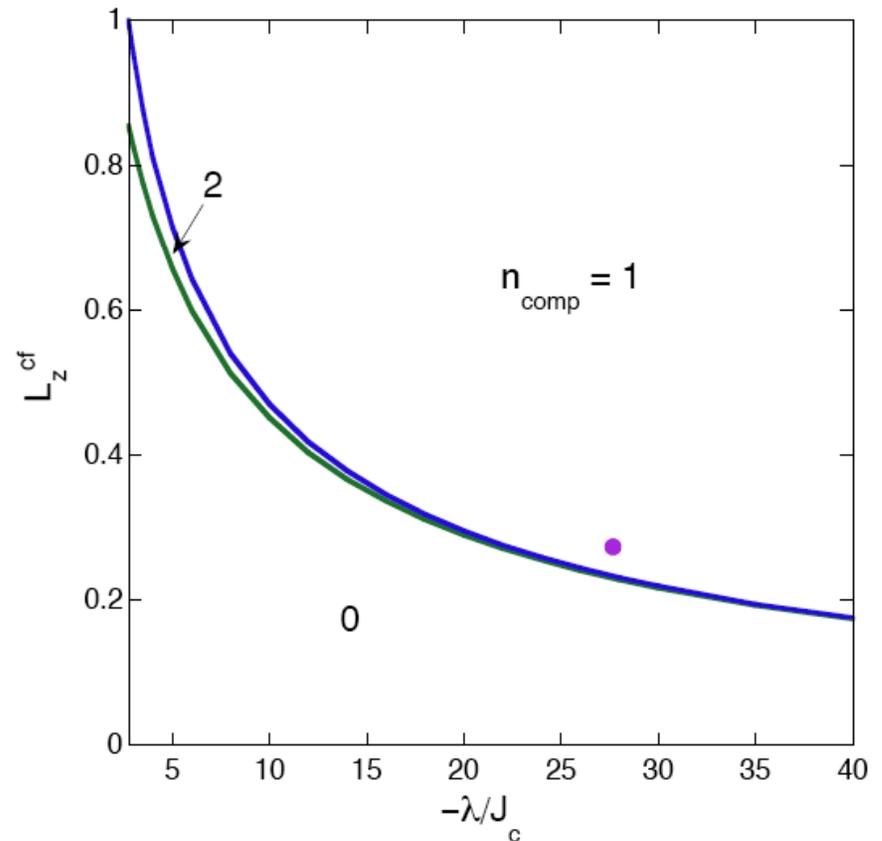
Our model predicts that an Fe(II)Fe(III) bimetallic oxalate may have two compensation points. This has recently been observed!

$$A = N(n\text{-}C_4H_9)_4$$
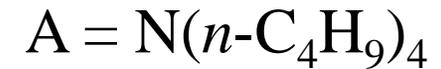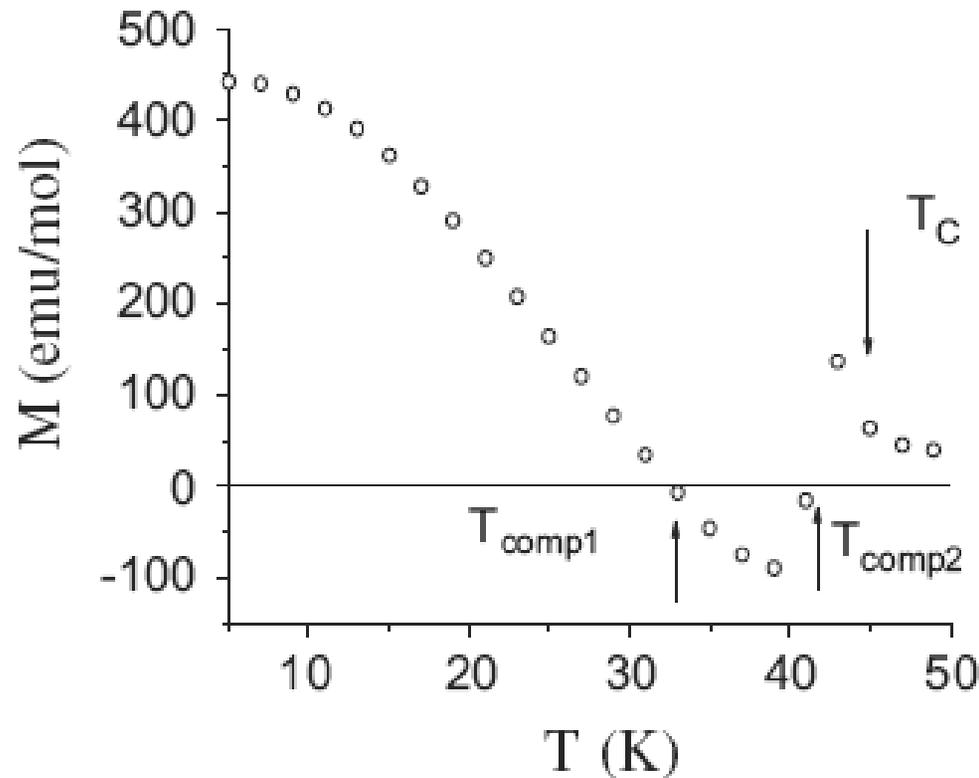
[Tang, He, Liang, Li, and Huang, *Physica B* **392**, 337 (2007)]

