# Oxide magnetoelectrics

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L. E. Hueso[5], L. C. Phillips[1], W. Yan[1], P. Martins[6], M. E. Vickers[1],
S. Lanceros-Mendez[6], S. S. Dhesi[3] and N. D. Mathur[1]

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[3]Diamond Light Source, Didcot
[4]Institute of Magnetism, Kyiv
[5]CIC nanoGUNE Consolider, San Sebastián
[6]BCmaterials, Bilbao

**Financial support:** THE ROYAL SOCIETY, EPSRC, erc

# Oxide magnetoelectrics

Background

Strain-control of local magnetism in manganite films

$La_{0.67}Sr_{0.33}MnO_3/BaTiO_3$

$La_{0.7}Ca_{0.3}MnO_3/BaTiO_3$

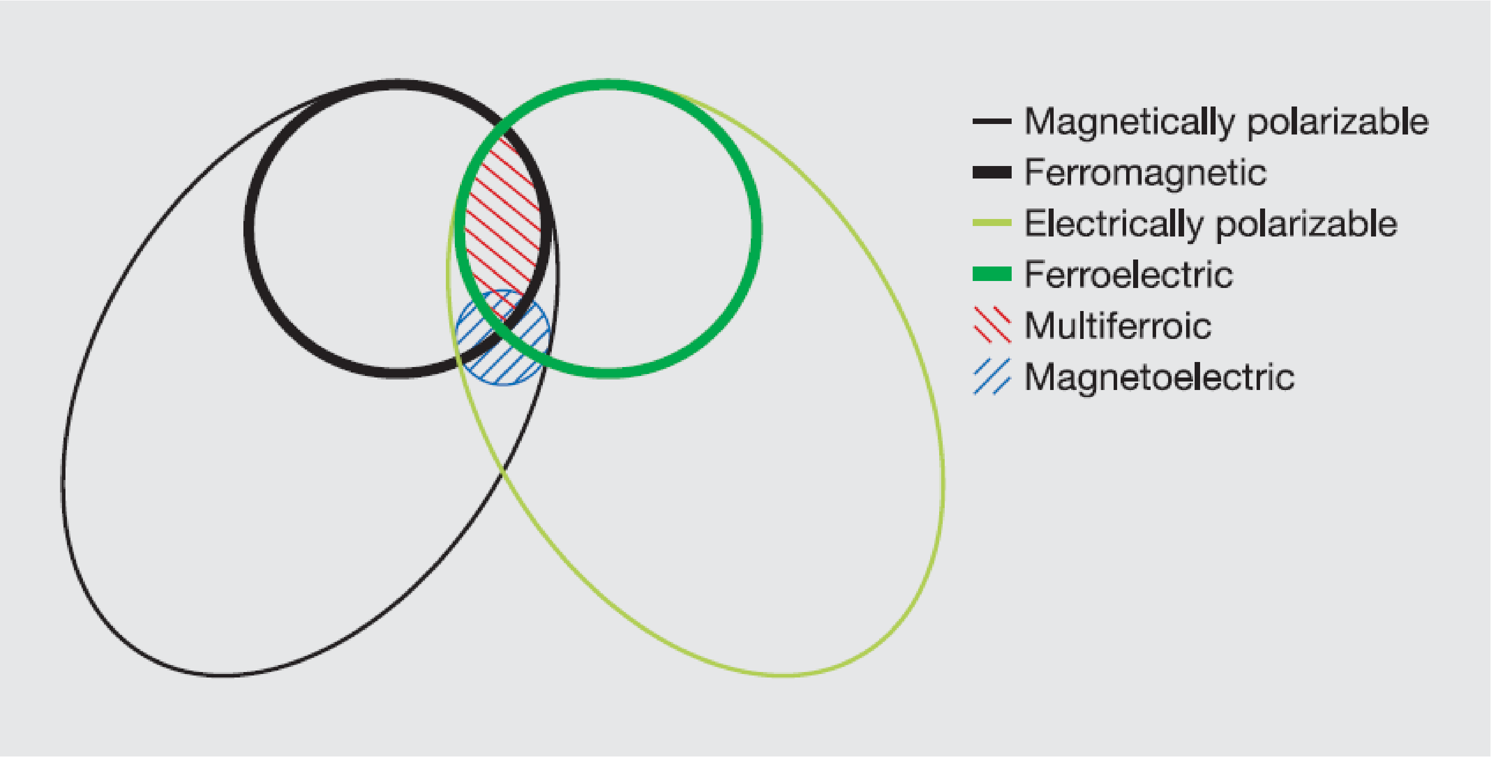
Strain-control of local magnetism in Ni films

$Ni/BaTiO_3$

$Ni/Pb(Mg_{1/3}Nb_{2/3})_{0.68}Ti_{0.32}O_3$

An electrocaloric diversion

# Multiferroic and magnetoelectric (ME) materials




W. Eerenstein *et al.* *Nature* **442**, 759 (2006)

**Direct ME effect:** *H* control of polarisation *P*

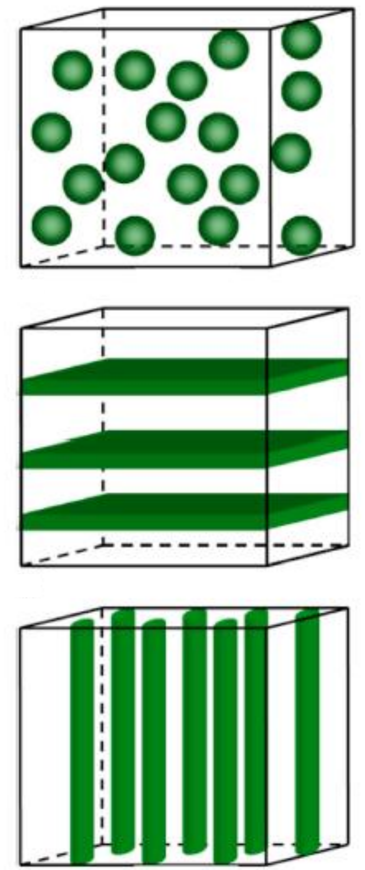
**Converse ME effect:** *E* control of magnetisation *M*

# Direct ME heterostructures

**Useful for energy efficient magnetic field sensors**

**Strain coupling**

- 0-3 composites
- 2-2 composites
- 1-3 composites

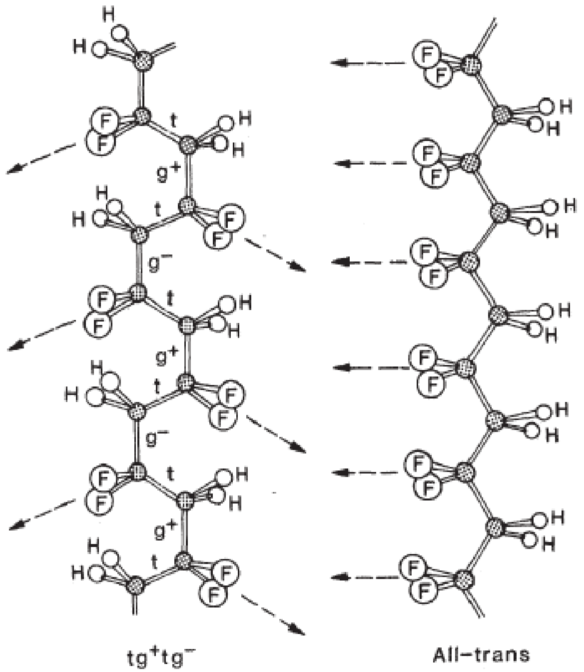


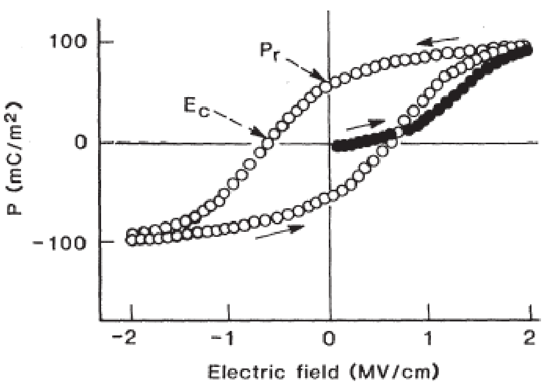
**ME coefficient $\alpha = \Delta P/\Delta H$**

C. W. Nan *et al.*, JAP **103**, 031101 (2008)

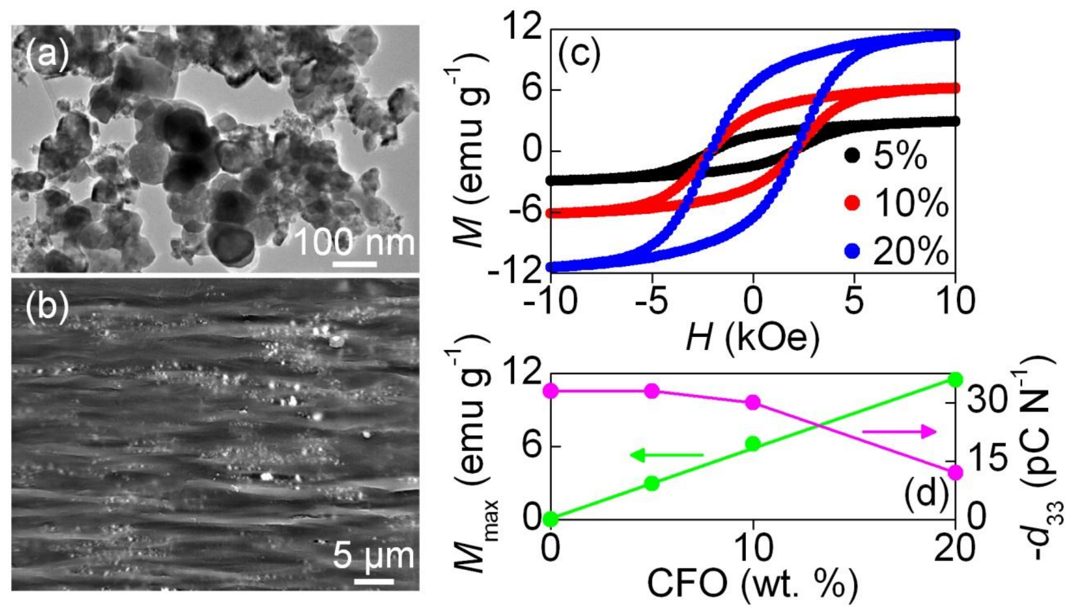
# Direct ME effects in $CoFe_2O_4$/PVDF composites

**polyvinylidene fluoride (PVDF)**




**0-3 ME composite**

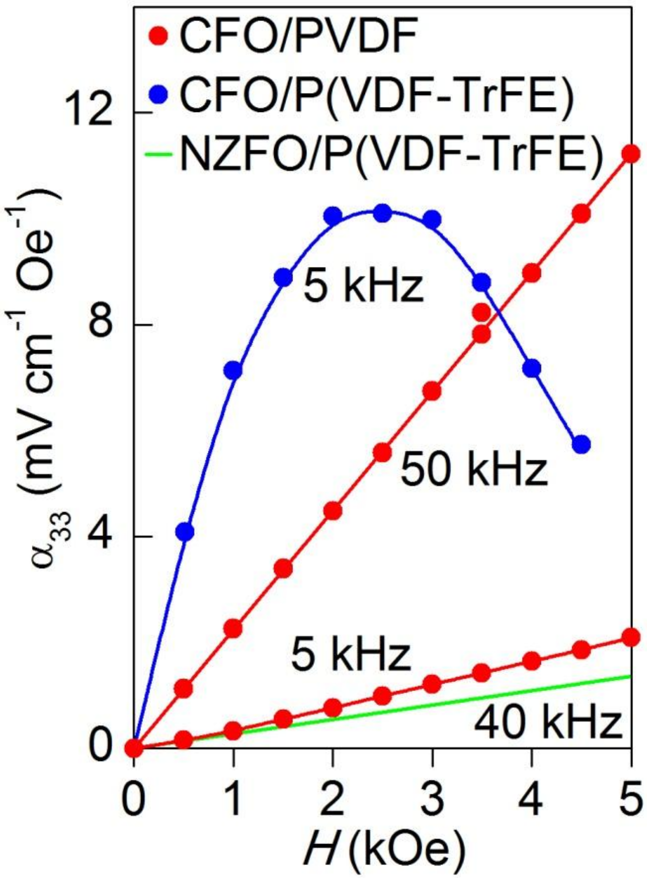



P. Martins *et al.*, JPhysD **44,** 482001 (2011)

P. Martins *et al.*, *J. Nanopart . Res.***15**, 1825 (2013)

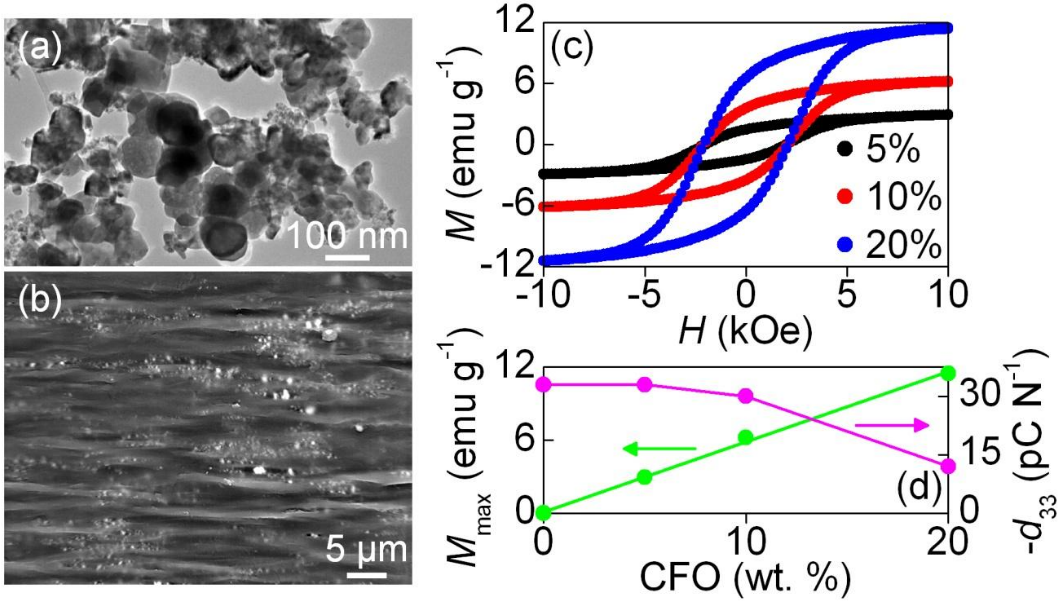
A. J. Lovinger, *Science* **220,** 1115 (1983)

# Direct ME effects in $CoFe_2O_4$/PVDF composites




**Large ME coefficients**

**0-3 ME composite**




P. Martins *et al.*, JPhysD **44,** 482001 (2011)

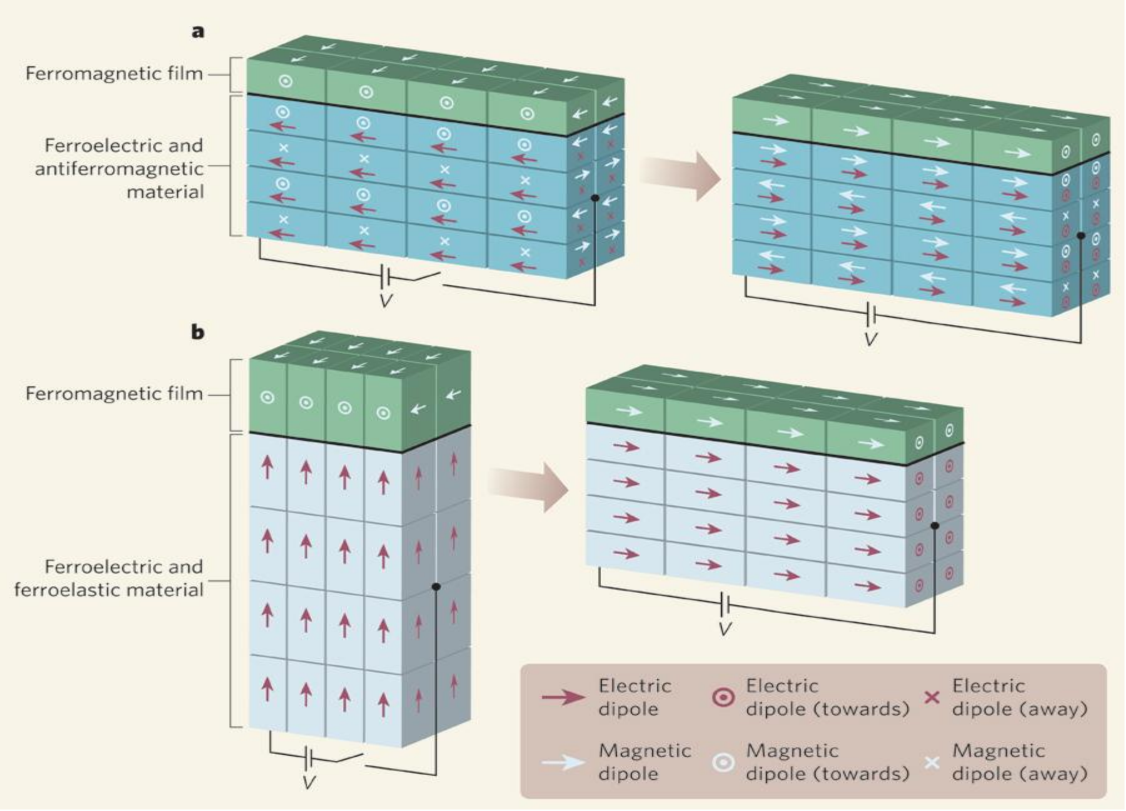
P. Martins *et al.*, *J. Nanopart . Res.***15**, 1825 (2013)

# Converse ME heterostructures

**Useful for energy efficient data storage**

Exchange coupling

Strain coupling

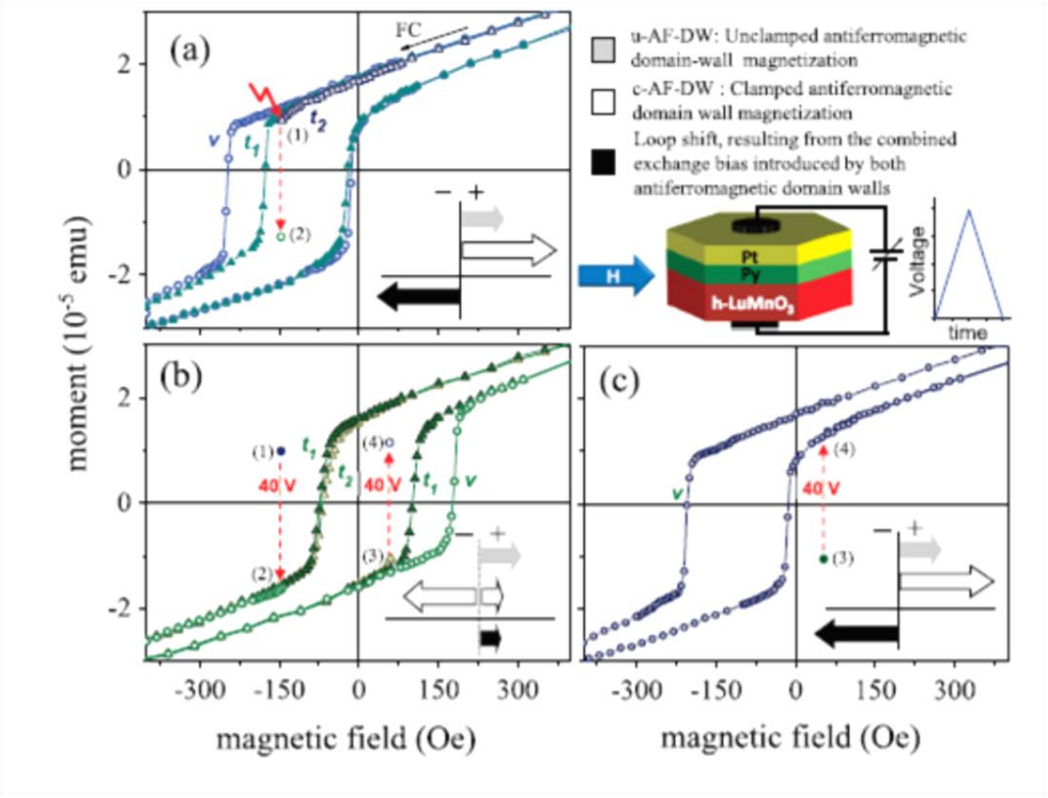



N. D. Mathur, *Nature* **591**, 454 (2008)

**ME coefficient $\alpha = \mu_0 \Delta M / \Delta E$**

# Exchange-coupling-mediated converse ME effects in Py

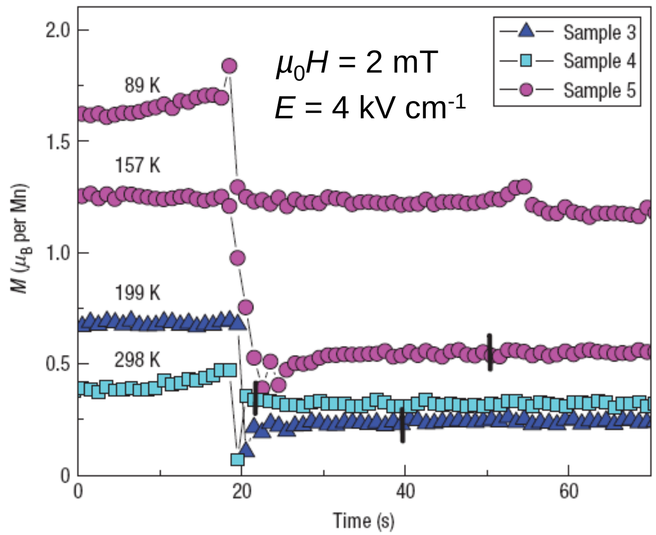
## Exchange bias in Py/$LuMnO_3$




V. Skumryev et al., *Phys. Rev. Lett.*, **106**, 057206 (2011)

# Strain-mediated converse ME effects in oxides

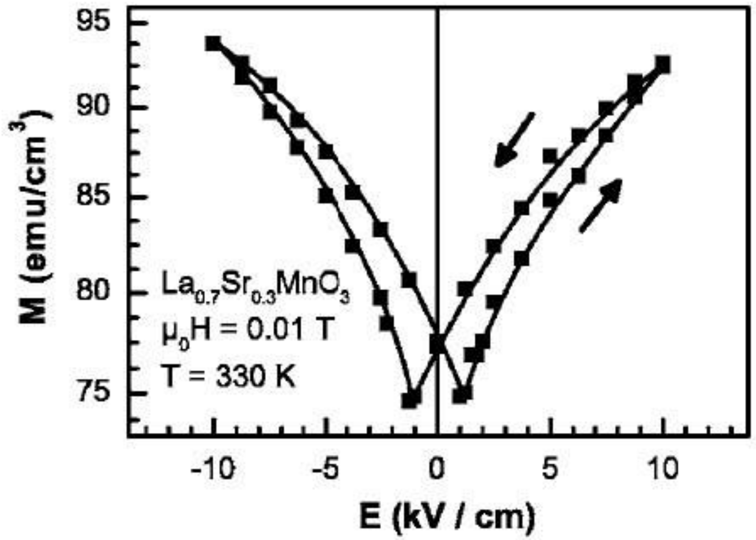
$La_{0.67}Sr_{0.33}MnO_3/BaTiO_3$




W. Eerenstein *et al., Nature Materials* **6**, 348 (2007)

**Sharp and persistent ME**

$La_{0.7}Sr_{0.3}MnO_3/Pb(Mg_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O_3$

