Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich

MATERIALS THEORY

Hidden magnetoelectric multipoles

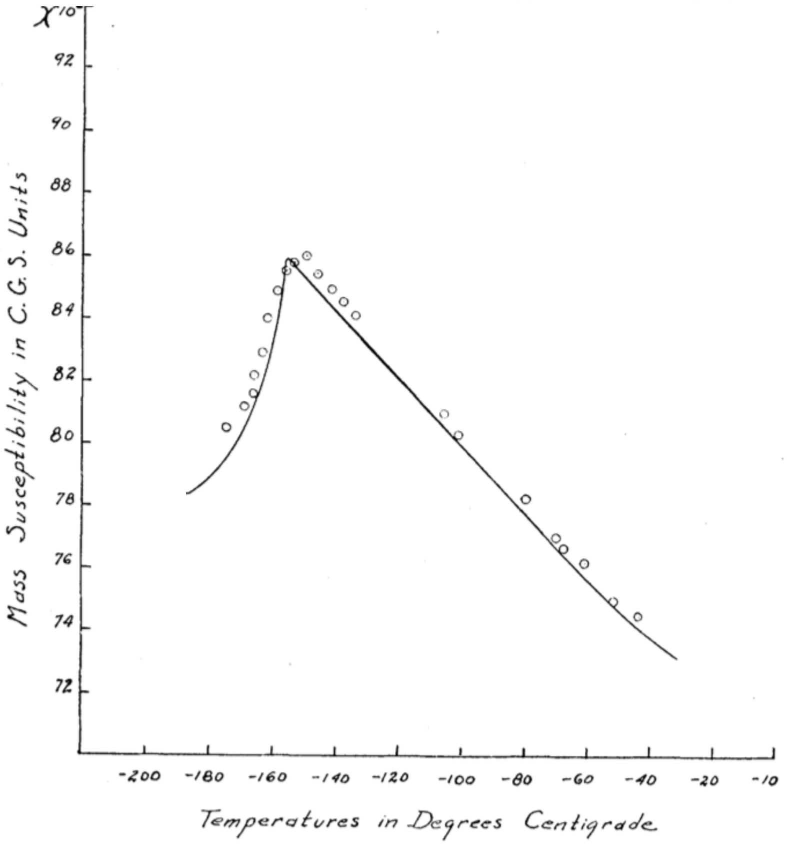
Nicola Spaldin
Materials Theory
ETH Zürich

1930s – weird magnetic response of some “non-magnetic” materials

NOVEMBER 1, 1933 PHYSICAL REVIEW VOLUME 44

The Magnetic Susceptibility of MnO as a Function of the Temperature

RAYEN WELCH TYLER, *University of Illinois*

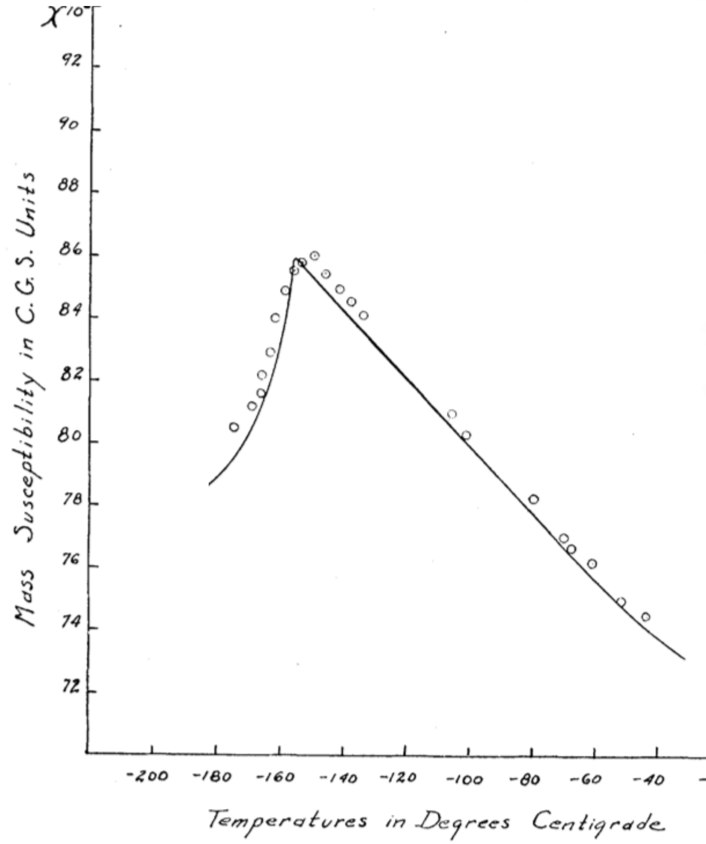


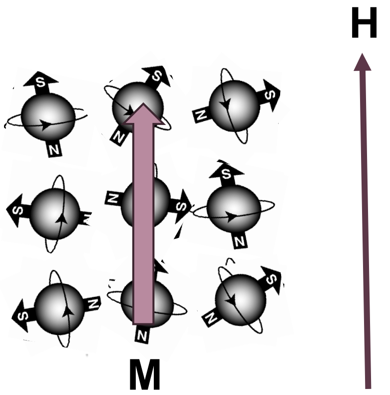
Understood at high temperature

NOVEMBER 1. 1933 PHYSICAL REVIEW VOLUME 44

The Magnetic Susceptibility of MnO as a Function of the Temperature

RAYEN WELCH TYLER, *University of Illinois*



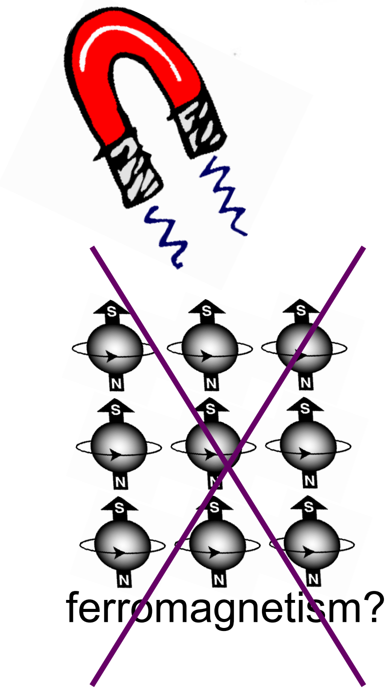


But not at low temperature

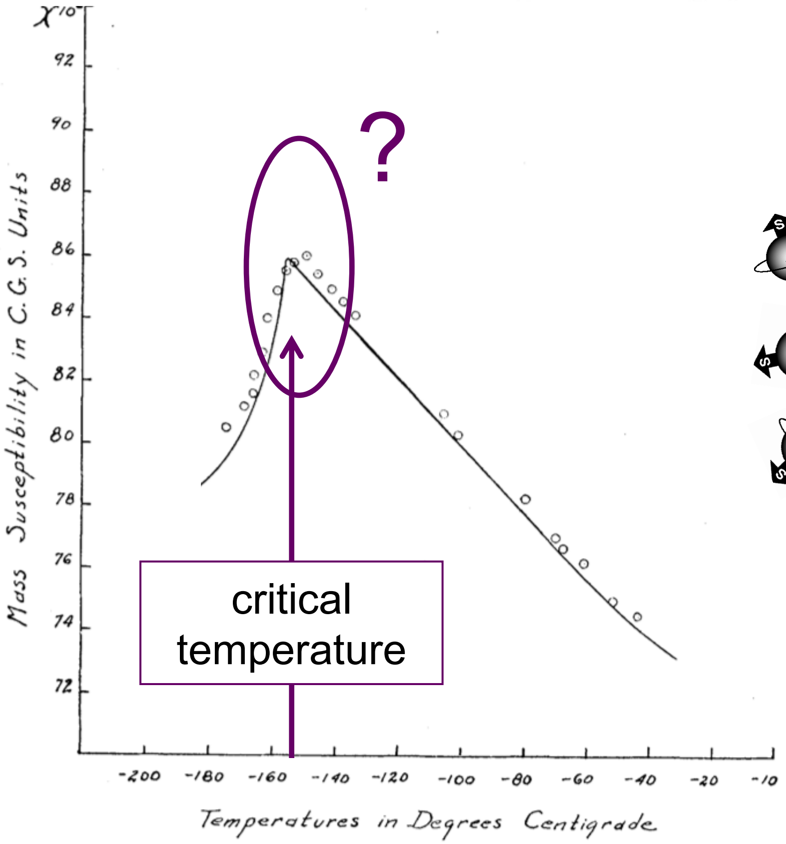
NOVEMBER 1. 1933 PHYSICAL REVIEW VOLUME 44

The Magnetic Susceptibility of MnO as a Function of the Temperature

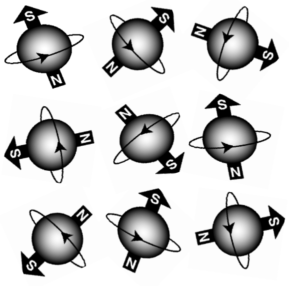
RAYEN WELCH TYLER, *University of Illinois*



ferromagnetism?

