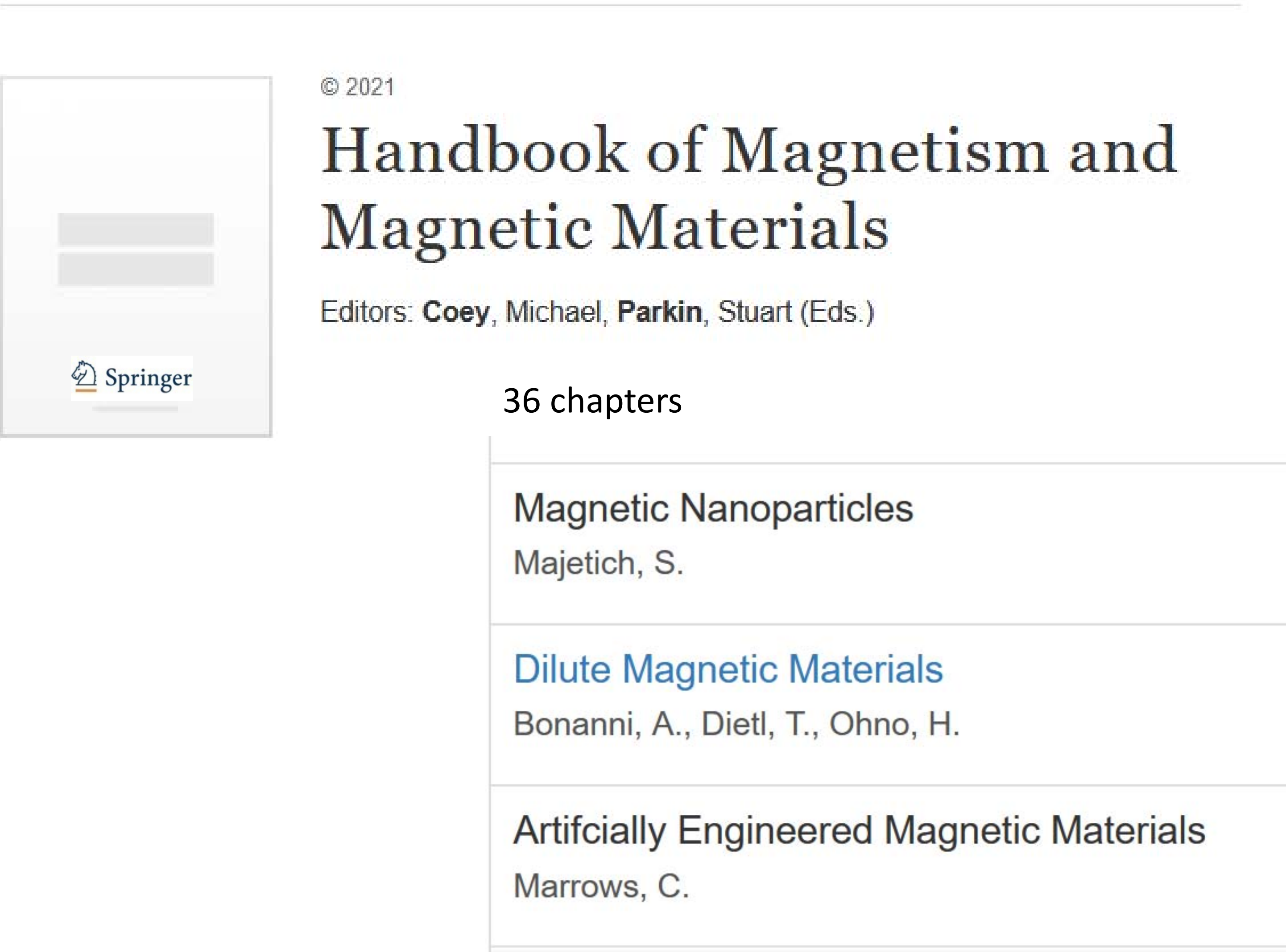
Electric-field effects on localized spins

Tomasz Dietl

1. International Centre for Interfacing
Magnetism and Superconductivity with Topological Matter ***MagTop***
at the Institute of Physics, Polish Academy of Sciences, Warsaw, Poland
www.MagTop.ifpan.edu.pl

2. WPI Advanced Institute for Materials Research
Tohoku University, Sendai, Japan

European Funds Smart Growth
Republic of Poland
FNP Foundation for Polish Science
European Union European Regional Development Fund
Alexander von Humboldt Stiftung / Foundation



© 2021

Handbook of Magnetism and Magnetic Materials

Editors: **Coey**, Michael, **Parkin**, Stuart (Eds.)

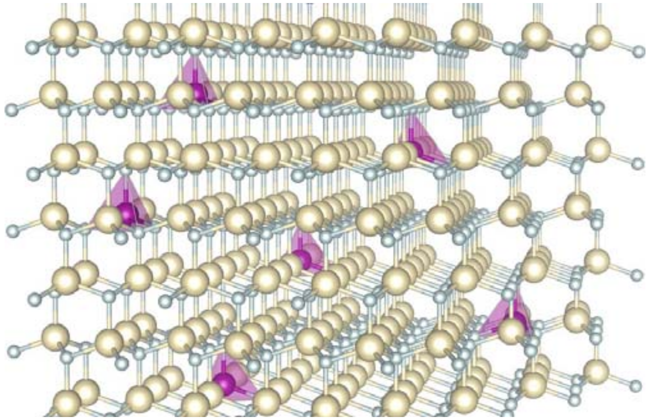
36 chapters

Magnetic Nanoparticles
Majetich, S.

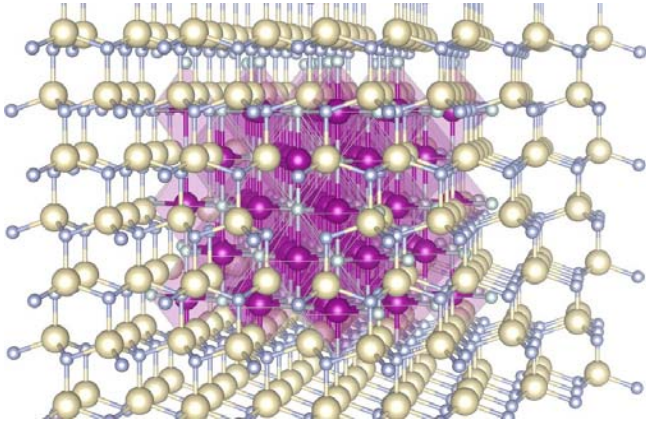
Dilute Magnetic Materials
Bonanni, A., Dietl, T., Ohno, H.

Artifcially Engineered Magnetic Materials
Marrows, C.

Spatial distribution of magnetic component



random

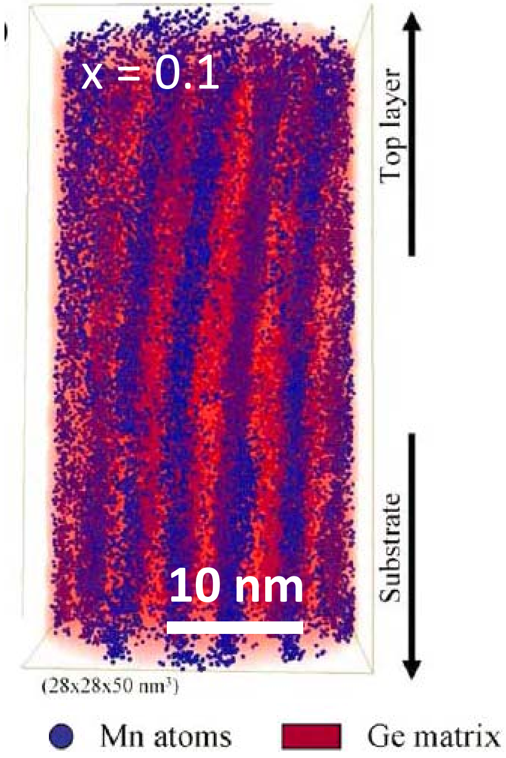


non-random

Aggregation of magnetic cations - nanocolumns

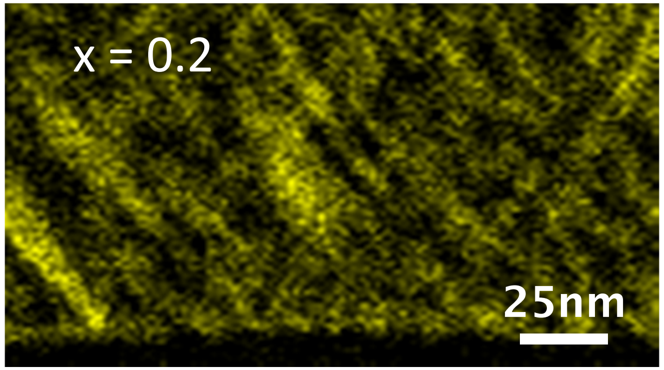
MBE growth (001)

$Ge_{1-x}Mn_x$



I. Mouton et al. [Rouen, Grenoble] JAP'2012

$Zn_{1-x}Cr_xTe$



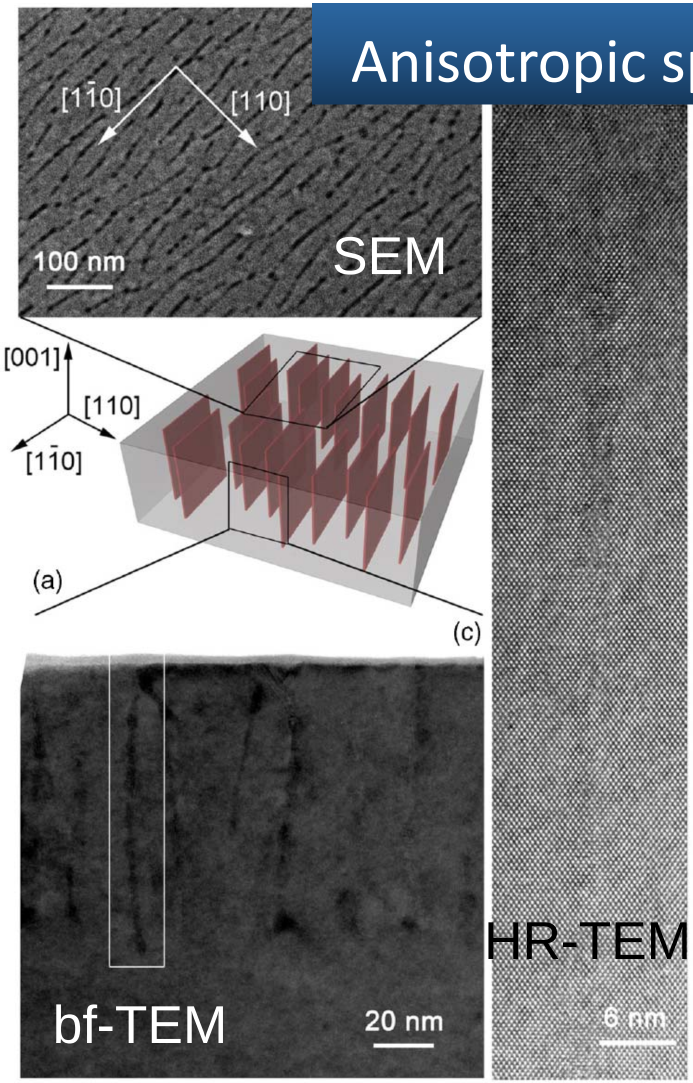
Y. Nishio et al. (Tsukuba) MRS Proc.'09

spinodal decomposition

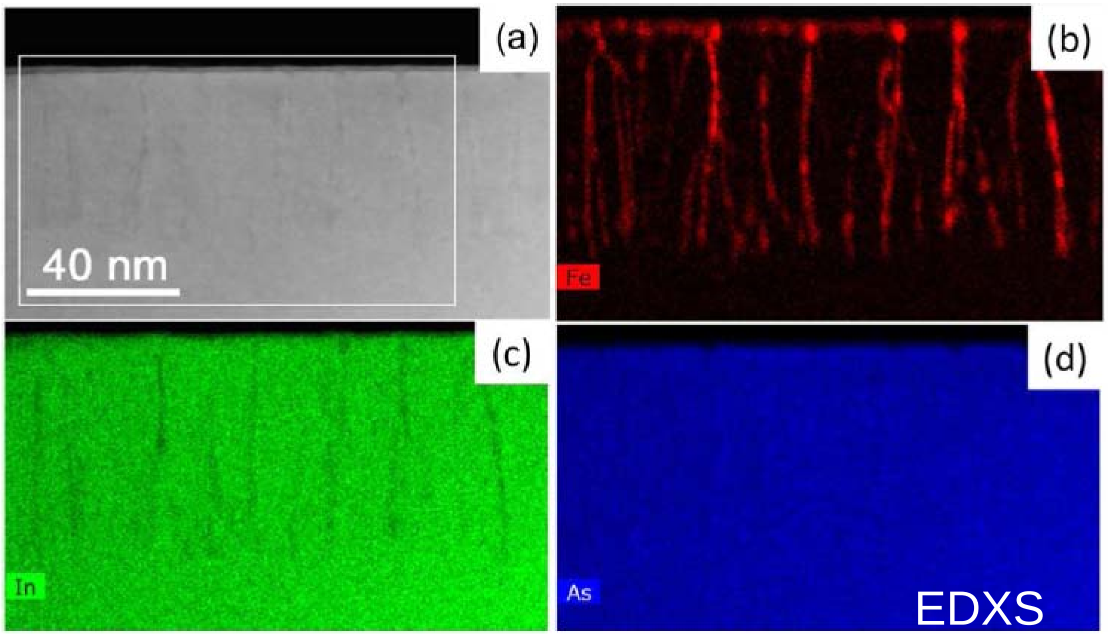
when self-organized growth of magnetic nanostructures will be competitive with top-down approaches dominating today?

T. Dietl et al., Spinodal nanodecomposition in semiconductors doped with transition metals, *Rev. Mod. Phys.* **87**, 1311 (2015)

Anisotropic spinodal decomposition



(001)$In_{1-x}Fe_xAs$, x = 0.04



Fe-rich nanoplates oriented along [-110]

[110] ≠ [-110] nematicity $D_{2d} \rightarrow C_{2v}$

Ye Yuan et al. [Dresden, Warsaw] PRMater'2018

Examples of nematicity

GaAs/Al$_x$Ga$_{1-x}$ As QW AMR in QHE/FQHE $D_{2d} \rightarrow C_{2v}$

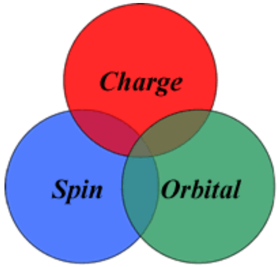
Ga$_{1-x}$Mn$_x$As magnetic anisotropy, AMR $D_{2d} \rightarrow C_{2v}$

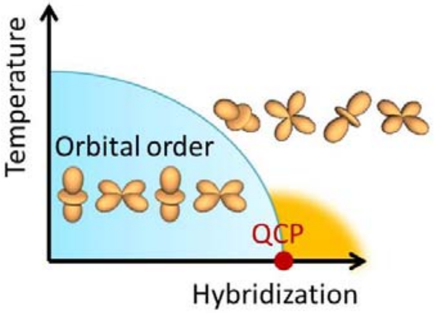
Cu$_x$Bi$_2$Se$_3$ anisotropy of sc gap $D_{3d} \rightarrow C_{2v}$

....