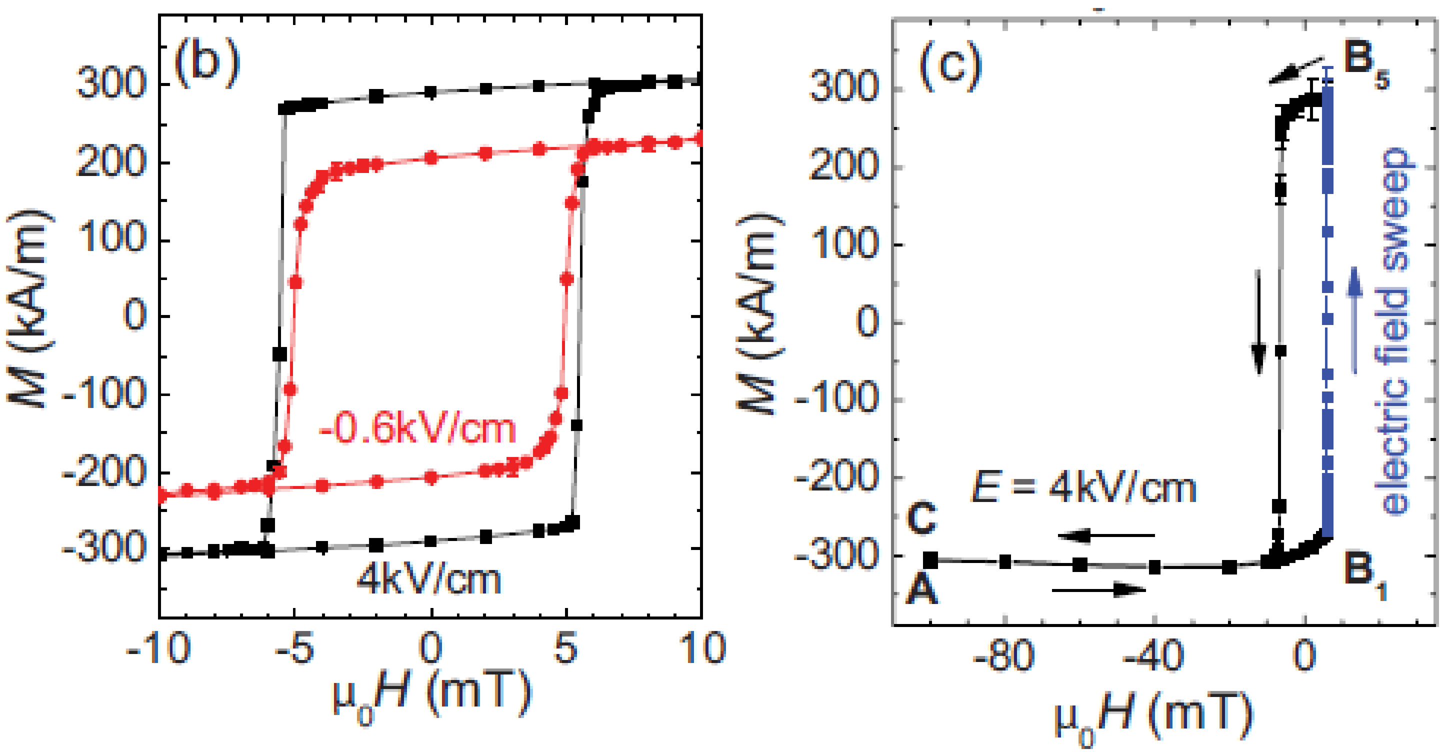



C. Thiele *et al.*, *Phys. Rev. B* **75**, 054408 (2007)

**Continuous and reversible ME**

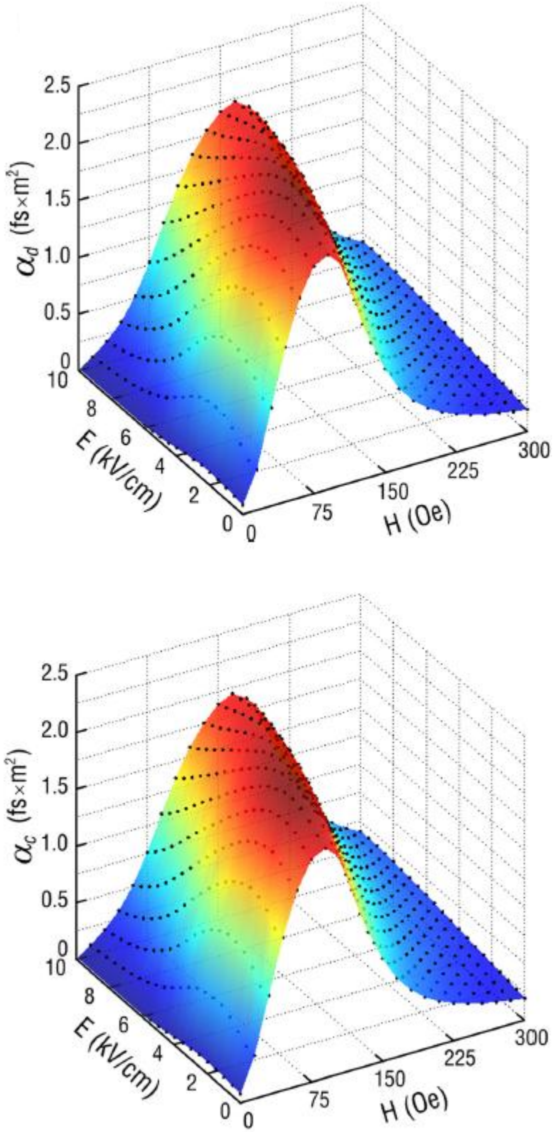
# Strain-mediated converse ME effects in Ni

**Strain in Ni/BTO**

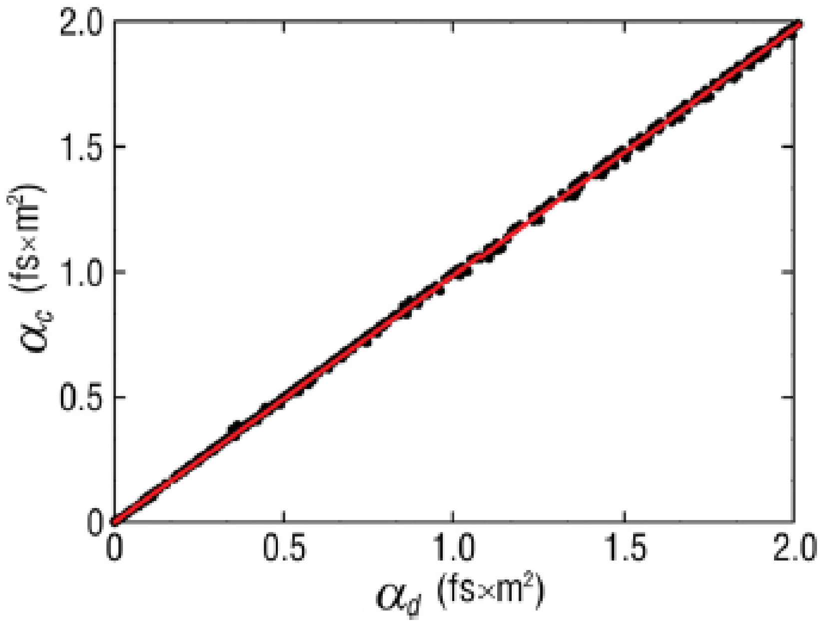



S. Geprägs *et al.*, *Appl. Phys. Lett.* **96**,142509 (2010)

# Direct and converse ME coefficients are equivalent




$Fe_{82}Ga_{18}/Pb(Zn_{1/3}Nb_{2/3})_{0.93}Ti_{0.07}O_3$

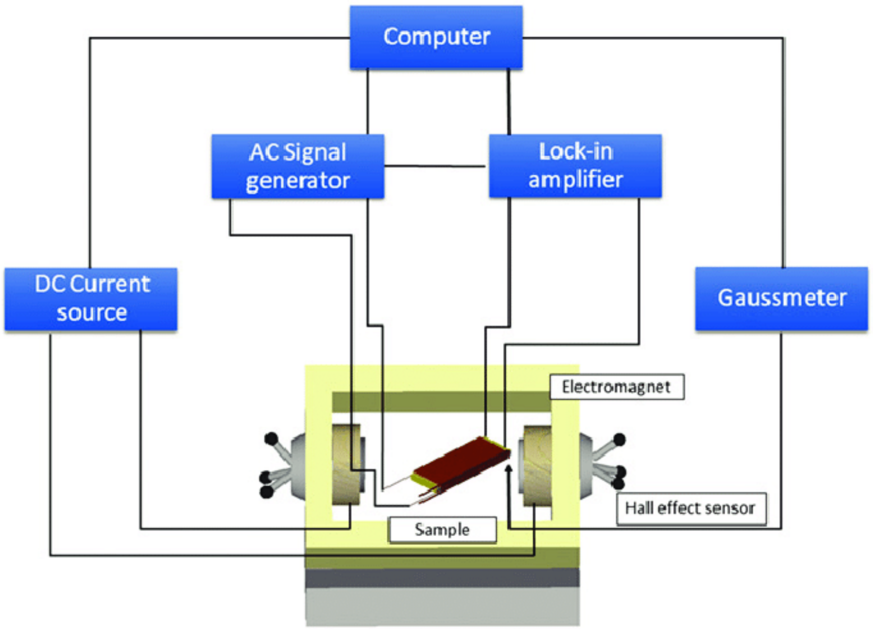



J. Lou *et al.*, APL **100**, 102907 (2012)

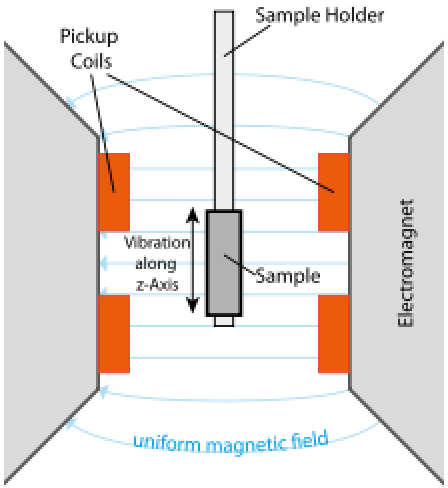
$$\Delta p/\Delta H = \mu_0 \Delta m/\Delta E$$

# Measuring ME effects

## Direct ME measurements



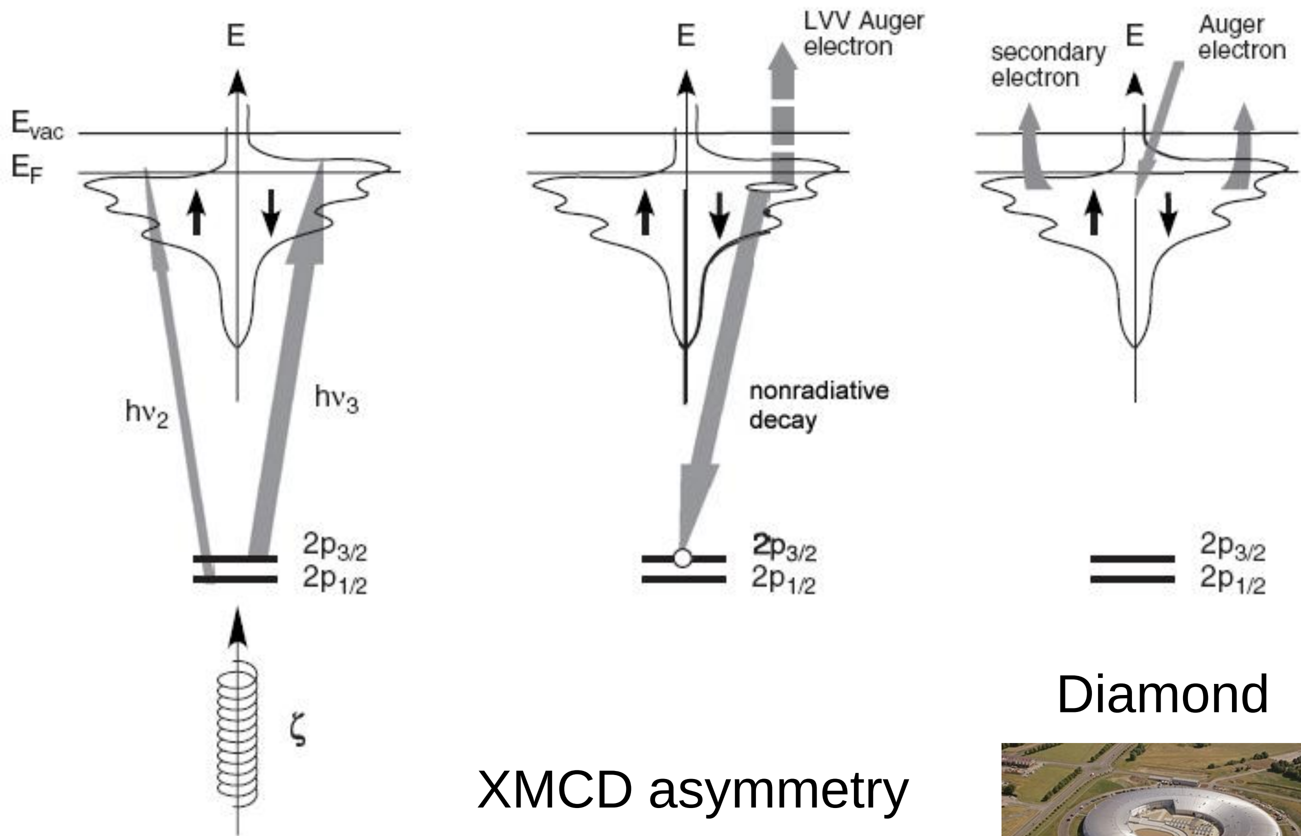

## Converse ME measurements




**Access to macroscopic behaviour**

# Imaging: PEEM-XMCD

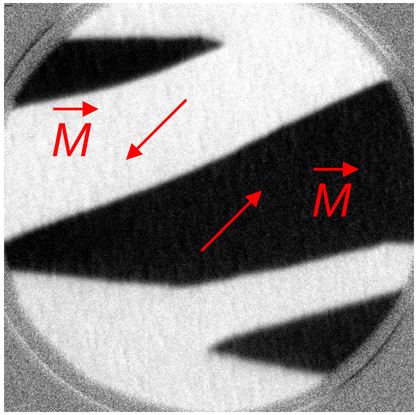
Photoexcitation Auger process Secondary electron emission




$$I \sim \vec{M} \cdot \vec{k}$$

LSMO/$NdGaO_3$

**k**




10 µm

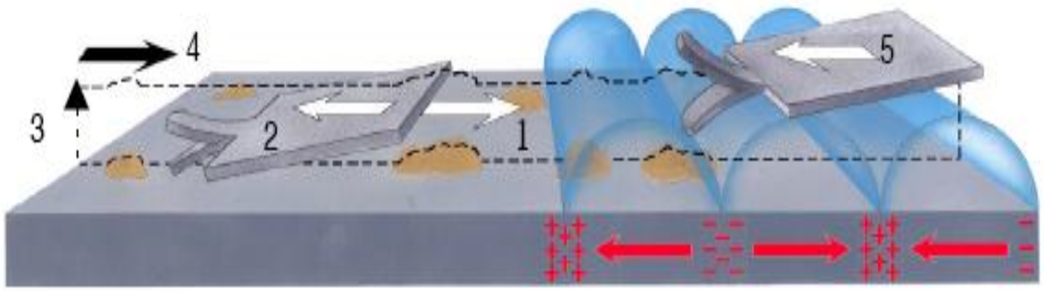
XMCD asymmetry

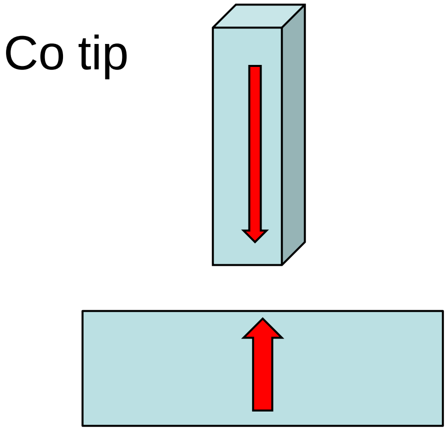
$$\left(I^{+} - I^{-}\right) / \left(I^{+} + I^{-}\right)$$

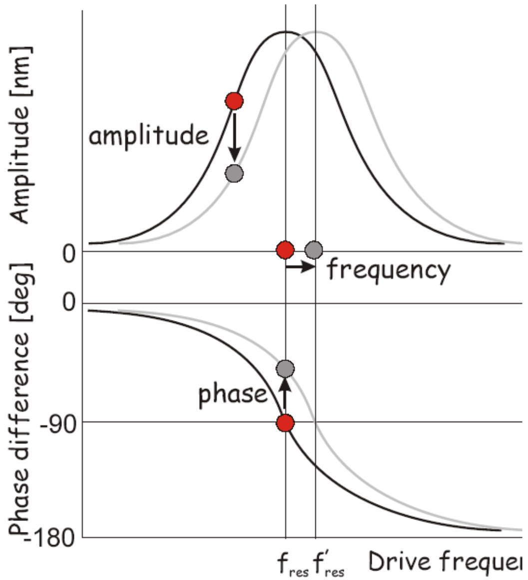
Diamond

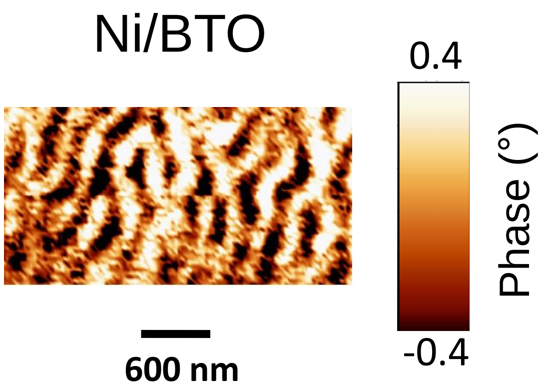
200 m

# Imaging: MFM


1
2
3
4
5


Co tip


Amplitude [nm]
amplitude
0
frequency
0
phase
-90
-180
Phase difference [deg]
Drive freque
$f_{res}$ $f'_{res}$