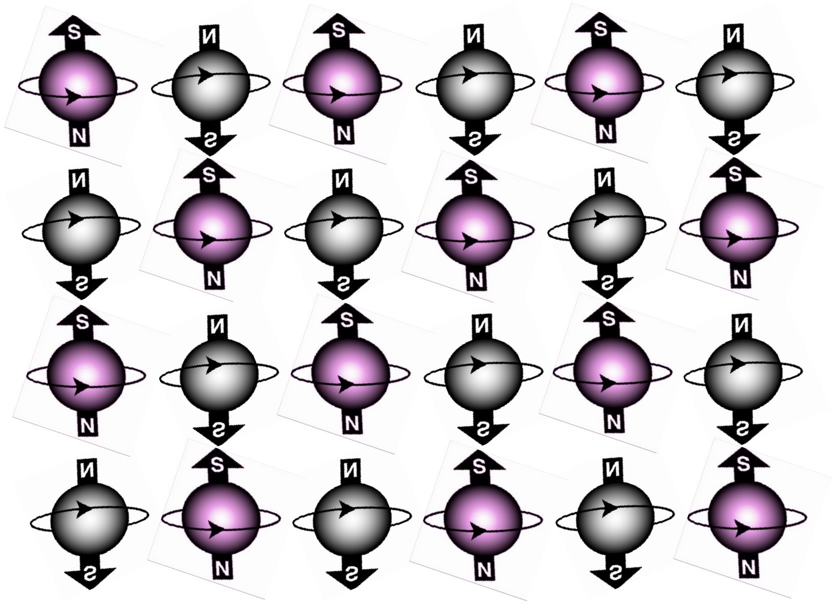


critical temperature



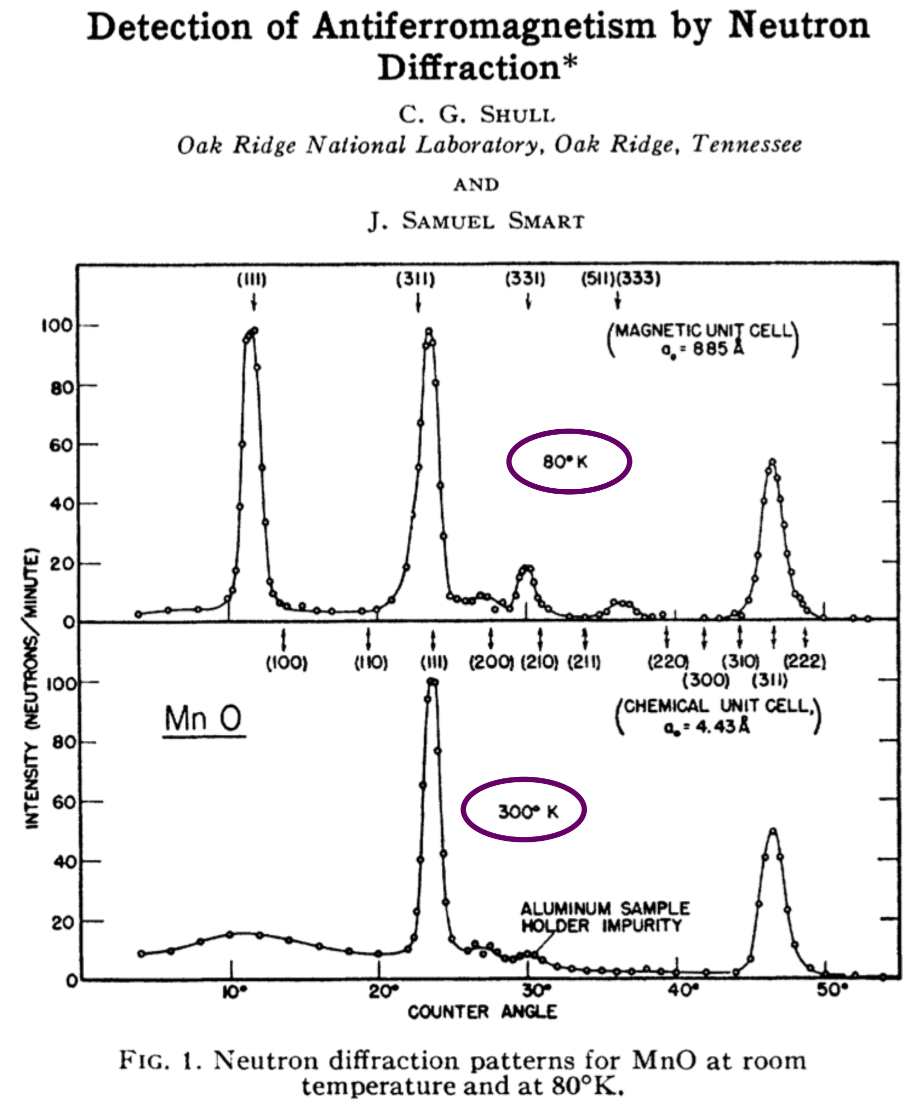
An early example of "hidden order"

In 1934 Louis Néel proposed a phase transition to *antiferromagnetism*…



…and showed that the observed susceptibility was consistent with such a magnetic ordering

First direct evidence 20 years later from neutron diffraction!



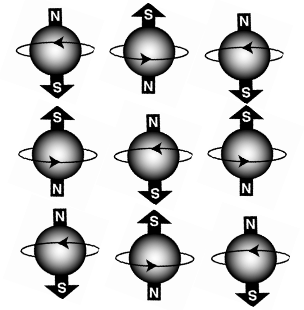
Detection of Antiferromagnetism by Neutron Diffraction*

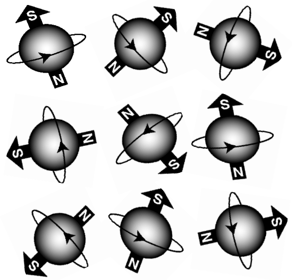
C. G. SHULL
Oak Ridge National Laboratory, Oak Ridge, Tennessee

AND

J. SAMUEL SMART

FIG. 1. Neutron diffraction patterns for MnO at room temperature and at 80°K.

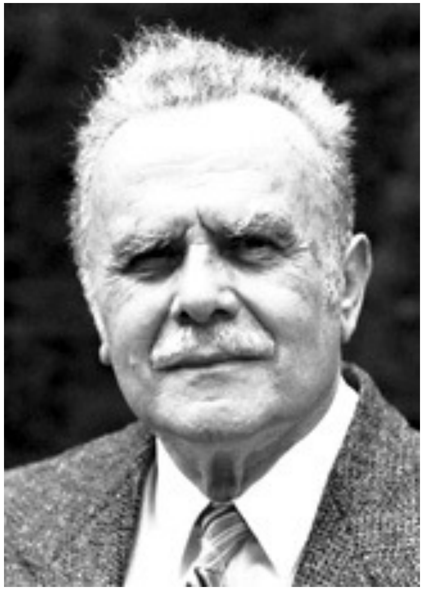




Nobel Prize 1994 – Clifford Shull and Bertram Brockhouse

“For development of the neutron diffraction technique”

“For the development of neutron spectroscopy”

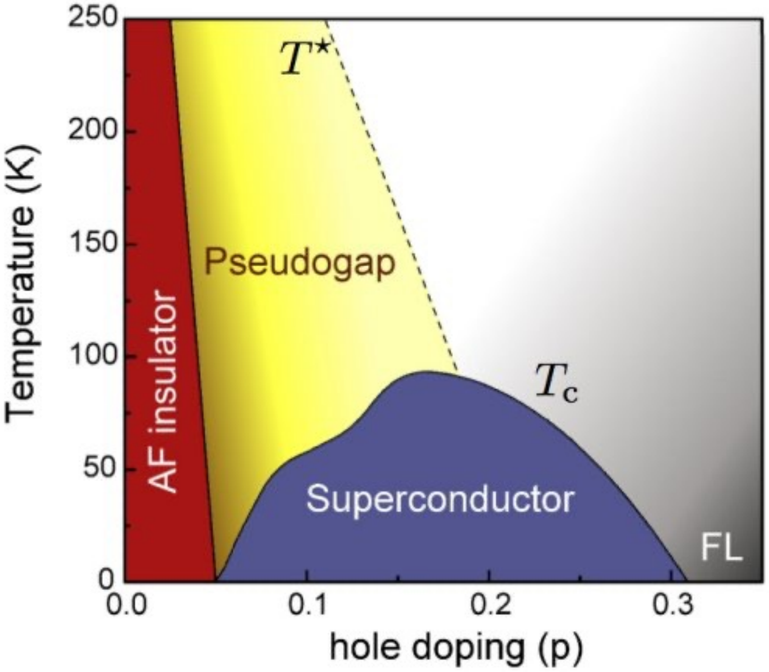


Nobel Prize 1970 – Louis Néel

“For fundamental work and discoveries concerning antiferromagnetism…”

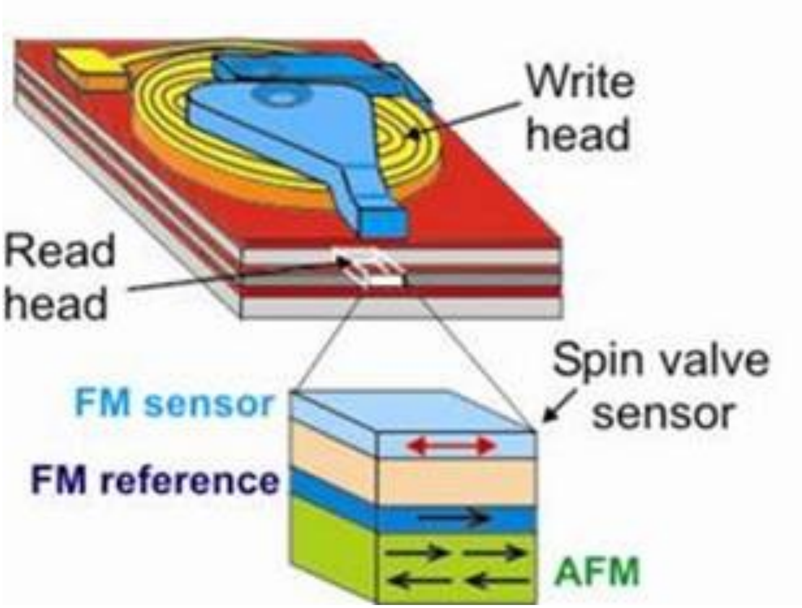
Antiferromagnets today

> A large number of antiferromagnetic materials is now known ... They are extremely interesting from the theoretical point of view but do not seem to have any applications.
>
> *L. Néel, Nobel lecture, 1970*



(Image from High-Magnetic Field Lab, Toulouse)

Exchange bias in GMR sensors



(Image from J. Stohr, SLAC)

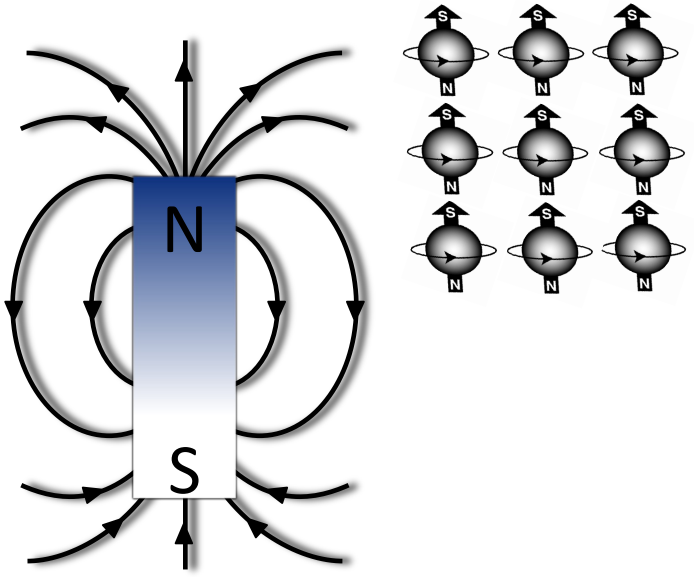
Are other kinds of magnetic order still hidden?

Probably ... but where to look?

Composite order, where $< A > = 0 \quad < B > = 0$

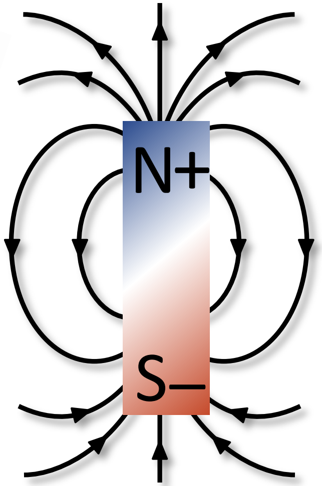
but $<A \otimes B> \neq 0$

An example: μ and r

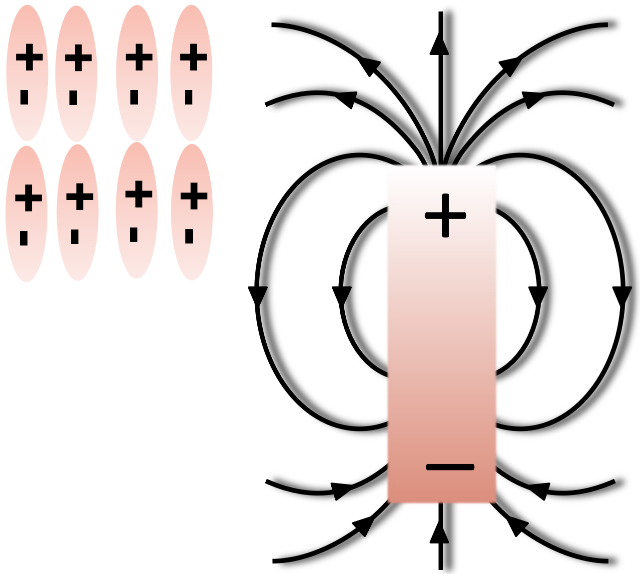


ferromagnetic

$\langle\mu\rangle \neq 0$



multiferroic



ferroelectric

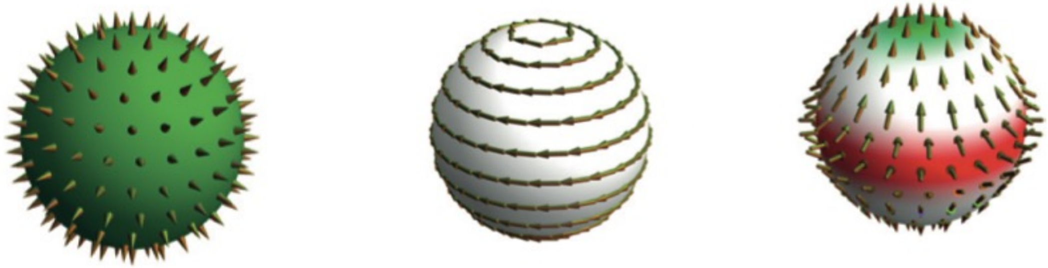
$\langle r\rangle \neq 0$

$\langle\mu\rangle \neq 0$ and $\langle r\rangle \neq 0$

Beyond Multiferroics

$\langle \mu \otimes r \rangle \neq 0$ even with $\langle\mu\rangle = 0$ and $\langle r\rangle = 0$

Such $<\mu \otimes r>$ order occurs in magnetoelectric multipoles



Outline

What are magnetoelectric multipoles?