Or is there another explanation for this behavior?

Spin-Wave Frequencies

Applying a 1/S and 1/S' expansion about the classical limit, we have evaluated the spin-wave frequencies of Fe(II)Fe(III) bimetallic oxalates.
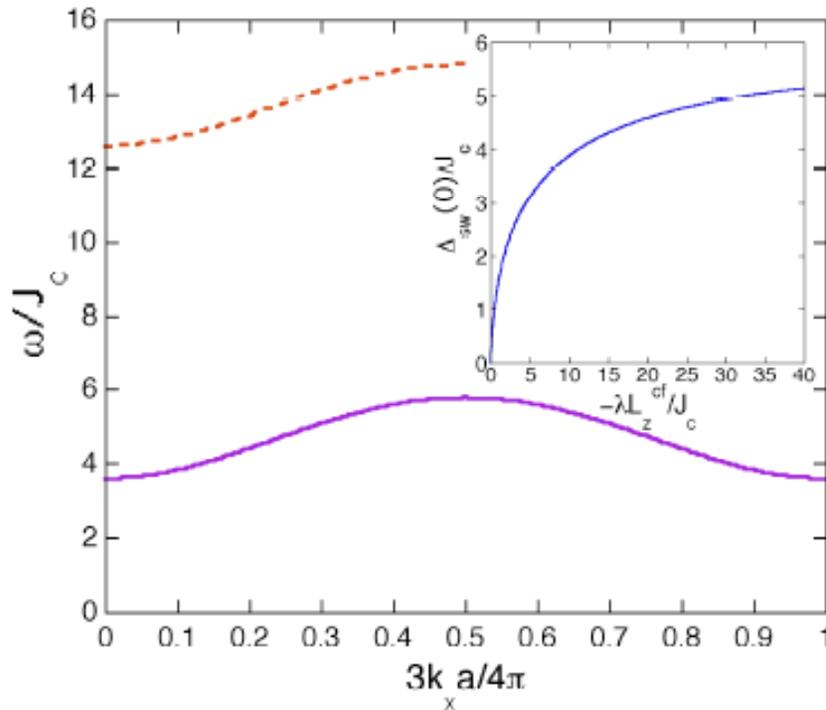
Using the parameters estimated above, we find the SW gap in zero field to be about 3.7 J_c = 1.65 meV.

If the interlayer coupling is weak, there should be little or no dispersion in the k_z direction.

Controlling the Magnetic Behavior

The persistence of negative magnetization in small fields is caused by (a) the spin-orbit energy cost for flipping **L** once it is aligned with the magnetic field and (b) the small matrix element for this dipole-allowed transition. The magnetic behavior can be controlled in at least three ways:

1. A cation can be chosen with the appropriate crystal field parameters γ, γ', and α to obtain a GNM or normal material.

2. In the negative magnetization state, **L** can be flipped by infrared light with energy $-2\lambda L_z^{cf} S = 14$ meV or wavelength 88 μm. That will in turn flip the spin and the magnetization.