Literature model:

spontaneous symmetry breaking by ordering of charge or spin or orbital … degrees of freedom at low temperatures

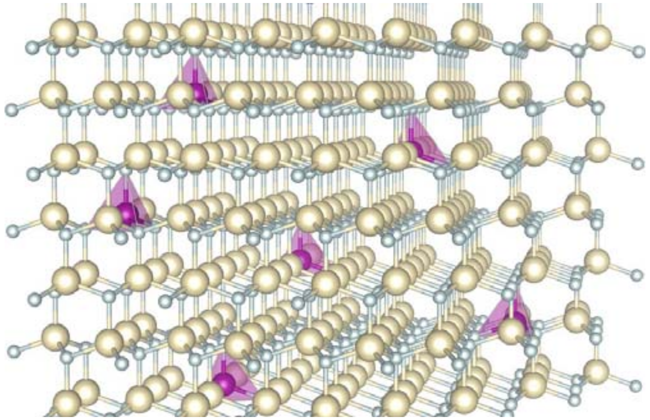




In most cases symmetry breaking (nematicity) originates from quenched anisotropic spinodal decomposition of alloy components/impurities/defects/… appearing during the growth

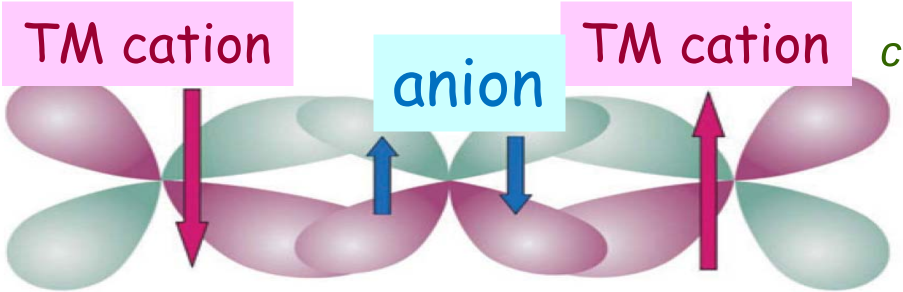
theory: *M. Birowska et al. [Warsaw] PRL’2012*
Ye Yuan et al. [Dresden, Warsaw] PRMater’2018

Random distribution, no carriers

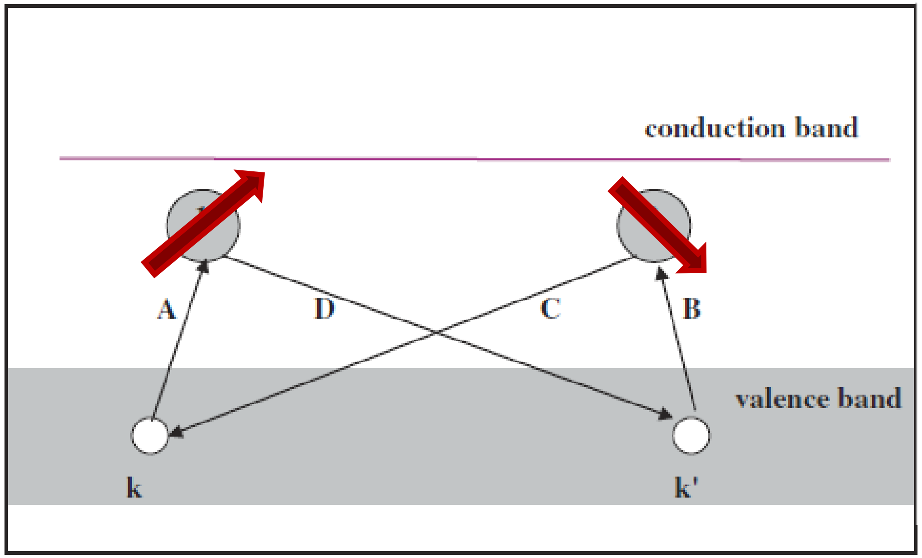


spin-spin interactions?

Superexchange in II-VI/III-V DMS



p-d hybridization



cf. P.W. Anderson, J.B. Goodenough, J. Kanamori

- always present in magnetic compounds
- 4th order in V_{pd}
- short range $J_{ij} = J_0\exp(-R_{ij}/b)$
- usually antiferromagnetic , e.g., for

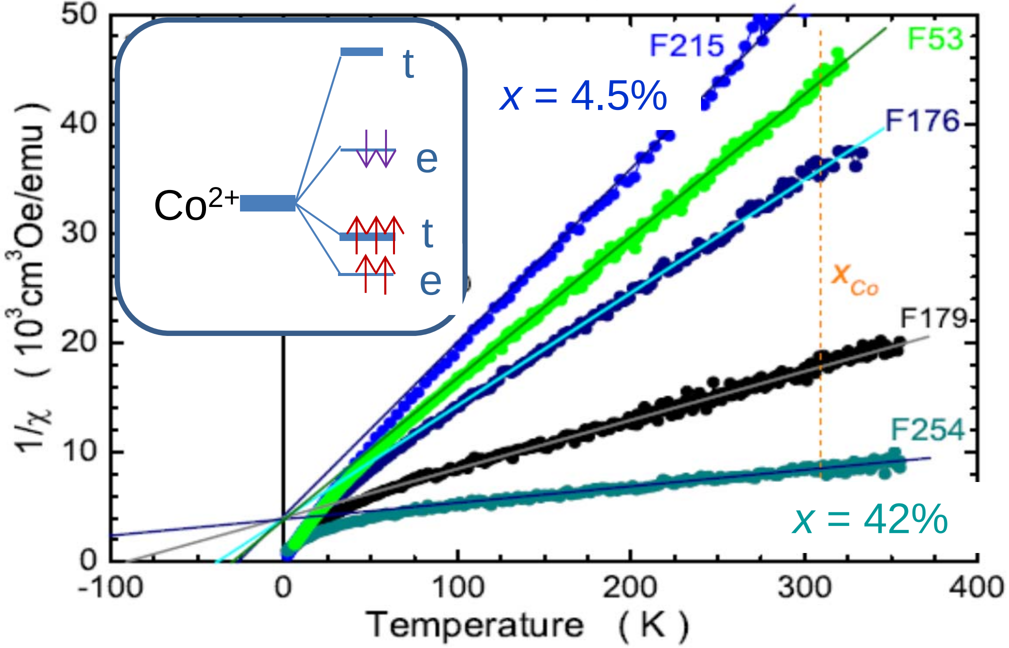
  Mn^{2+},Fe^{3+}, Co^{2+} in tetrahedral DMS

  J. Spałek et al. [Purdue, Krakow, Warsaw] PRB'1986
  B.E. Larson et al. [Harvard] PRB'1988
- can be ferromagnetic, e.g., for
  Mn^{3+}, Cr^{2+}, V^{2+} in tetrahedral DMS

  J. Blinowski et al. [Warsaw, Schottky] PRB'1996

wz-$Zn_{1-x}Co_xO$ – $1/\chi$ vs. T AF superexchange

grown by ALD at 160°C, low electron density



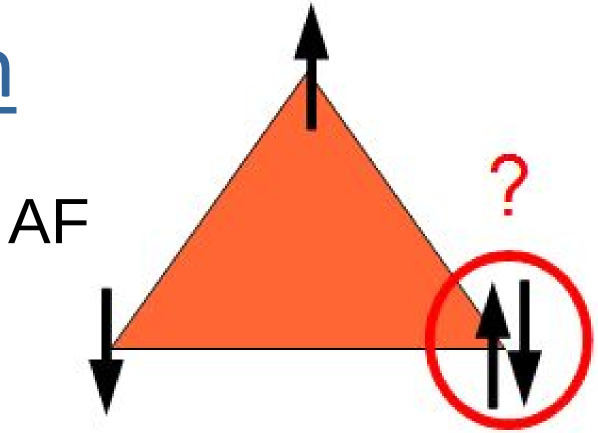
- $\Theta_{CW} < 0$ => AF interactions
- common intersection ➔ random Co distribution
- $T_c \ll \Theta_{CW}$
- ferro features under specific growth conditions
  - Co inclusions
  - uncompensated spins at surface of AF CoO nanocrystals

T. D. et al. [Warsaw, Singapore] PRB'2007

M. Sawicki et al. [Warsaw] PRB'2013
cf. A. Ney et al. [Duisburg-Essen, Pacific, Grenoble] PRL'2008

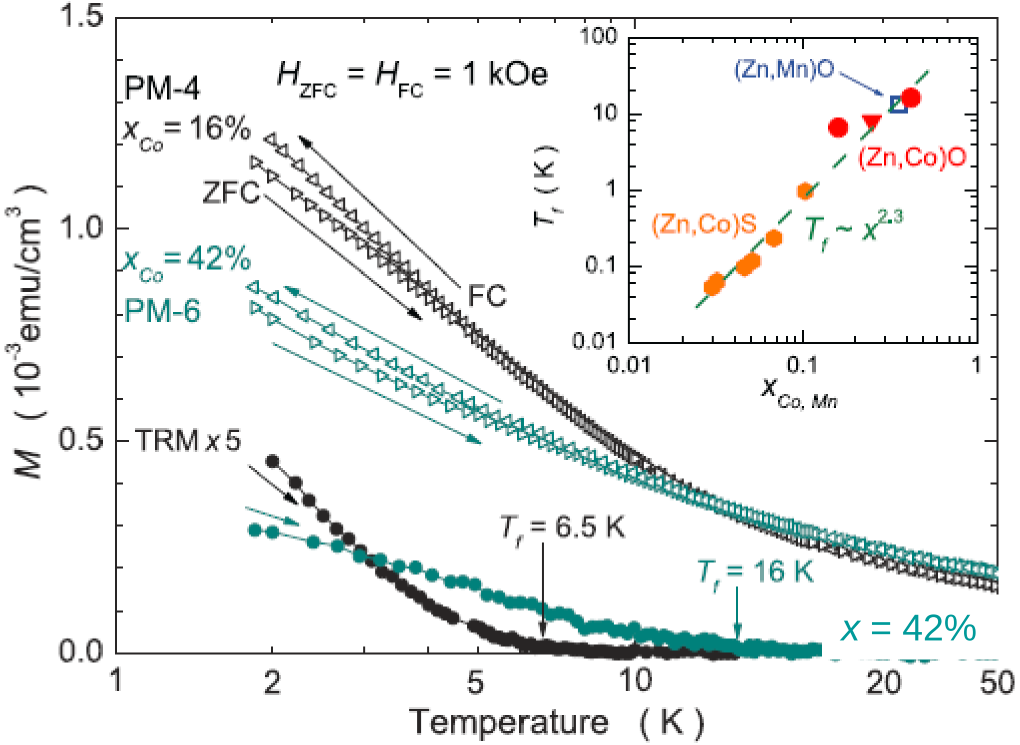
Random antiferromagnets

Frustration



e.g., C. Lacroix, P. Mendels, F. Mila "Introduction to Frustrated Magnetism", Springer 2011

Spin-glass freezing in $Zn_{1-x}Co_xO$



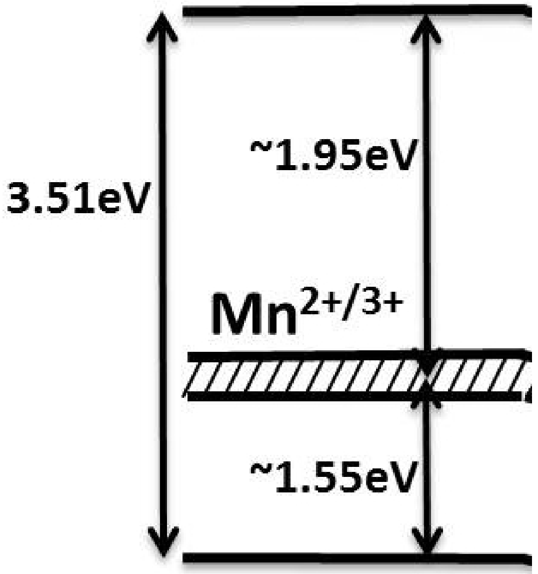
$T_f << \Theta_{CW}$

M. Sawicki et al. [Warsaw] PRB’2013

Semiinsulating GaN:Mn by AMMONO/Unipress

M. Zajac et al. [Warsaw] APL'2001
A. Wolos et al. [Warsaw] PRB'2004

Mn – deep acceptor in GaN)-:



Mn – ideal for making S.I. GaN (-:

M. Zajac et al. [AMMONO/Unipress] Prog. Crys. Growth'2018


ieee spectrum 7.10

THE MAGAZINE OF TECHNOLOGY INSIDERS

HOW A LITTLE COMPANY IN POLAND MAKES THE SEMICONDUCTOR INDUSTRY'S HOT NEW ROCK

The Crystal That Will Change Everything

THE TROUBLE WITH MULTICORE MICROPROCESSORS

DECODING THE NEANDERTHAL GENOME

R. Dwilinski

Magnetism and its control in wz-$Ga_{1-x}Mn_xN$ epilayers

Collaborators:

D. Sztenkiel, M. Foltyn, G. P. Mazur,
K. Gas, C. Śliwa, M. Sawicki

R. Adhikari, A. Bonanni

JKU Linz

MOVPE/Adv. charac.