What properties do the magnetoelectric multipoles cause?

Can we directly measure them?

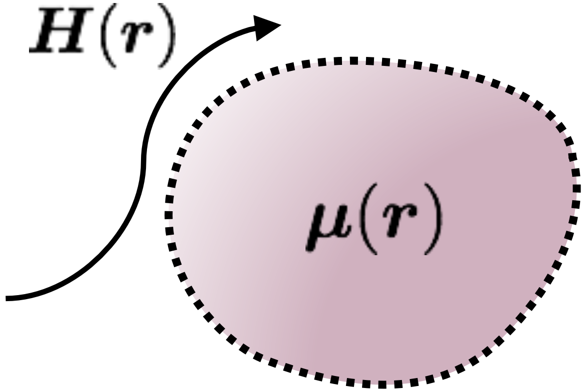
How does a magnetic material interact with a magnetic field?

In general, the interaction energy is

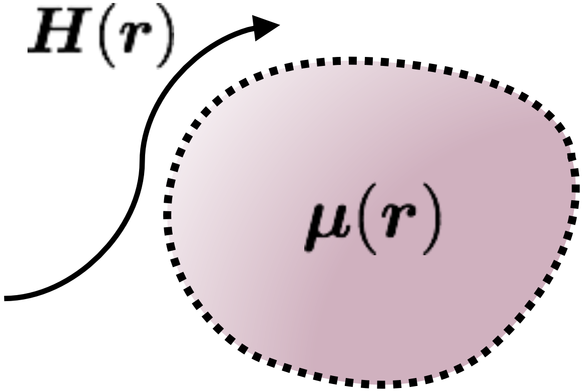
magnetization density

$$E_{\text{int}} = -\int \boldsymbol{\mu}(\boldsymbol{r}) \cdot \boldsymbol{H}(\boldsymbol{r})\, d^3\boldsymbol{r}$$

magnetic field



How does a magnetic material interact with a magnetic field?



In general, the interaction energy is

magnetization density

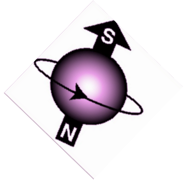
$$E_{\text{int}} = -\int \boldsymbol{\mu}(\boldsymbol{r})\cdot\boldsymbol{H}(\boldsymbol{r})\,d^3\boldsymbol{r}$$

magnetic field

and usually we write this as

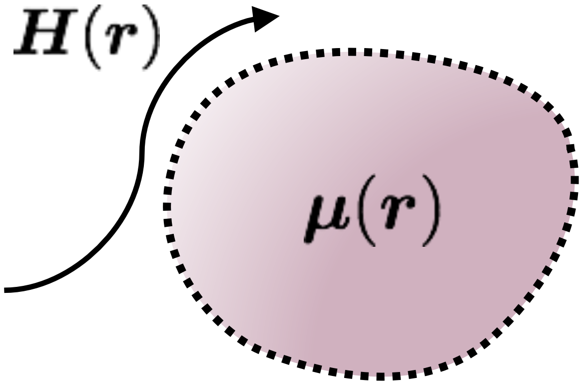
$$= -\int \boldsymbol{\mu}(\boldsymbol{r})\cdot\boldsymbol{H}(0)\,d^3\boldsymbol{r}$$
$$= -\boldsymbol{m}\cdot\boldsymbol{H}(0)$$

where $\boldsymbol{m} = \int \boldsymbol{\mu}(\boldsymbol{r})d^3\boldsymbol{r}$



is the magnetic dipole moment

How does a magnetic material interact with a magnetic field?



But we’ve ignored spatial variations in $\boldsymbol{H}$!

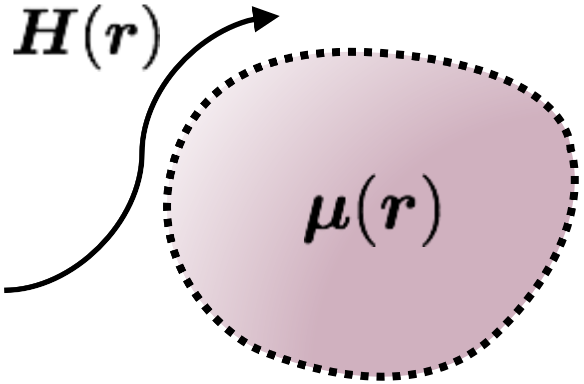
If they matter: make a multipole expansion for the interaction energy of a magnetization density with the magnetic field, in powers of the field gradient:

$$\begin{aligned} E_{\text{int}} &= -\int \boldsymbol{\mu}(\boldsymbol{r})\cdot\boldsymbol{H}(\boldsymbol{r})\,d^3\boldsymbol{r} \\ &= -\int \boldsymbol{\mu}(\boldsymbol{r})\cdot\boldsymbol{H}(0)\,d^3\boldsymbol{r} - \int r_i\mu_j(\boldsymbol{r})\partial_i H_j(0)\,d^3\boldsymbol{r} - \ldots \\ &= -\boldsymbol{m}\cdot\boldsymbol{H}(0) \end{aligned}$$

usual dipolar Zeeman term

extra terms in the interaction energy

What are the extra terms in the interaction energy?



$$\begin{aligned} E_{\text{int}} &= -\int \boldsymbol{\mu}(\boldsymbol{r}) \cdot \boldsymbol{H}(r)\, d^3\boldsymbol{r} \\ &= -\int \boldsymbol{\mu}(\boldsymbol{r}) \cdot \boldsymbol{H}(0)\, d^3\boldsymbol{r} - \int r_i \mu_j(\boldsymbol{r}) \partial_i H_j(0)\, d^3\boldsymbol{r} - \ldots \end{aligned}$$

a 9-component tensor

$$\mathcal{M}_{ij} = \int r_i \mu_j(\vec{r})\, d^3\vec{r}$$

the magnetoelectric multipole tensor

The $< \mu \otimes r >$ order can be described in terms of *magnetoelectric multipoles*

Convenient to decompose $\mathcal{M}_{ij} = \int r_i \mu_j(\vec{r})\, d^3\vec{r}$ into its irreducible parts:

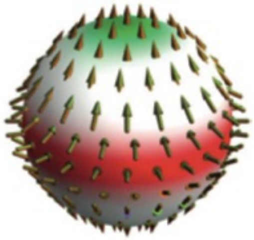
$$a = \frac{1}{3}\int \boldsymbol{r}\cdot\boldsymbol{\mu}(\boldsymbol{r})d^3\boldsymbol{r} \qquad \boldsymbol{t} = \frac{1}{2}\int \boldsymbol{r}\times\boldsymbol{\mu}(\boldsymbol{r})d^3\boldsymbol{r} \qquad q_{ij} = \frac{1}{2}\int\left[r_i\mu_j + r_j\mu_i - \frac{2}{3}\delta_{ij}\boldsymbol{r}\cdot\boldsymbol{\mu}(\boldsymbol{r})\right]d^3\boldsymbol{r}$$

magnetoelectric monopole moment

$$-a(\nabla\cdot\boldsymbol{H})_{\boldsymbol{r}=0}$$

magnetoelectric toroidal moment

$$-\boldsymbol{t}\cdot[\nabla\times\boldsymbol{H}]_{\boldsymbol{r}=0}$$



magnetoelectric quadrupole moment

$$-q_{ij}(\partial_i H_j + \partial_j H_i)_{\boldsymbol{r}=0}$$

N. A. Spaldin, M. Fechner, E. Bousquet, A. Balatsky and L. Nordström, PRB 88, 094429 (2013)

Outline

What properties do the magnetoelectric multipoles cause?

Can we directly measure them?

What next?

Outline

What properties do the magnetoelectric multipoles cause?

- Linear Magnetoelectric Effect
- Surface Magnetism

Can we directly measure them?

What next?

Property I: The linear magnetoelectric effect

$$\boxed{\begin{aligned} P_i &= \alpha_{ij} H_j \\ M_i &= \alpha_{ji} E_j \end{aligned}}$$

α is the magnetoelectric tensor

non-zero only in the absence of space-inversion and time-reversal symmetries

Property I: The linear magnetoelectric effect

$$\boxed{\begin{array}{l} P_i = \alpha_{ij} H_j \\ M_i = \alpha_{ji} E_j \end{array}}$$

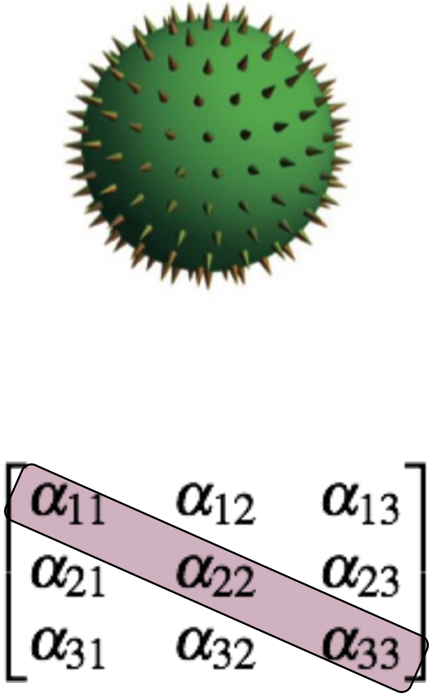
α is the magnetoelectric tensor

non-zero only in the absence of space-inversion and time-reversal symmetries

form of the tensor determined by structural and magnetic symmetry

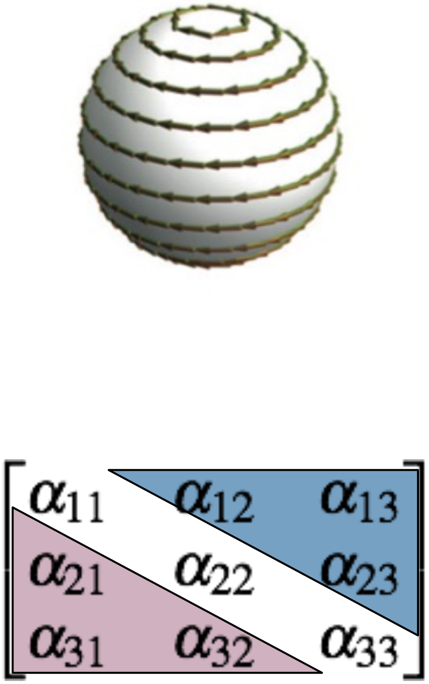
$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$$

By symmetry, when magnetoelectric multipoles exist, and order ferroically, the linear magnetoelectric tensor is non-zero (and vice versa)