14 meV

L **S** **S'**
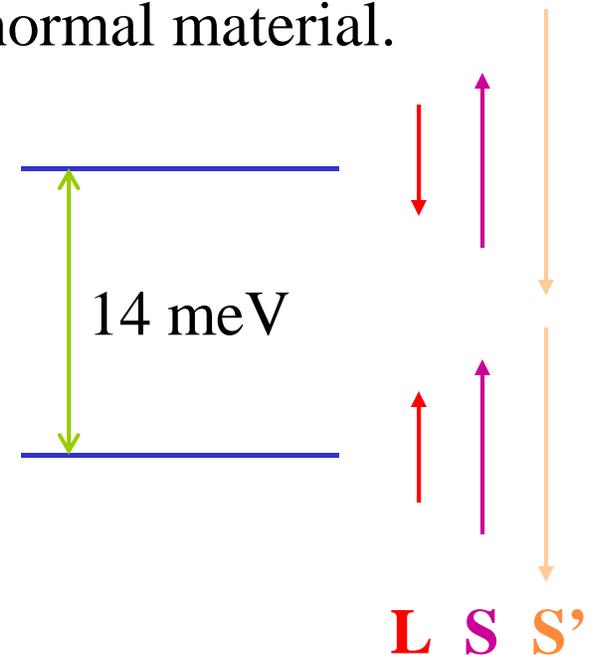
3. Uni-axial strain with crystal-field potential V_s will mix the doublet eigenstates $|\psi_1\rangle$ and $|\psi_2\rangle$:

$$V_s = \eta(x^2 - y^2) \propto \eta \cos 2\phi \sin^2 \theta$$

$$H^{mixing} = \begin{pmatrix} \epsilon_{1\sigma} & \xi \\ \xi & \epsilon_{2\sigma} \end{pmatrix}$$

This mixing will lower the angular momentum of the ground-state doublet and increase the magnetic compensation temperature. It will eventually transform a GNM material into a normal one.
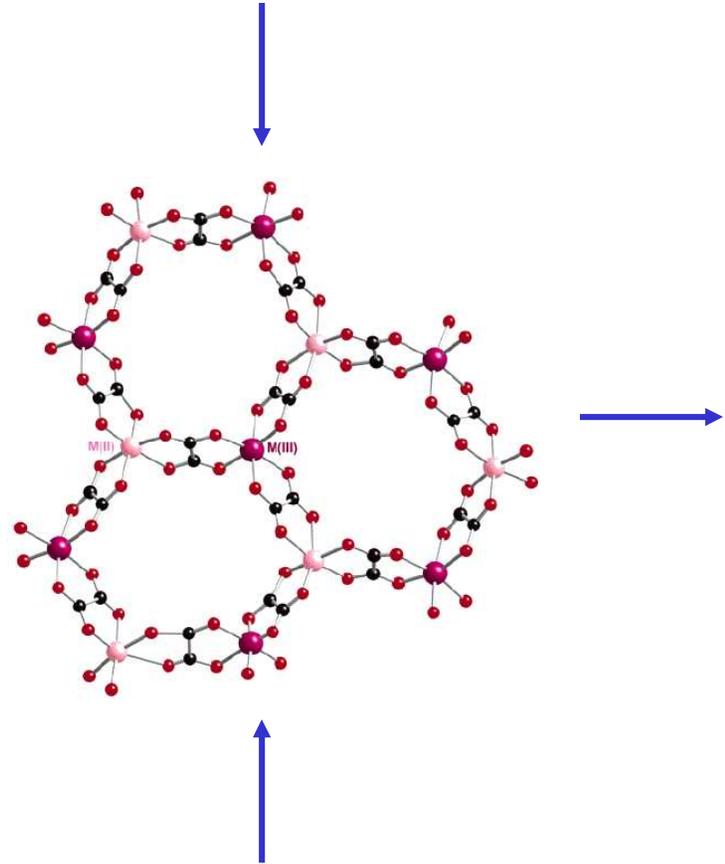
Jahn-Teller Transition