D. Hommel

PORT
Polish Center for
Technology Development

MBE

N. Gonzalez Szwacki, J. A. Majewski

Ga-subsitutional Mn acceptor in wurtzite GaN

☐ forms mid-gap Mn^{2+}/Mn^{3+} (A^{-}/A^{0}) level (impurity band)

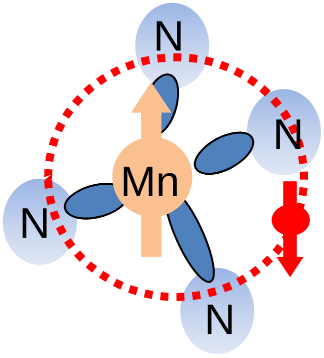
T. Graf et al. [Schottky] pss'2003; Wolos et al. [Warsaw] PRB'2004

➔ GaN:Mn excellent semi-insulating material
(up to at least 10% of Mn)

☐ hole binding energy: mostly *p-d* hybridization

➔ Zhang-Rice polaron; $Mn^{3+} = Mn^{2+} + h$

T. D. et al. [Warsaw, Tohoku] PRB'2002

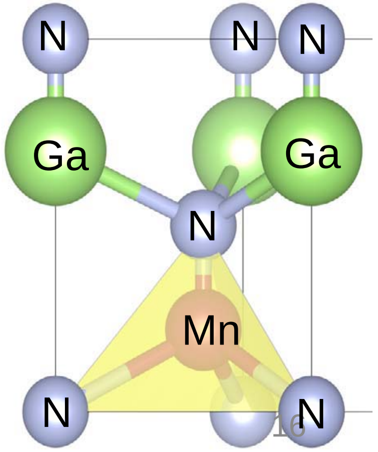


☐ Mn^{3+} high spin configuration $^{5}T_{2}$ ($S = 2$, $L = 2$)
confirmed by high-field EPR, EXAFS, XANES, XES

A. Bonanni et al. [Linz, Warsaw,Grenoble] PRB'2010'2011, Sci. Rep.'2012

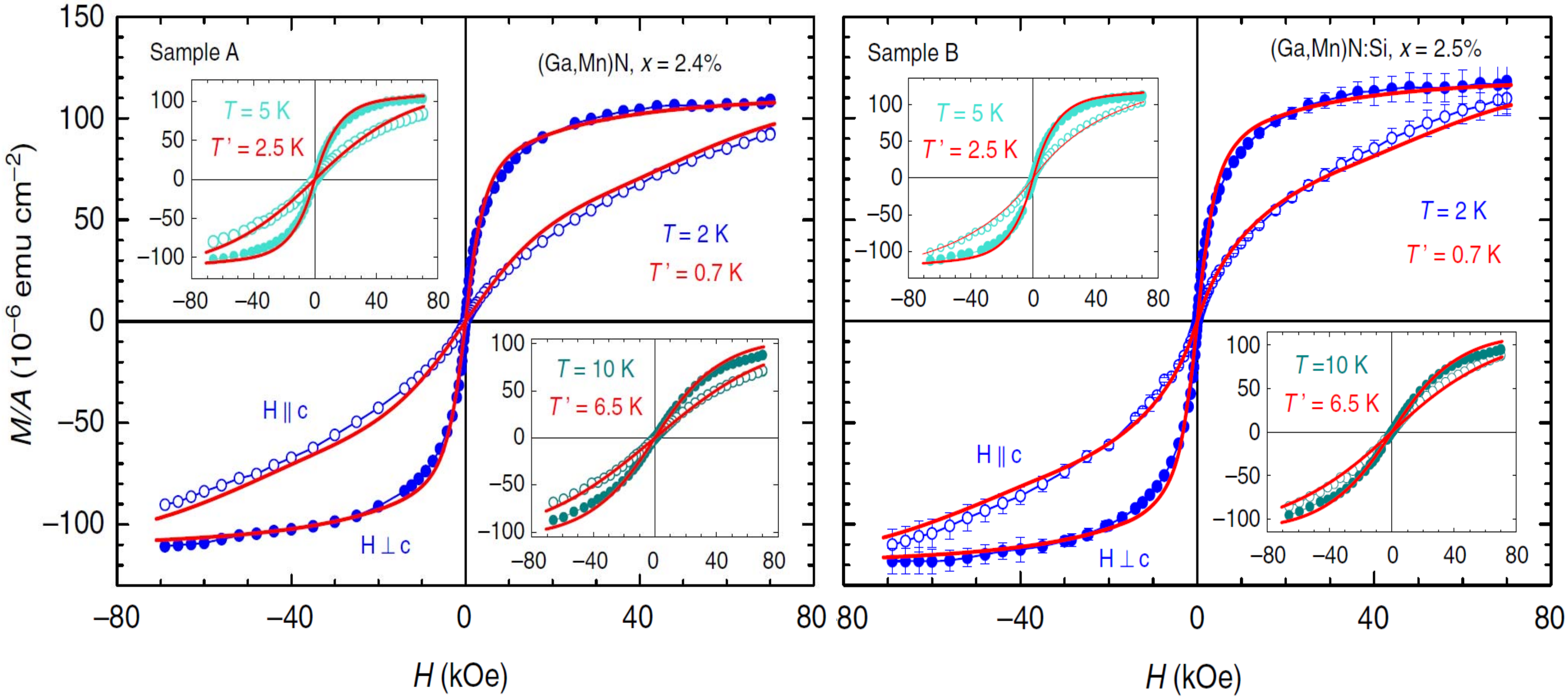
➔ Jahn-Teller distortion along one of <100> cubic axes
➔ wz trigonal distortion along [111] cubic axis

J. Gosk et al. [Warsaw] PRB'2005; W. Stefanowicz et al. [Warsaw, Linz] PRB'2010
cf. F. Virot et al. [Marseille, Mostaganem] JPC'2010



☐ crystal-field parameters known [x-ray, optics, *M(T,H)*]

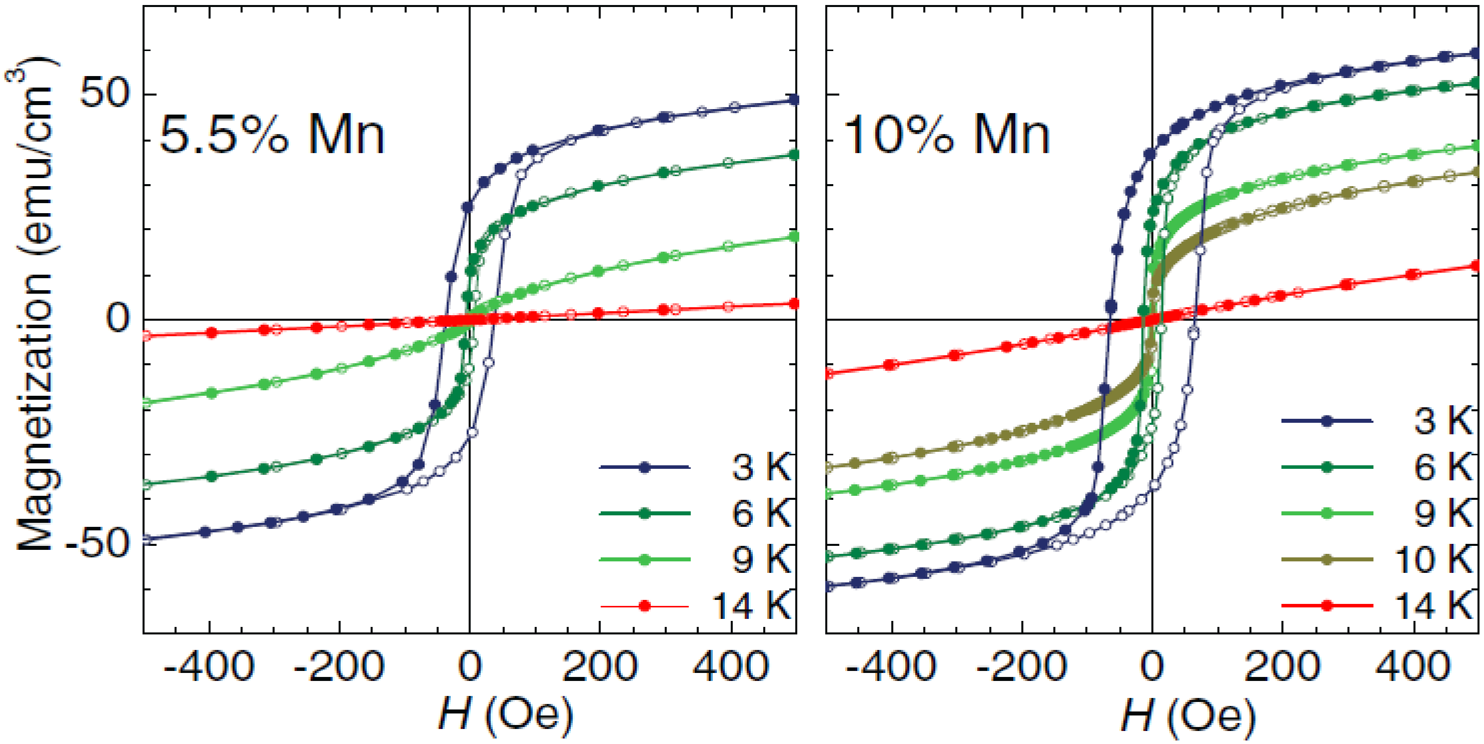
$M(T,H)$ in paramagnetic in wz-Ga$_{1\text{-}x}$Mn$_x$N: exp. vs. theory



Mn^{3+} $\mathcal{H} = \mathcal{H}_{\mathrm{TE}} + \mathcal{H}_{\mathrm{JT}} + \mathcal{H}_{\mathrm{TR}} + \mathcal{H}_{\mathrm{SO}} + \mathcal{H}_{\mathrm{Z}}$

Mn^{2+} ~ 10%, Mn^{3+} ~ 90%

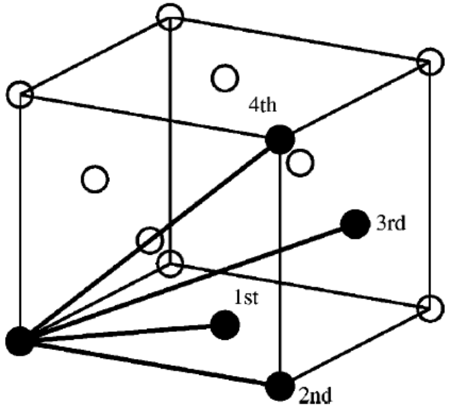
Exp.: Low temperature ferromagnetism in wz-$Ga_{1-x}Mn_xN$



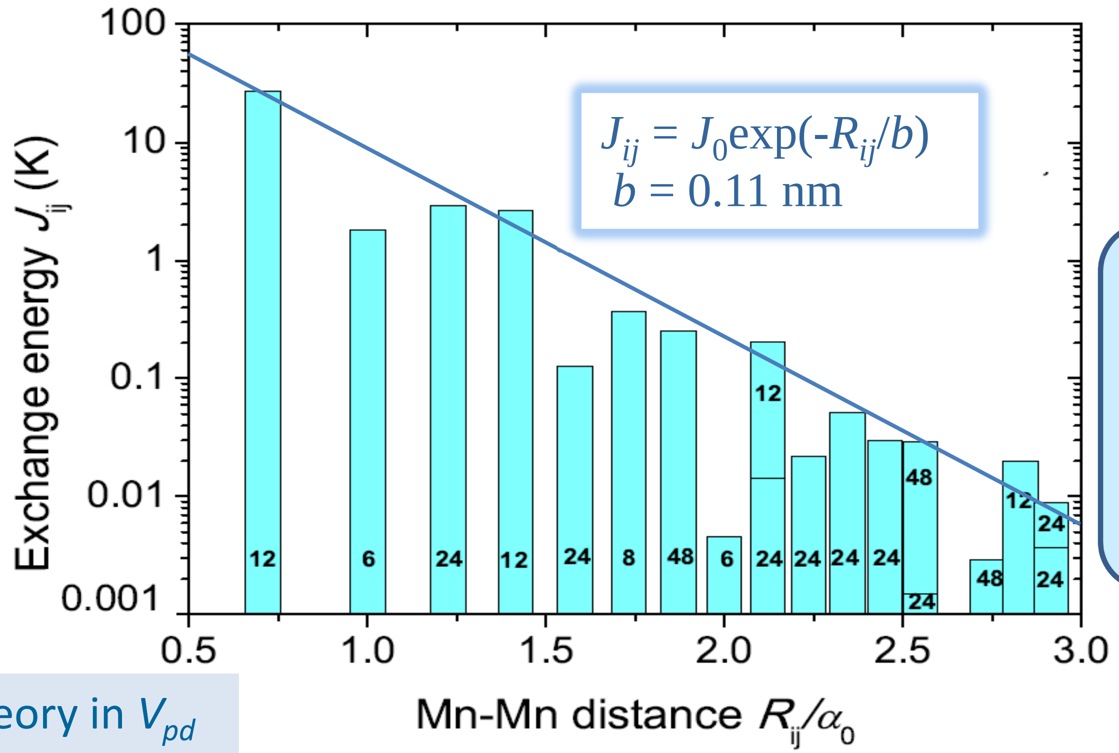
A. Bonanni et al., M. Sawicki et al. [Linz, Warsaw, Bremen, Athens] PRB'2011, 2012,2013
cf. E. Sarigiannidou et al. [Grenoble] PRB'2006

Theory: Ferromagnetic superexchange in $Ga_{1-x}Mn_xN$ with Mn^{3+} TBA

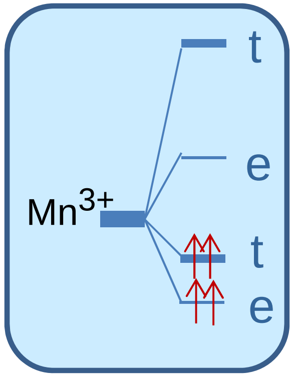
$$H_{ij} = -J_{ij}\mathbf{S}_i\mathbf{S}_j$$



fcc



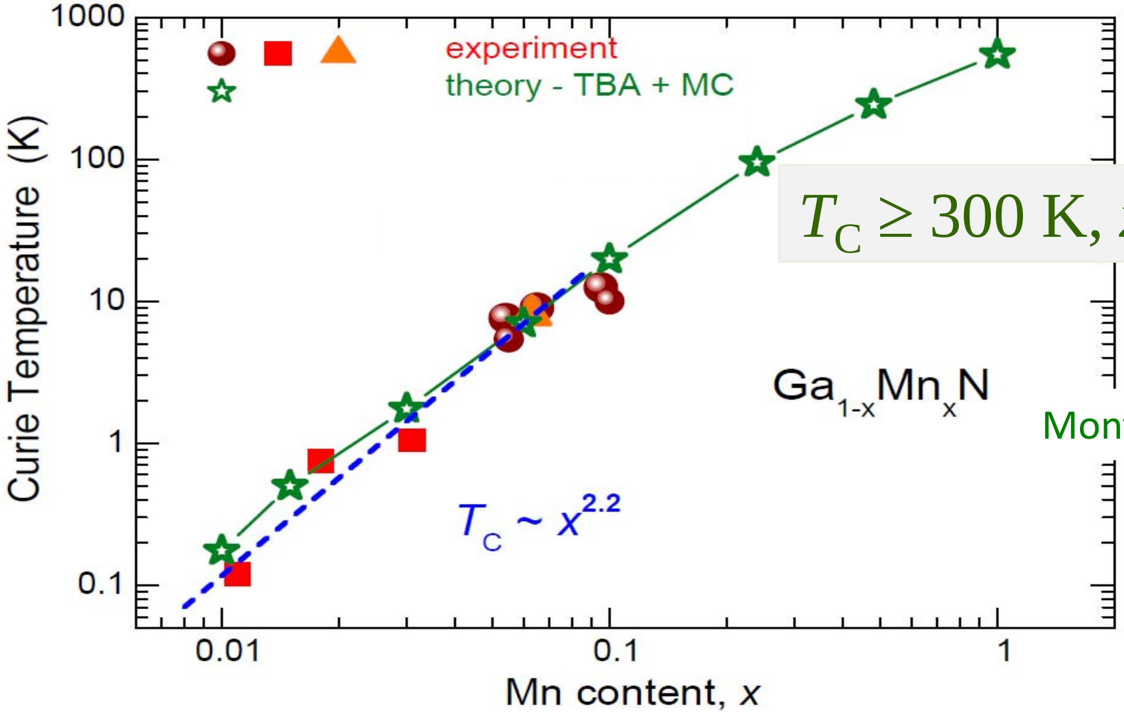
$J_{ij} = J_0\exp(-R_{ij}/b)$
$b = 0.11$ nm