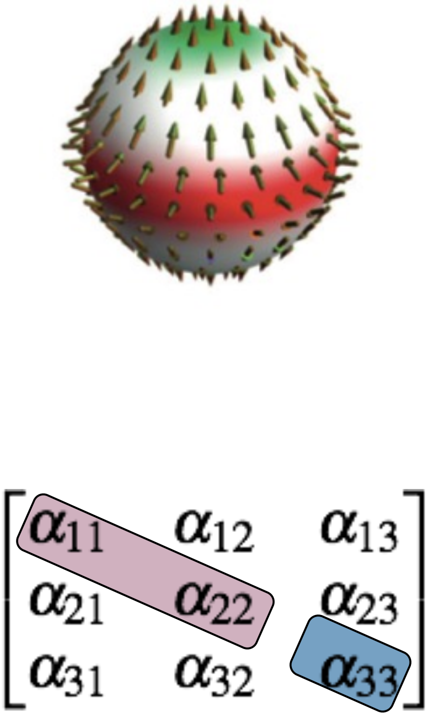
$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$$

isotropic, diagonal



$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$$

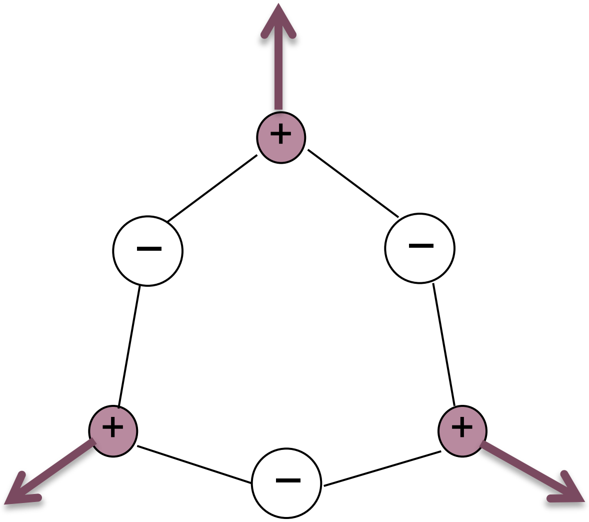
anti-symmetric, off-diagonal



$$\begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$$

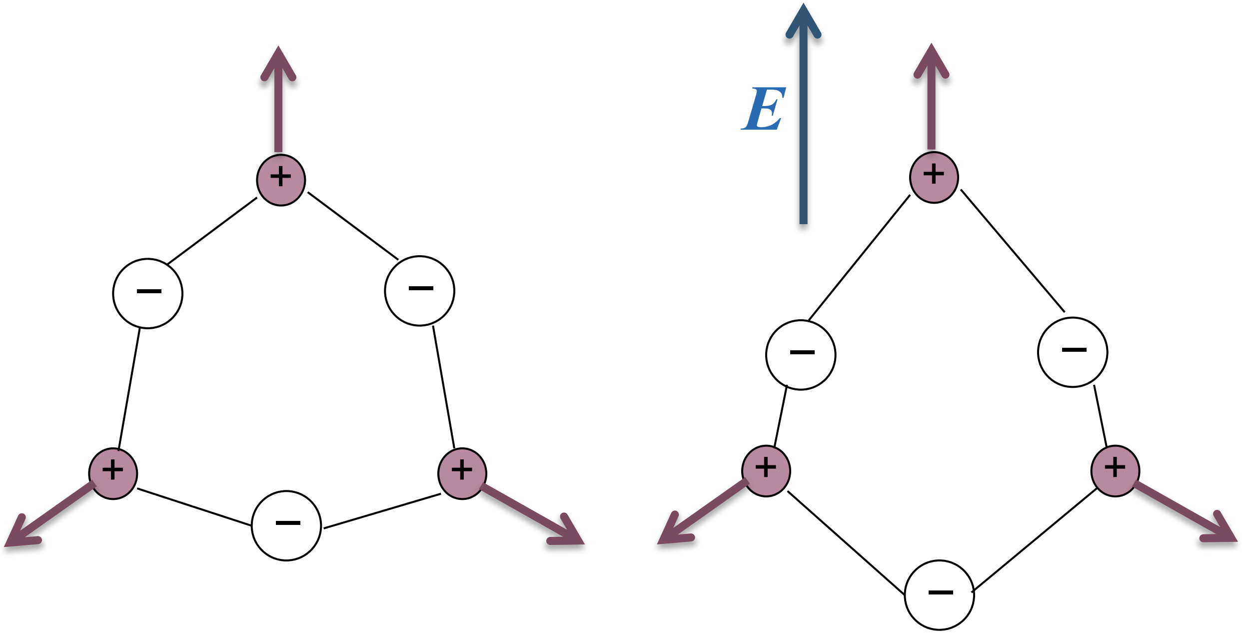
traceless

Possibly helpful cartoon connecting linear magnetoelectric effect and magnetoelectric monopole



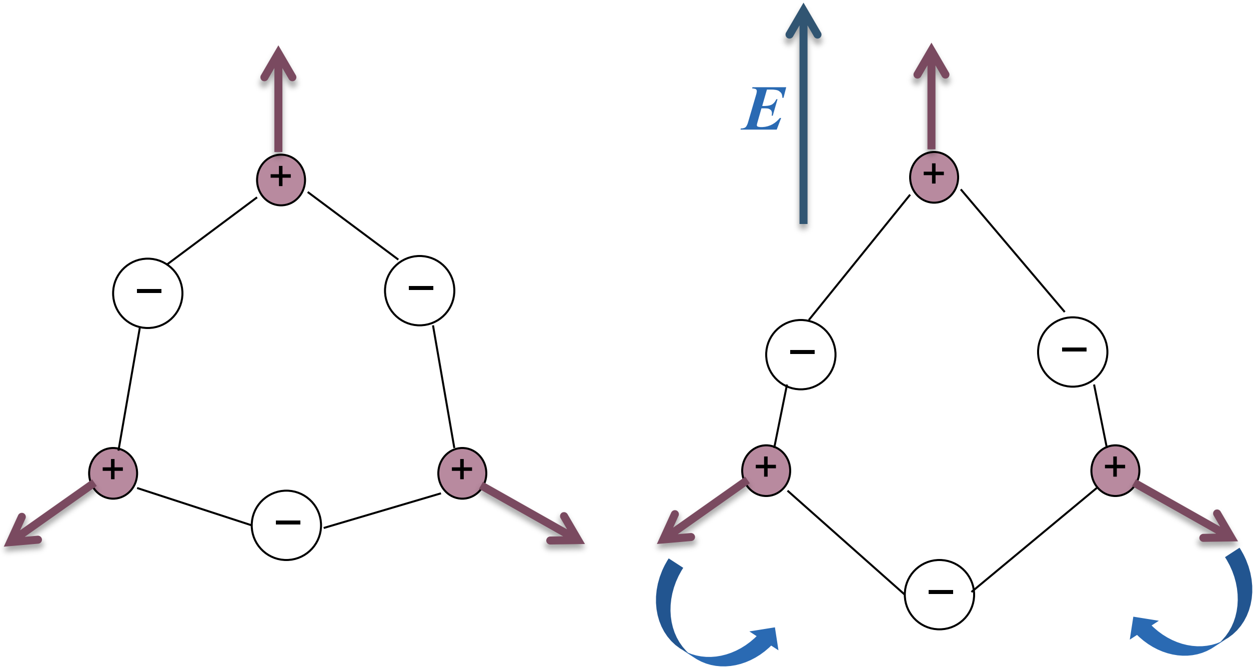
180^o TM-O-TM
interaction is AFM

Possibly helpful cartoon connecting linear magnetoelectric effect and magnetoelectric monopole



180º TM-O-TM interaction is AFM

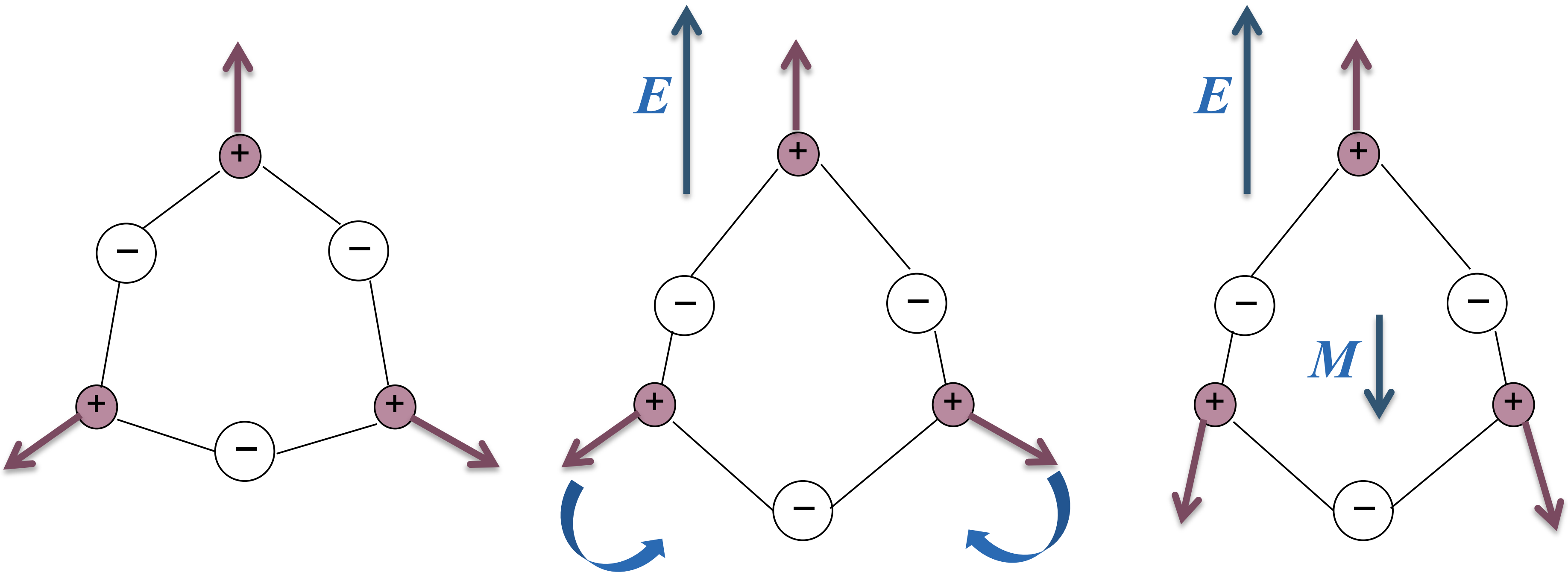
Possibly helpful cartoon connecting linear magnetoelectric effect and magnetoelectric monopole



180^{o} TM-O-TM
interaction is AFM

90^{o} TM-O-TM
interaction is FM

Possibly helpful cartoon connecting linear magnetoelectric effect and magnetoelectric monopole

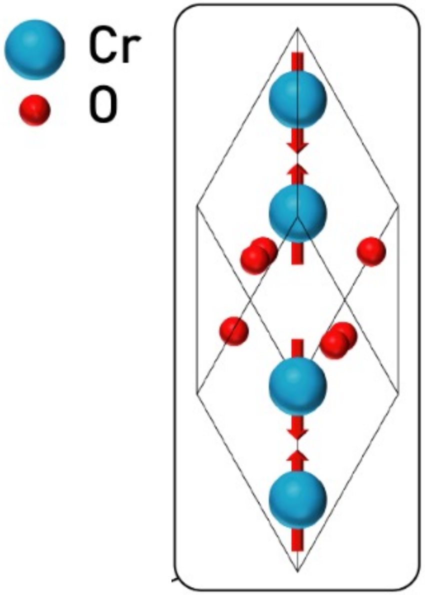


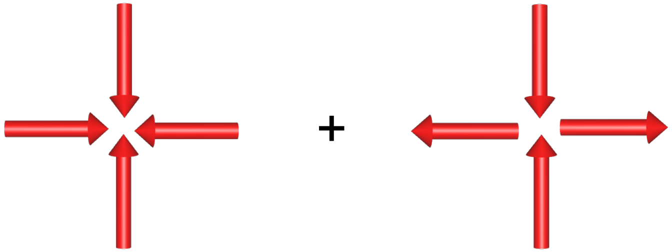
180° TM-O-TM
interaction is AFM

90° TM-O-TM
interaction is FM

diagonal
magnetoelectric
response!

