Giant Negative Magnetization in a Layered Molecular-Based Magnet

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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.

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 $S$).
What are the Bimetallic Oxalates?

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 $\text{ox} = \text{C}_2\text{O}_4$ molecules.  

$[\text{Tamaki et al., J. Am. Chem. Soc. 114, 6974 (1992)}]$
The magnetic coupling depends primarily on the species of transition metals:

<table>
<thead>
<tr>
<th>M(II)M'(III)</th>
<th>orbitals</th>
<th>magnetic order</th>
<th>transition temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(II)Cr(III)</td>
<td>3d^5, 3d^3</td>
<td>FM or canted</td>
<td>T_c = 6 K</td>
</tr>
<tr>
<td>Fe(II)Fe(III)</td>
<td>3d^6, 3d^5</td>
<td>Ferrimagnet</td>
<td>30 K &lt; T_c &lt; 48 K</td>
</tr>
<tr>
<td>Mn(II)Fe(III)</td>
<td>3d^5, 3d^5</td>
<td>weak AF</td>
<td></td>
</tr>
<tr>
<td>Fe(II)Mn(III)</td>
<td>3d^6, 3d^4</td>
<td>AF</td>
<td>T_c = 21 K</td>
</tr>
<tr>
<td>Ni(II)Mn(III)</td>
<td>3d^8, 3d^4</td>
<td>Ferrimagnet</td>
<td>T_c = 21 K</td>
</tr>
<tr>
<td>V(II)V(III)</td>
<td>3d^3, 3d^2</td>
<td>Ferrimagnet</td>
<td>T_c = 11 K</td>
</tr>
<tr>
<td>Co(II)Cr(III)</td>
<td>3d^7, 3d^3</td>
<td>FM</td>
<td>T_c = 5 K</td>
</tr>
<tr>
<td>V(II)Cr(III)</td>
<td>3d^3, 3d^3</td>
<td>AF coupling</td>
<td>no order</td>
</tr>
<tr>
<td>Mn(II)V(III)</td>
<td>3d^5, 3d^2</td>
<td>FM</td>
<td>T_c &lt; 2 K</td>
</tr>
</tbody>
</table>
For a single cation $A = \text{NBu}_4 = \text{N}(n\text{-C}_4\text{H}_9)_4$, the transition temperatures are shown below:

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

\[ \text{[BETS]}_3[\text{MnCr(C}_2\text{O}_4)_3] \]


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:

[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-C\textsubscript{n}H\textsubscript{2n+1})\textsubscript{4}[Fe(II)Fe(III)ox\textsubscript{3}] compounds, the interlayer spacing grows from 8.2 to 10.2 Å as \textit{n} increases from 3 to 5. But the ferrimagnetic transition temperature then \textit{increases} from 35 to 48 K. [Mathonière \textit{et al.}, \textit{Inorg. Chem.} \textbf{35}, 1201 (1996)]

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

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

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.

Giant Negative Magnetization

[Mathonière et al., Inorg. Chem. 35, 1201 (1996)]
Some Fe(II)Fe(III) compounds exhibit GNM, others do not!

<table>
<thead>
<tr>
<th>A</th>
<th>$T_c$</th>
<th>GNM?</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N(n$-$C_{n}H_{2n+1})_4$ ($n = 3$)</td>
<td>35 K</td>
<td>no</td>
</tr>
<tr>
<td>$P(C_6H_5)_4$</td>
<td>37 K</td>
<td>no</td>
</tr>
<tr>
<td>$As(C_6H_5)_4$</td>
<td>35 K</td>
<td>no</td>
</tr>
<tr>
<td>$N(n$-$C_{n}H_{2n+1})_4$ ($n = 4$ or 5)</td>
<td>45, 48 K</td>
<td>yes</td>
</tr>
<tr>
<td>$N(C_6H_5CH_2)(n$-$C_{4}H_{9})_3$</td>
<td>44 K</td>
<td>yes</td>
</tr>
<tr>
<td>$(C_6H_5)_3PNP(C_6H_5)_3$</td>
<td>45 K</td>
<td>$T_{comp} = 28$ K</td>
</tr>
<tr>
<td>$P(n$-$C_{4}H_{9})_4$</td>
<td>45 K</td>
<td>$T_{comp} = 30$ K</td>
</tr>
</tbody>
</table>
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 hierarchy 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 $J_c S \cdot S'$, spin-orbit coupling $\lambda S \cdot L$ ($\lambda < 0$, 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 $48^\circ$. 
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 \((\gamma-\gamma')/|\alpha|\). \(L_z^{\text{cf}} = |\langle \psi_i | L_z | \psi_i \rangle|\) can vary from 0 to 2.
Below the curve $\gamma' = |\alpha|^2$, 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:

\[
H_{\text{II}} = \lambda \mathbf{L} \cdot \mathbf{S} + 3J_c \langle S'_z \rangle S_z \quad H_{\text{III}} = 3J_c \langle S_z \rangle S'_z
\]

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

\[
M = \langle 2S_z + L_z \rangle \quad M' = 2\langle S'_z \rangle
\]

In zero field, we adopt the convention that \( M < 0 \) and \( M' > 0 \).
The ferrimagnetic transition $T_c$ and compensation temperatures $T_{\text{comp}}$ are shown on the right. $T_c/J_c$ depends only on $-\lambda L_z^{\text{cf}}/J_c$.

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

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 $n_{\text{comp}}$ where $M^{\text{avg}}$ goes through 0 is given by

- $0 \leq L_z^{\text{cf}} < 0.51$: $n_{\text{comp}} = 0$
- $0.51 < L_z^{\text{cf}} < 0.54$: $n_{\text{comp}} = 2$
- $0.54 < L_z^{\text{cf}} < 1$: $n_{\text{comp}} = 1$
- $1 < L_z^{\text{cf}} \leq 2$: $n_{\text{comp}} = 0$
These results are summarized in the “phase diagram:”

There are two regions with $n_{\text{comp}} = 1$:

(i) strong spin-orbit coupling and $L_z^{\text{cf}} < 1$
(ii) weak spin-orbit coupling and $L_z^{\text{cf}} > 1$.

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 \( T_c = 45 \text{ K} \) and \( T_{\text{comp}}/T_c = 0.62 \), we then estimate

\[ J_c = 0.45 \text{ meV}, \quad L_{z,\text{cf}} = 0.274 \]

The critical value of \( L_{z,\text{cf}} \) below which \( n_{\text{comp}} = 0 \) is about 0.23. So the GNM compounds are just inside the region with \( n_{\text{comp}} = 1 \).

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!

\[ A = N(n-C_4H_9)_4 \]

[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 $3.7 \, J_c = 1.65 \, \text{meV}$.

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 $\gamma$, $\gamma'$, and $\alpha$ to obtain a GNM or normal material.

2. In the negative magnetization state, $L$ can be flipped by infrared light with energy $-2\lambda L_z^{cf} S = 14 \text{ meV}$ or wavelength 88 $\mu$m. That will in turn flip the spin and the magnetization.
3. Uni-axial strain with crystal-field potential $V_s$ will mix the doublet eigenstates $|\psi_1>$ and $|\psi_2>$:

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

$$H^{mixing} = \begin{pmatrix} \epsilon_1 \sigma & \xi \\ \xi & \epsilon_2 \sigma \end{pmatrix}$$

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 $\xi$ 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.