Ni/BTO
0.4
-0.4
Phase (°)
600 nm

# Oxide magnetoelectrics

Background

Strain-control of local magnetism in manganite films

LSMO/BTO

LCMO/BTO

Strain-control of local magnetism in Ni films

Ni/BTO

Ni/PMN-PT

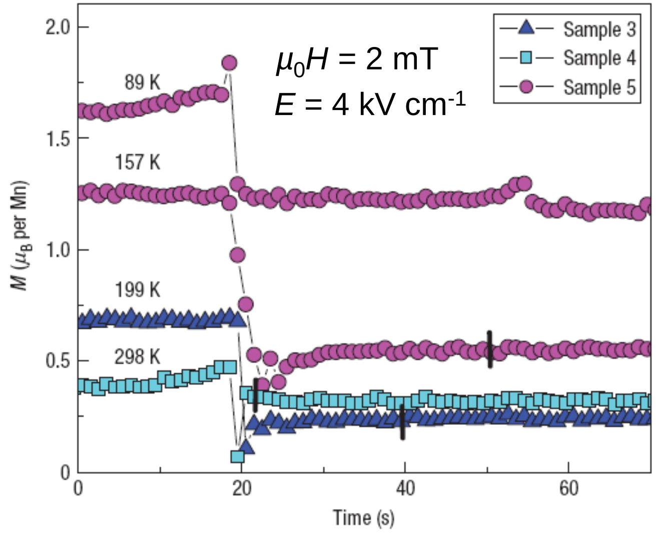
An electrocaloric diversion

# Strain-mediated converse ME effects in oxides

**Mainly studied using bulk magnetometry**

| Ferromagnetic film |
|---|
| Ferroelectric substrate |

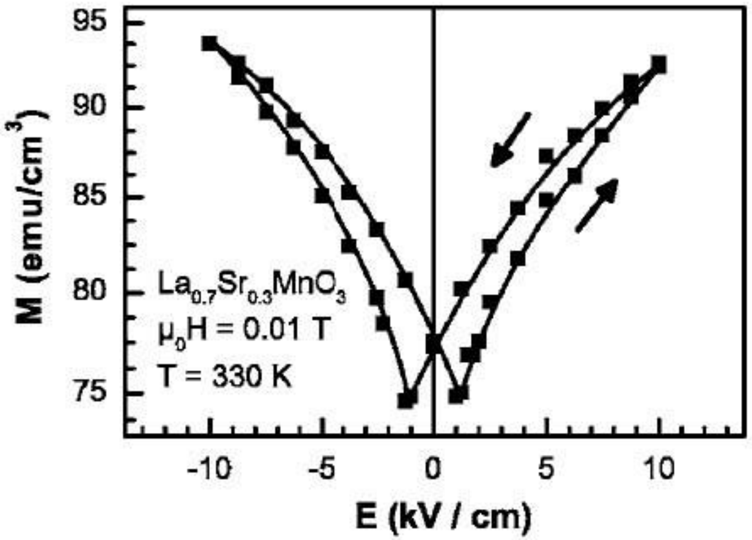
$La_{0.67}Sr_{0.33}MnO_3/BaTiO_3$




W. Eerenstein *et al., Nature Materials* **6**, 348 (2007)

**Sharp and persistent ME**

$La_{0.7}Sr_{0.3}MnO_3/Pb(Mg_{1/3}Nb_{2/3})_{0.72}Ti_{0.28}O_3$



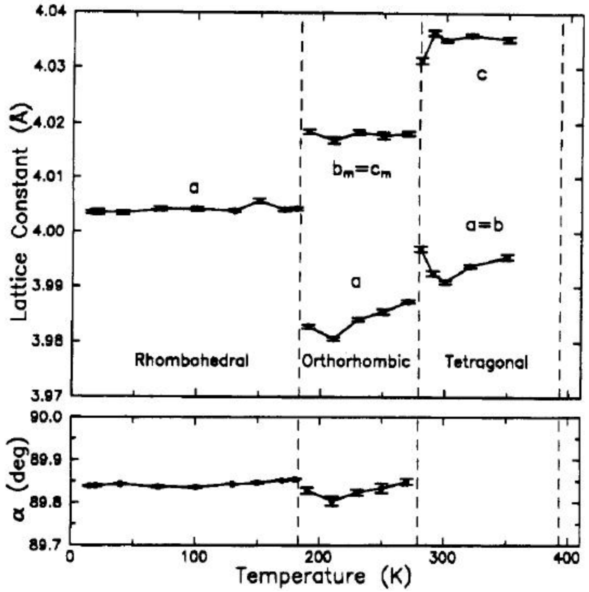

C. Thiele *et al.*, *Phys. Rev. B* **75**, 054408 (2007)

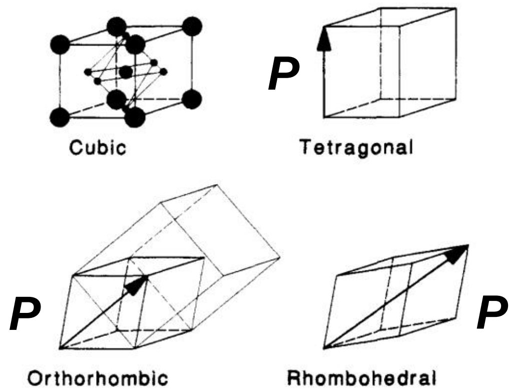
**Continuous and reversible ME**

**Role of substrate microstructure**

# Ferromagnetic films on $BaTiO_3$ substrates

## Structural transitions BTO

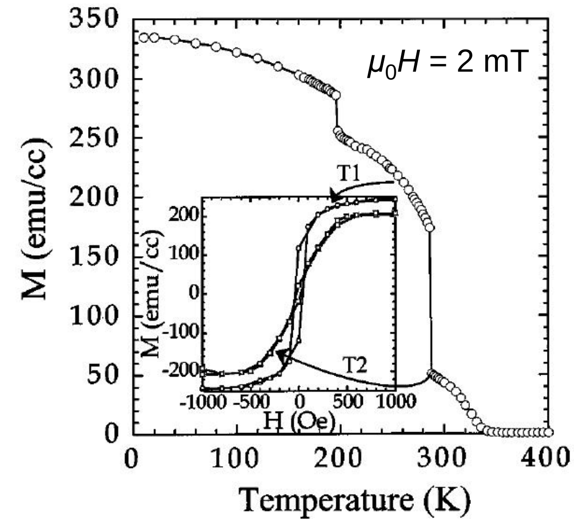



G. H. Kwei *et al.*, *J. Phys. Chem.* **97**, 2368 (1993)

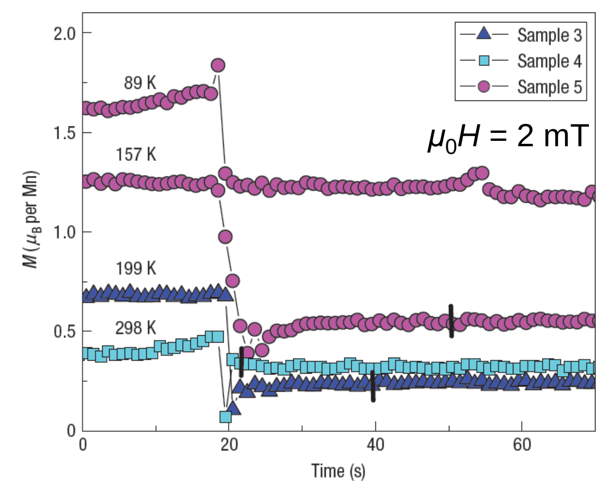
## Magnetic changes LSMO/BTO

*T*-driven




M. K. Lee *et al. Appl. Phys. Lett.* **77**, 3547 (2000)

*E*-driven



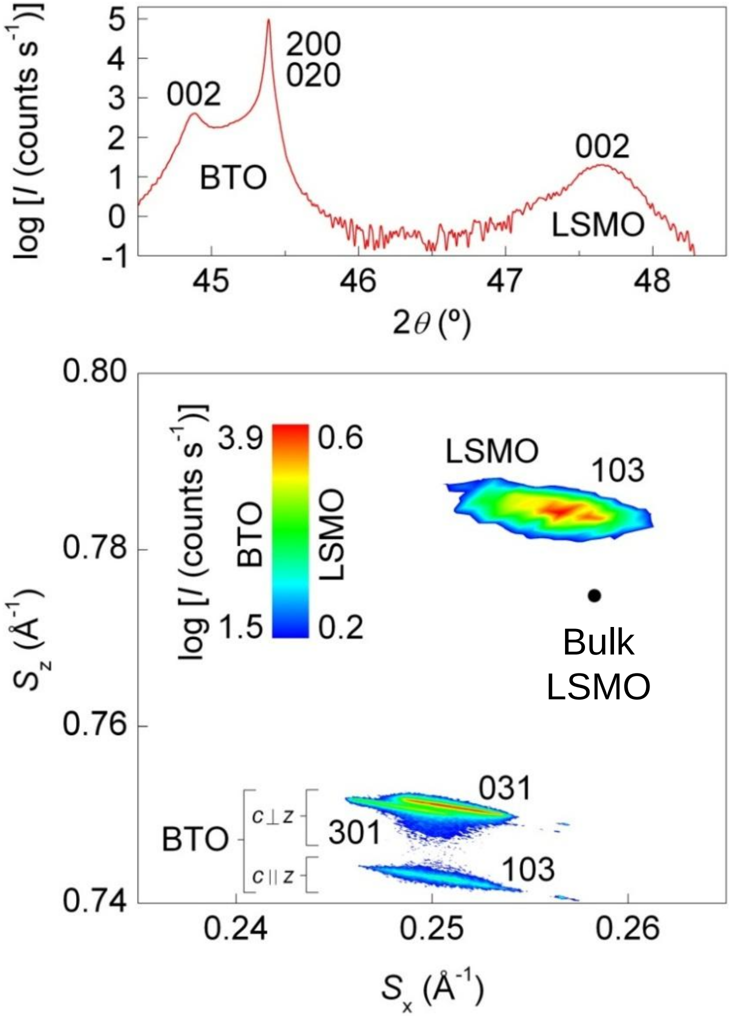

W. Eerenstein *et al. Nature Materials* **6**, 348 (2007)

# LSMO/BTO

## Samples grown by PLD

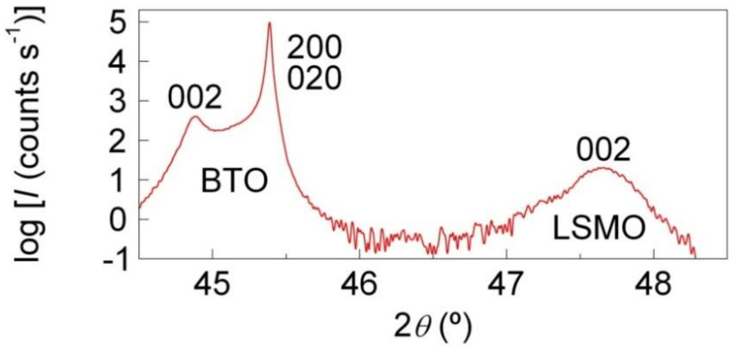
| |
|---|
| 55 nm $La_{0.67}Sr_{0.33}MnO_3$ |
| 0.5 mm $BaTiO_3$ (001) |

## XRD



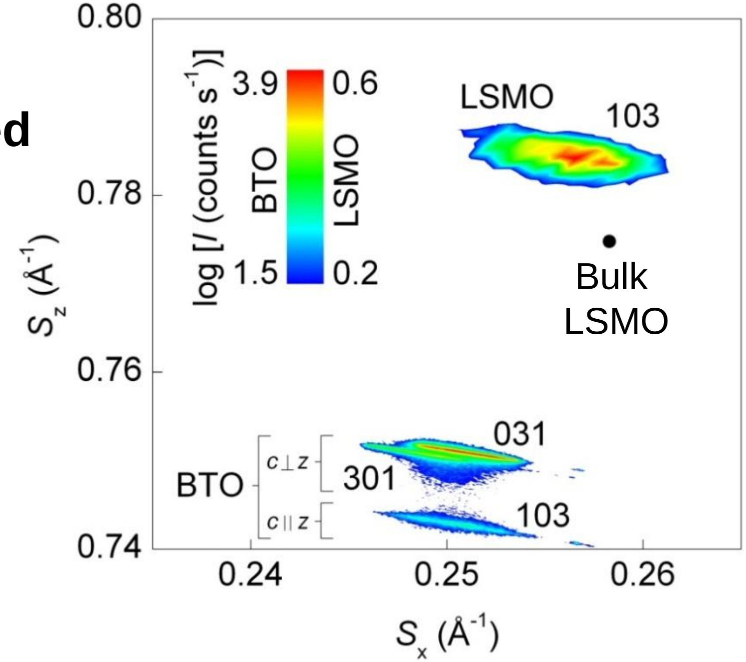
# Structural properties tetragonal phase

**Majority *c*-domains in plane**

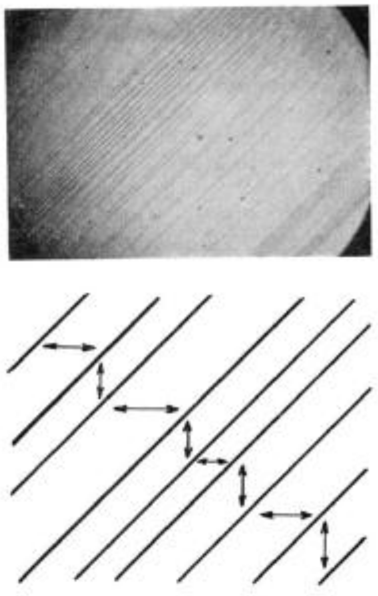



**Almost fully-relaxed LSMO**

**Twinned BTO**




Microstructure

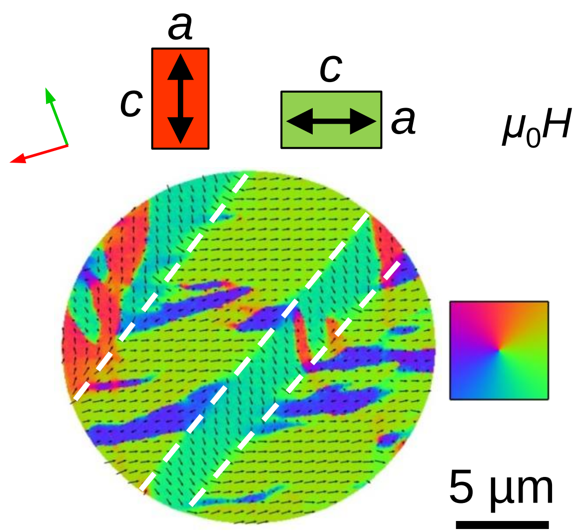


W. J. Merz, PRB **95**, 690 (1954)

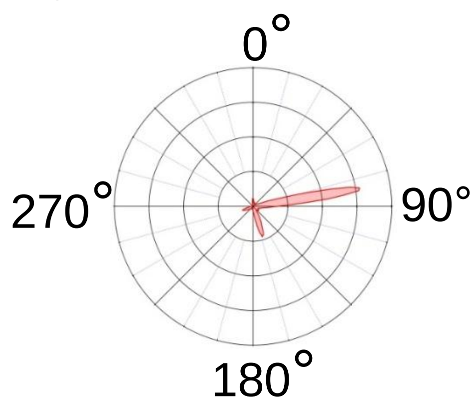
# Magnetic anisotropy tetragonal phase

Strain → Local magnetic anisotropy

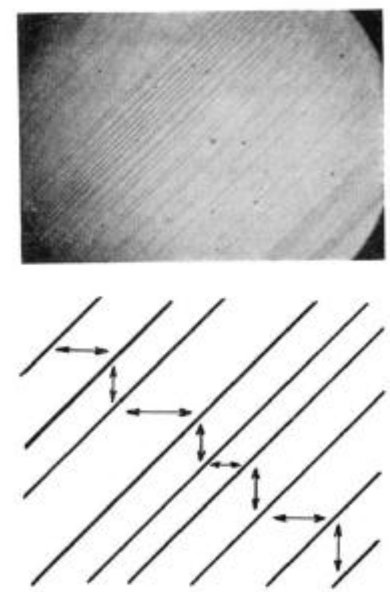
**PEEM-XMCD**




$\mu_0 H$ = 0 T



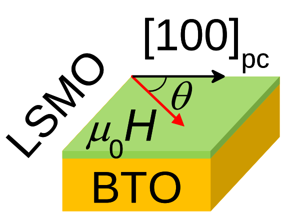

Microstructure

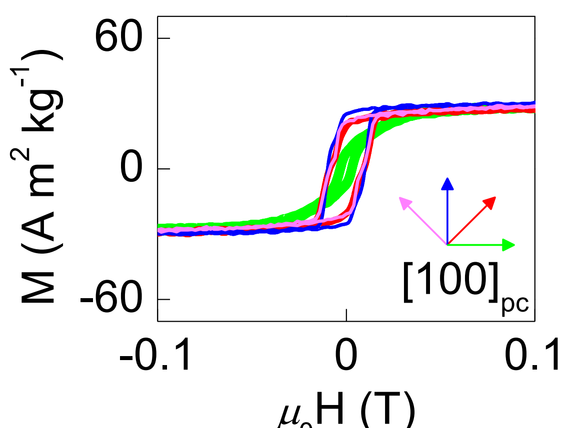


W. J. Merz, PRB **95**, 690 (1954)

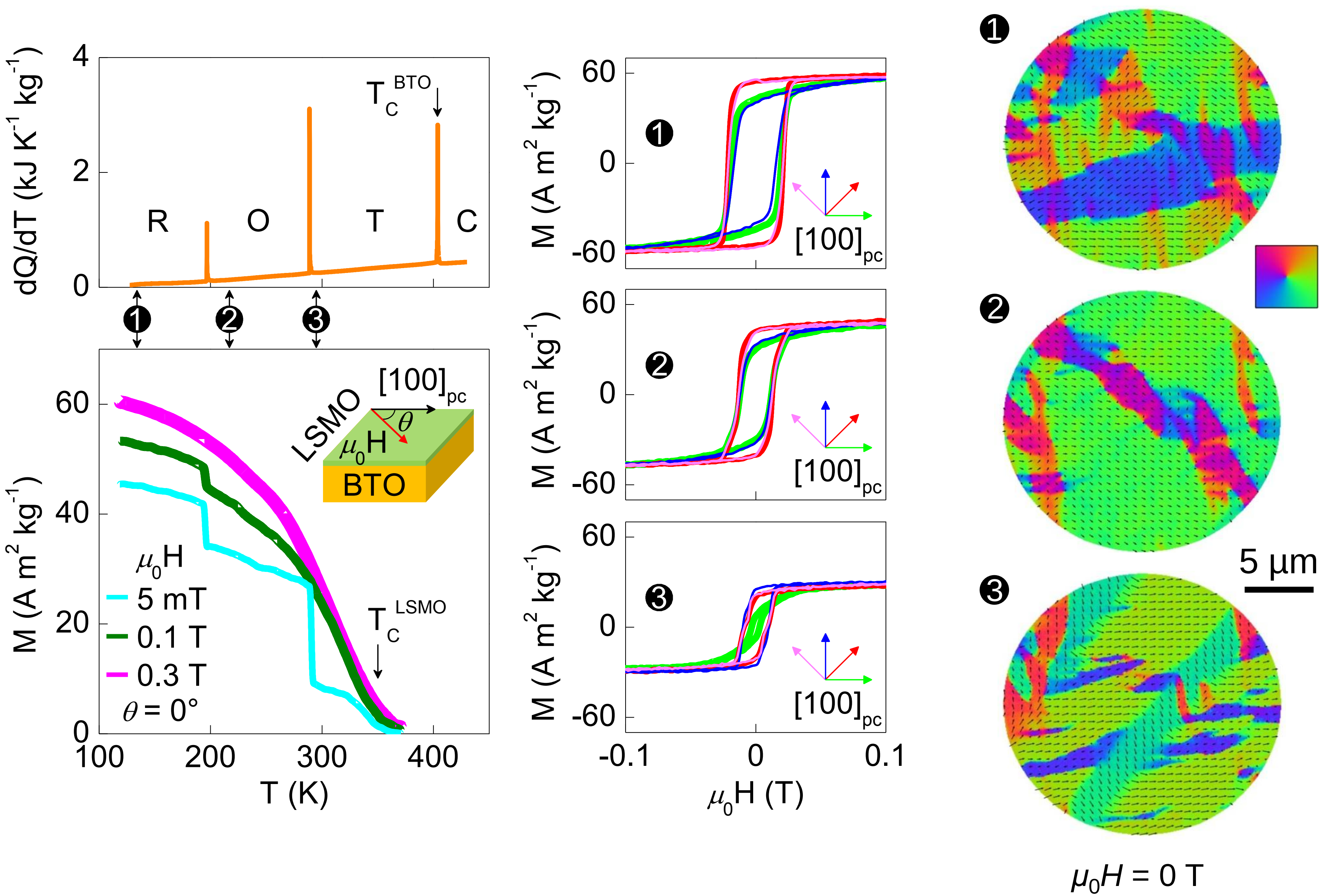
Domain population → Bulk magnetic anisotropy