4th order perturb. theory in V_{pd}
parameters from XAS, PE

S. Stefanowicz et al. [Warsaw, Bremen, Athens] PRB'2013

Ferromagnetism of semi-insulating wz-$Ga_{1-x}Mn_xN$ with Mn^{3+} expl/theory



$T_C \geq 300$ K, $x \geq 0.6$

Monte-Carlo J_{ij} up to 16th nn

MOVPE
and MBE grown

ferromagnetic superexchange

M. Sawicki et al. [Warsaw, Linz, Bremen, Athens] PRB'2012,2013

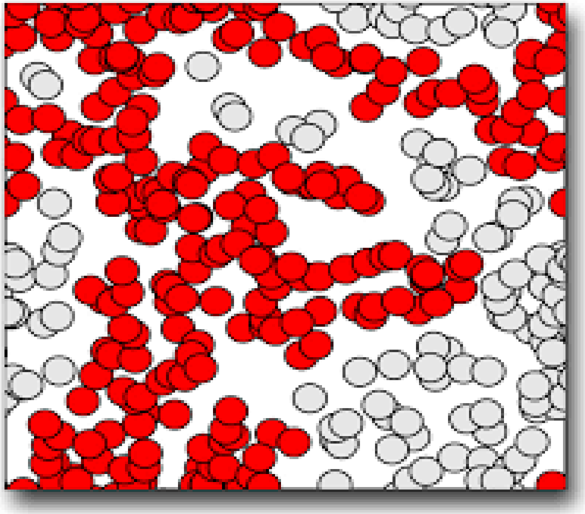
also $[(Bi,Sb)(Cr,V)]_2(Te,Se)_3$

Room temperature ferromagnetic features in DMS (or in nominally non-magnetic semiconductors or oxides) result from spinodal decomposition or contamination

G. Karczewski et al. [Warsaw, Wuerzburg] JSNM'2003
T. Dietl et al. [Warsaw,Osaka,Linz,Grenoble, Tsukuba,Tokyo] Rev. Mod. Phys.'2015

Random ferromagnets

Percolation



e.g., A. Aharony, D. Stauffer "Introduction To Percolation Theory" Taylor & Francis, 2003

Percolation theory of dilute magnets $A_{1-x}TM_x$

percolation theory

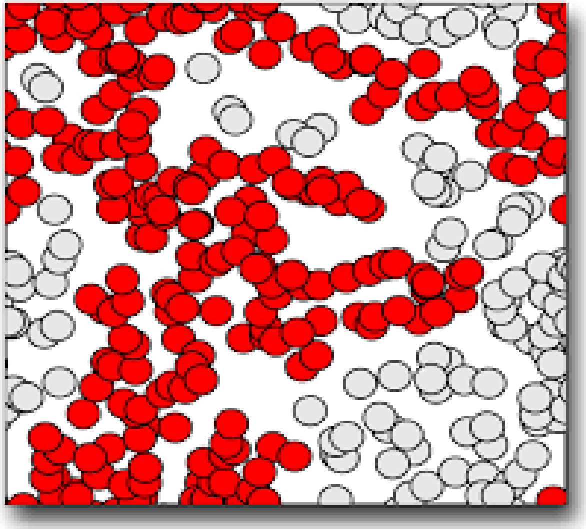
(overlapping spheres)

$r_{ij}^{(cr)} = 0.87(N_0x)^{-1/3}$

$J_{ij} = J_0\exp(-r_{ij}/b)$

spins *ij* talk if $J_{ij} \geq T$

$T_c = T_0\exp[-0.87(N_0x)^{-1/3}/b]$



I.Ya. Korenbilt et al. [Leningrad] Phys. Lett.' 1973

Testing percolation theory in wz-$Ga_{1-x}Mn_xN$

percolation theory

(overlapping spheres)

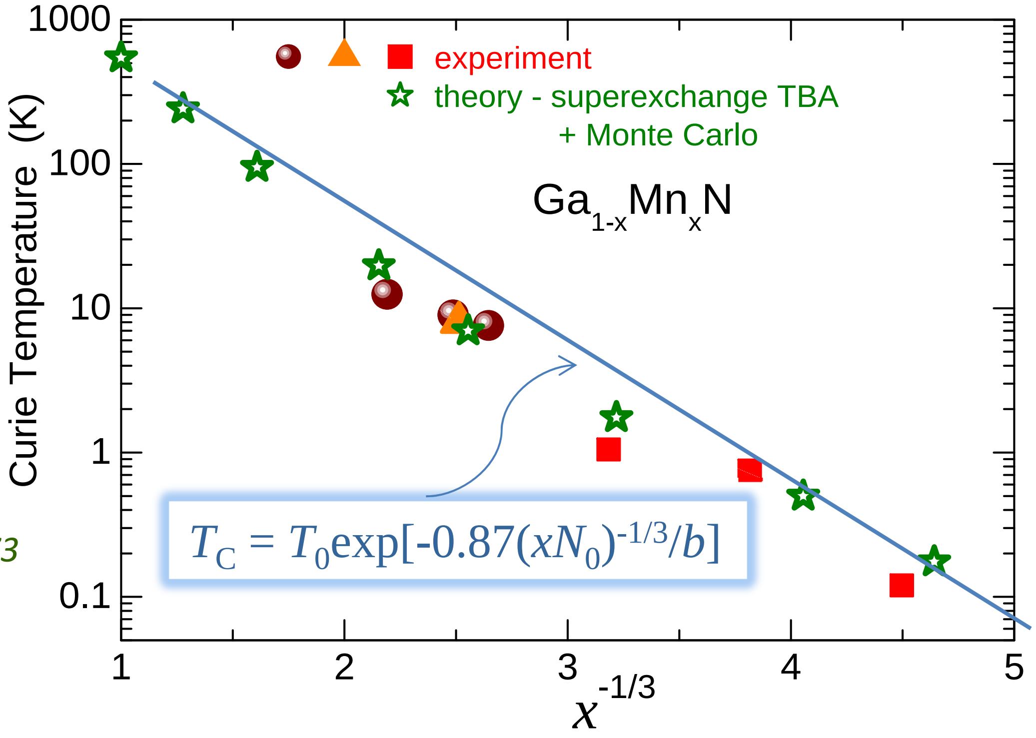
$r_{ij}^{(cr)} = 0.87(N_0x)^{-1/3}$

$J_{ij} = J_0\exp(-r_{ij}/b)$

spins *ij* talk if $J_{ij} \geq T$

$T_c = T_0\exp[-0.87(N_0x)^{-1/3}/b]$

I.Ya. Korenbilt et al. [Leningrad] Phys. Lett.' 1973

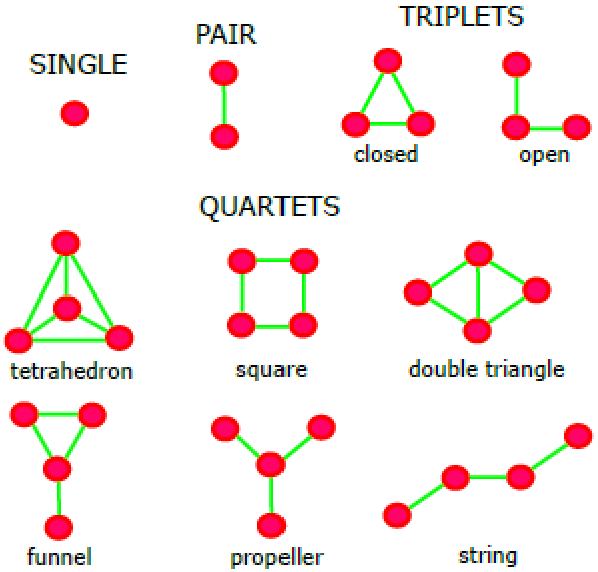


$T_C = T_0\exp[-0.87(xN_0)^{-1/3}/b]$

random Mn distribution proven

Two computational developments for *M*(*H*)

M(***H***) from quantum levels of ferro coupled



D. Sztenkiel arXiv:2006.12945
also NJP -112309.R1 (2020)

M(***H***) from atomistic LLG eqn. for coupled classical spins

$$\frac{\partial \mathbf{S}_i}{\partial t} = -\frac{\gamma}{1+\alpha_G^2}[\mathbf{S}_i \times \mathbf{H}^i_{eff} + \alpha_G \mathbf{S}_i \times (\mathbf{S}_i \times \mathbf{H}^i_{eff})]$$

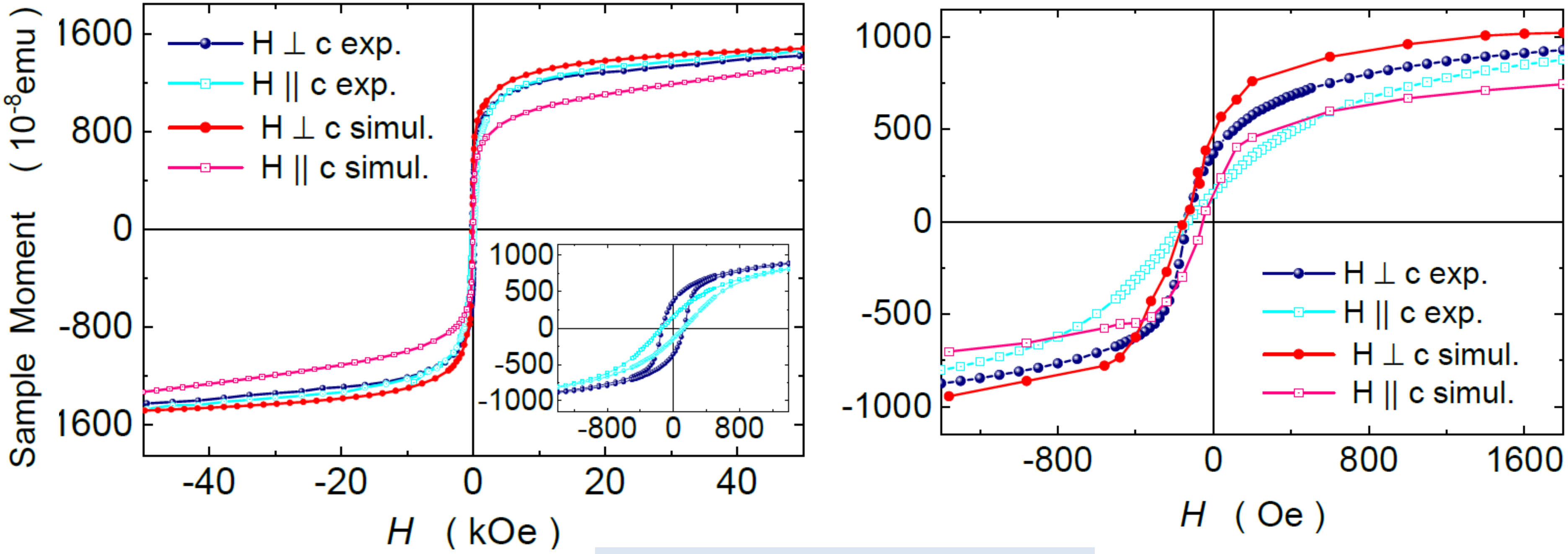
$$\mathbf{H}^i_{\text{eff}} = -\frac{1}{\mu_S}\frac{\partial \mathcal{H}}{\partial \mathbf{S}_i} + \mathbf{H}^i_{th}(t)$$

$$\mathcal{H} = \mathcal{H}_{\text{Exch}} + \mathcal{H}_{\text{Trig}} + \mathcal{H}_{\text{JT}} + \mathcal{H}_{\text{Z}}$$

$$\mathcal{H}_{\text{Exch}} = -\sum_{i\neq j} J_{i,j}\mathbf{S}_i\mathbf{S}_j$$

D. Sztenkiel et al., JEMS 2020
cf. R. F. L. Evans et al. [York] JPC'2014

Experimental (blue) vs. atomistic LLG (red) $M(\boldsymbol{H})$ at 2 K, x = 6%



8640 Mn spins, t = 280 ns

➔ hystereses due to in-plane barriers caused by JT effect

[macrospin model would give square hysteresis]

Electric field effects in wz-Ga$_{1\text{-}x}$Mn$_x$N

D. Sztenkiel et al., Nat. Commun. ***7****, 13232 (2016); JEMS 2020*

$$M_E^{(i)} = \alpha_{ji}\mathcal{E}_j + \beta_{jki}\mathcal{E}_j B_k + \ldots$$

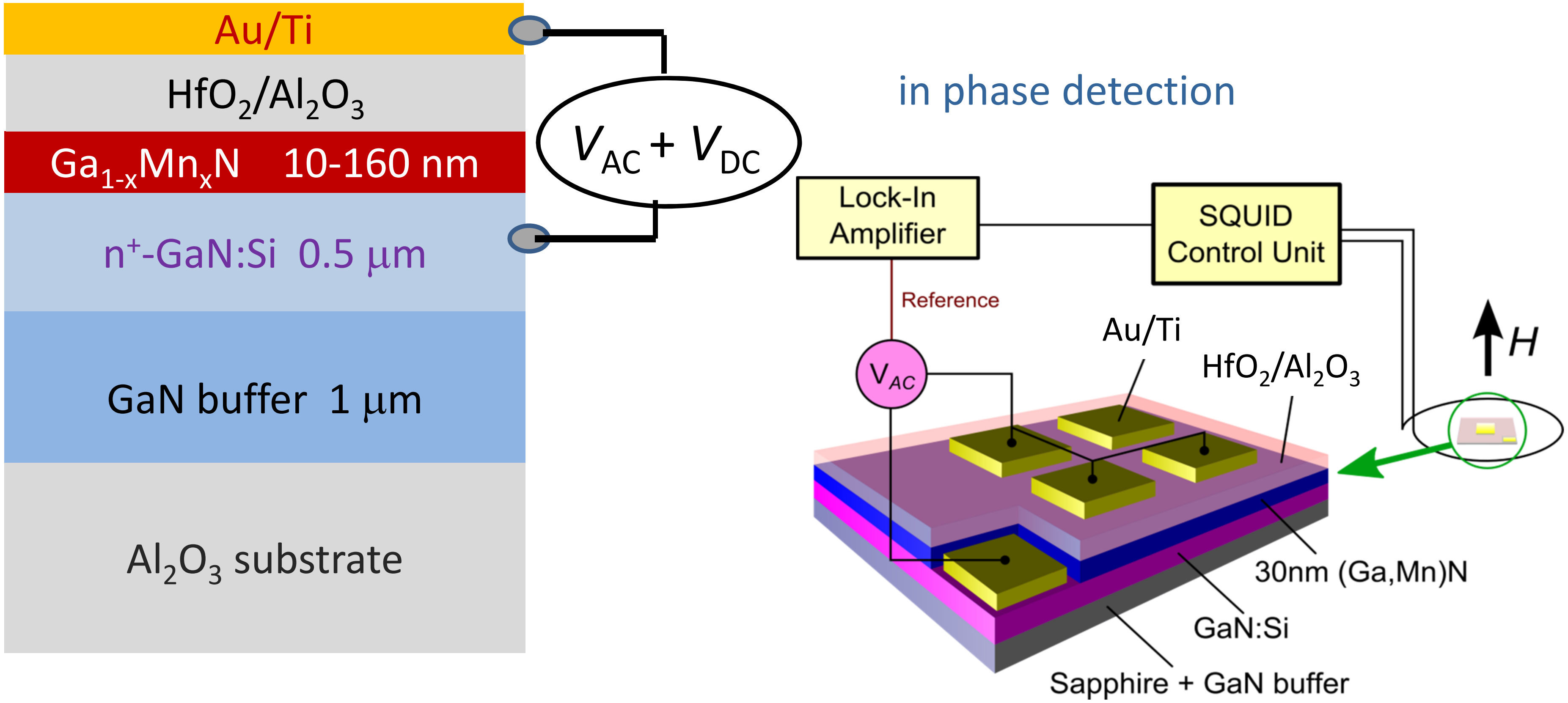
$$\alpha_{ji} \neq 0 \text{ if } \mathcal{T} \text{ and } \mathcal{I} \text{ broken}$$

