Spin-Charge Coupling in Transition Metal Vanadates

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Projects

1. Magnetoelectric materials
2. Magnetism in semiconductors
3. Magnetic nanoparticles for biomedical applications
Magnetoelectric coupling
Coupling between magnetic and electric fields is well understood in a vacuum

\[ \nabla \cdot E = \rho \]
\[ \nabla \cdot B = 0 \]
\[ \nabla \times E = -\frac{\partial B}{\partial t} \]
\[ \nabla \times B = \mathbf{J} + \frac{\partial \mathbf{E}}{\partial t} \]
Magnetoelectric coupling in matter

Pierre Curie (1894): “Sur la symetrie dans les phenomenes physiques, symetrie d’un champ electrique et d’un champ magnetique” postulated induction of magnetization by an electric field and vice-versa.

Can a **static** magnetic field induce an electric polarization? Conversely, can a **static** electric field induce a magnetization?

More generally, how are magnetism and polarization coupled in real materials?
Consider a formal expansion of the interaction potential $V(E,H)$

$$V = \alpha_{ij} E_i H_j + \beta_{ijk} E_i H_j H_k + \gamma_{ijk} E_i E_j H_k + \delta_{ijkl} E_i E_j H_k H_l + \ldots$$

In materials

$$H \leftrightarrow M \quad E \leftrightarrow P$$
Magnetodielectric coupling

How are $\varepsilon$ and $M$ coupled at a mean field level?

First try: Couple electric dipole moment ($P$) to *uniform* magnetization ($M$)

$$F = \frac{P^2}{2\varepsilon_0} - P \cdot E + \gamma P^2 M^2 \quad \Rightarrow \quad \Delta \varepsilon \propto M^2$$

More generally, coupling $P$ to the spin-spin correlation function:

$$F = \frac{P^2}{2\varepsilon_0} - P \cdot E + P^2 \sum_q g(q) \langle M_q M_{-q} \rangle$$
Why is a linear magnetoelectric coupling unexpected?

**Macroscopic** Magnetization breaks time reversal symmetry while polarization breaks spatial inversion symmetry.

**Microscopic** Partially filled d-electron shells suppress off-centre distortions.
Electron orbitals and magnetism

d orbitals

from: chem.wisc.edu
Magnetoelectric coupling

**Symmetric** $S_i \cdot S_j$

**Exchange Striction**

Towards a microscopic model of magnetoelectric interactions in Ni$_3$V$_2$O$_8$

A. B. Harris, T. Yildirim, A. Aharony, and O. Entin-Wohlman

$$\mathcal{H}_{\gamma_p} = \frac{1}{2} Q_{\gamma_p} \sum_{\alpha \beta} \sum_{ij} \frac{\partial X_{\alpha \beta}(i,j)}{\partial Q_{\gamma_p}} S_{\alpha}(i)S_{\beta}(j)$$

Ferroelectricity in an Ising Chain Magnet

Y. J. Choi, H. T. Yi, S. Lee, Q. Huang, V. Kiryukhin, and S.-W. Cheong
Magnetoelectric coupling

Antisymmetric $S_i \times S_j$

Dzyaloshinskii-Moriya interaction

Spin-current

\[ \sum_{ia} D^a(r) \cdot [S_i \times S_{i+a}] \]

Role of the Dzyaloshinskii-Moriya interaction in multiferroic perovskites

I. A. Sergienko and E. Dagotto

\[ \vec{P} \propto \vec{e}_{ij} \times (\vec{S}_i \times \vec{S}_j) \]

Spin Current and Magnetoelectric Effect in Noncollinear Magnets

Hosho Katsura, Naoto Nagaosa, and Alexander V. Balatsky
Materials Science
Roughly 100,000,000,000,000,000,000 combinations of 10 atom compounds.

NEED RATIONAL SEARCH
Transition metal oxides

3d Transition metals
d electrons for magnetism
Plentiful, safe, many valence states

Oxides
Oxygen has large electronegativity
Typically stable under ambient conditions
Vanadium oxides

$[V] = [Ar]3d^34s^2$

Easily switch between stable oxidation states.

Battery applications

From: wikipedia
Vanadates

Vanadium oxide structure with V in +5 oxidation state ([V$^{5+}$]=[Ar]).

Orthovanadate

Relative ion sizes in materials

From: wikipedia

O$^{2-}$

Ca$^{2+}$

Fe$^{2+}$

V$^{5+}$
Why are transition metal vanadates good candidates for magnetoelectric studies?