**VSM**



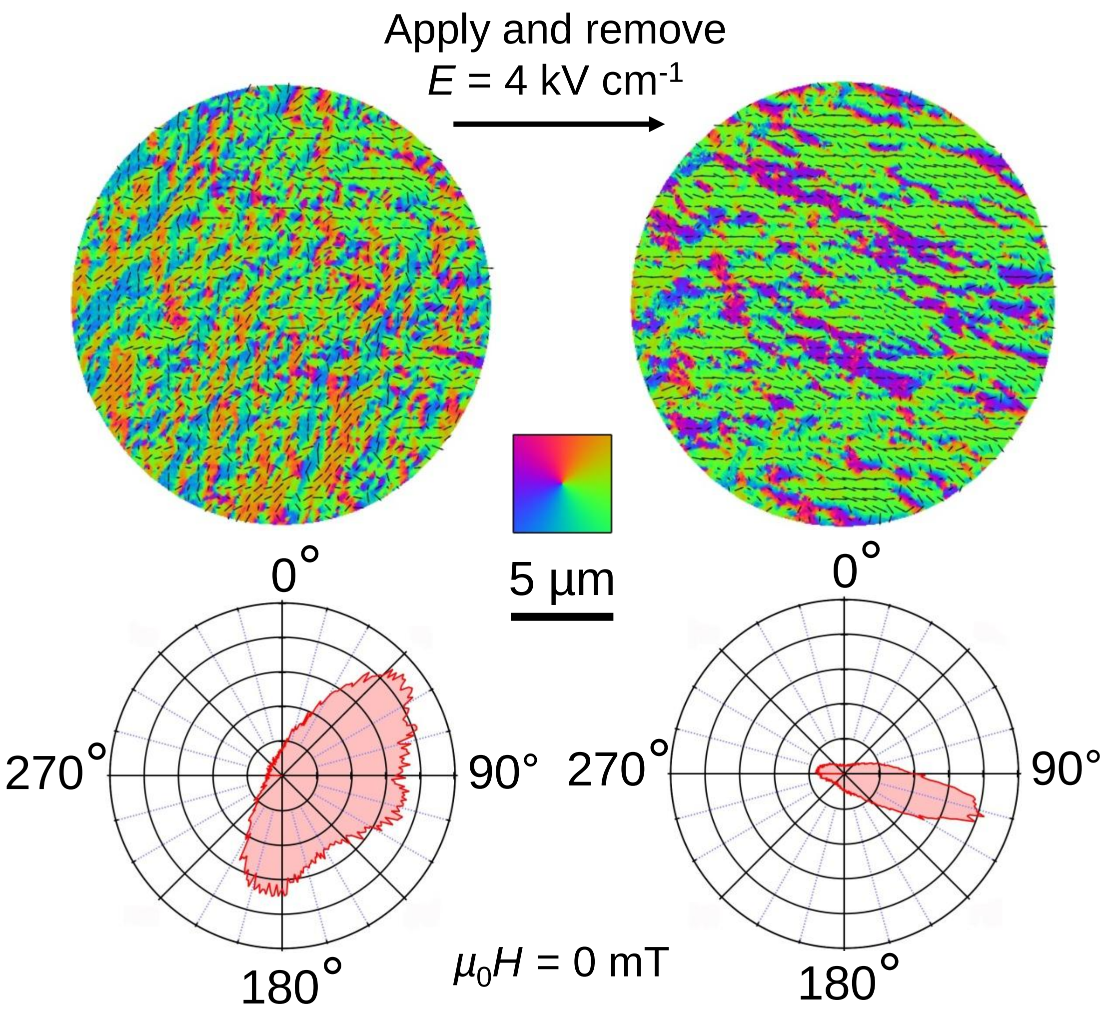



# Temperature control of local magnetic anisotropy

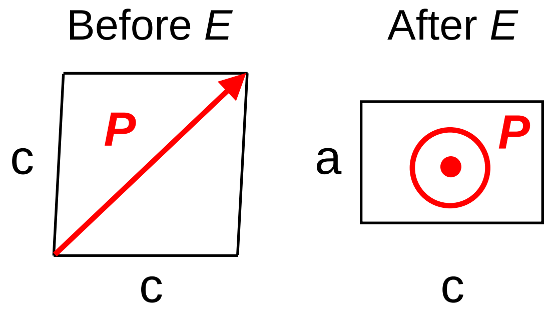


# Electric-field control of local magnetic anisotropy

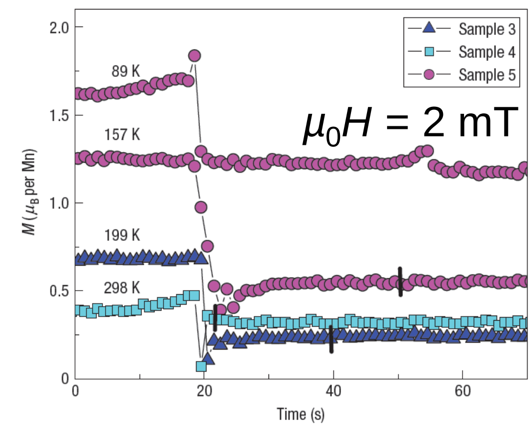
## PEEM-XMCD $T$ = 200 K (O)


## Schematics




## VSM

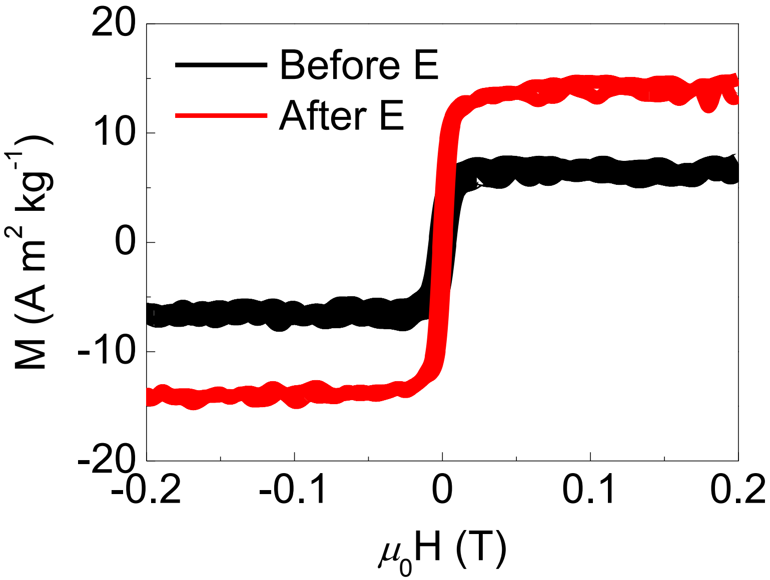


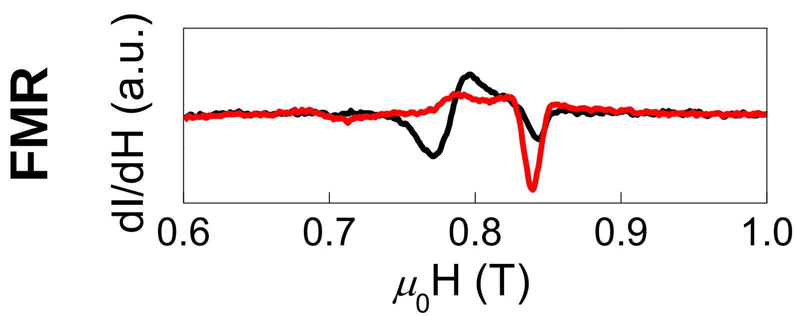

W. Eerenstein *et al.*,
*Nature Materials* **6**, 348 (2007)

# Electric-field control of magnetization

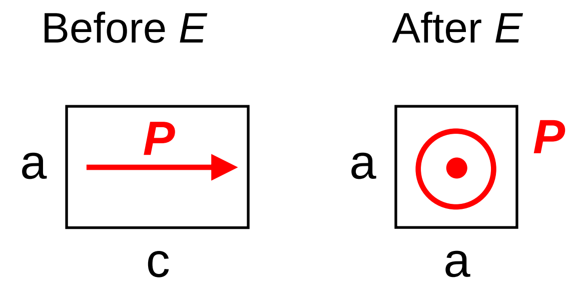
## VSM $T$ = 294 K (T)

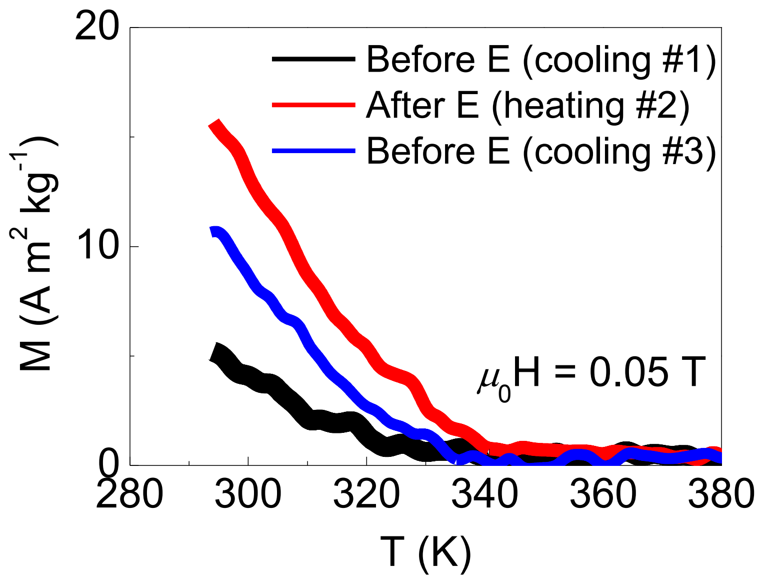
Apply and remove $E$ = 4 kV cm$^{-1}$




## Schematics



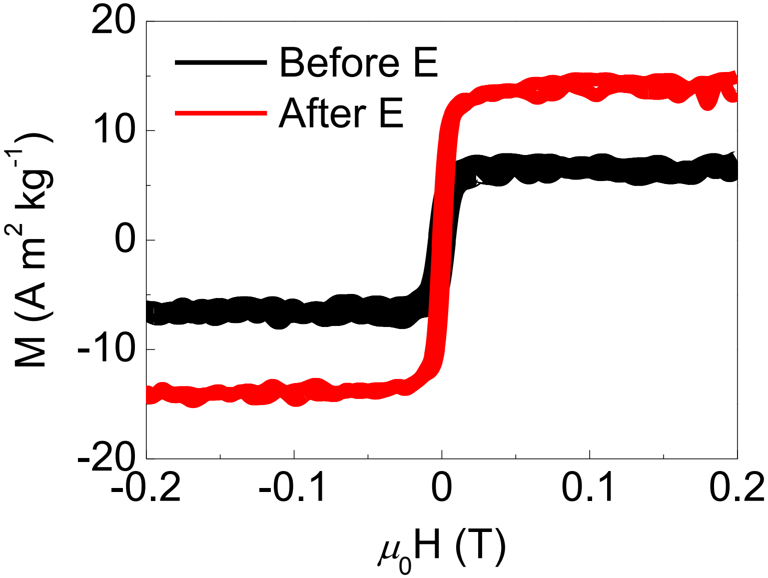




$E$-field-induced increase in $T_C$

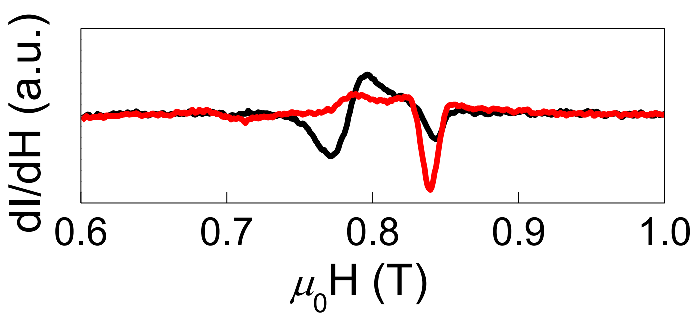
# Electric-field control of magnetization

## VSM *T* = 294 K (T)

Apply and remove *E* = 4 kV cm$^{-1}$

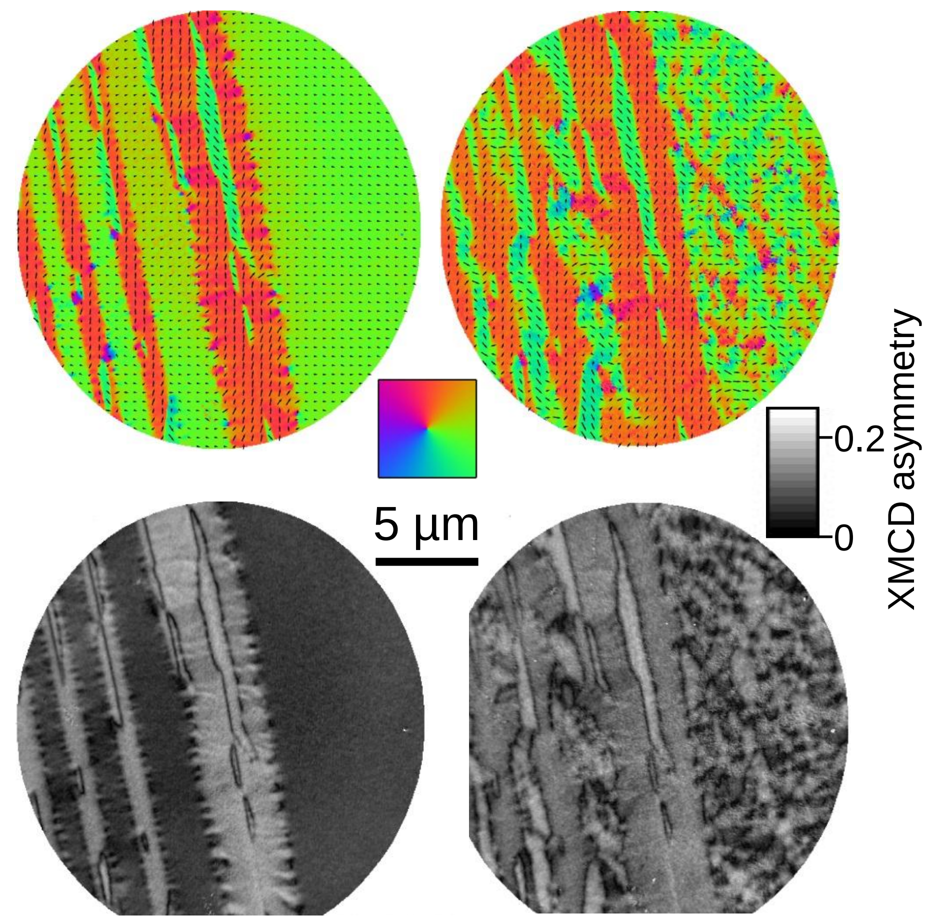



**FMR**




## PEEM-XMCD *T* = 294 K (T)

Apply and remove *E* = 2 kV cm$^{-1}$



# Oxide magnetoelectrics

Background

Strain-control of local magnetism in manganite films

LSMO/BTO

LCMO/BTO

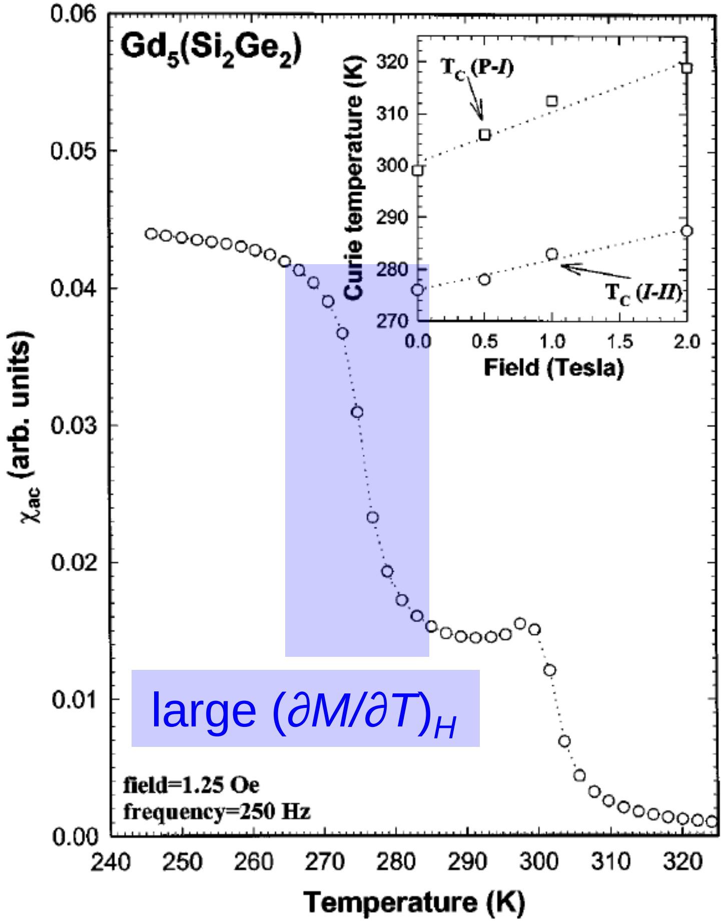
Strain-control of local magnetism in Ni films

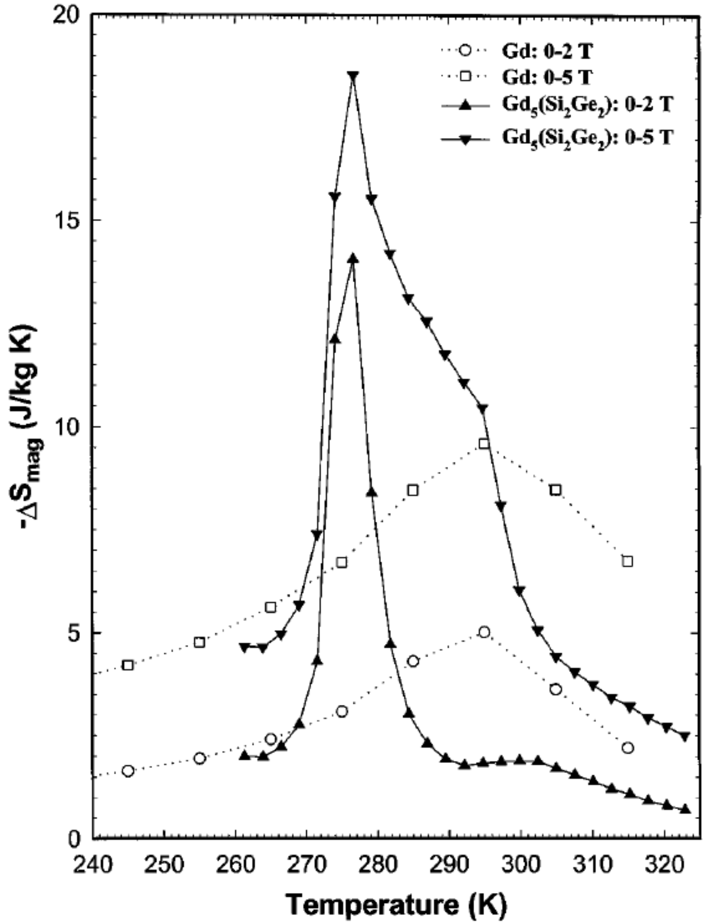
Ni/BTO

Ni/PMN-PT

# Giant magnetocaloric effects

**First-order magnetostructural transition:** large $(\partial M/\partial T)_H$




V. K. Pecharsky *et al., Phys. Rev. Lett.* **78**, 4494 (1997)

# Giant magnetocaloric materials

| Material | $T_t$ (K) | $\Delta S/\mu_0\Delta H$ (J $K^{-1}$ $kg^{-1}$ $T^{-1}$) | Reference |
|---|---|---|---|
| $Gd_5Si_2Ge_2$ | 276 | -3.8 | Pecharsky *et al.* PRL **78**, 4494 (1997) |
| $Gd_5Si_1Ge_3$ | 136 | -13.6 | Pecharsky *et al.* APL **70**, 3299 (1997) |
| MnAs | 318 | -6.4 | Wada *et al.* APL **79**, 3302 (2001) |
| $Mn_{1.24}Fe_{0.71}P_{0.46}Si_{0.54}$ | 320 | -3.6 | Tegus *et al. Nature* **415**, 150 (2002) |
| $MnCoGeB_{0.02}$ | 277 | -9.5 | Trung *et al.* APL **96**, 172504 (2010) |
| $LaFe_{11.57}Si_{1.43}H_{1.3}$ | 291 | -5.6 | Fujita *et al.* PRB **67**, 104416 (2003) |
| $CoMnSi_{0.95}Ge_{0.05}$ | 215 | 1.8 | Sandeman *et al.* PRB **74**, 224436 (2006) |
| $Ni_{53}Mn_{23}Ga_{24}$ | 295 | -3.6 | Hu *et al.* PRB **64**, 132412 (2001) |
| $Ni_{50}Mn_{37}Sn_{13}$ | 299 | 3.8 | Krenke *et al. Nat. Mat.* **4**, 450 (2005) |
| $Ni_{50}Mn_{34}In_{16}$ | 219 | 2.4 | Moya *et al.* PRB **75**, 184412 (2007) |
| LCMO | 259 | -0.87 | Zhang *et al.* APL **69**, 3596 (1996) |