$$\beta_{jki} \neq 0 \text{ if } \mathcal{I} \text{ broken}$$

$$\boxed{\mathcal{I} \text{ broken in wz crystals}}$$

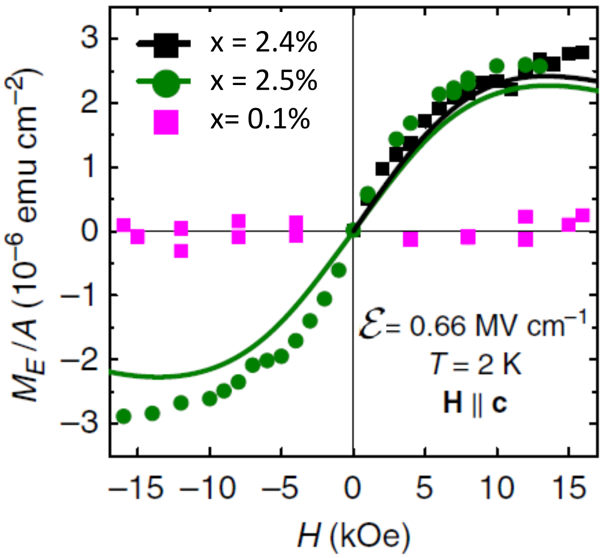
Capacitor structure and expl set-up

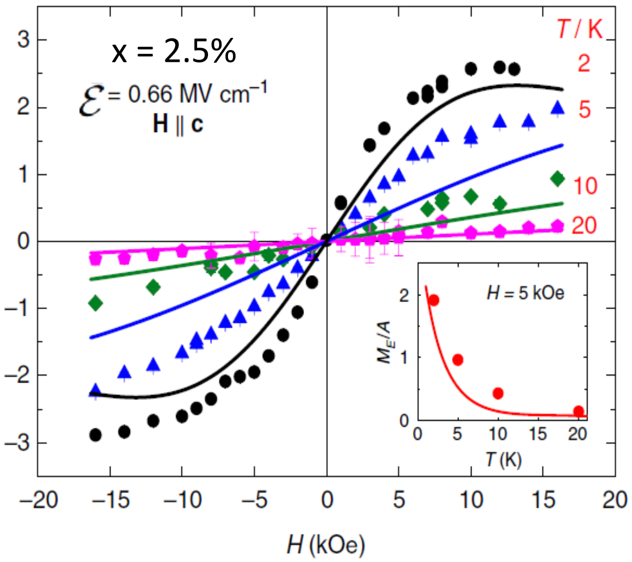
in phase detection

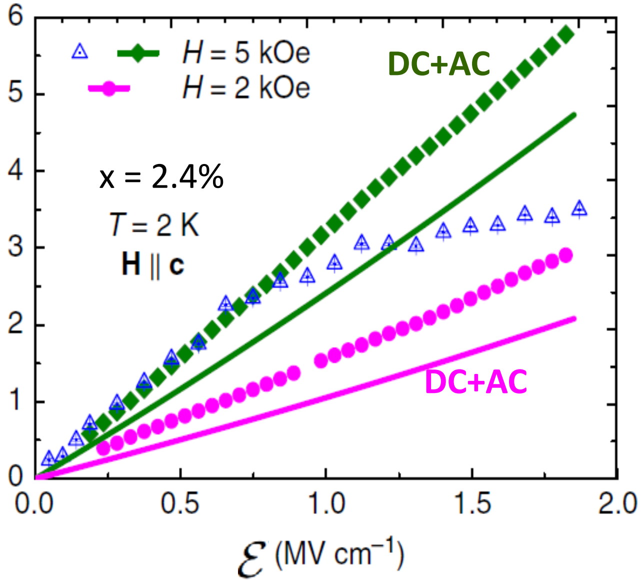


M_E in paramagnetic $Ga_{0.98}Mn_{0.02}N$ – exp. vs. theory

$$M_E^{(i)} = \cancel{\alpha_{ji}\mathcal{E}_j} + \beta_{jki}\mathcal{E}_j B_k + \ldots$$



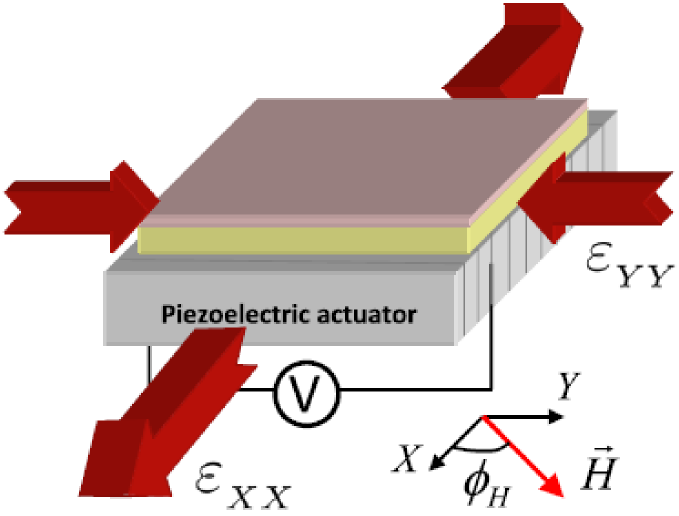


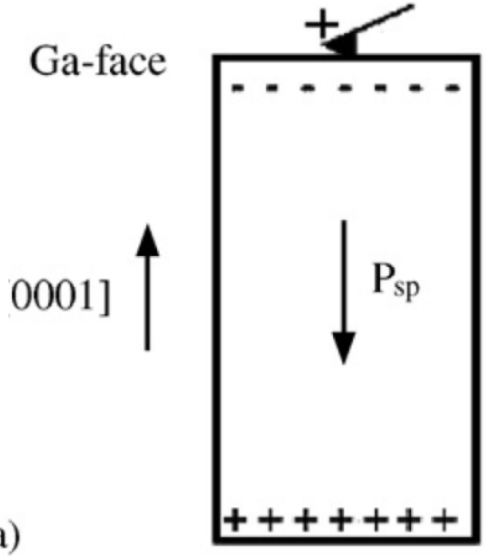


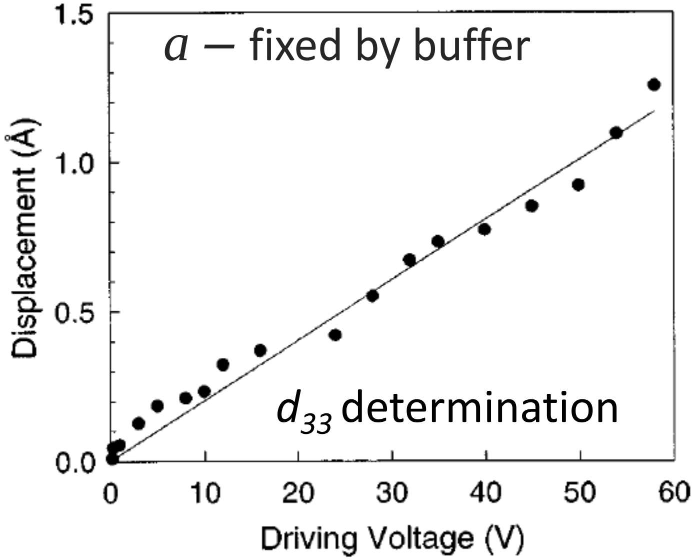
$M_E^{(max)} \approx 0.04 M_{Sat}$

no adjustable parameters

Piezoelectricity of wz-GaN





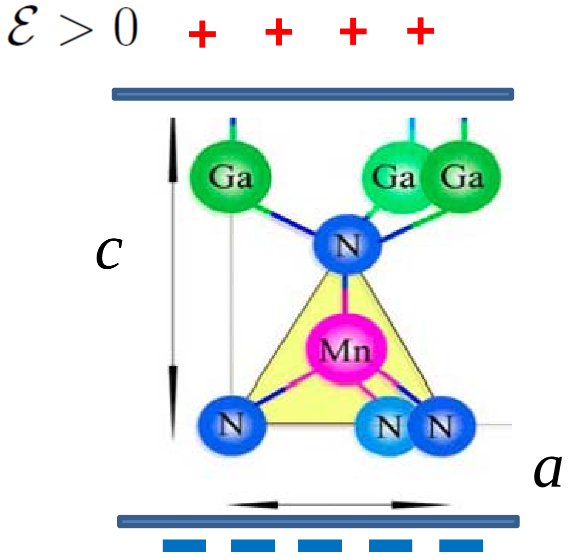


a – fixed by buffer

d_{33} determination

I.L. Guy et al. [Macquarie U.] APL'1999

Piezo-electromagnetic effect (PEME) in wz-$Ga_{1-x}Mn_xN$



The dominant effect of the electric field:

$$\mathcal{H}_{\mathrm{Trig}} \propto c(\mathcal{E})/a - (8/3)^{1/2}$$

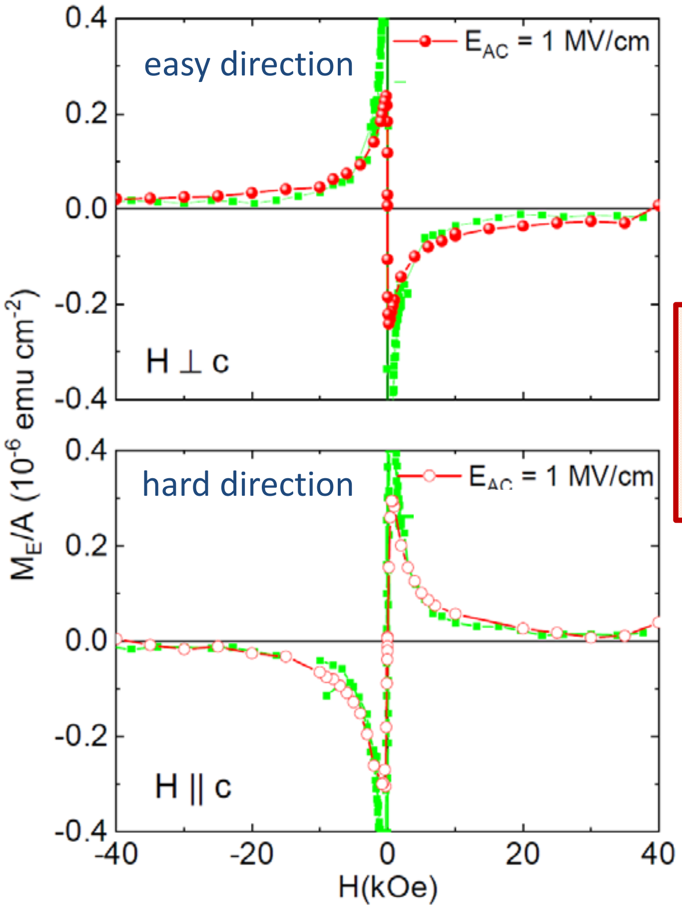
$$\Delta c(\mathcal{E})/c = d_{33}\mathcal{E}$$

ε_{33} up to 0.1%

Electric field effects in ferromagnetic wz-$Ga_{1-x}Mn_xN$

$x = 6\%$

$T = 2$ K

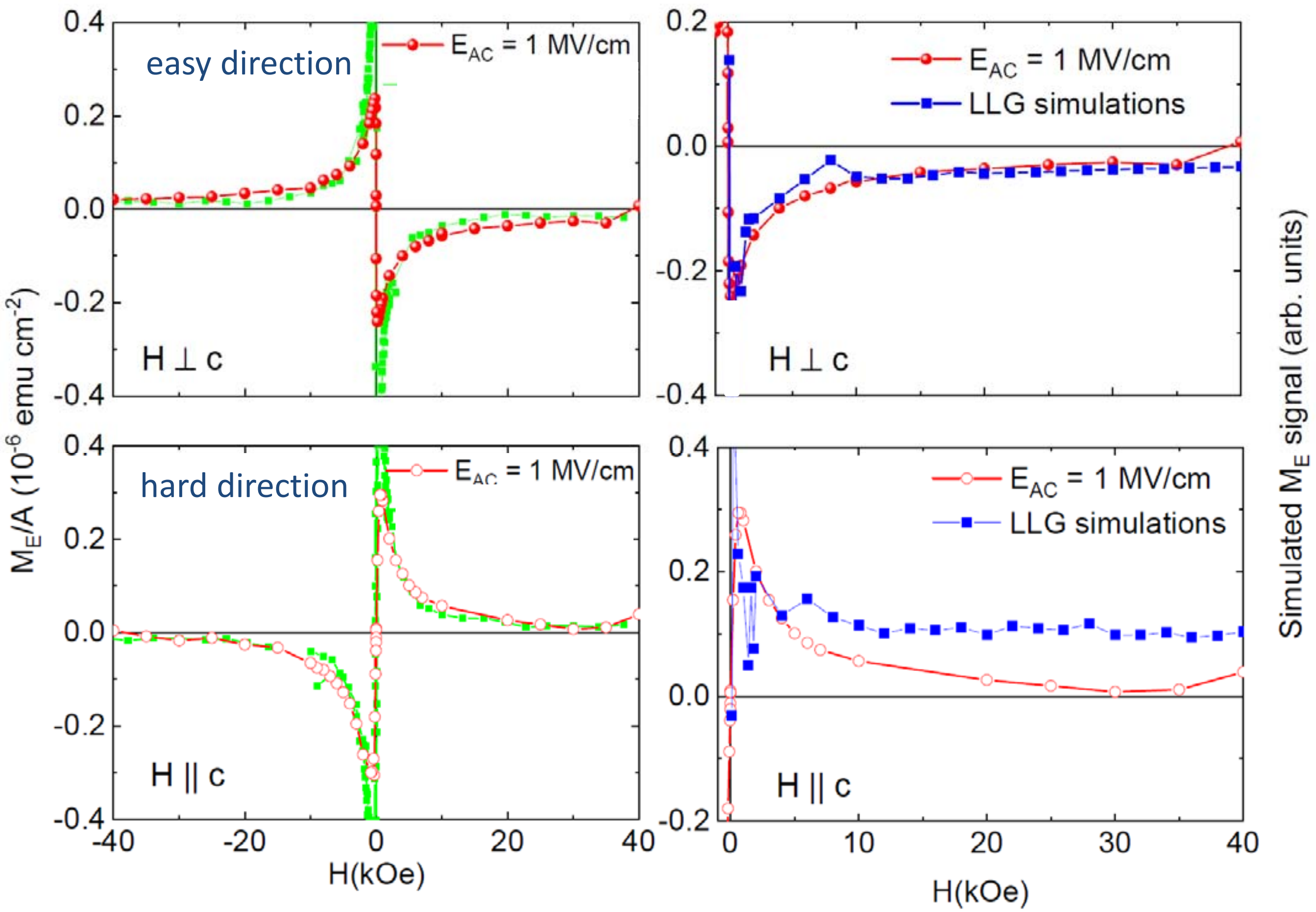


- opposite sign of $\Delta M_{\perp}(\mathcal{E})$ and $\Delta M_{\parallel}(\mathcal{E})$
- vanish in high fields