An example: Cr_2O_3

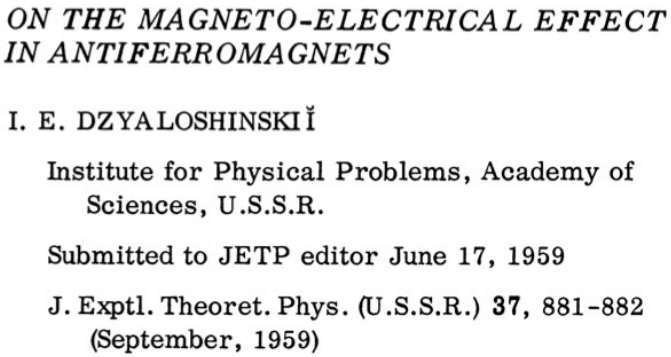




expect magnetoelectric monopole and z^2 quadrupole

$$\alpha = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix} + \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$$

First prediction and measurement of ME effect in Cr_2O_3



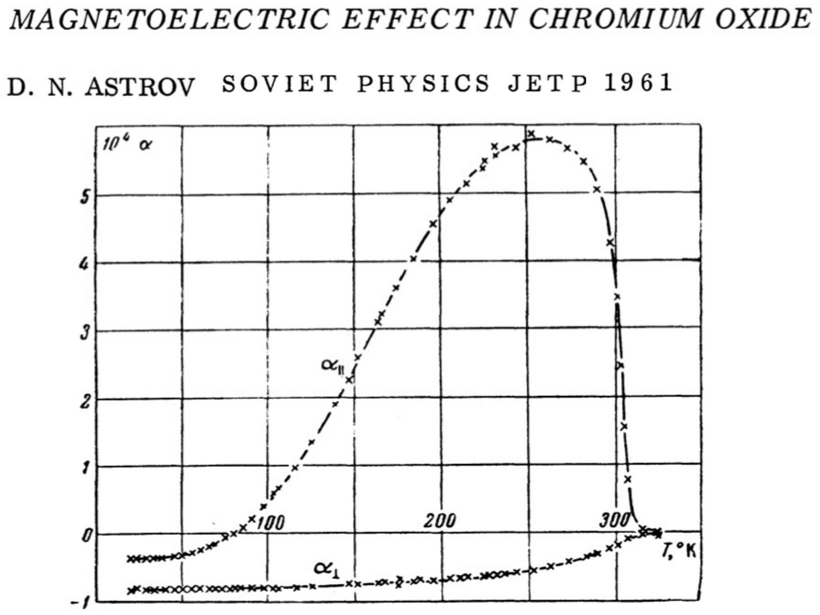
ON THE MAGNETO-ELECTRICAL EFFECT IN ANTIFERROMAGNETS

I. E. DZYALOSHINSKIĬ

Institute for Physical Problems, Academy of Sciences, U.S.S.R.

Submitted to JETP editor June 17, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **37**, 881-882 (September, 1959)



MAGNETOELECTRIC EFFECT IN CHROMIUM OXIDE

D. N. ASTROV SOVIET PHYSICS JETP 1961

FIG. 2

diagonal and uniaxial with $\alpha_{11} = \alpha_{22} \neq \alpha_{33}$

as expected:

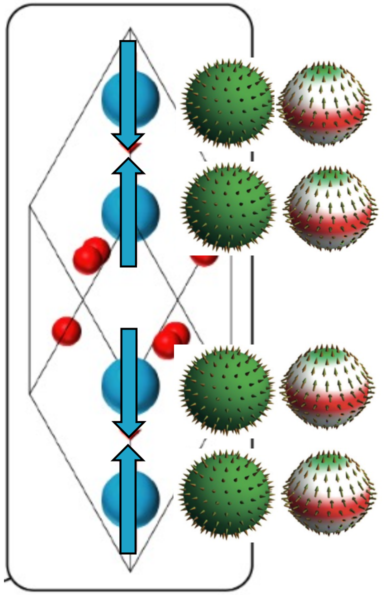
$$\alpha = \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix} + \begin{bmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{bmatrix}$$

Calculated magnetoelectric monopole / quadrupole in Cr_2O_3

Local moments at the atomic sites:

$$a = \frac{1}{3}\int \boldsymbol{r}\cdot\boldsymbol{\mu}(\boldsymbol{r})d^3\boldsymbol{r}$$

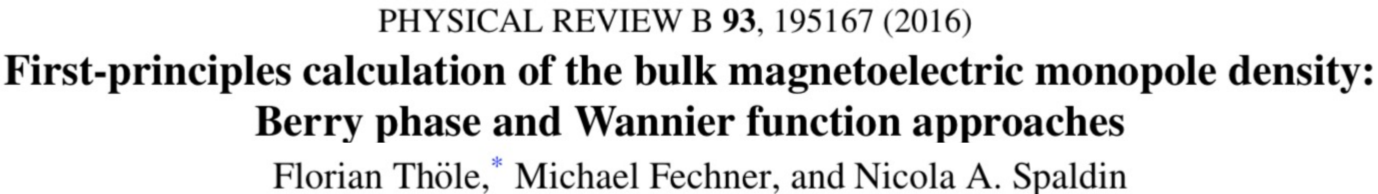
$$q_{ij} = \frac{1}{2}\int\left[r_i\mu_j + r_j\mu_i - \frac{2}{3}\delta_{ij}\boldsymbol{r}\cdot\boldsymbol{\mu}(\boldsymbol{r})\right]d^3\boldsymbol{r}$$



Calculate in sphere around the atom

All non-zero with the same sign (μ_B . nm)

“ferromonopolar” and “ferroquadrupolar” as expected



PHYSICAL REVIEW B **93**, 195167 (2016)

First-principles calculation of the bulk magnetoelectric monopole density: Berry phase and Wannier function approaches

Florian Thöle,[*] Michael Fechner, and Nicola A. Spaldin

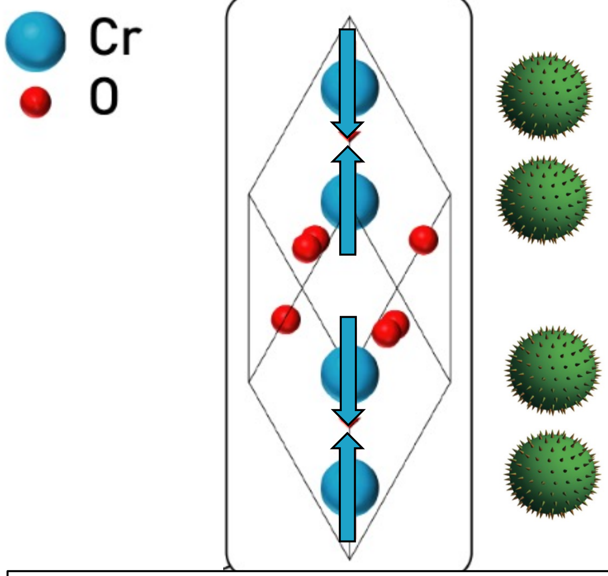
Aside: hidden *anti-ferro-mono/quadrupolar* order in Fe_2O_3

Hidden orders and (anti-)Magnetoelectric Effects in Cr_2O_3 and α-Fe_2O_3

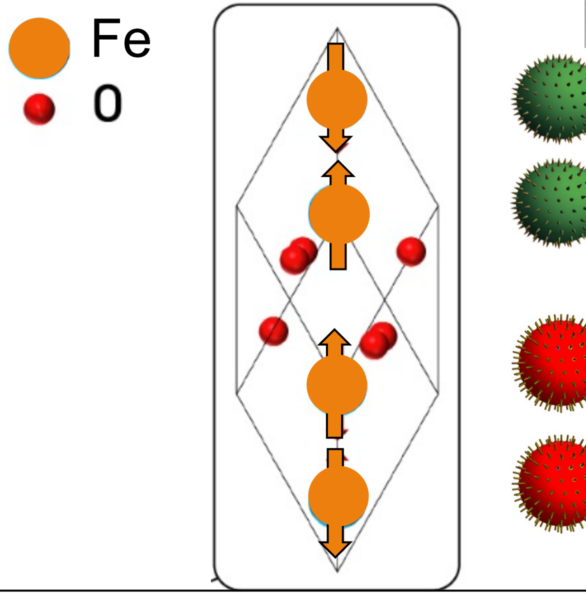
Xanthe H. Verbeek,* Andrea Urru, and Nicola A. Spaldin

arXiv:2303.00513

Cr_2O_3



Fe_2O_3



antiferromonopolar “hidden order”! (Bulk “Monopolization” is zero)

should manifest as a non-zone center magnetoelectric response

spatially varying electric field should induce homogeneous magnetization

pattern of antiferromonopolar order different from dipolar AFM order

Outline

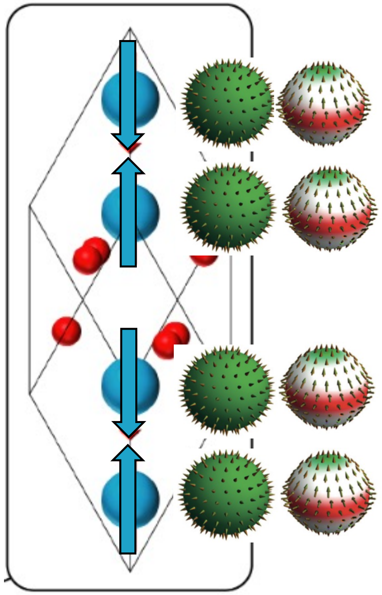
What are magnetoelectric multipoles?

Why are they interesting?

- Relationship to the magnetoelectric effect.
- Surface magnetism

Can they be measured? An example: Measuring the magnetoelectric monopole through its magnetoelectric response in Cr_2O_3

Calculated magnetoelectric monopole / quadrupole in Cr_2O_3

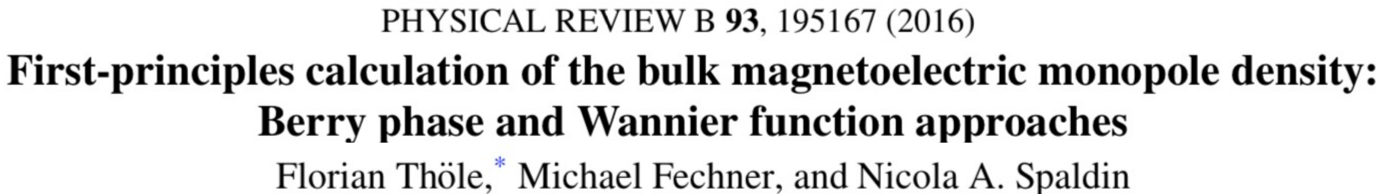


Local moments at the atomic sites: $a = \frac{1}{3}\int \boldsymbol{r}\cdot\boldsymbol{\mu}(\boldsymbol{r})d^3\boldsymbol{r}$

- Calculate in sphere around the atom
- All non-zero with the same sign (μ_B . nm)
- “ferromonopolar” and “ferroquadrupolar” as expected

Bulk “Monopolization” / “Quadrupolization” / ME Multipolization (monopole / quadrupole moment per unit volume):

- Berry phase calculation analogous to polarization
- (or cheat and sum over local dipole moment times position)
- Also non-zero consistent with linear ME response (μ_B / nm^2)