**Few materials, suffer hysteresis**

# Magnetocaloric effects in manganites

Available online at www.sciencedirect.com
ScienceDirect
ELSEVIER
Journal of Magnetism and Magnetic Materials 308 (2007) 325–340
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Review

Review of the magnetocaloric effect in manganite materials

Manh-Huong Phan[a,*], Seong-Cho Yu[b]

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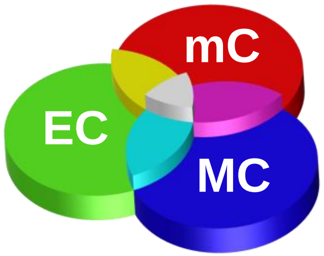
Received 26 June 2006
Available online 17 August 2006

## Multicaloric Perovskite Oxides

E. Stern-Taulats, D. Mukherjee, M.H. Phan and X. Moya
in preparation (2019)

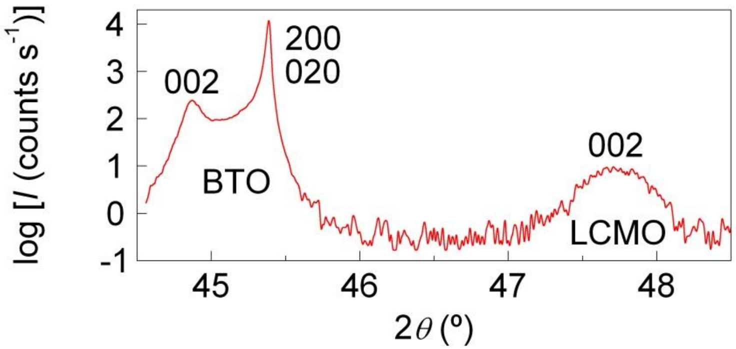


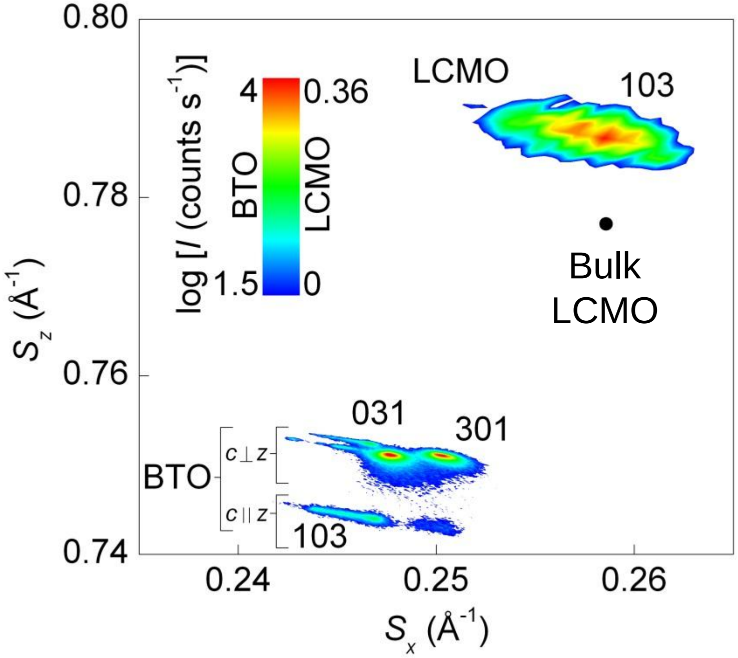
# LCMO/BTO

## Samples grown by PLD

| |
|---|
| 34 nm $La_{0.7}Ca_{0.3}MnO_3$ |
| 0.5 mm $BaTiO_3$ (001) |

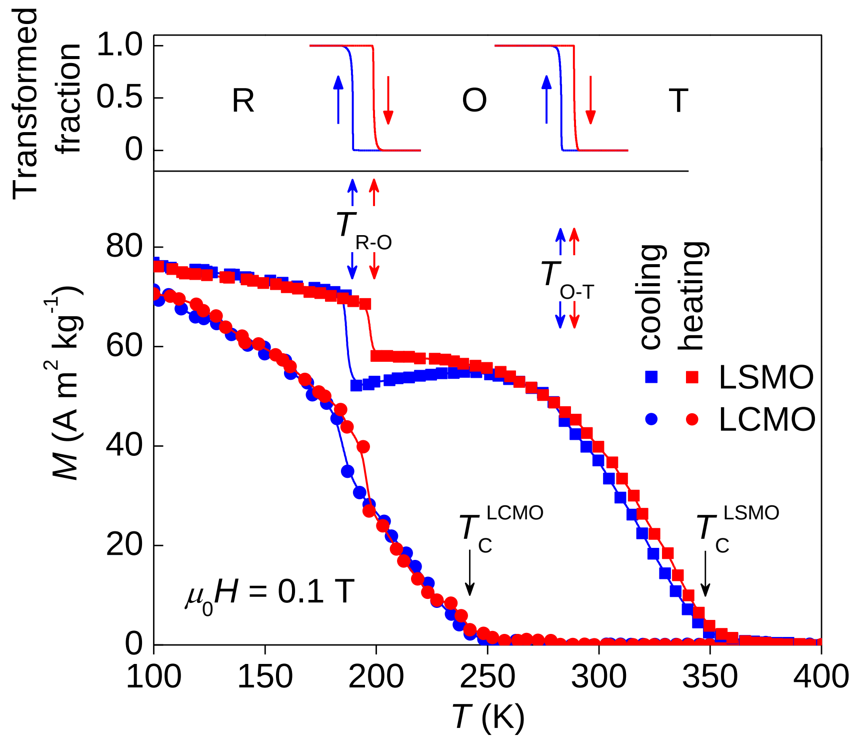
## XRD



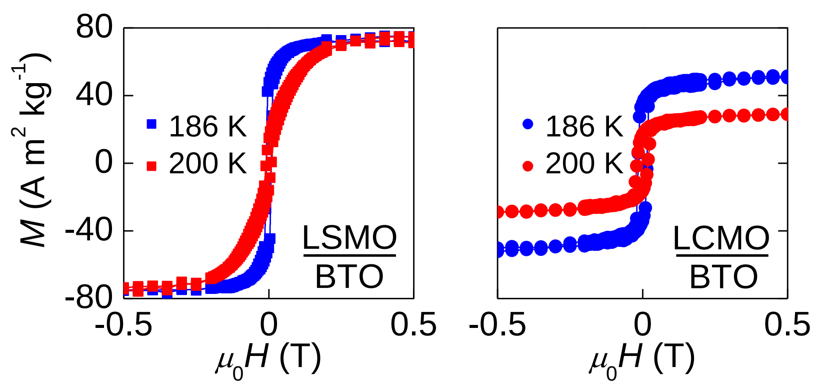



# Macroscopic magnetic properties

***M*(*T*)**




***M*(*H*)**

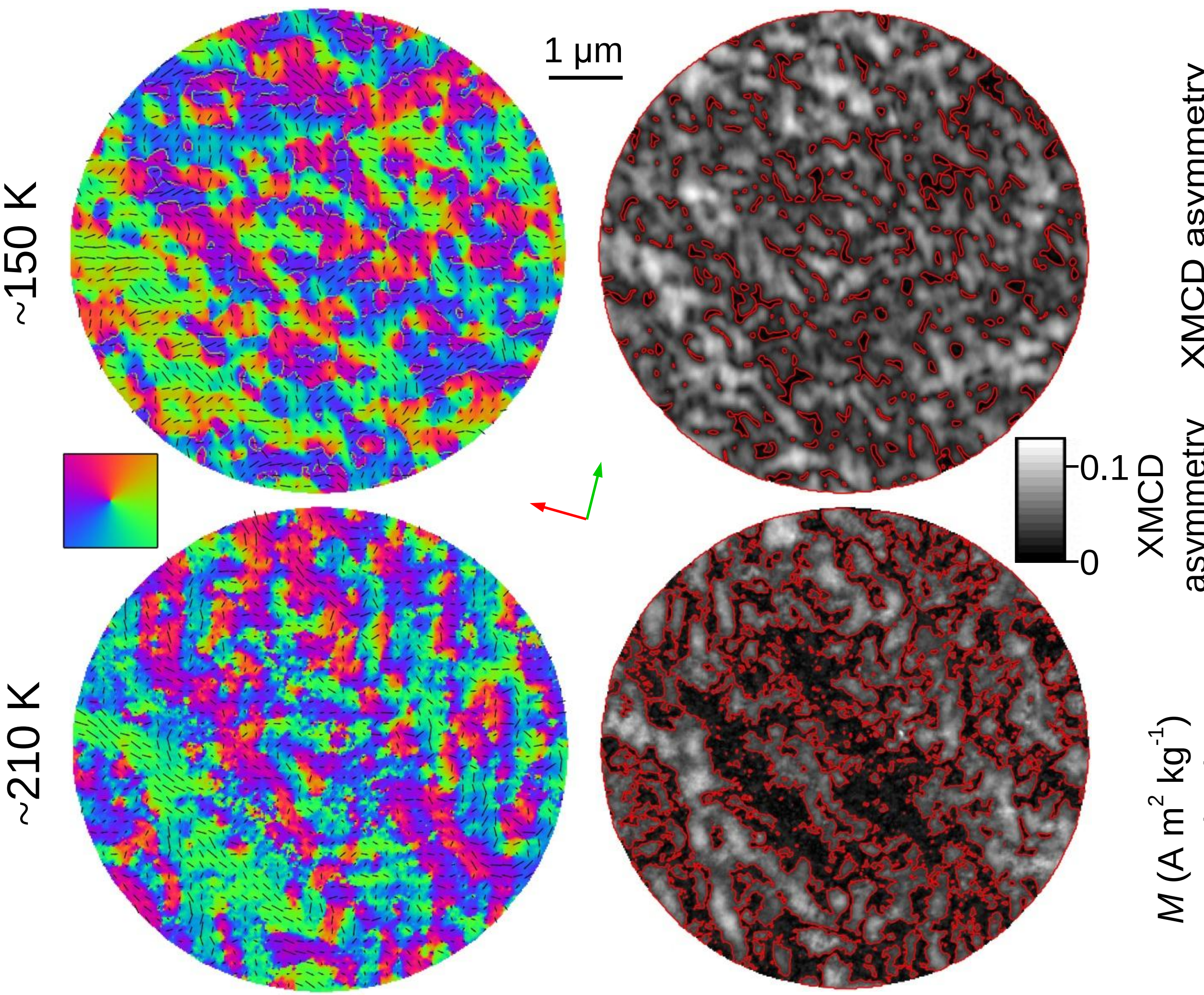



LSMO
Anisotropy change

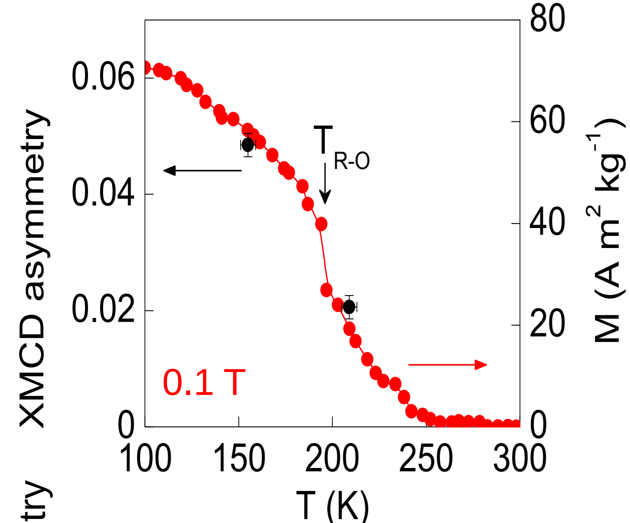
LCMO
Entropy change

# Temperature-driven phase interconversion

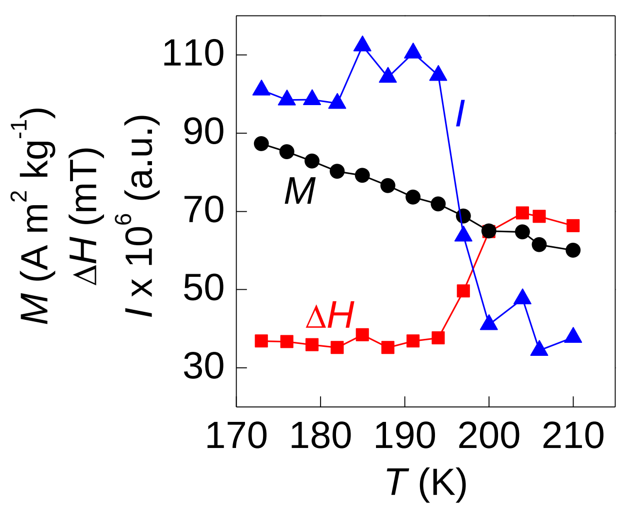
## LCMO/BTO PEEM-XMCD




$\mu_0 H = 0$ T




## FMR

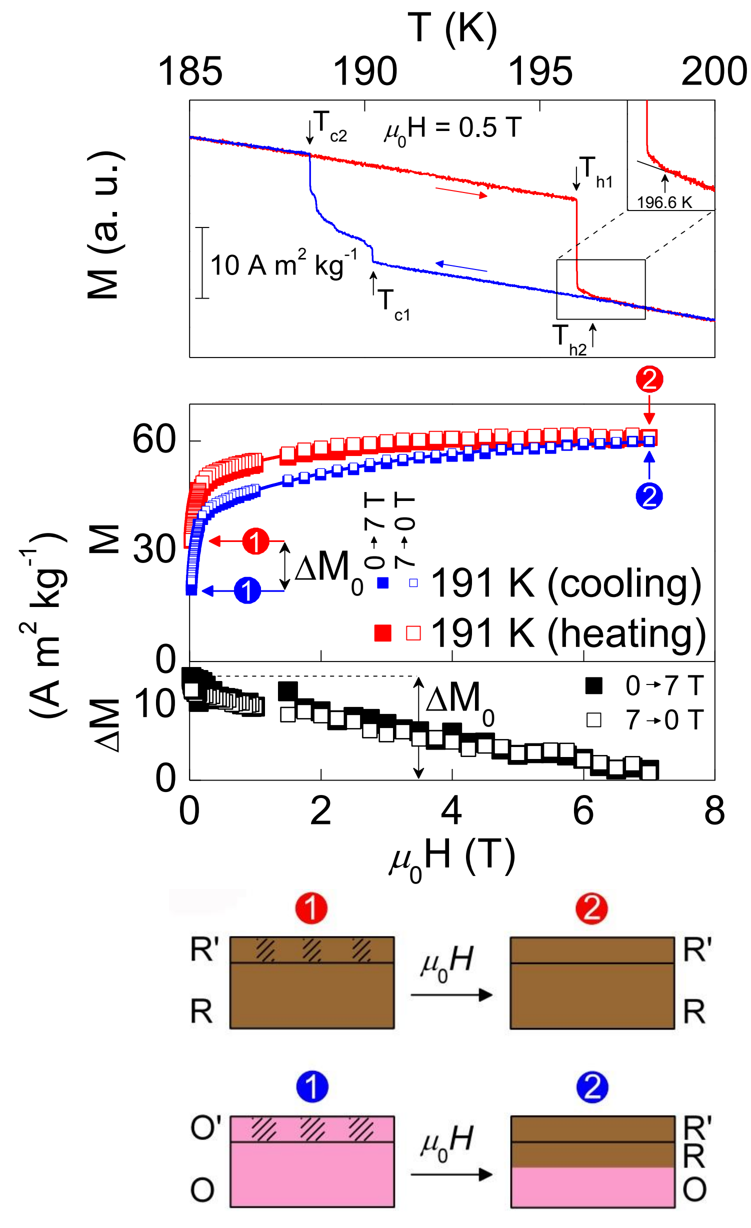


# Magnetic-field-driven phase interconversion

**Detail of transition in *M*(*T*)**

**Drive transition directly**
**Reversible**

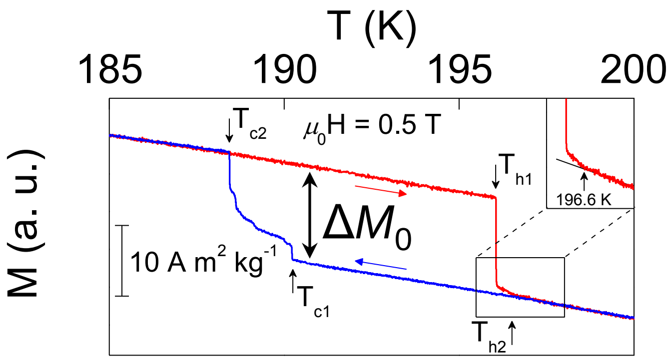
**Schematics**



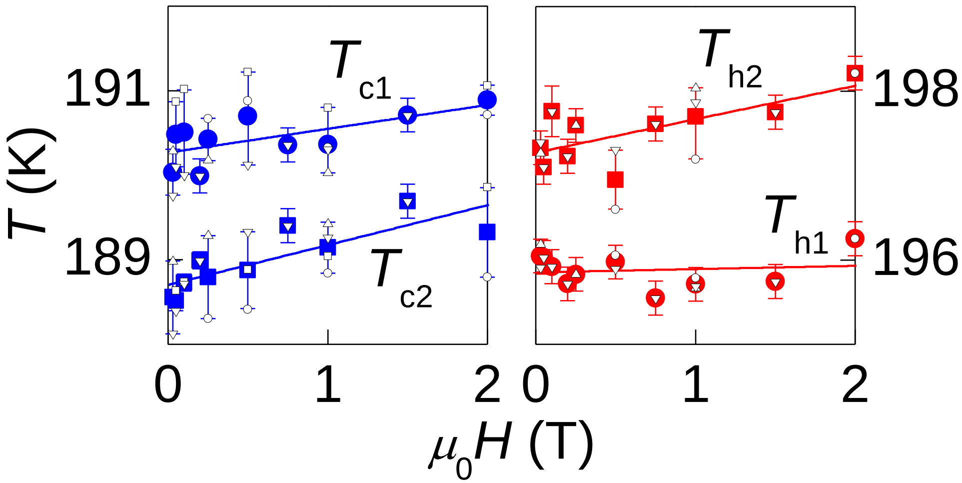

Feedback

# Quantifying the MC effect (1)

**Detail of transition in *M*(*T*)**




**Clausius-Clapeyron:** $$\frac{dT_0}{\mu_0 dH} = -\frac{\Delta M_0}{\Delta S}$$




$\Delta M_0 \sim 13.5$ A m$^2$ kg$^{-1}$

$$\frac{dT_0}{\mu_0 dH} \sim 0.4 \text{ K T}^{-1}$$

↓

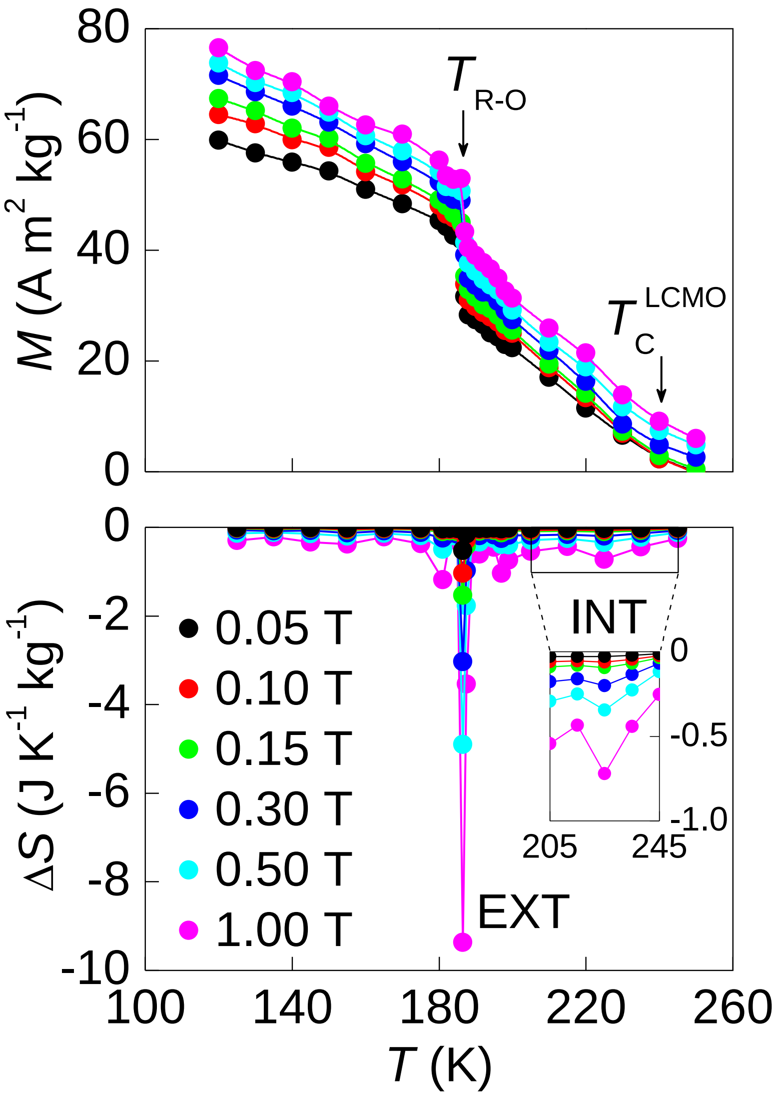
$\Delta S/\mu_0\Delta H \sim -9$ J K$^{-1}$ kg$^{-1}$ T$^{-1}$