$$M_E^{(\mathrm{max})} \approx 0.003 M_{\mathrm{Sat}}$$

Exp. results vs. atomistic LLG

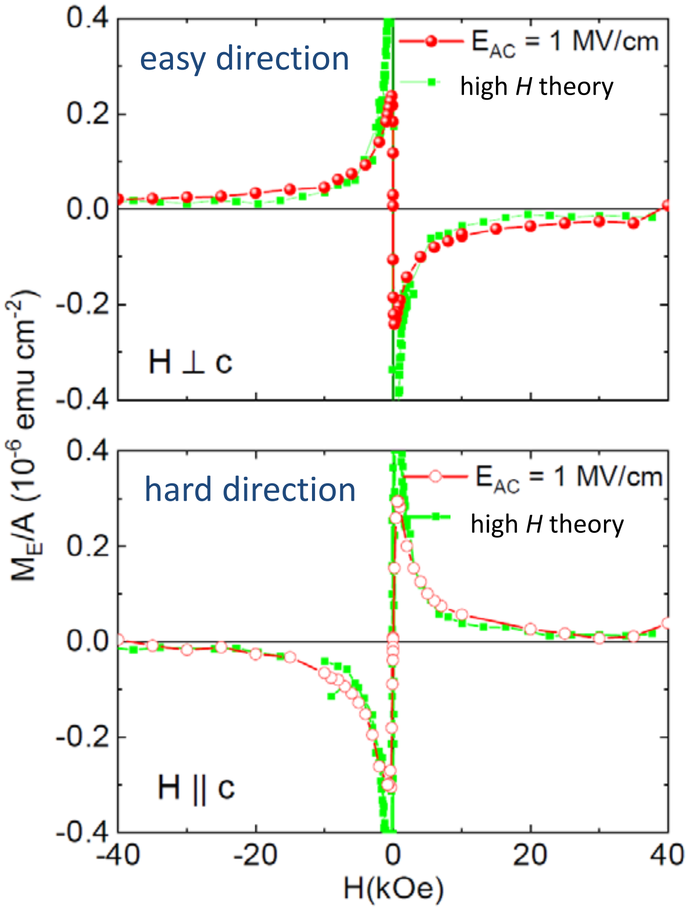
x = 6%
T = 2 K



Exp. results vs. qualitative model

$x = 6\%$

$T = 2$ K



$$\boldsymbol{M} = \boldsymbol{M}(\boldsymbol{H}_{\text{eff}}) = \boldsymbol{M}(\boldsymbol{H}+\boldsymbol{H}_{\text{an}})$$

$$M_E^{(i)} = \frac{\partial M_i}{\partial \boldsymbol{H}_{\text{eff}}}\frac{\partial \boldsymbol{H}_{\text{eff}}}{\partial \mathcal{E}}\mathcal{E}$$

$$\boldsymbol{H}_{\text{TR}} = b[c(\mathcal{E})/a-(8/3)^{1/2}][-M_x, M_z]$$

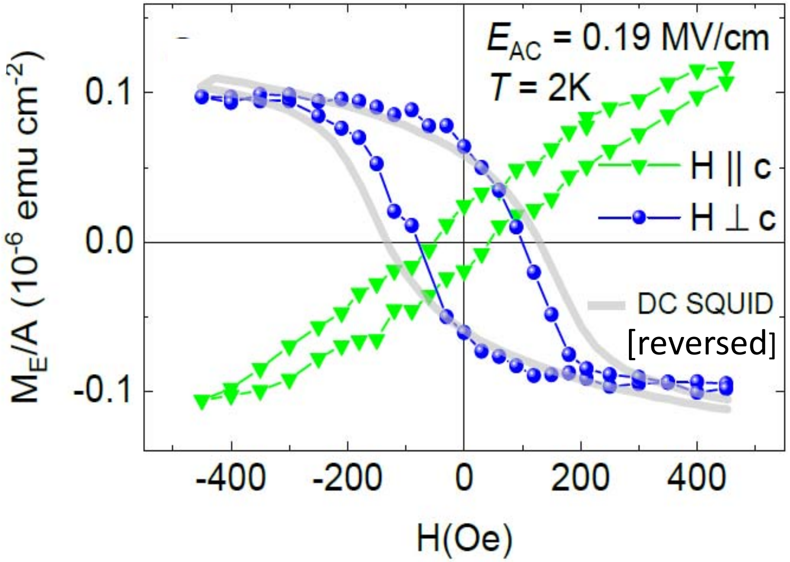
$$M_E^{(x)} = -b\frac{\partial M_x}{\partial H_{\text{eff}}^{(x)}}M_x d_{33}(c/a)\mathcal{E}$$

$$M_E^{(z)} = b\frac{\partial M_z}{\partial H_{\text{eff}}^{(z)}}M_z d_{33}\mathcal{E}$$

in high fields $\dfrac{\partial M_{x,z}}{\partial \boldsymbol{H}_{\text{eff}}} \rightarrow \dfrac{\partial M_{x,z}}{\partial \boldsymbol{H}}$

PEME in weak *H* fields

x = 6%



$$M_E^{(x)} = -b\frac{\partial M_x}{\partial H_{\text{eff}}^{(x)}} M_x d_{33}(c/a)\mathcal{E}$$

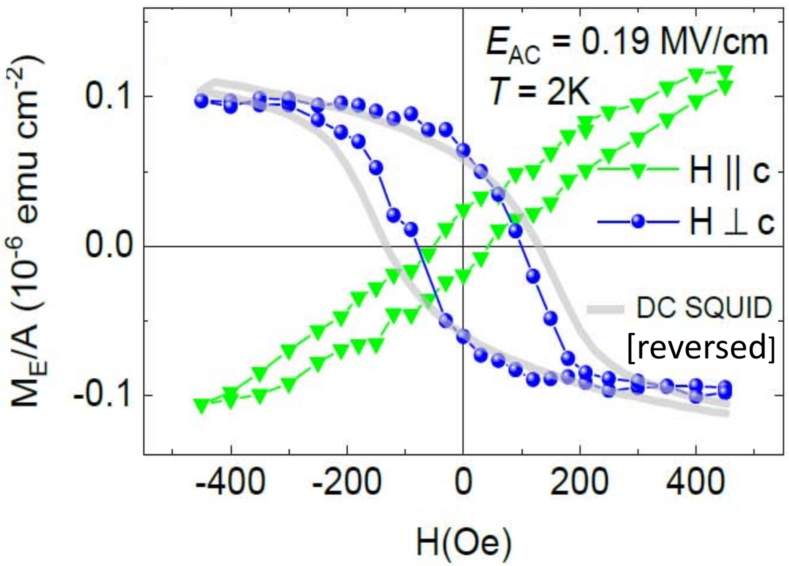
$$M_E^{(z)} = b\frac{\partial M_z}{\partial H_{\text{eff}}^{(z)}} M_z d_{33}\mathcal{E}$$

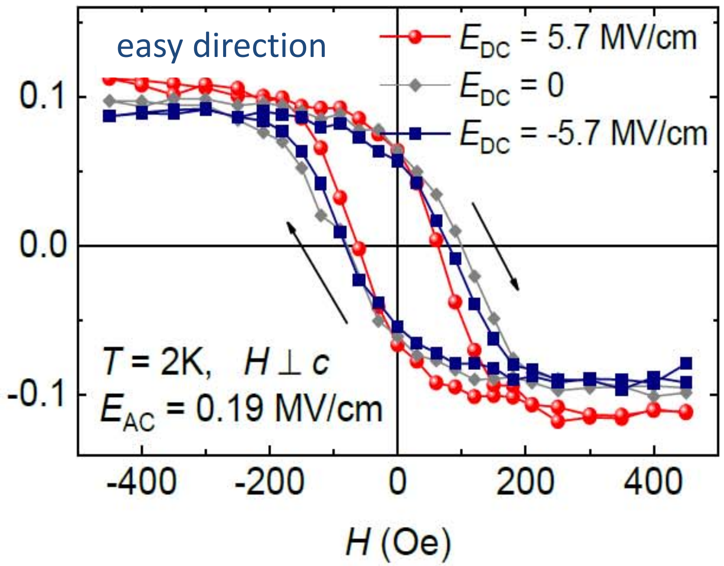
in weak magnetic fields time-reversal symmetry broken only by ***M***

$$M_E^{(i)} = \alpha_{ji}\mathcal{E}_j + \cancel{\beta_{jki}\mathcal{E}_j B_k} + \ldots$$

PEME in weak *H* fields

x = 6%





in weak magnetic fields time-reversal symmetry broken only by ***M***

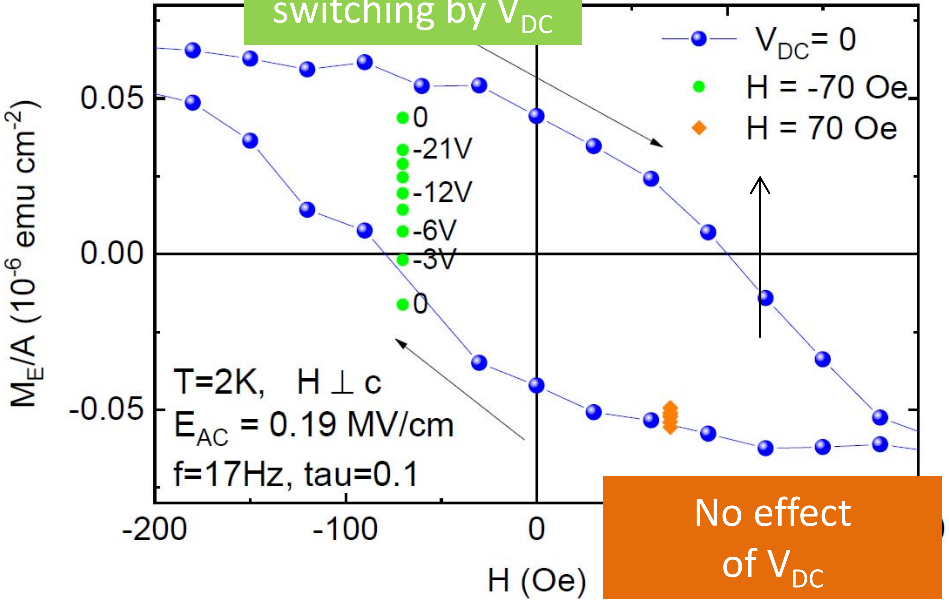
$$M_E^{(i)} = \alpha_{ji}\mathcal{E}_j + \cancel{\beta_{jki}\mathcal{E}_j B_k} + \ldots$$

hysteresis width determined by JT

➔ independent of $\mathcal{E}_{\mathrm{DC}}$

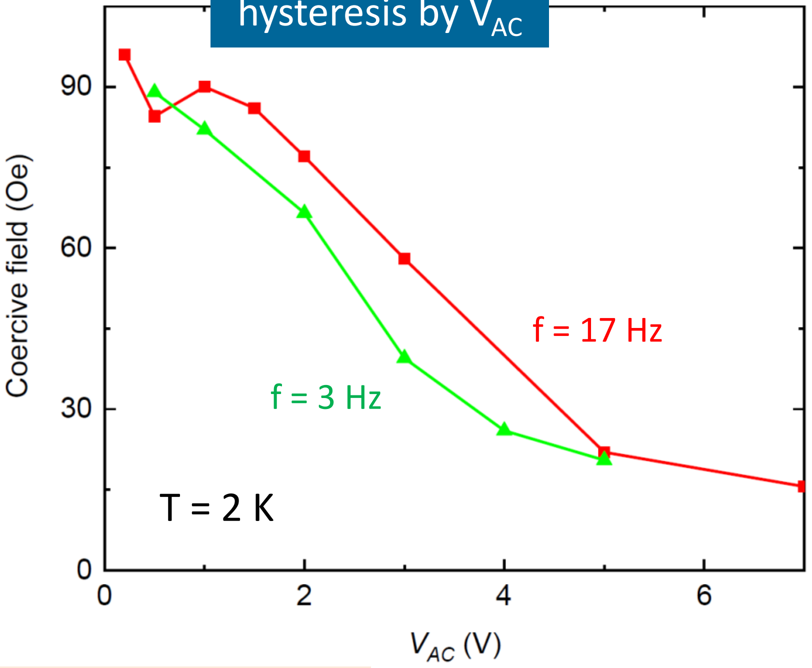
Magnetization switching

x = 6%



Magnetization switching by V_{DC}

No effect of V_{DC}

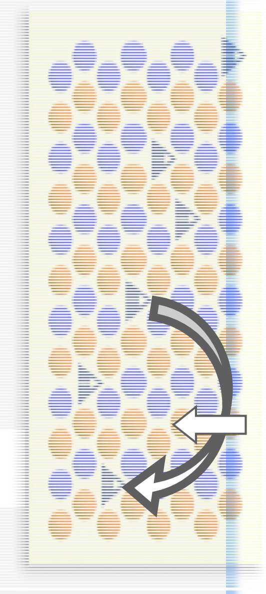


Narrowing of hysteresis by V_{AC}

Models:

- heating by capacitor charging
- precessional switching *D. Sztenkiel et al. JEMS 2020*

Hole-mediated ferromagnetism in Mn-doped semiconductors



- holes due to Mn itself

$\mathrm{(In,Mn)As}$; $\mathrm{(Ga,Mn)As}$ *H. Ohno et al. [IBM, Tohoku] PRL'92, APL'96* T_C up to 200 K

$\mathrm{(Sb,Mn)_2Te_3}$; $\mathrm{(Bi,Mn)_2Te_3}$ *Choi et al. [Ulsan] pps(b)'04* T_C up to 20 K

- holes due to acceptor impurities

$\mathrm{(Cd,Mn)Te{:}N}$, $\mathrm{(Zn,Mn)Te{:}P}$ T_C up to 5 K

TD, Cibert et al. [Grenoble, Warsaw] PRB'97, PRL'97, PRL'03

$\mathrm{(K,Ba)(Zn,Mn)_2As_2}$ *K. Zhao al. [Beijing, Columbia U.] Nat. Commun.'13* T_C up to 230 K