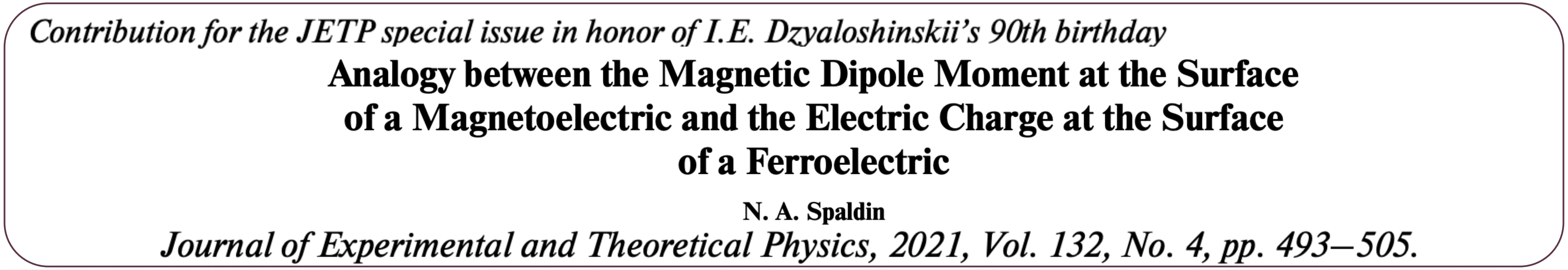
PHYSICAL REVIEW B **93**, 195167 (2016)

First-principles calculation of the bulk magnetoelectric monopole density: Berry phase and Wannier function approaches

Florian Thöle,* Michael Fechner, and Nicola A. Spaldin

Surface Magnetic Dipole Moment

BULK	SURFACE
Ferroelectric polarization	Electric charge
depends on ρ times r	
Magnetoelectric multipolization	Magnetic dipole
depends on μ times r	



Contribution for the JETP special issue in honor of I.E. Dzyaloshinskii's 90th birthday

Analogy between the Magnetic Dipole Moment at the Surface of a Magnetoelectric and the Electric Charge at the Surface of a Ferroelectric

N. A. Spaldin

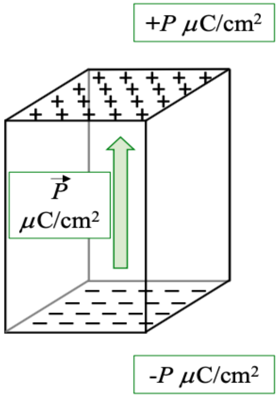
Journal of Experimental and Theoretical Physics, 2021, Vol. 132, No. 4, pp. 493–505.

Property II. The bulk magnetoelectric multipolization leads to a surface magnetic dipole mom

BULK

Ferroelectric polarization

depends on ρ times r

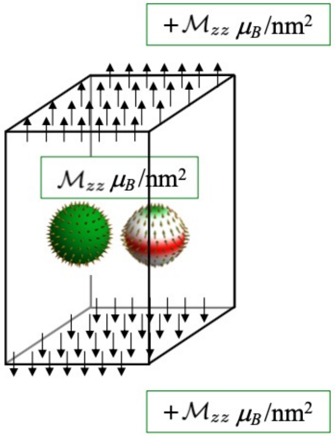


SURFACE

Electric charge, ρ

Magnetoelectric multipolization

depends on μ times r



Magnetic dipole, μ

Contribution for the JETP special issue in honor of I.E. Dz

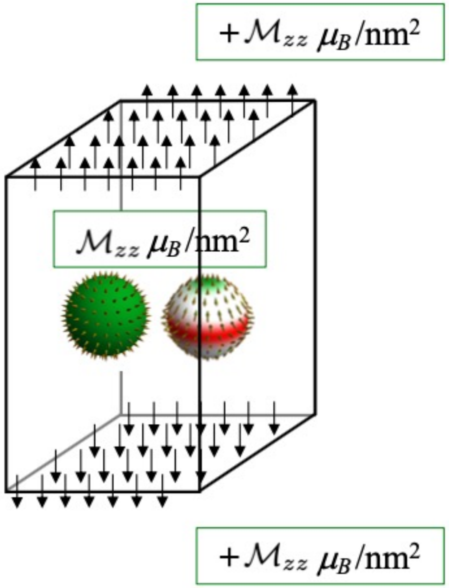
Analogy between the Magnetic Surface
of a Magnetoelectric and the Electric Charge at the Surface
of a Ferroelectric

N. A. Spaldin

Journal of Experimental and Theoretical Physics, 2021, Vol. 132, No. 4, pp. 493–505.

Property II. Intrinsic surface magnetization in Cr_2O_3

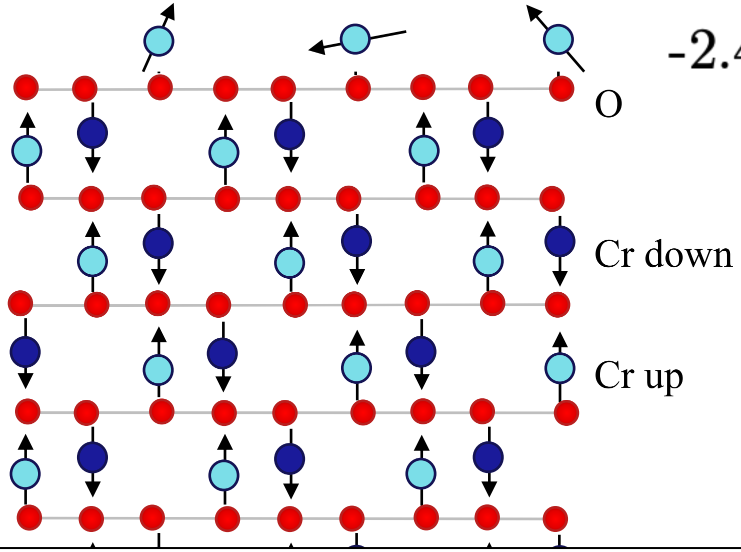
There is an intrinsic surface magnetization associated with the magnetoelectric multipoles in a magnetoelectric antiferromagnet

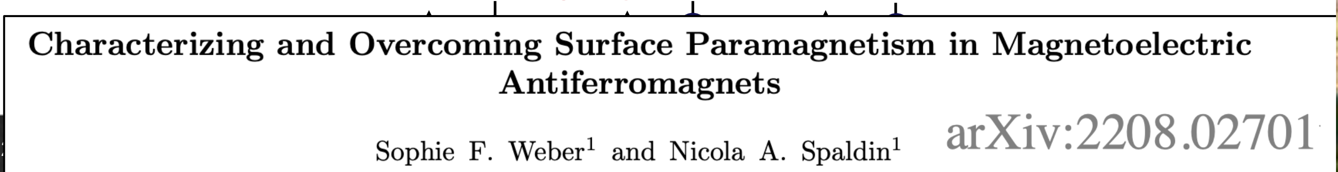


Predict for (001) Cr_2O_3:

Surface magnetization = $+12.0\ \mu_B/\mathrm{nm}^2$

$-2.4\ \mu_B/\mathrm{nm}^2$





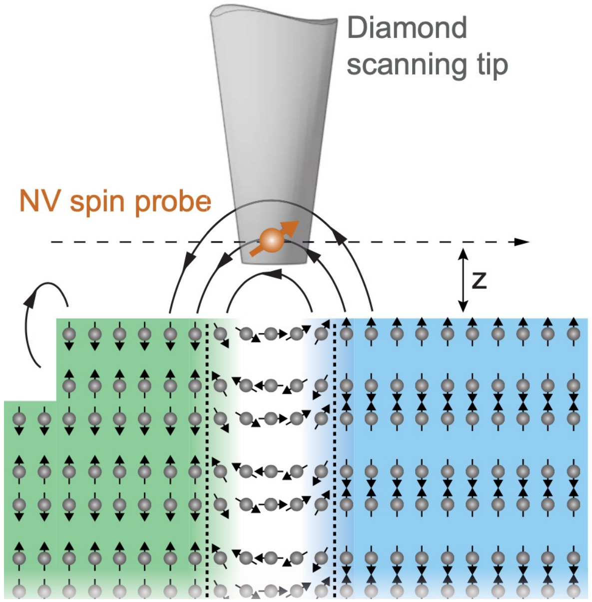
Characterizing and Overcoming Surface Paramagnetism in Magnetoelectric Antiferromagnets

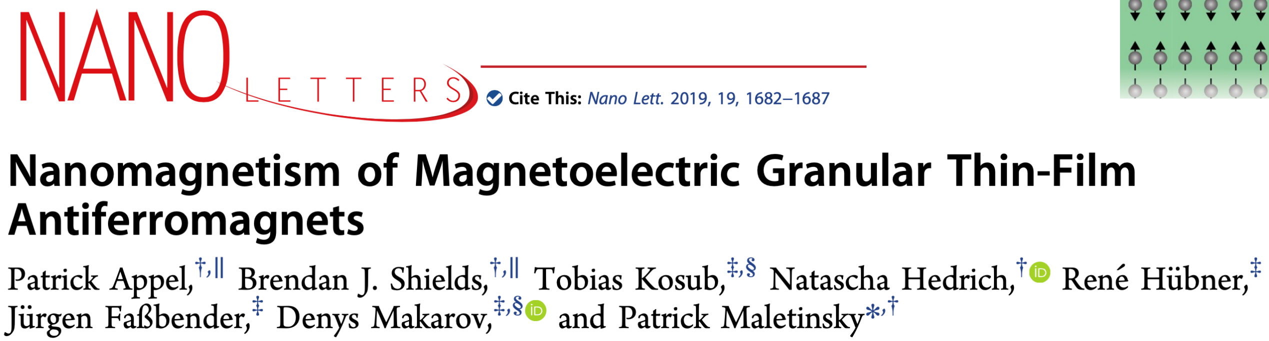
Sophie F. Weber[1] and Nicola A. Spaldin[1]

arXiv:2208.02701

Measurement of intrinsic surface magnetization

Predicted value of -2.4 μ_B/nm^2 very close to value measured using Nv magnetometry!



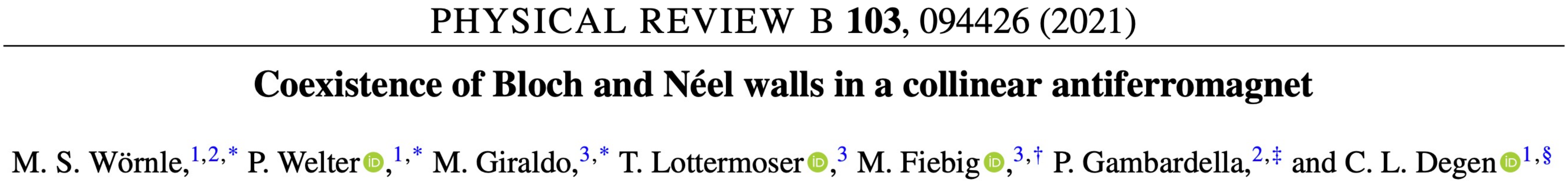


NANO LETTERS

Cite This: *Nano Lett.* 2019, 19, 1682–1687

Nanomagnetism of Magnetoelectric Granular Thin-Film Antiferromagnets

Patrick Appel,[†,‖] Brendan J. Shields,[†,‖] Tobias Kosub,[‡,§] Natascha Hedrich,[†] René Hübner,[‡] Jürgen Faßbender,[‡] Denys Makarov,[‡,§] and Patrick Maletinsky[*,†]



PHYSICAL REVIEW B **103**, 094426 (2021)

Coexistence of Bloch and Néel walls in a collinear antiferromagnet

M. S. Wörnle,[1,2,*] P. Welter,[1,*] M. Giraldo,[3,*] T. Lottermoser,[3] M. Fiebig,[3,†] P. Gambardella,[2,‡] and C. L. Degen[1,§]

Outline

What properties do the magnetoelectric multipoles cause?