1. Vanadium is associated with strong charge-lattice coupling (e.g. ultrafast MIT transition in VO$_2$ nanostructures)

2. V$^{5+}$ ions are non-magnetic, so the magnetic moments arise only from the transition metal.

3. Properties of oxides (e.g. M-O-M magnetic superexchange) are very well studied, the materials are stable, and they can be synthesized as single crystals.
Outline

1. Orthovanadates with TM in +2 oxidation state

2. Orthovanadates with TM in +3 oxidation states

3. Vanadates with TM in +2 oxidation state
\( \text{TM}^{2+} \text{ orthovanadates (TM}_3\text{V}_2\text{O}_8 \)
TM lattice

Two different types of TM sites
Co$_3$V$_2$O$_8$
$\text{Ni}_3\text{V}_2\text{O}_8$
$N_i_3V_2O_8$ polarization

\[ P_b (\mu C/m^2) \]

\[ H=0 \ T \]
\[ H=1 \ T \]
\[ H=2 \ T \]
\[ H=3 \ T \]
\[ H=4 \ T \]
\[ H=5 \ T \]
Polarization isotherms

H || a

T = 2 K

H (T)

P_b (μC/m²)

H || c

T = 4 K

T = 5 K

P_b (μC/m²)

H (T)
Spin structure and polarization direction
\[ V = \sum \gamma a_\gamma \sigma_H \sigma_L \sin(\phi_H - \phi_L) P_\gamma \]

\[ \sigma_H, \sigma_L \text{ are magnetic order parameters} \]

\[ P_b = \sigma_H \sigma_L \]
\( \text{Ni}_3\text{V}_2\text{O}_8 \) multiferroic transition
TM$^{3+}$ orthovanadates (TMVO$_4$)
Magnetic transitions in FeVO$_4$

\[ \chi (10^{-2} \text{ emu/mole Oe}) \]

\[ T (K) \]

- AF$_2$
- AF$_1$
- PM

Graph showing the magnetic susceptibility $\chi$ as a function of temperature $T$ for different magnetic fields (5T, 1T, and 100 Oe). The graph highlights the magnetic transitions at various temperatures.
Electrical and dielectric properties
Ferroelectric properties

\[ P \left( \mu \text{C m}^{-2} \right) \]

\[ E_p = \pm 360 \, \text{KV/m} \]

\[ T_{N2} \]

\[ T \text{ (K)} \]

Graph showing ferroelectric properties with various applied fields.

- \( E_p = +360 \, \text{KV/m} \)
- \( E_p = -360 \, \text{KV/m} \)

Legend:
- \( H=0 \, \text{T} \)
- \( H=10 \, \text{kOe} \)
- \( H=30 \, \text{kOe} \)
- \( H=50 \, \text{kOe} \)
Magnetoelectric coupling in FeVO$_4$

\[ V = 2 \sum \gamma r_{\gamma} |\sigma_1 \sigma_2| \sin(\phi_2 - \phi_1) P_{\gamma} \]

\[ P \vec{1} \Rightarrow \text{No symmetry restrictions on } \vec{P} \]
CrVO$_4$
TM$^{2+}$ vanadates (TMV$_2$O$_6$)
$\text{CuV}_2\text{O}_6$
Conclusions

Many transition metal vanadates show strong spin-charge-lattice coupling.

In some cases, this can lead to magnetically-induced ferroelectric order, with a resulting *multiferroic* ground state.

The coupling between electric polarization and magnetization can be understood by a Landau model depending on the underlying crystal symmetry.
Open questions

1. What is the switching speed between ferroelectric polarization states? Between magnetization states?

2. What are the fundamental mechanisms giving rise to spin-charge-lattice coupling in these systems? Can this coupling be strengthened?
Magnetoelectric coupling in low symmetry systems

FeVO$_4$ (and NiV$_2$O$_6$) have P$_1$ symmetry, so the direction of the spontaneous polarization is determined by the details of the magnetoelectric interaction.
Doping studies on P1 vanadates

$$\text{Fe}^{3+} \text{ V}^{5+} \text{ O}^{2-}$$

$$\text{Sc}^{3+}, \text{ Mn}^{3+}, \text{ Ti}^{4+}$$

$$\text{Co}^{3+}, \text{ Cr}^{3+}$$
Graduate Student Collaborators

Current
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