# Quantifying the MC effect (2)

$$\Delta S = \mu_0 \int_0^H \left(\frac{\partial M}{\partial T}\right)_{H'} dH'$$

INT ~ - 0.7 J $K^{-1}$ $kg^{-1}$ $T^{-1}$

EXT ~ - 9 J $K^{-1}$ $kg^{-1}$ $T^{-1}$



# Giant magnetocaloric materials

| Material | $T_t$ (K) | $\Delta S/\mu_0\Delta H$ (J K$^{-1}$ kg$^{-1}$ T$^{-1}$) | Reference |
|---|---|---|---|
| $Gd_5Si_2Ge_2$ | 276 | -3.8 | Pecharsky *et al.* PRL **78**, 4494 (1997) |
| $Gd_5Si_1Ge_3$ | 136 | -13.6 | Pecharsky *et al.* APL **70**, 3299 (1997) |
| MnAs | 318 | -6.4 | Wada *et al.* APL **79**, 3302 (2001) |
| $Mn_{1.24}Fe_{0.71}P_{0.46}Si_{0.54}$ | 320 | -3.6 | Tegus *et al.* *Nature* **415**, 150 (2002) |
| $MnCoGeB_{0.02}$ | 277 | -9.5 | Trung *et al.* APL **96**, 172504 (2010) |
| $LaFe_{11.57}Si_{1.43}H_{1.3}$ | 291 | -5.6 | Fujita *et al.* PRB **67**, 104416 (2003) |
| $CoMnSi_{0.95}Ge_{0.05}$ | 215 | 1.8 | Sandeman *et al.* PRB **74**, 224436 (2006) |
| $Ni_{53}Mn_{23}Ga_{24}$ | 295 | -3.6 | Hu *et al.* PRB **64**, 132412 (2001) |
| $Ni_{50}Mn_{37}Sn_{13}$ | 299 | 3.8 | Krenke *et al.* *Nat. Mat.* **4**, 450 (2005) |
| $Ni_{50}Mn_{34}In_{16}$ | 219 | 2.4 | Moya *et al.* PRB **75**, 184412 (2007) |
| LCMO | 259 | -0.87 | Zhang *et al.* APL **69**, 3596 (1996) |

# Giant magnetocaloric materials

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| $Ni_{50}Mn_{34}In_{16}$ | 219 | 2.4 | Moya *et al.* PRB **75**, 184412 (2007) |
| LCMO/BTO | 186 | -9 | **Extrinsic** |

X. Moya *et al.*, *Nature Materials* **12**, 52 (2013)

# Oxide magnetoelectrics

Background

Strain-control of local magnetism in manganite films

LSMO/BTO

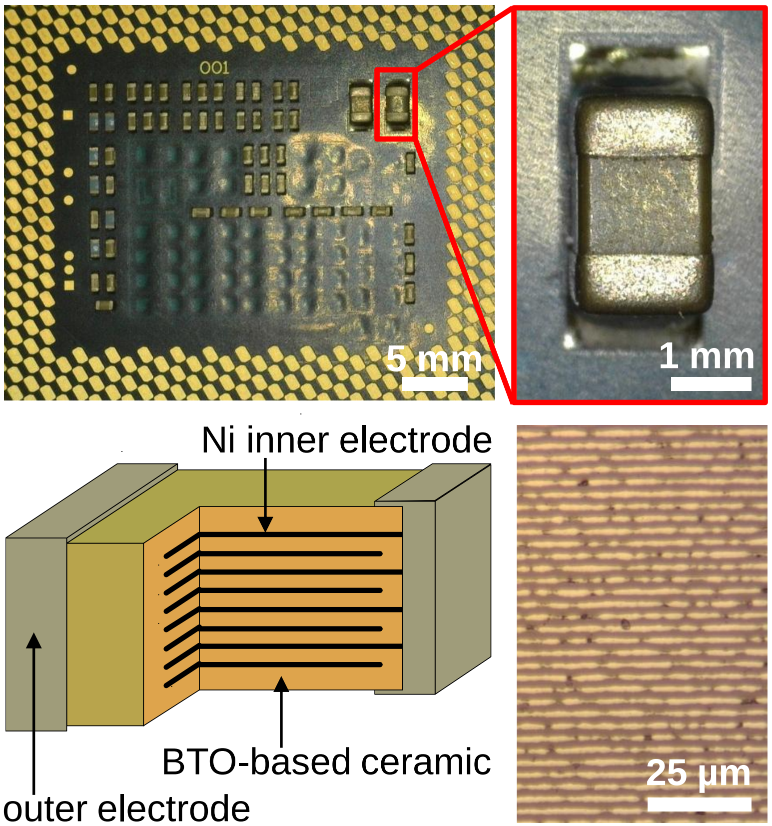
LCMO/BTO

Strain-control of local magnetism in Ni films

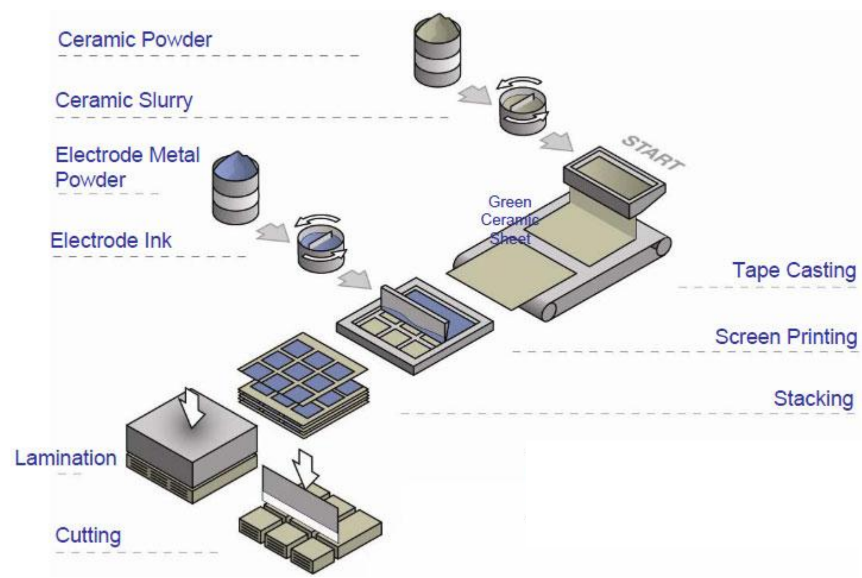
Ni/BTO

Ni/PMN-PT

# Ni/BTO multilayer capacitors




## Fabrication

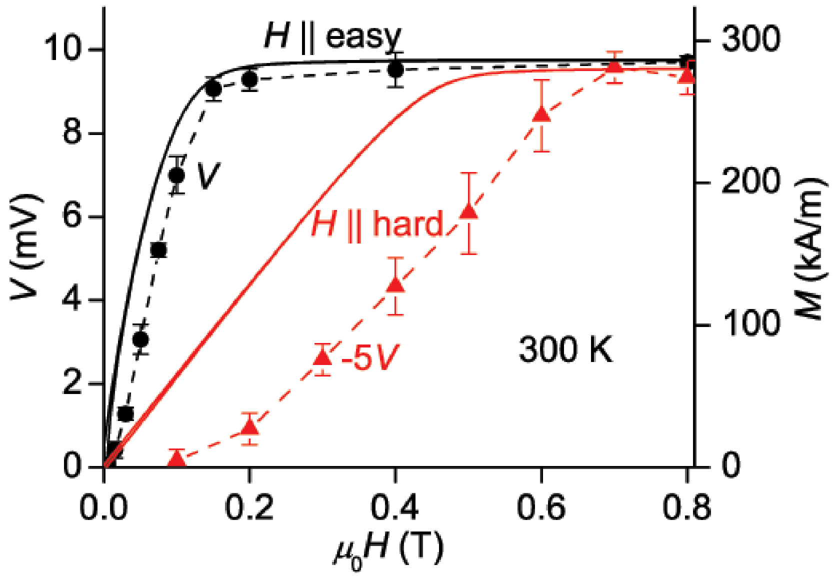



X. Moya *et al.*, *MRS Bulletin* **43**, 291 (2018)

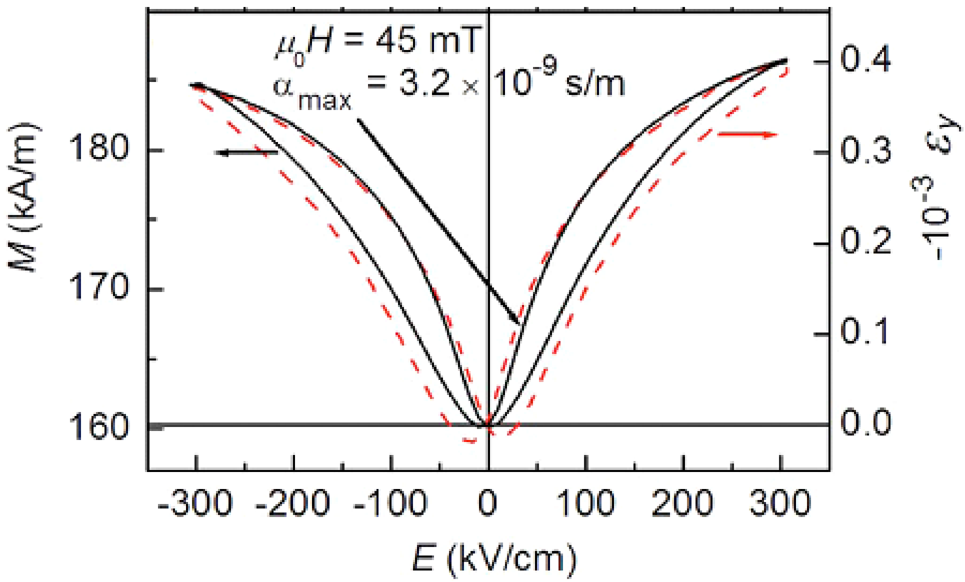
# Ni/BTO multilayer capacitors

Strain coupling via:

Piezoelectricity in doped BTO dielectric
Magnetostriction in Ni electrodes

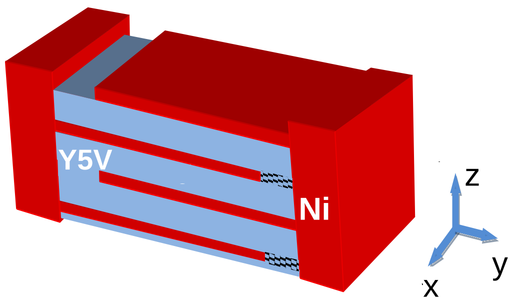


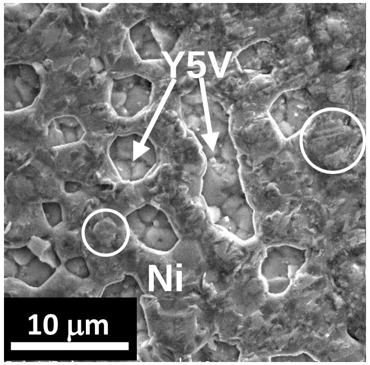

**Direct effect**
*Nature Materials* **7** (2008) 93

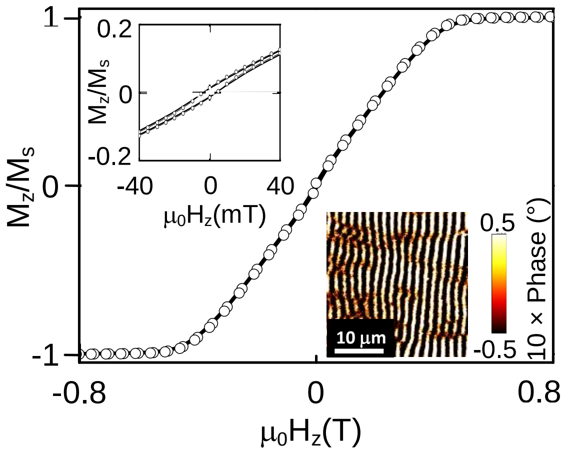



**Converse effect**
*Appl Phys Lett* **93** (2008) 173501

# MLC characterization



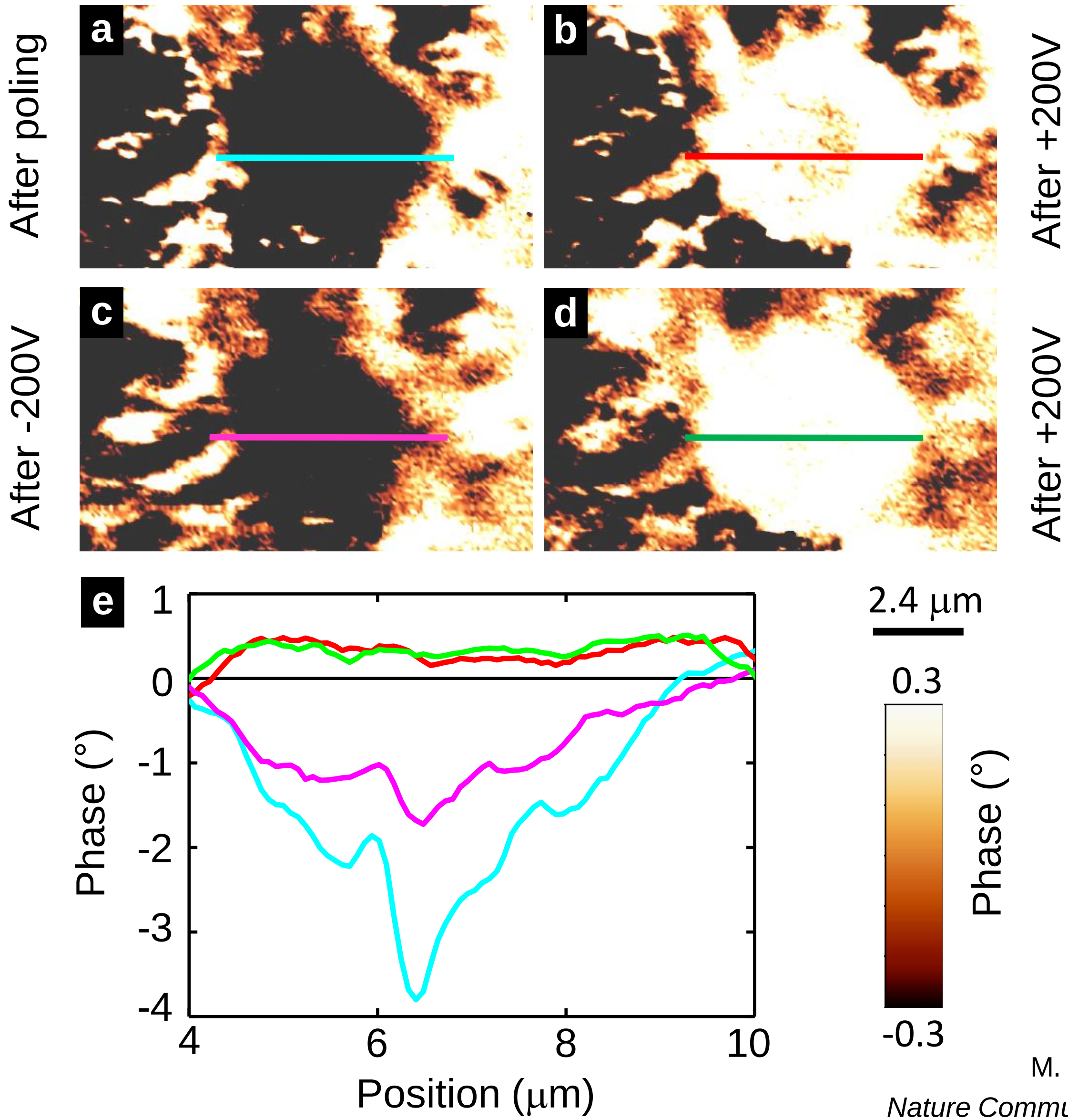



# Non-volatile *M* reversal with no applied *H*

$\mathbf{H_f}$ from surrounding domains

$\mathbf{H_k}$ from strain

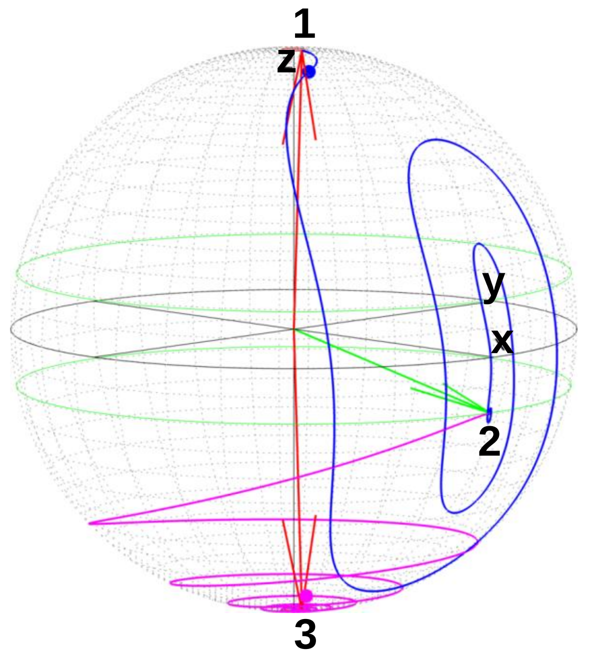



M. Ghidini *et al.*,
*Nature Communications* **4**, 1453 (2013)

# Model

$$\mathbf{H}_{\mathrm{k}} = \frac{2K}{\mu_0 M_{\mathrm{s}}} \cos\theta \ \ \hat{\mathbf{z}}$$

- end of 1 ns ramp to $K_{\mathrm{lo}}$
- end of 1 ns ramp to $K_{\mathrm{hi}}$




$\mathbf{H}_{\mathrm{f}}$ = 100 Oe

$$|\Delta K| / K_{\mathrm{hi}} = 96\%$$

$|M_z|/M_s$ ~ 99.9% switched in 41.8 ns

M. Ghidini *et al.*,
*Nature Communications* **4**, 1453 (2013)

# Oxide magnetoelectrics

Background

Strain-control of local magnetism in manganite films

LSMO/BTO

LCMO/BTO

Strain-control of local magnetism in Ni films

Ni/BTO

Ni/PMN-PT

# Sample preparation

RT Ni deposition by e-beam assisted thermal evaporation on ferroelectric single-crystal substrates

UHV-MBE chamber
$P_{base}$ = 1.5 x$10^{-10}$ mbar

N.-J. Steinke, R. Mansell,
C. H. W. Barnes
(Cavendish Lab.)