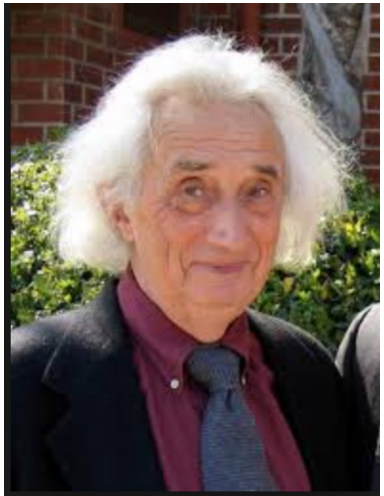
Can we directly measure them?

What next?

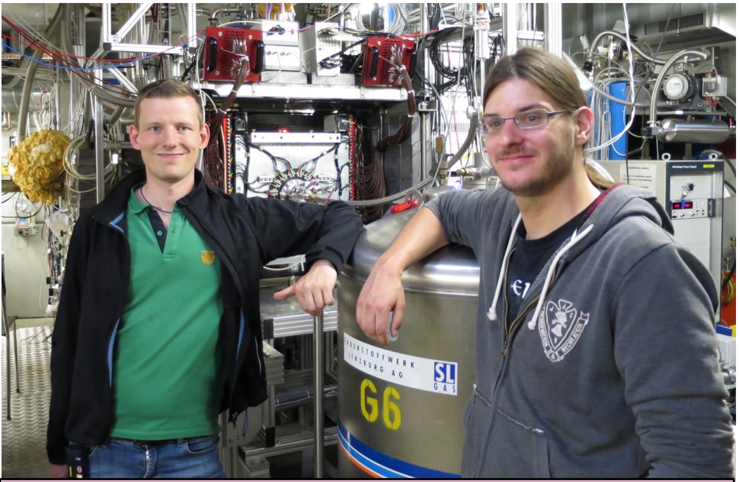
Ongoing: Spherical neutron polarimetry, with Andrea Urru, Henrik Ronnow et al.

Compton scattering, with Sayantika Bhowal, Urs Staub, Steve Collins et al.

An attempt to measure the magnetoelectric monopole with muons

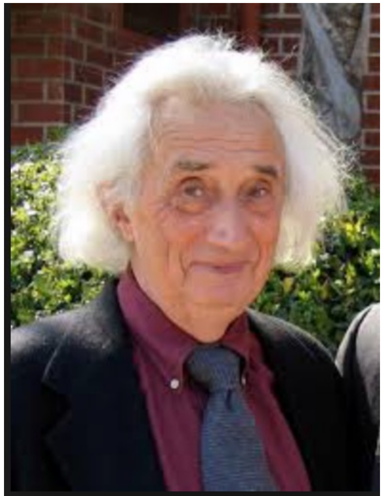


Igor Dzyaloshinskii

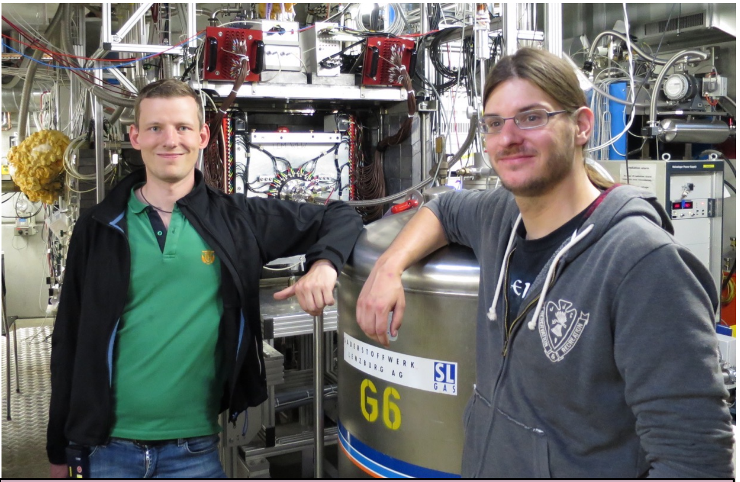


Michael Fechner and Quintin Meier

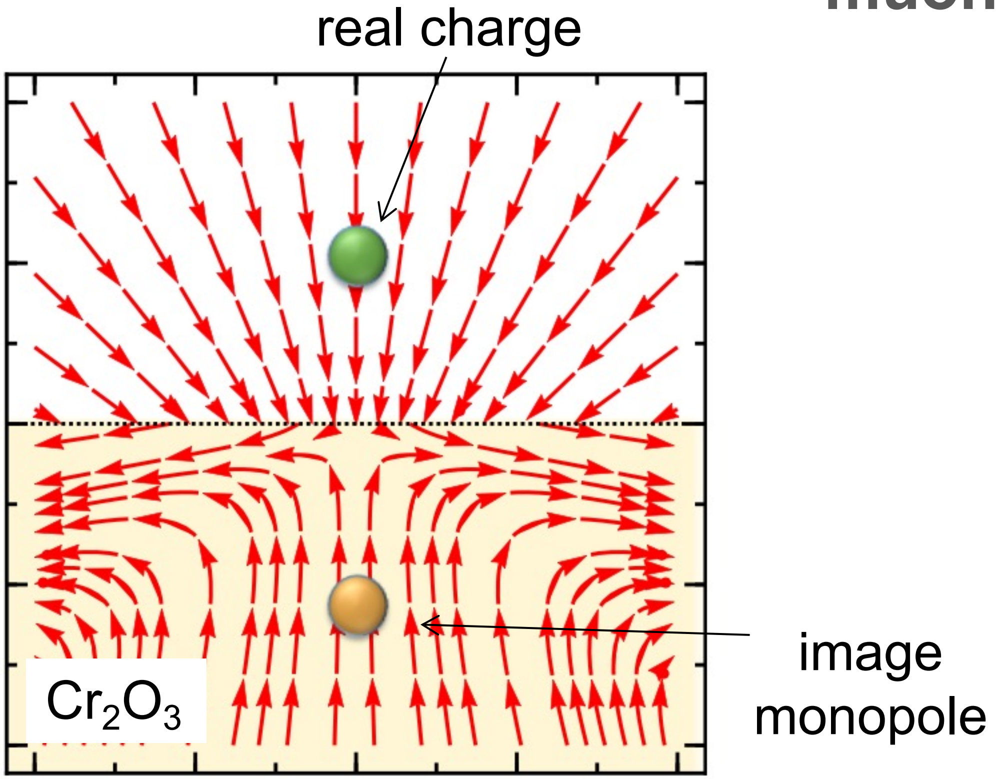
An attempt to measure the magnetoelectric monopole with muons



Igor Dzyaloshinskii



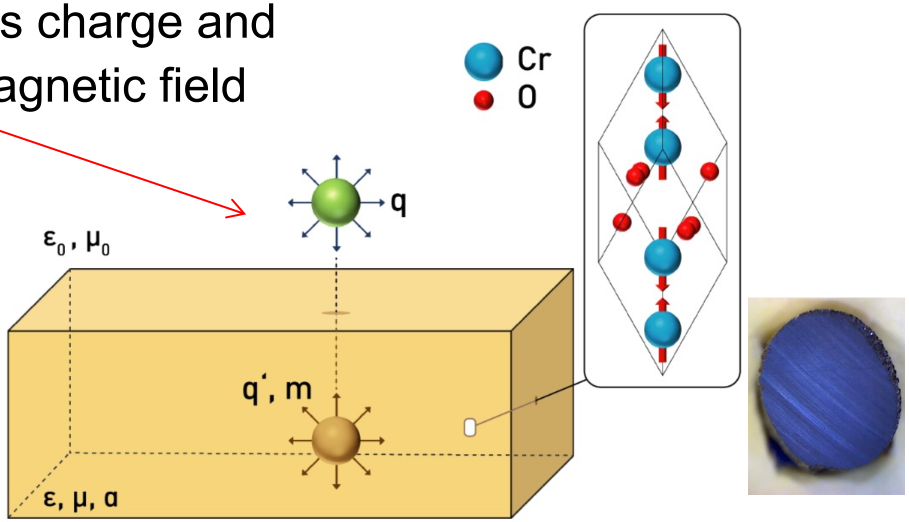
Michael Fechner and Quintin Meier



Charge on the surface induces image monopole in Cr_2O_3 and “monopolar” external field