A spontaneous Jahn-Teller (JT) transition will also mix the doublet eigenstates with ξ proportional to the distortion of the O atoms. For $L_z^{cf} > 0.3$, the JT distortion would be quenched by the spin-orbit coupling. For $0.25 < L_z^{cf} < 0.3$, there will be two JT transitions with C_3 symmetry recovered at low and high temperatures.
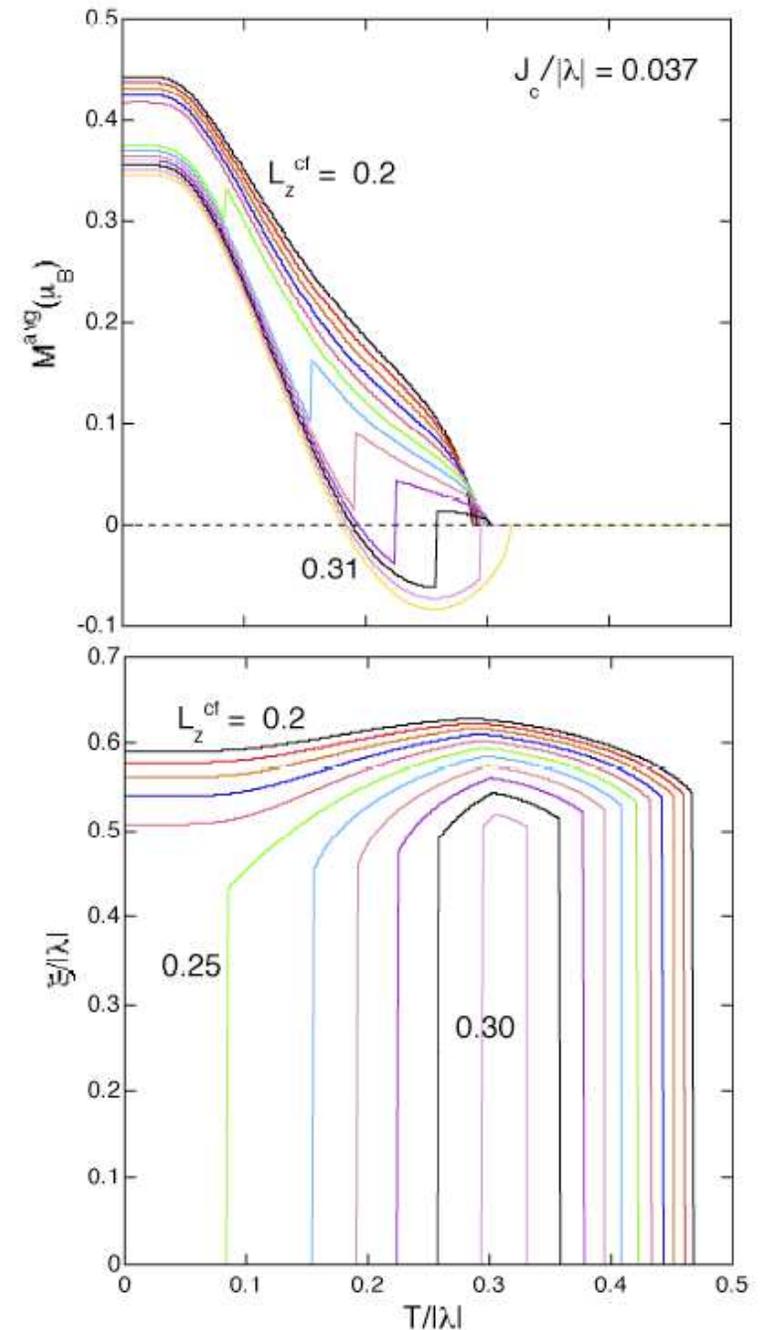
A first-order JT distortion may be the real explanation for the two compensation points observed by Tang *et al.*
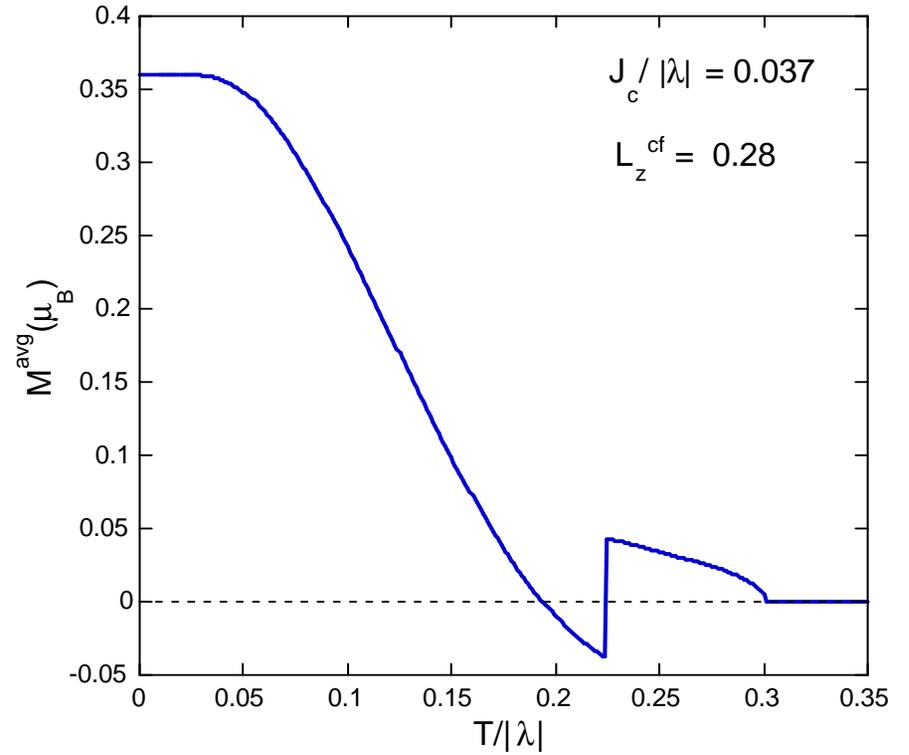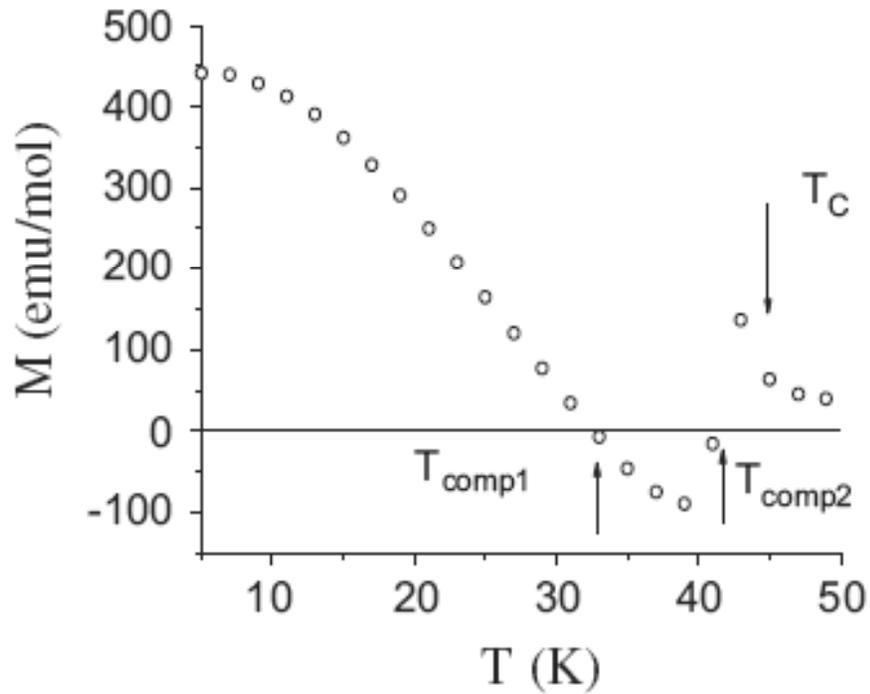
Conclusions

- The orbital angular momentum L_z^{cf} of the ground-state orbital doublet of Fe(II)Fe(III) bimetallic oxalates depends on the crystal-field potential.

- Fe(II)Fe(III) bimetallic oxalates exhibit GNM when L_z^{cf} exceeds a critical value.

- The spin-orbit coupling within each plane on the Fe(II) sites is responsible for the magnetic ordering of well-separated bimetallic planes. A spin-wave gap of about 1.65 meV is associated with the spin-orbit coupling.

- The negative magnetization state can be optically flipped.

- The compensation temperature can be controlled by uni-axial strain.

- There is evidence for a first-order JT transition.