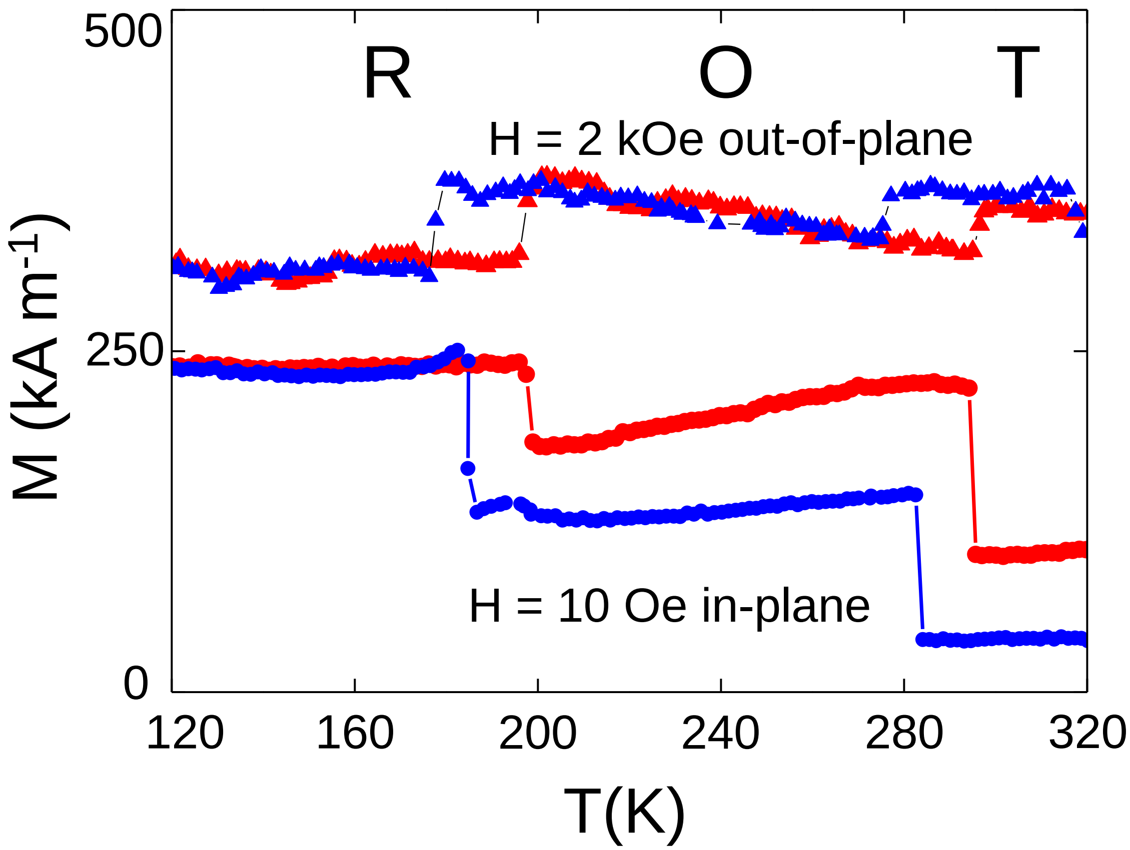
**Ni/BTO**

**NiBT1=NiBT2**

Cu(4 nm)/Ni(100 nm)/BTO (0.5 mm)

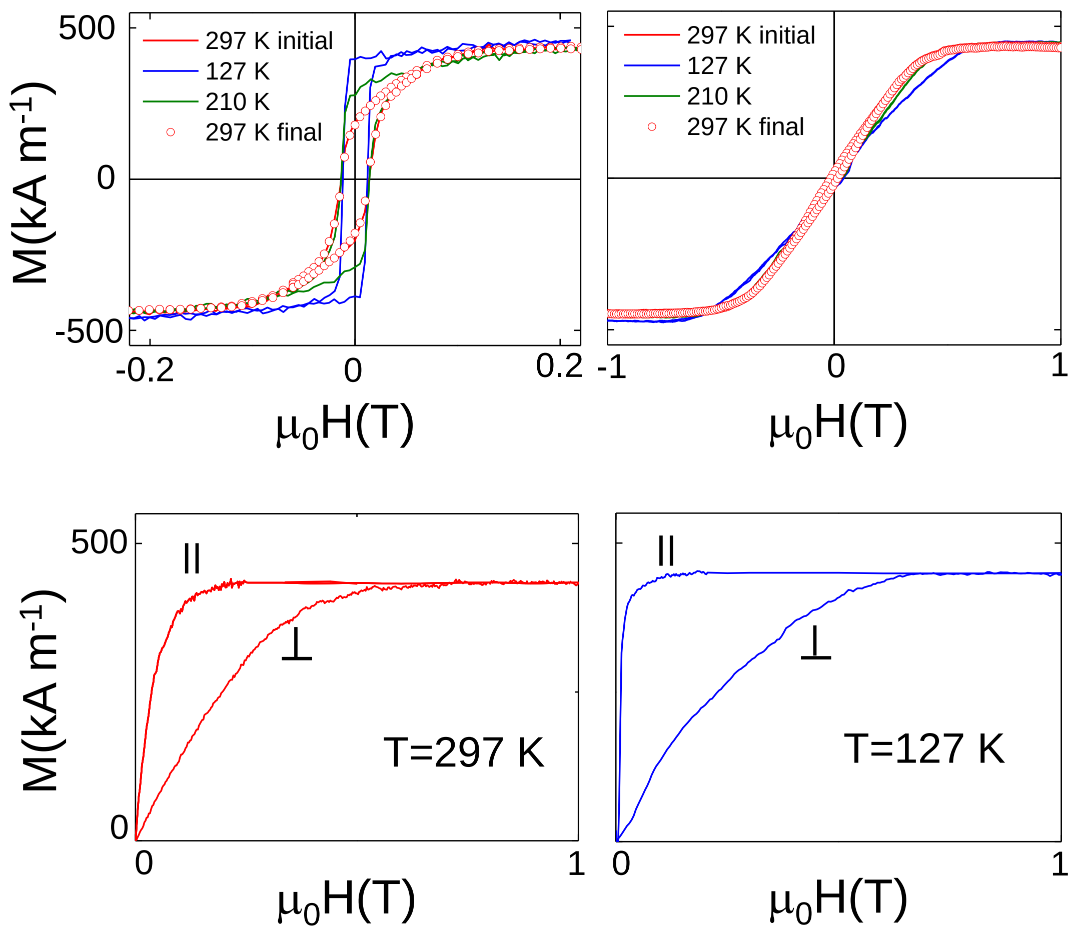
# Polycrystalline Ni on single-crystal BTO

*M*(*T*) from VSM



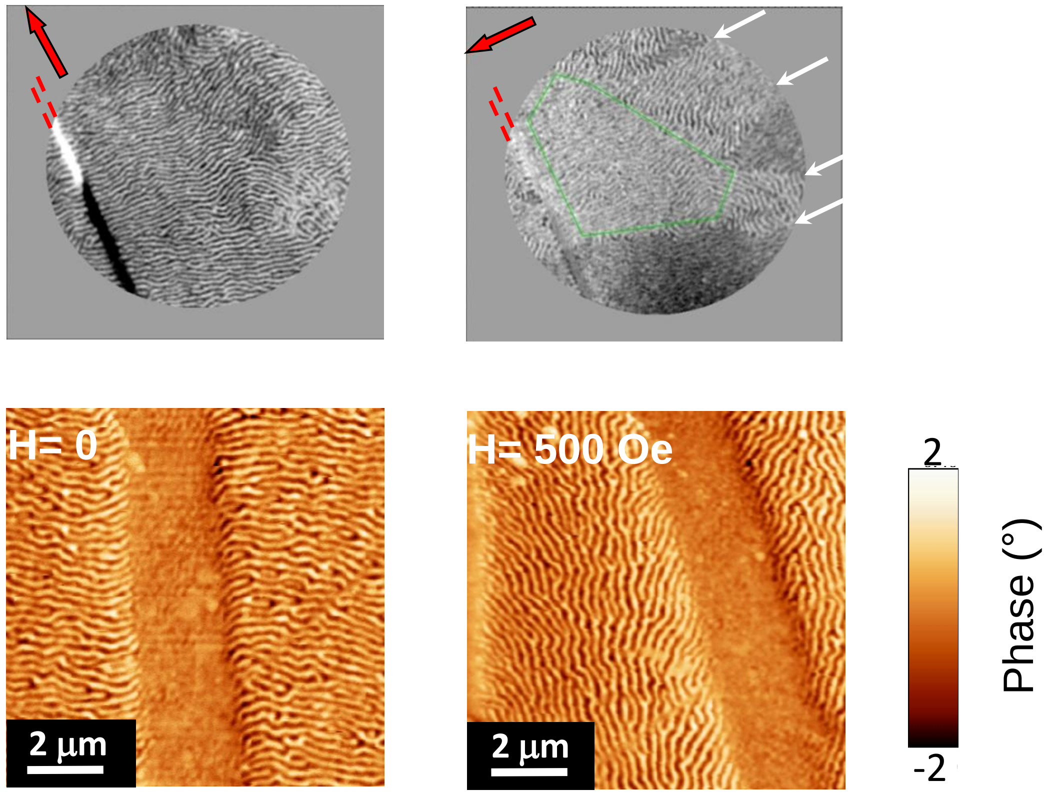
# Polycrystalline Ni on single-crystal BTO

*M*(*H*) from VSM on changing *T*



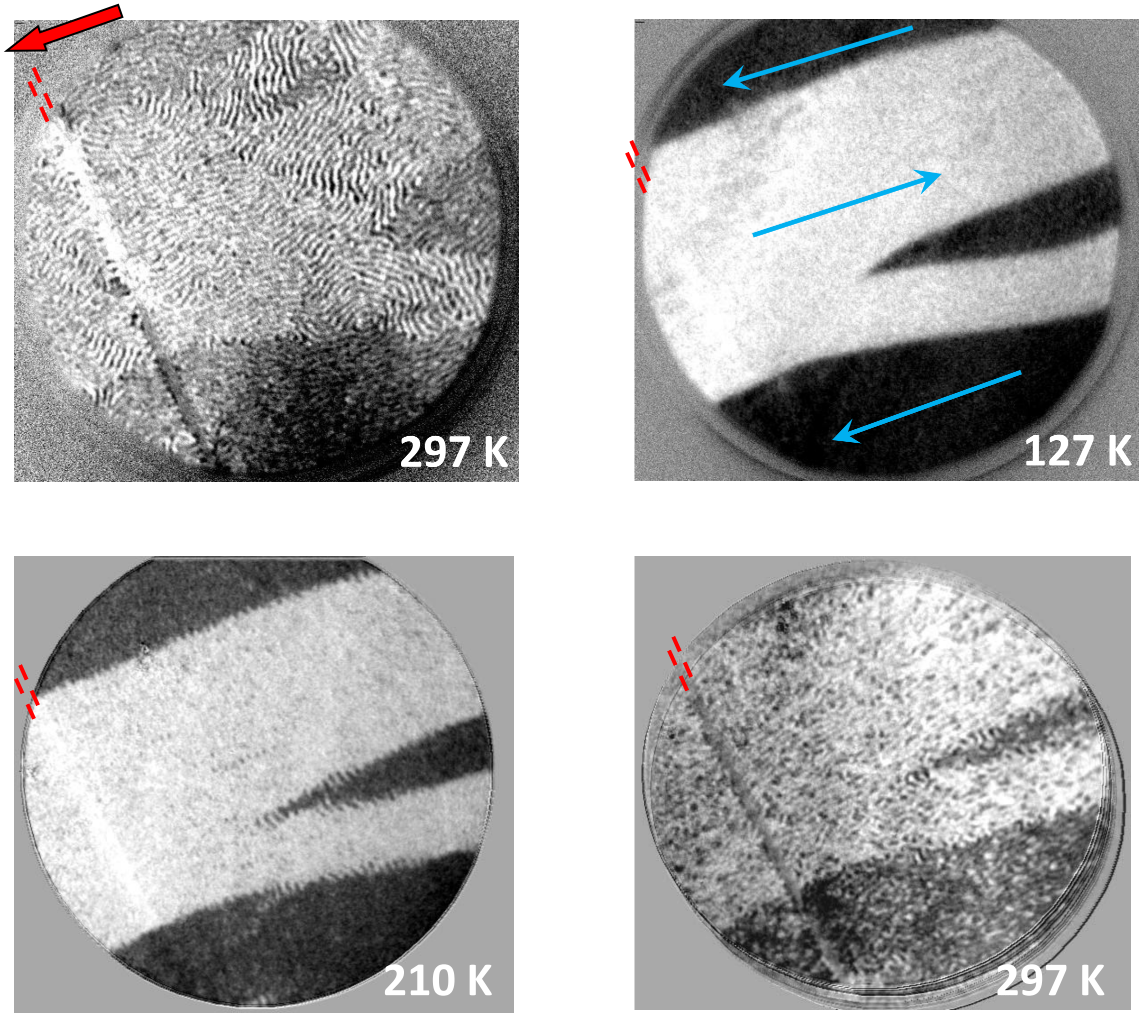
# Polycrystalline Ni on single-crystal BTO

Magnetic maps using XMCD-PEEM and MFM




Room-temperature stripe width ⇒ $K_z$ = 22 kJ $m^{-3}$ ⇒ $\sigma \sim 0.5$ GPa

# Magnetic maps on changing *T*



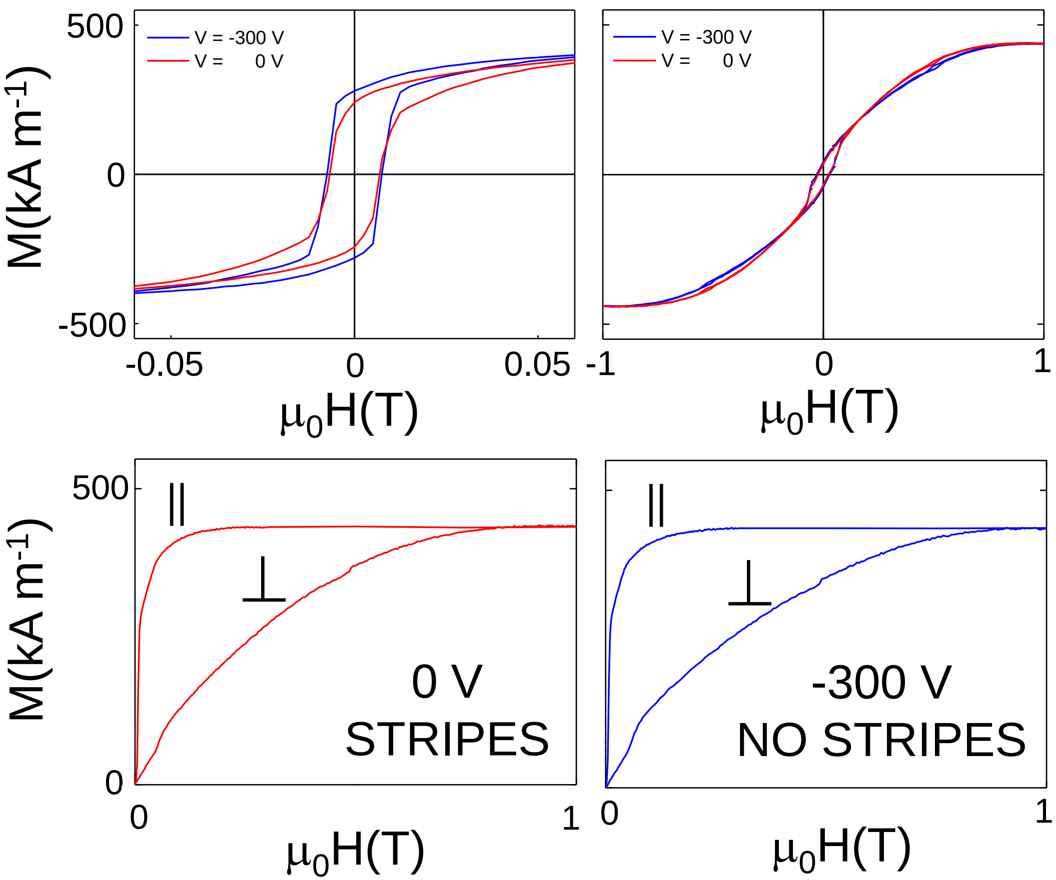

T

R

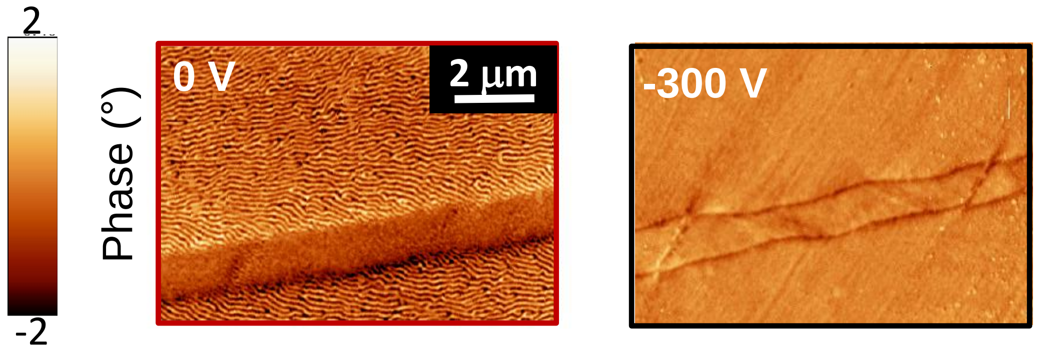
O

T

# VSM and MFM on changing E



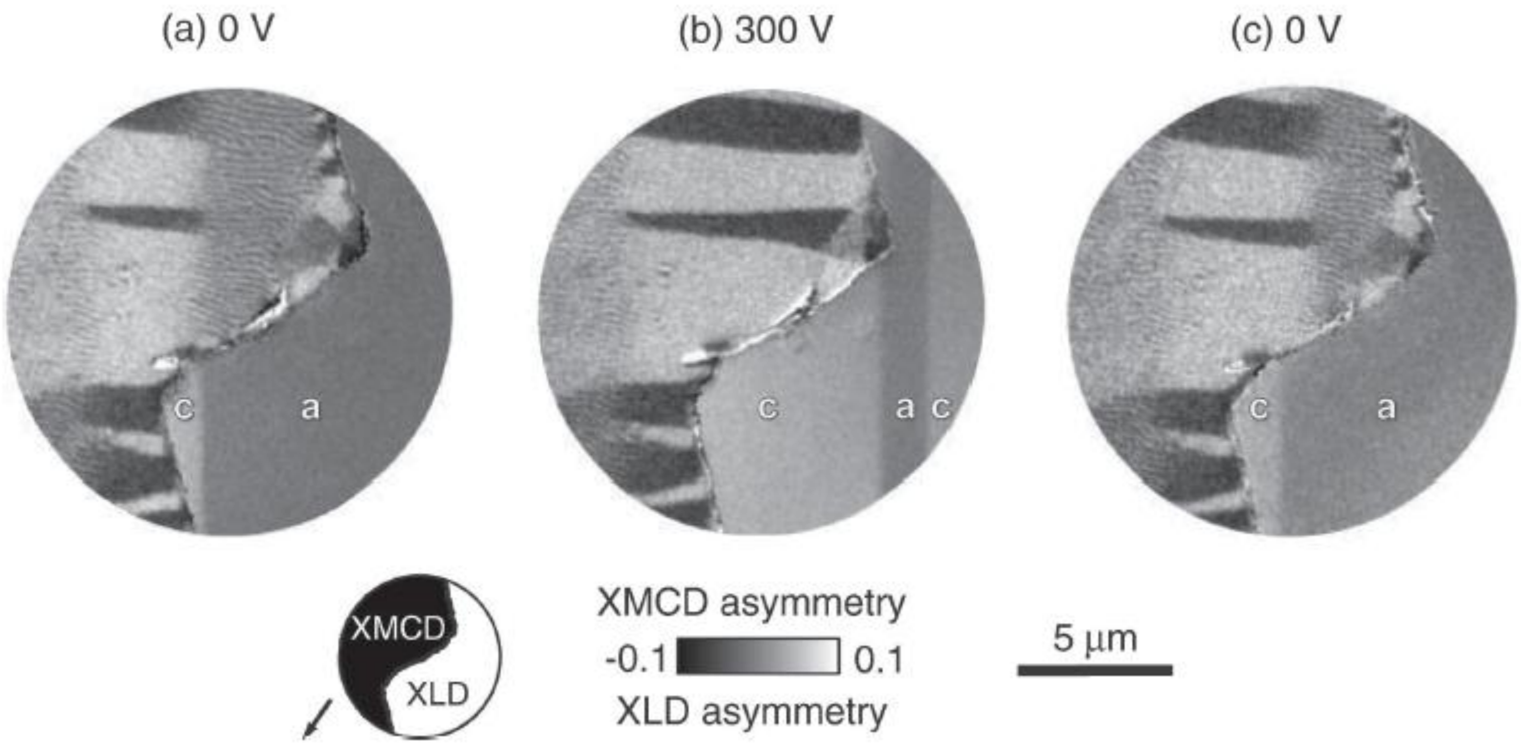

Not all BTO domains switch
Changes with E suppressed




~1% change from $c_{BTO}$ to $a_{BTO}$
Similar to change on cooling

# Repeatable volatile switching of stripes

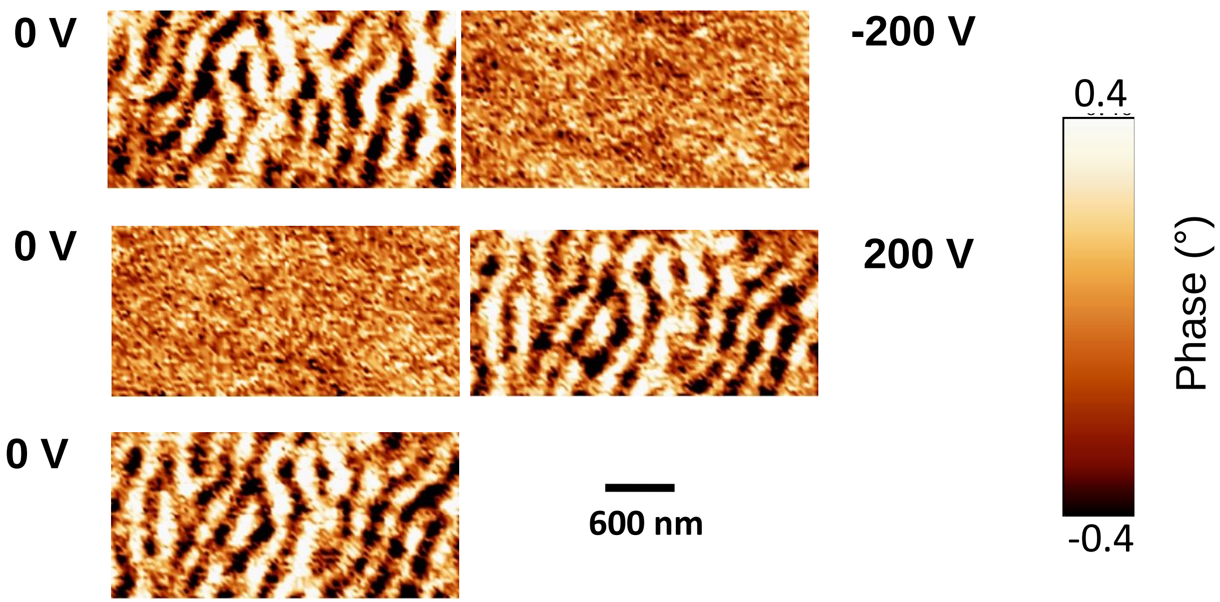
PEEM XMCD and XLD at different E
Stripe domains switch on and off