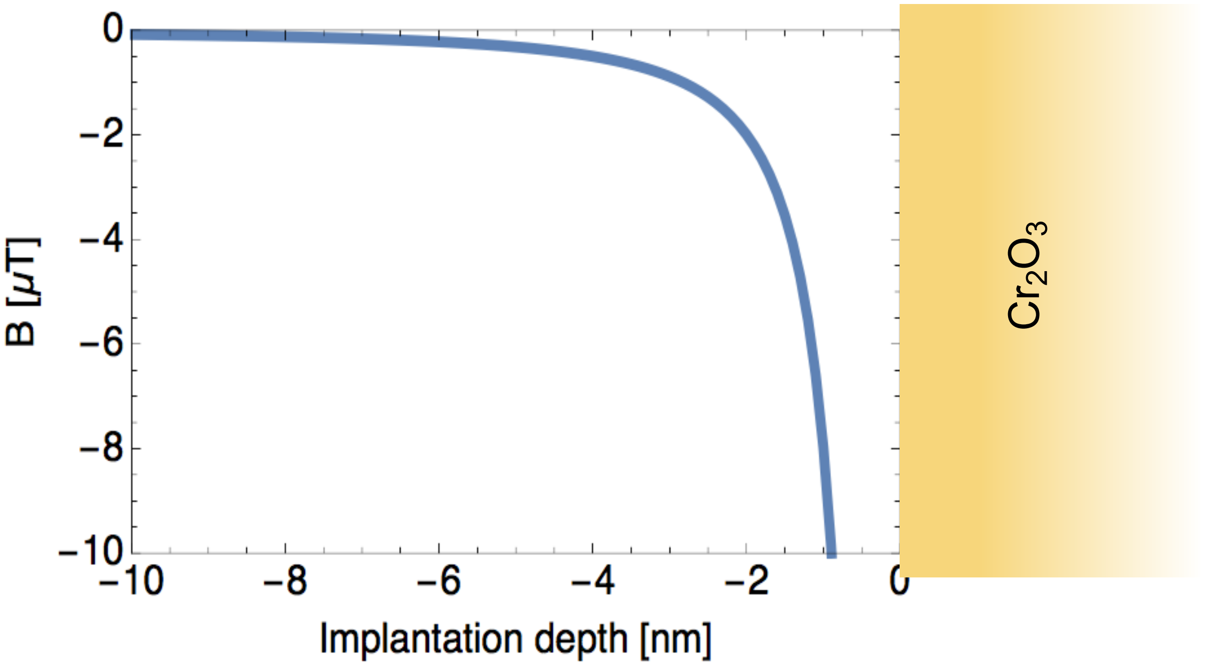
Try to detect using muon spin resonance

muon both provides charge and
detects induced magnetic field



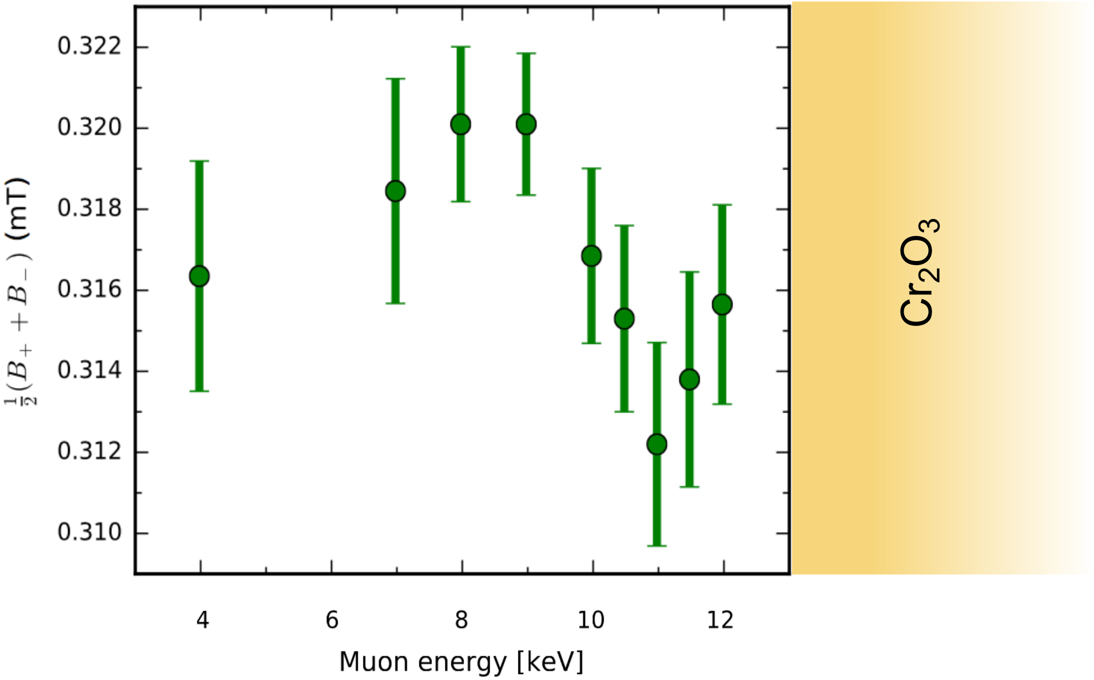
Hubertus Luetkens

Calculated field strength at charge +e above Cr_2O_3 surface



Q. Meier et al., *Search for the magnetic monopole at a magnetoelectric surface*, PRX **9**, 011011 (2019)

Did we find the monopolar field?



Measured local fields in solid N_2 layer above Cr_2O_3 are *not inconsistent* with the existence of the monopole

Q. Meier et al., *Search for the magnetic monopole at a magnetoelectric surface,* PRX **9**, 011011 (2019)

Outline

What properties do the magnetoelectric multipoles cause?

Can we directly measure them?

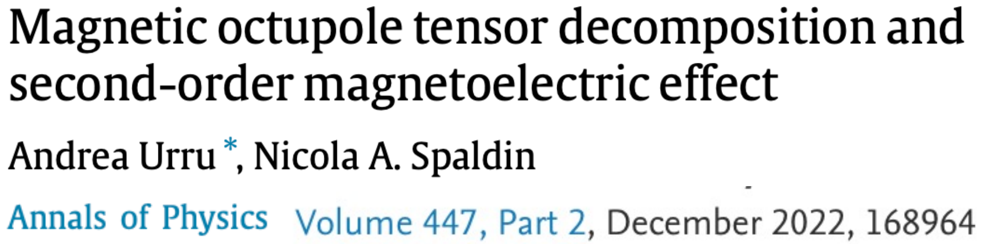
What next?

Well, we can keep expanding in our multipole expansion...

Continuing to the next term in the multipole expansion:

$$
\begin{aligned}
E_{\text{int}} &= -\int \boldsymbol{\mu}(\boldsymbol{r}) \cdot \boldsymbol{H}(r)\, d^3\boldsymbol{r} \\
&= -\int \boldsymbol{\mu}(\boldsymbol{r}) \cdot \boldsymbol{H}(0)\, d^3\boldsymbol{r} - \int r_i \mu_j(\boldsymbol{r}) \partial_i H_j(0)\, d^3\boldsymbol{r} - \\
&\qquad - \int \mu_i(\mathbf{r}) r_j r_k \partial_j \partial_k H_i(0)\, d^3\mathbf{r}
\end{aligned}
$$

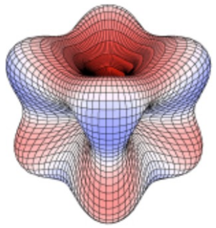
“r” appears twice!!



Magnetic octupole tensor decomposition and second-order magnetoelectric effect

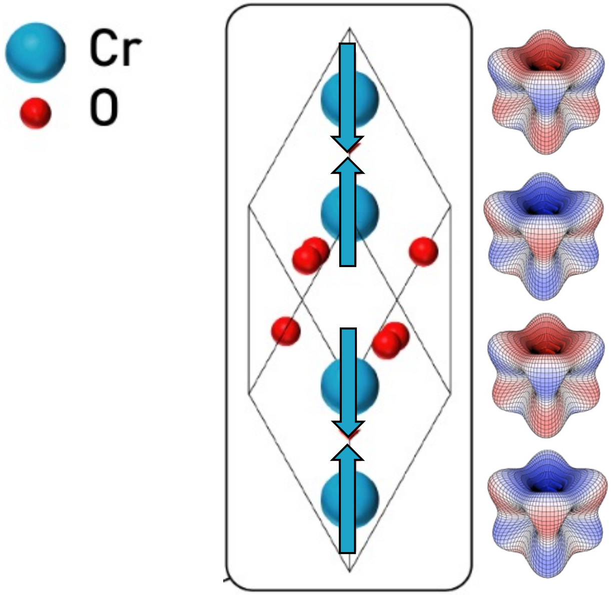
Andrea Urru *, Nicola A. Spaldin

Annals of Physics Volume 447, Part 2, December 2022, 168964

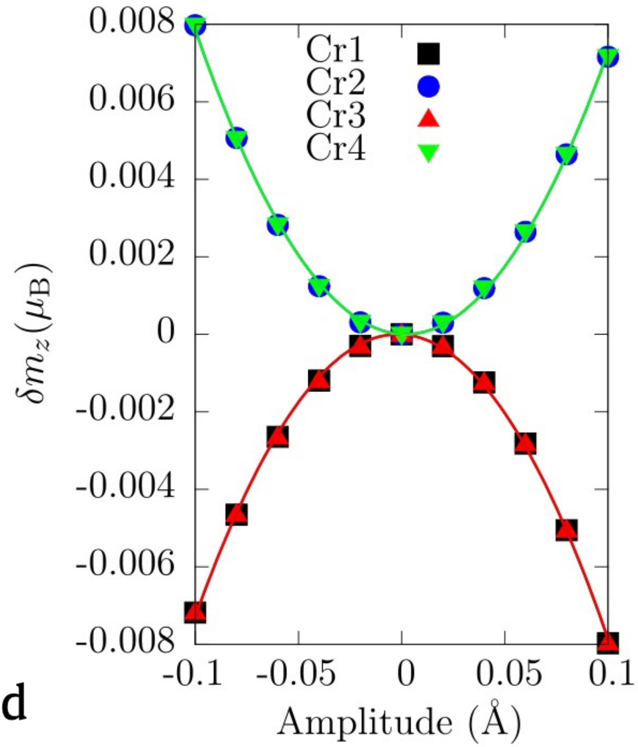


Cr_2O_3 has hidden *anti-ferro-magnetooctupolar* order

Cr_2O_3



leads to “hidden” quadratic anti-magnetoelectric response:



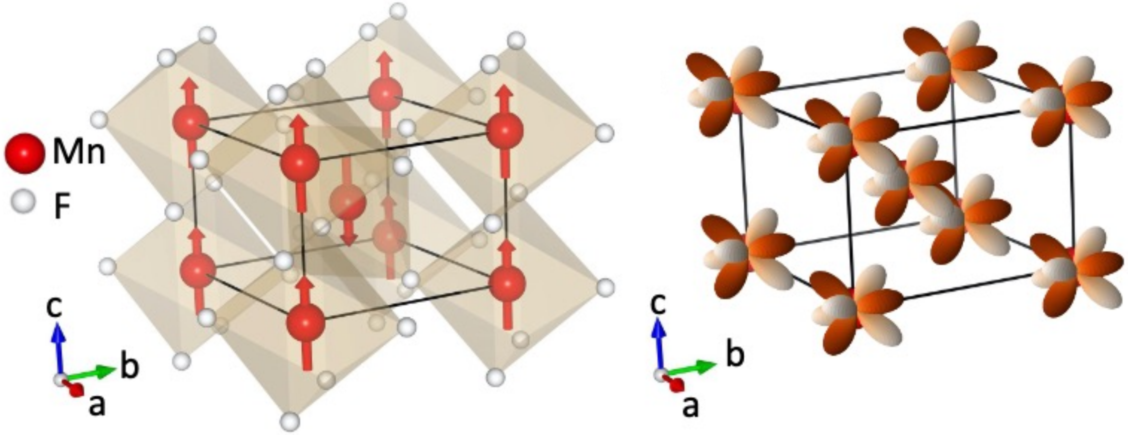
Magnetic octupole tensor decomposition and second-order magnetoelectric effect

Andrea Urru *, Nicola A. Spaldin

Annals of Physics Volume 447, Part 2, December 2022, 168964

Ferro-magneto-octupolar materials exist

An example: MnF_2



S. Bhowal and N. A. Spaldin, arXiv:2212.0375

What is special about ferro-magneto-octupolar materials?

An example: MnF_2

centrosymmetric

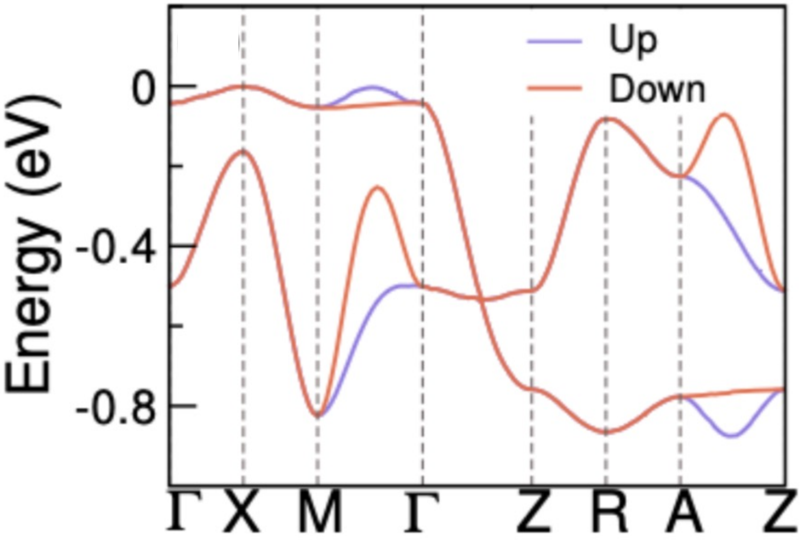
time-reversal symmetry broken even though dipoles order AFM

quadratic magnetoelectric effect

piezomagnetic

non-relativistic spin splitting

magnetic Compton profile



S. Bhowal and N. A. Spaldin, arXiv:2212.0375

Summary and Open Questions

In non-centrosymmetric antiferromagnets, the magnetoelectric multipoles form a kind of “hidden multiferroic order”

What do the magnetoelectric multipoles do?
- Magnetoelectric response
- Intrinsic surface magnetization

Can they be measured?
- N_V magnetometry?
- Muon spin resonance?
- Neutron scattering?
- Compton scattering?

Körber Stiftung
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CSCS Centro Svizzero di Calcolo Scientifico Swiss National Supercomputing Centre
ETH zürich
JOACHIM HERZ STIFTUNG
Swiss National Science Foundation

Got a centrosymmetric AFM? Then look for ferroic magnetic octupoles!

(Top secret: magnetic hexadecapoles are looking interesting too...)