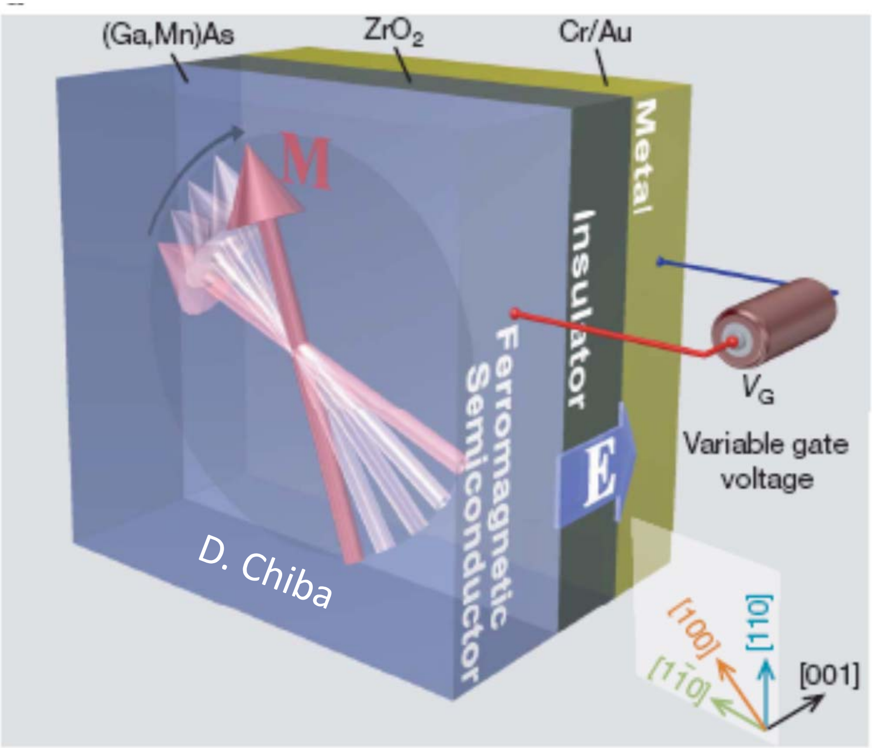
- holes due to cation vacancies IV-VI, [I-II]-V

$\mathrm{(Pb,Sn,Mn)Te}$ *T. Story et al. [Warsaw] PRL'86* T_C up to 10 K

$\mathrm{(Ge,Mn)Te}$ *Y. Fukuma et al. [Yamaguchi] APL'08* T_C up to 200 K

$\mathrm{[Li(Zn,Mn)]As}$ *Z. Deng et al. [Beijing, Columbia, Tokyo, Vancouver] Nature Comm.'11* T_C up to 50 K

Magnetization manipulation by gating



D. Chiba

$$\mathrm{div}\boldsymbol{\mathcal{E}}(z) = \rho(z)/\epsilon \Rightarrow T_{\mathrm{C}}(z)$$

also multilayers, interfaces, junctions, …

cf. T. Dietl, H. Ohno, RMP'2014
F. Matsukura, Y. Tokura, H. Ohno, Nat. Nano.'2015

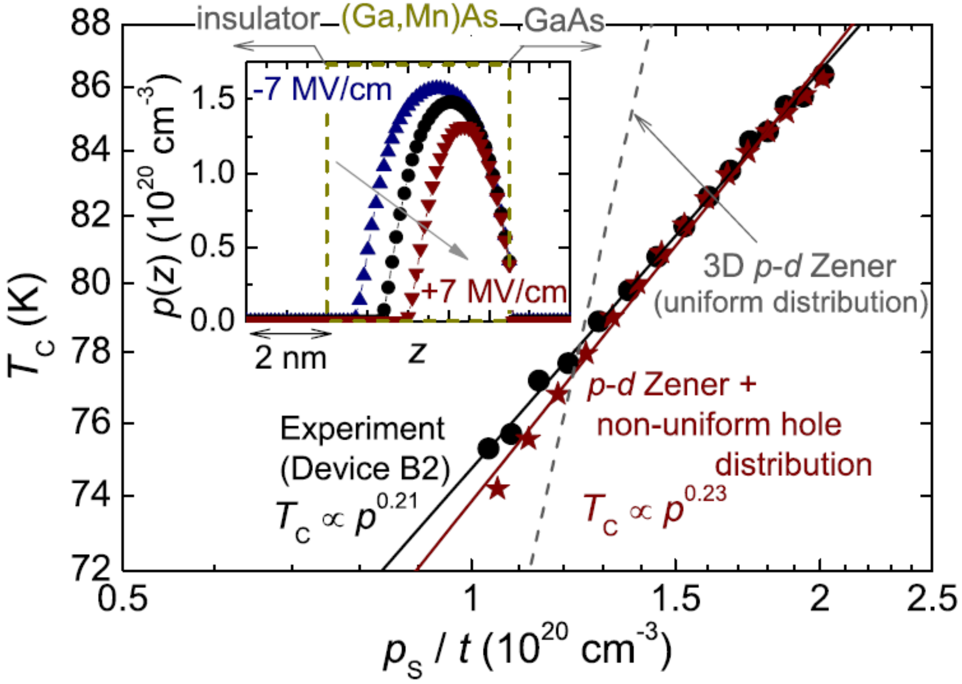
Carrier-mediated T_C in non-uniform systems

Phase coherence length

$$\bar{T}_\mathrm{C} = \frac{\int dz T_\mathrm{C}[\rho(z)] \int dz \rho^2(z)}{[\int dz \rho(z)]^2}$$

M. Sawicki et al. [Tohoku, Warsaw] Nat. Phys.'2010

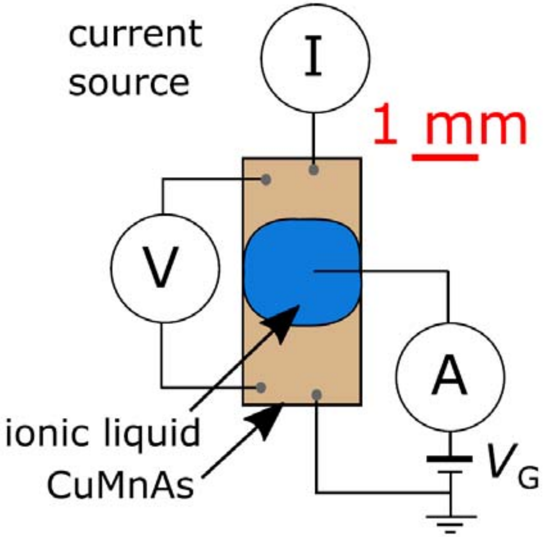
T_C in $Ga_{1-x}Mn_xAs$ MOS structure

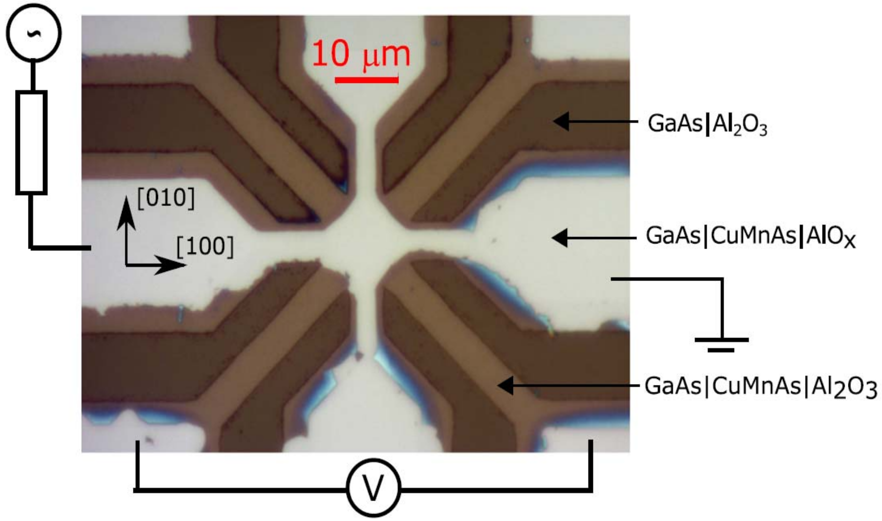


Y. Nishitani et al. [Tohoku, Warsaw] PRB.'2010

Gating semimetalic CuMnAs at 300 K

MBE: 10 nm tetragonal CuMnAs on (001) GaAs protected by 2.5 nm oxidized Al





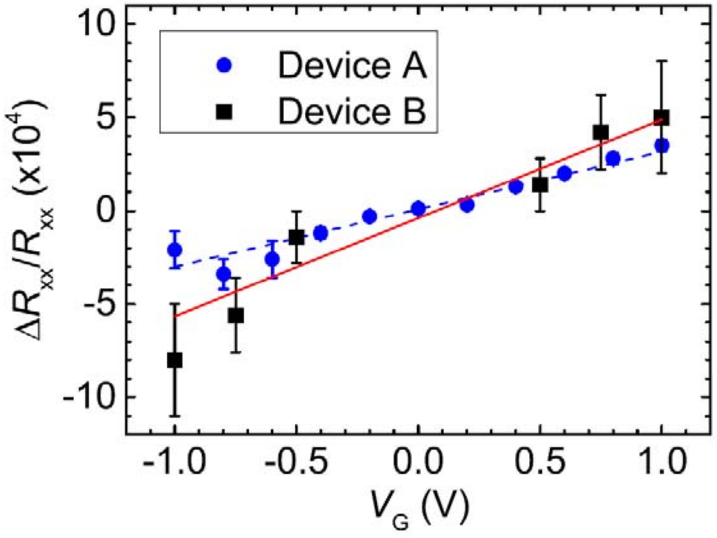
ionic liquid DEME-TFSI

$C/S = (4.4 \pm 0.8) \times 10^{-7}$ F/cm^2

$p_{\mathrm{Hall}} = (5 \pm 1)\cdot 10^{21}$ cm^{-3}

M. Grzybowski et al. [Warsaw, Nottingham] AIP Adv.'2019

Field effect and mobility at room temperature



field mobility

$$\mu_E = \frac{L}{fWC/S} \frac{1}{R_{xx}^2} \frac{\partial R_{xx}}{\partial V_G}$$

	μ_H (cm^2/V s)	μ_E (cm^2/V s)
Device A	. . .	3.7 ± 1
Device B	3.4 ± 0.7	3.7 ± 1

as $\mu_H = \mu_E$ no evidence for:

- -- multicarrier transport
- -- anomalous Hall effect
- -- electrochemical interfacial reactions

M. Grzybowski et al. [Warsaw, Nottingham] AIP Adv.’2019

Summary: concepts in dilute magnetic materials

spinodal decomposition

self-organization

high T_C ferromagnetism

anisotropic spinodal decomposition

nematicity

antiferromagnetic superexchange

ferromagnetic superexchange

frustration

percolation

dilute ferromagnetic insulators

dilute ferromagnetic p-type semiconductors

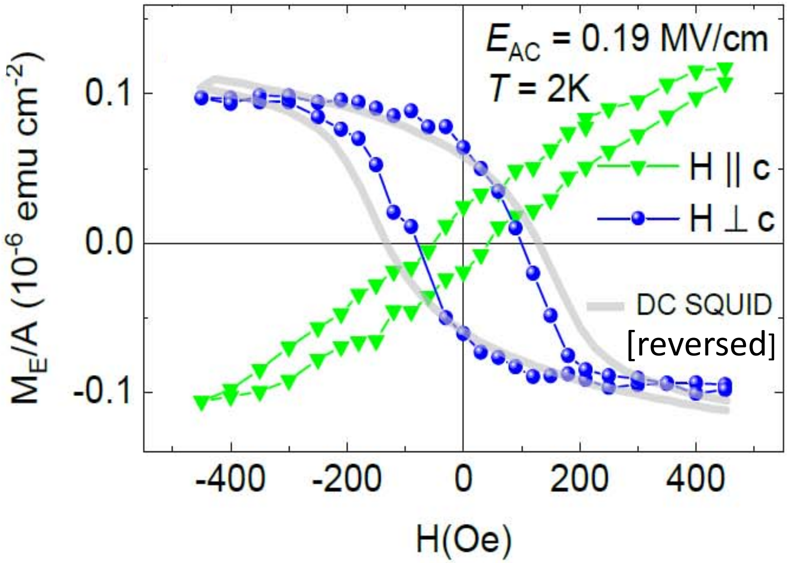
piezo-electromagnetic effects

gating effects

T_C in electrically non-uniform systems

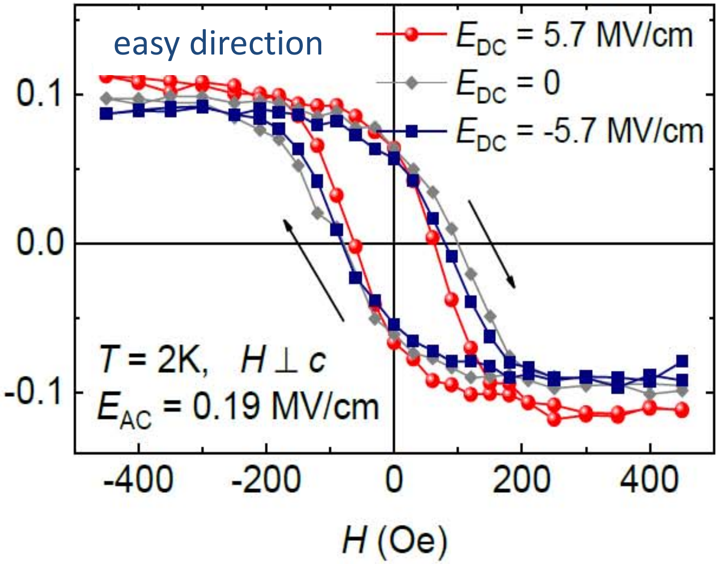
PEME in weak *H* fields

x = 6%



in weak magnetic fields time-reversal symmetry broken only by ***M***

$$M_E^{(i)} = \alpha_{ji}\mathcal{E}_j + \cancel{\beta_{jki}\mathcal{E}_j B_k} + \ldots$$