M. Ghidini *et al.*,
Advanced Materials **27**, 1460 (2015)

# Repeatable non-volatile switching of stripes

MFM at different E
Stripe domains switch on and off at 0 V




M. Ghidini *et al.*,
Advanced Materials **27**, 1460 (2015)

# Oxide magnetoelectrics

Background

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LSMO/BTO

LCMO/BTO

Strain-control of local magnetism in Ni films

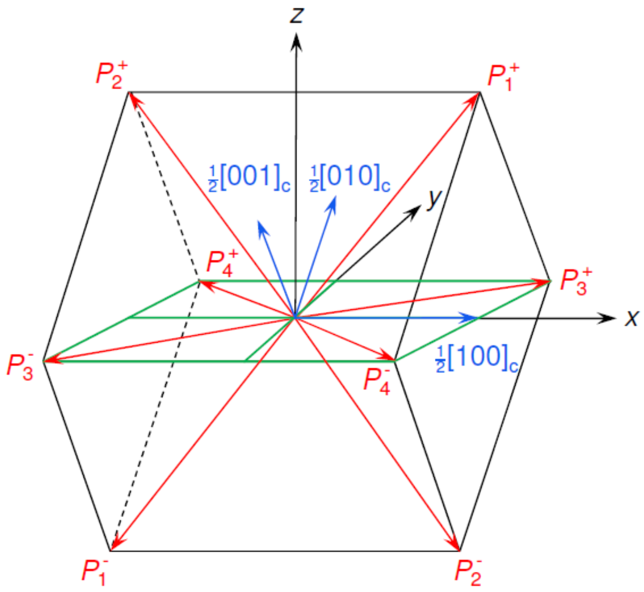
Ni/BTO

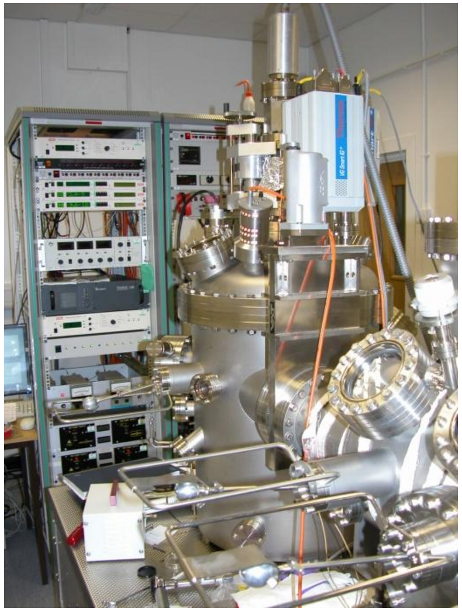
Ni/PMN-PT

# Ni/PMN-PT $(011)_{pc}$

RT Ni deposition by e-beam assisted
thermal evaporation
on ferroelectric single-crystal substrates

Cu(3 nm)/Ni(10 nm)/PMN-PT (0.3 mm)

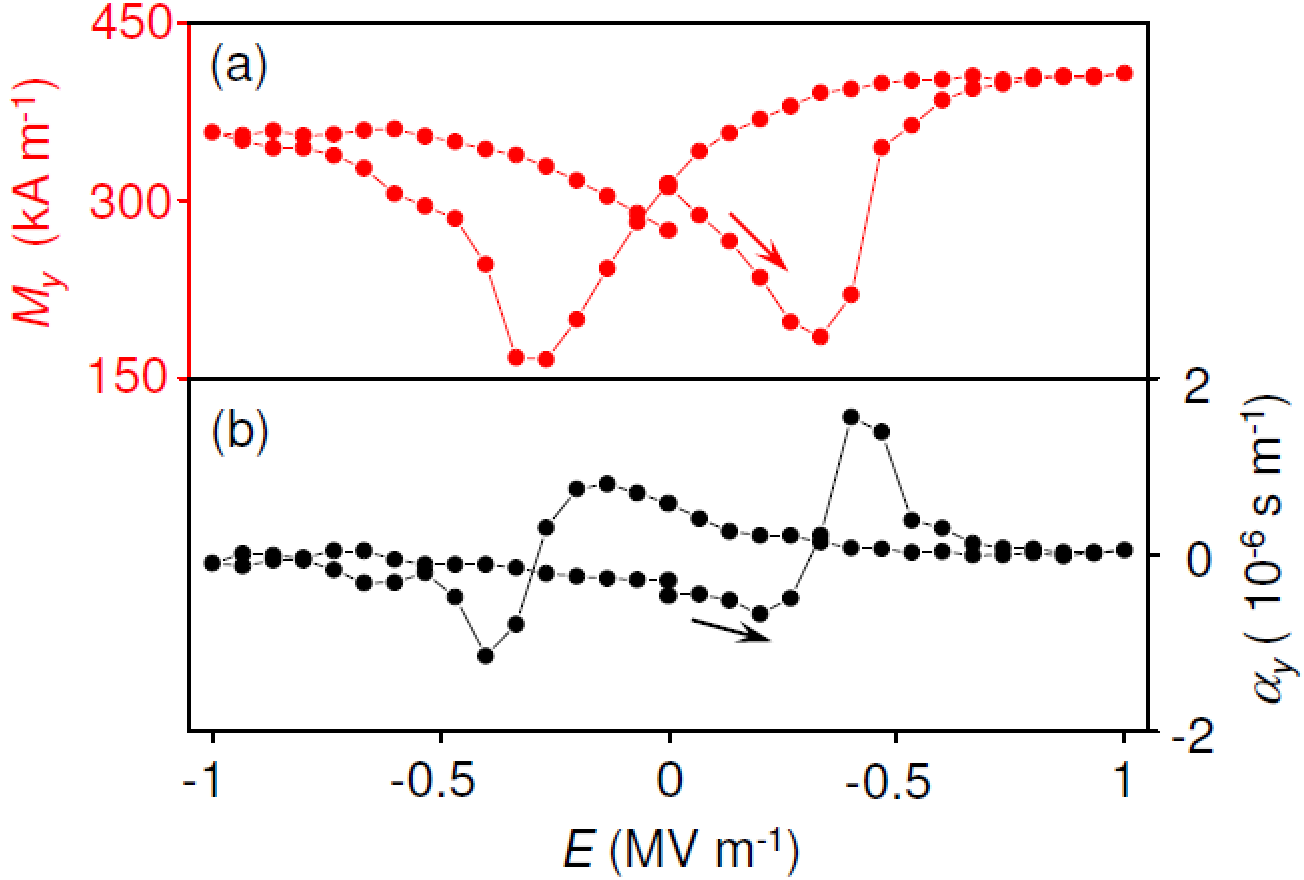


UHV-MBE chamber
$P_{base}$ = 1.5 x$10^{-10}$ mbar

N.-J. Steinke, R. Mansell,
C. H. W. Barnes
(Cavendish Lab.)

# Macroscopic ME effects in Ni/PMN-PT



# Global and local magnetization

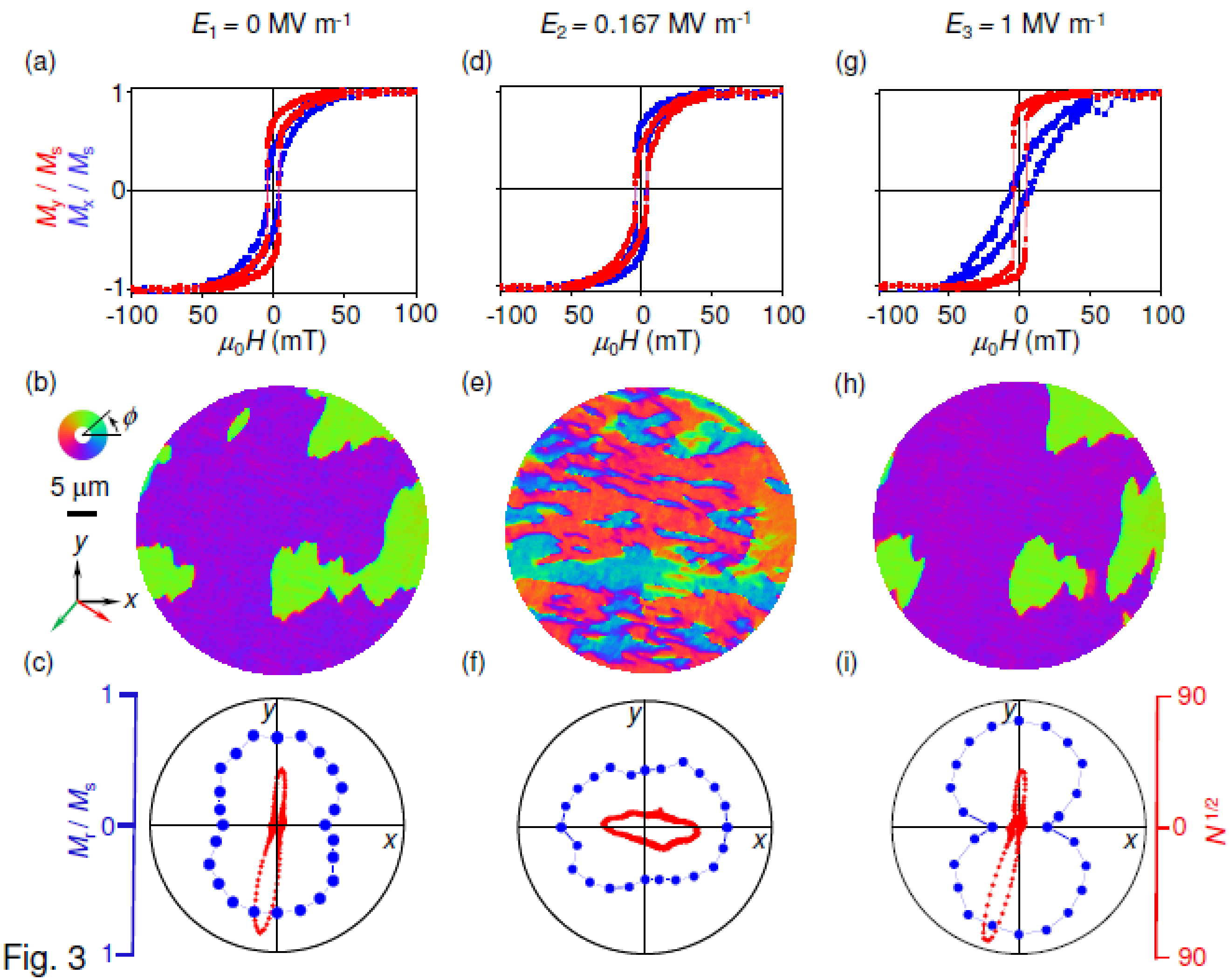
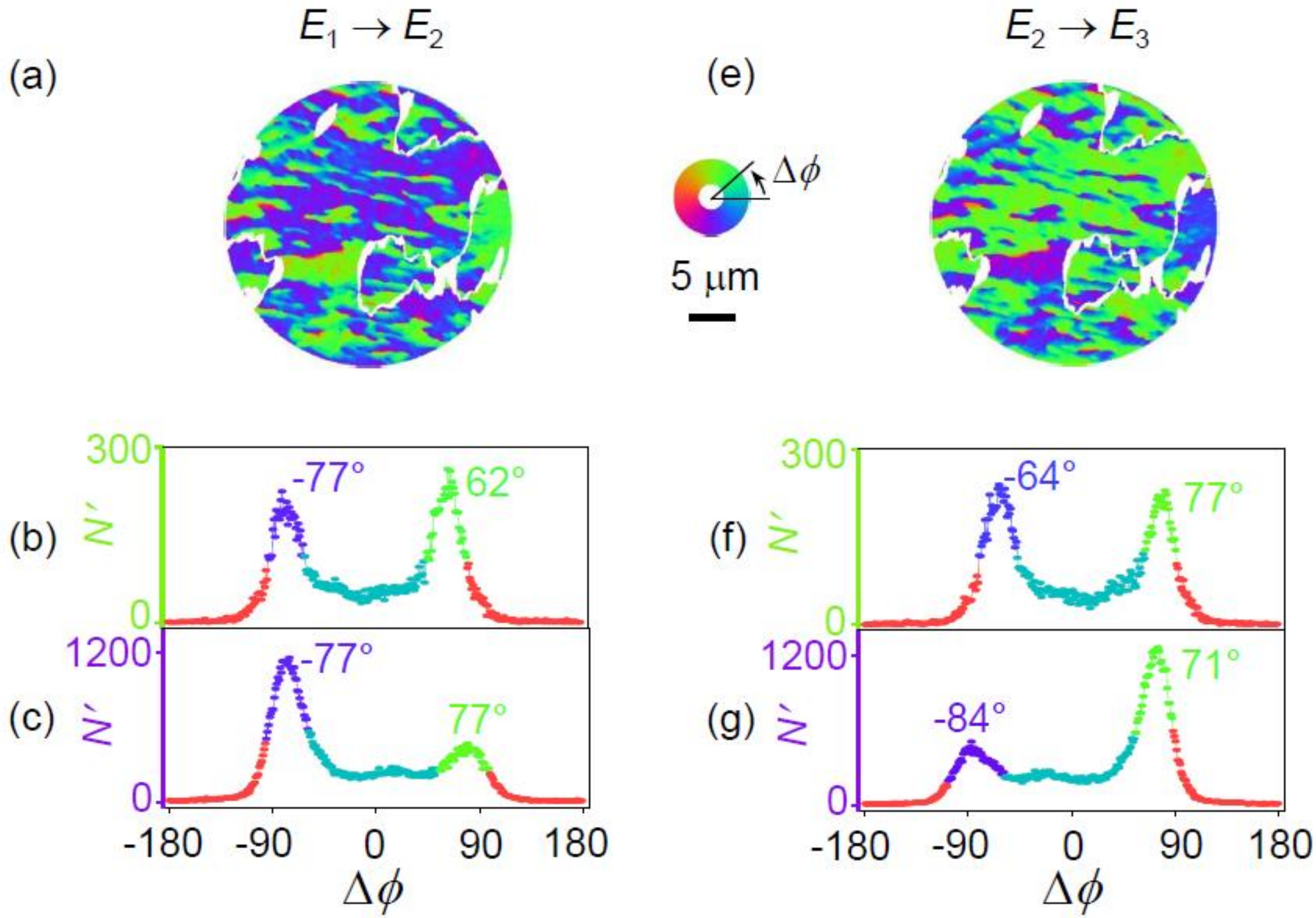


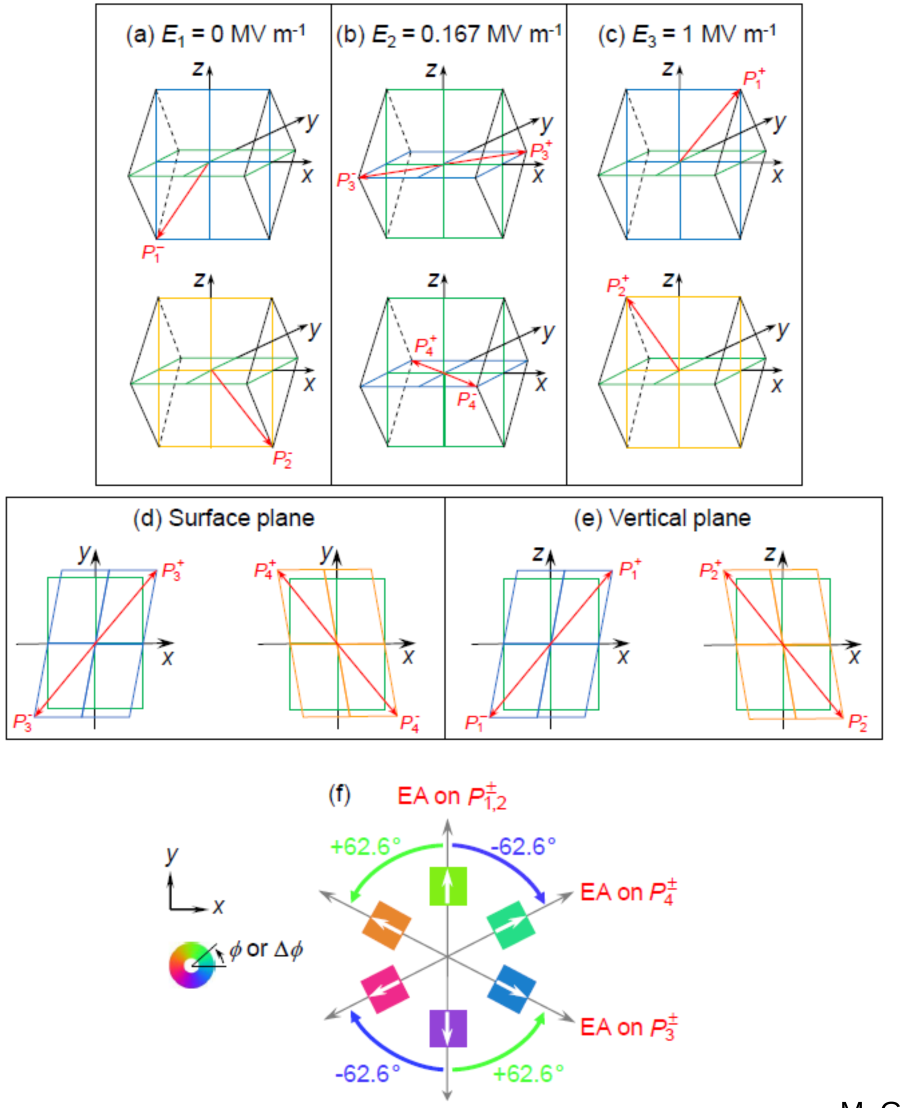
Fig. 3

# Changes in local magnetization




M. Ghidini *et al., Nature Materials* 2019,
doi.org/10.1038/s41563-019-0374-8

# Shear-strain-mediated ME effects




M. Ghidini *et al.*, *Nature Materials* 2019,
doi.org/10.1038/s41563-019-0374-8

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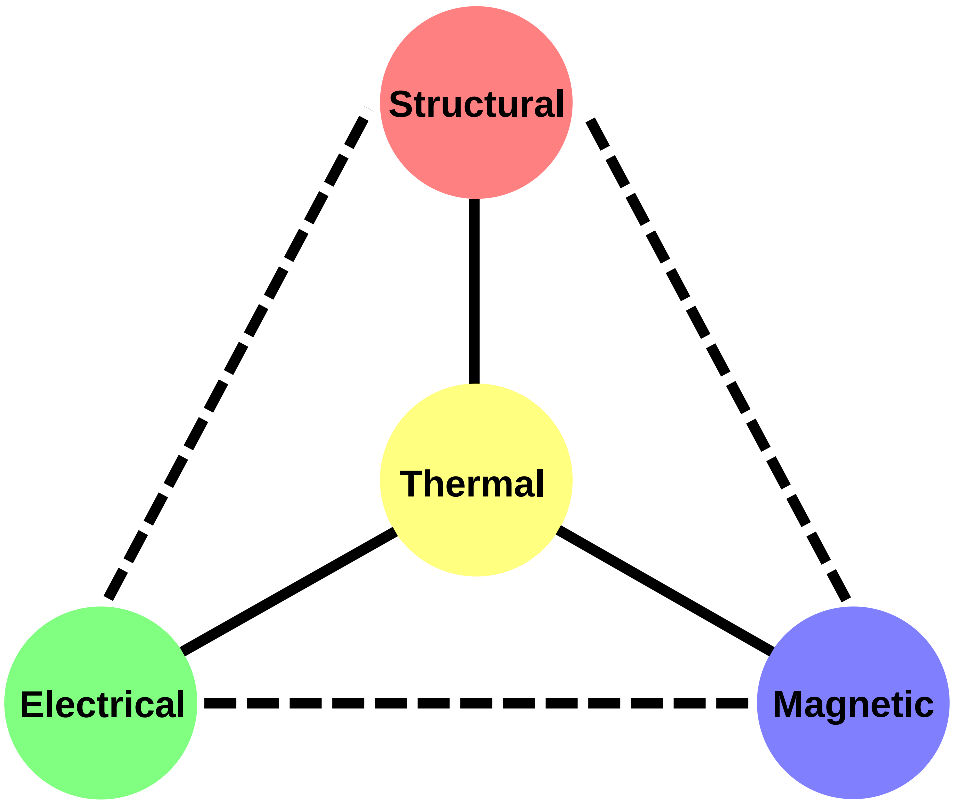
Ni/PMN-PT

# Oxide magnetoelectrics

Extremely fertile playground for direct and converse ME effects



# The Times They Are A-Changin'

Bob Dylan, 1964

I used to be so hot