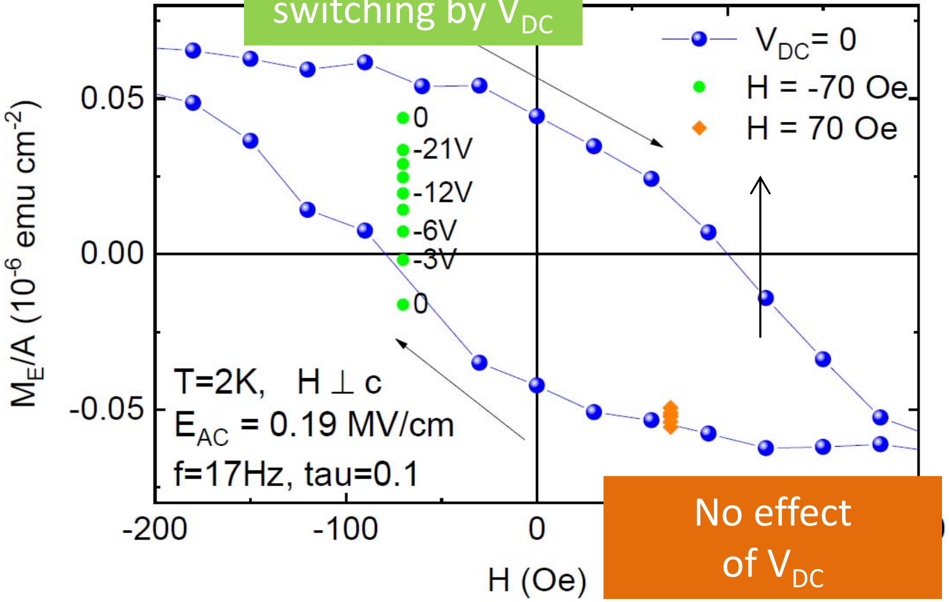


hysteresis width determined by JT

➔ independent of $\mathcal{E}_{DC}$

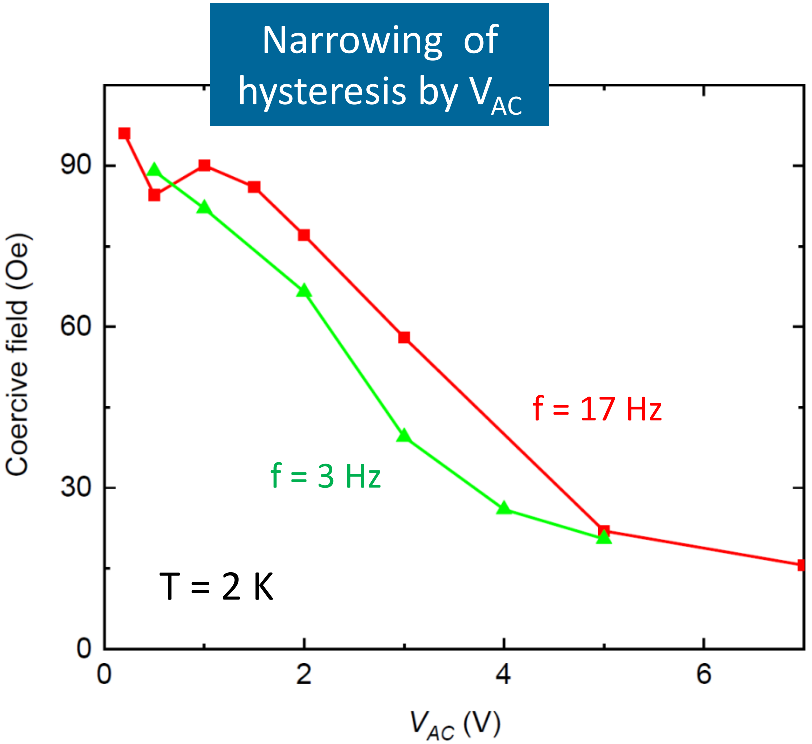
Magnetization switching

x = 6%



Magnetization switching by V_{DC}

No effect of V_{DC}

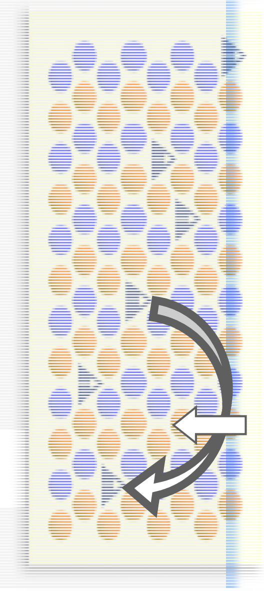


Narrowing of hysteresis by V_{AC}

Models:

- heating by capacitor charging
- precessional switching *D. Sztenkiel et al. JEMS 2020*

Hole-mediated ferromagnetism in Mn-doped semiconductors



- holes due to Mn itself

(In,Mn)As; (Ga,Mn)As *H. Ohno et al. [IBM, Tohoku] PRL'92, APL'96* T_C up to 200 K

$(Sb,Mn)_2Te_3$; $(Bi,Mn)_2Te_3$ *Choi et al. [Ulsan] pps(b)'04* T_C up to 20 K

- holes due to acceptor impurities

(Cd,Mn)Te:N, (Zn,Mn)Te:P T_C up to 5 K

TD, Cibert et al. [Grenoble, Warsaw] PRB'97, PRL'97, PRL'03

$(K,Ba)(Zn,Mn)_2As_2$ *K. Zhao al. [Beijing, Columbia U.] Nat. Commun.'13* T_C up to 230 K

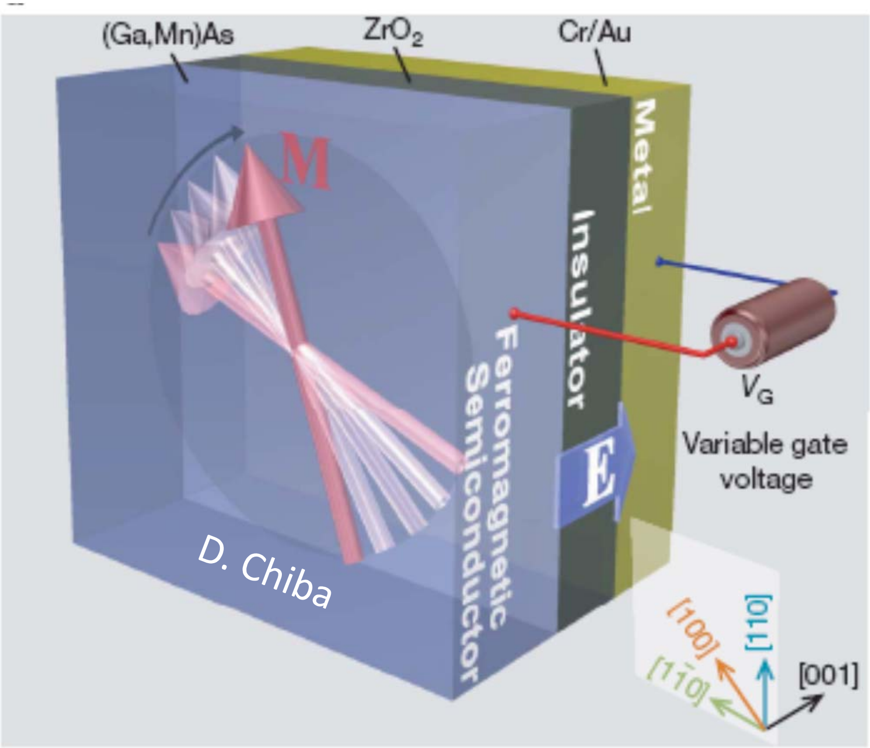
- holes due to cation vacancies IV-VI, [I-II]-V

(Pb,Sn,Mn)Te *T. Story et al. [Warsaw] PRL'86* T_C up to 10 K

(Ge,Mn)Te *Y. Fukuma et al. [Yamaguchi] APL'08* T_C up to 200 K

[Li(Zn,Mn)]As *Z. Deng et al. [Beijing, Columbia, Tokyo, Vancouver] Nature Comm.'11* T_C up to 50 K

Magnetization manipulation by gating



D. Chiba

$$\mathrm{div}\boldsymbol{\mathcal{E}}(z) = \rho(z)/\epsilon \Rightarrow T_\mathrm{C}(z)$$

also multilayers, interfaces, junctions, …

cf. T. Dietl, H. Ohno, RMP'2014
F. Matsukura, Y. Tokura, H. Ohno, Nat. Nano.'2015

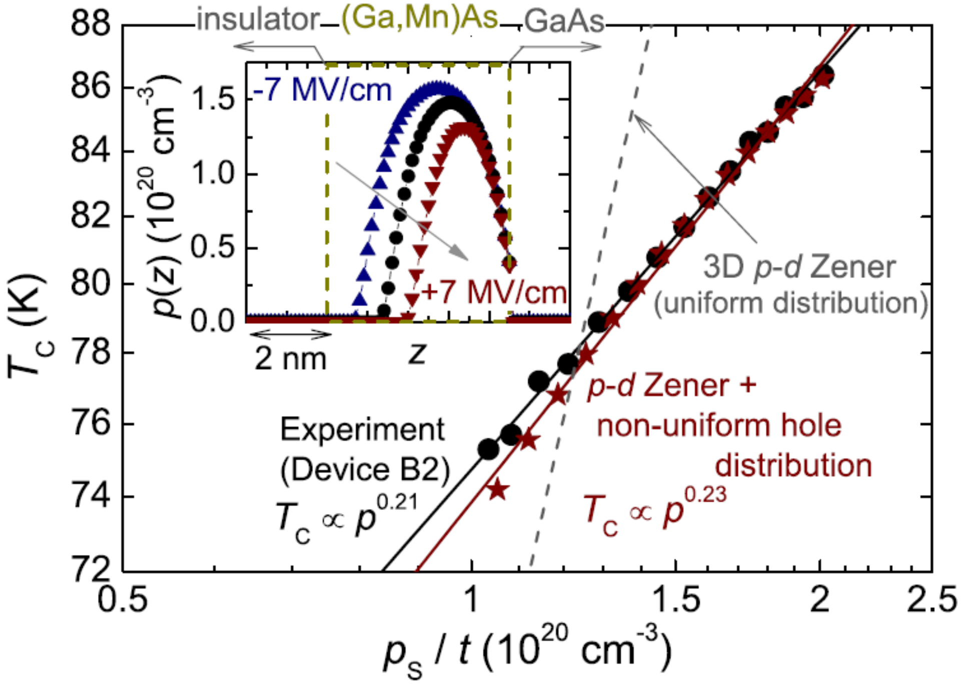
Carrier-mediated T_C in non-uniform systems

Phase coherence length

$$\bar{T}_C = \frac{\int dz T_C[\rho(z)] \int dz \rho^2(z)}{[\int dz \rho(z)]^2}$$

M. Sawicki et al. [Tohoku, Warsaw] Nat. Phys.'2010

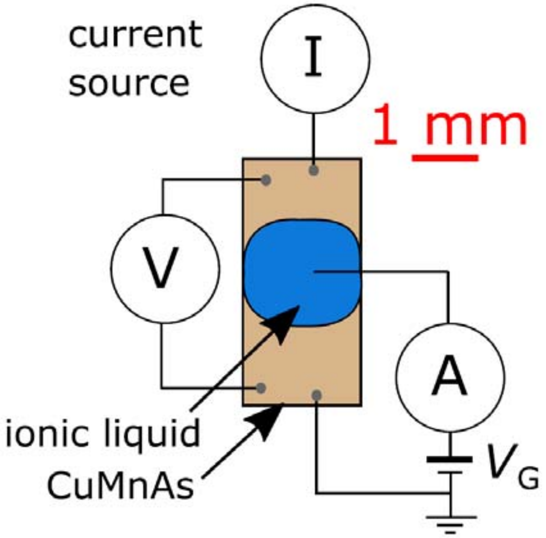
T_C in $Ga_{1-x}Mn_xAs$ MOS structure

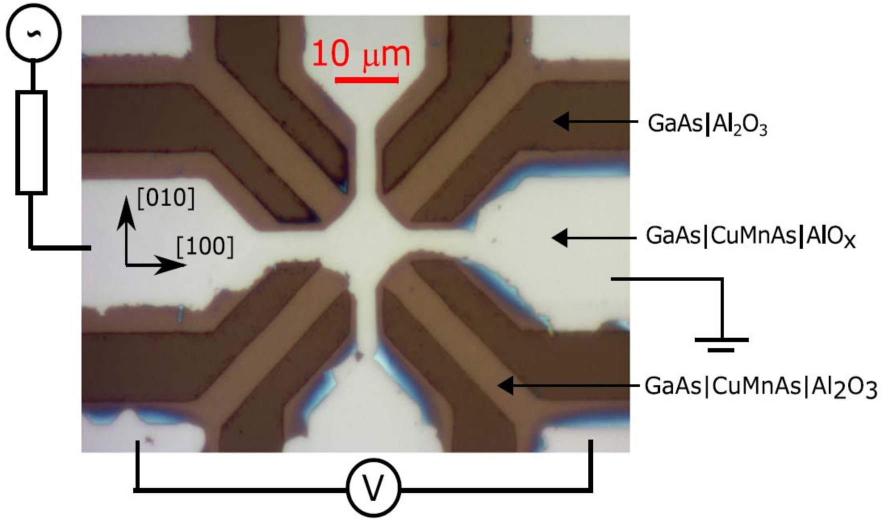


Y. Nishitani et al. [Tohoku, Warsaw] PRB.'2010

Gating semimetalic CuMnAs at 300 K

MBE: 10 nm tetragonal CuMnAs on (001) GaAs protected by 2.5 nm oxidized Al





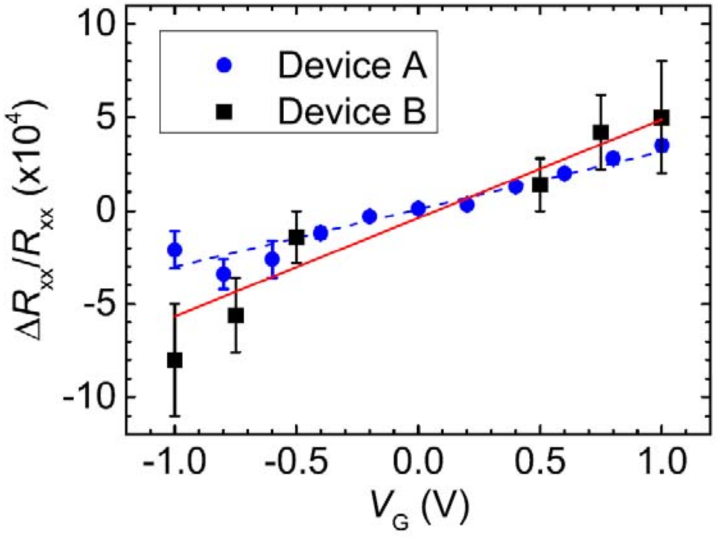
ionic liquid DEME-TFSI

$C/S = (4.4 \pm 0.8) \times 10^{-7}$ F/cm^2

$p_{\mathrm{Hall}} = (5 \pm 1)\cdot 10^{21}$ cm^{-3}

M. Grzybowski et al. [Warsaw, Nottingham] AIP Adv.'2019

Field effect and mobility at room temperature



field mobility

$$\mu_E = \frac{L}{fWC/S} \frac{1}{R_{xx}^2} \frac{\partial R_{xx}}{\partial V_G}$$

	μ_H (cm^2/V s)	μ_E (cm^2/V s)
Device A	. . .	3.7 ± 1
Device B	3.4 ± 0.7	3.7 ± 1

as $\mu_H = \mu_E$ no evidence for:

-- multicarrier transport

-- anomalous Hall effect

-- electrochemical interfacial reactions

M. Grzybowski et al. [Warsaw, Nottingham] AIP Adv.'2019

Summary: concepts in dilute magnetic materials

spinodal decomposition

self-organization

high T_C ferromagnetism

anisotropic spinodal decomposition

nematicity

antiferromagnetic superexchange

ferromagnetic superexchange

frustration

percolation

dilute ferromagnetic insulators

dilute ferromagnetic p-type semiconductors

piezo-electromagnetic effects

gating effects

T_C in electrically non-uniform systems