REVIEW *and* EFFECTS OF COMPETING FERRO- AND ANTI-FERROMAGNETIC INTERACTIONS IN MAGNETIC SEMICONDUCTORS

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FERROMAGNETIC DMS

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Ohno Semiconductor Spintronics ERATO Project of JST
Humboldt Foundation

OUTLINE / ISSUES

1. Why ferromagnetic semiconductors?
2. Understanding of carrier-controlled diluted ferromagnetic semiconductors
3. Nanoscale fluctuations
   - -- electrostatic disorder
   - -- magnetic disorder
4. Nanoscale phase separations

ICT - ways to go

- **improving existing technologies**

- **disruptive technologies**

many ideas around ….
which will win – unknown …

SPINTRONICS
exploiting spin, not only charge

- Storing *and* processing and transferring of classical information

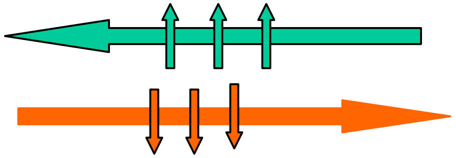
  -- manipulation with magnetization

- Storing *and* processing and transferring of quantum information

  -- manipulation with single spins

electronic and/or nuclear spins

→ Low power memories, processors, and interconnects

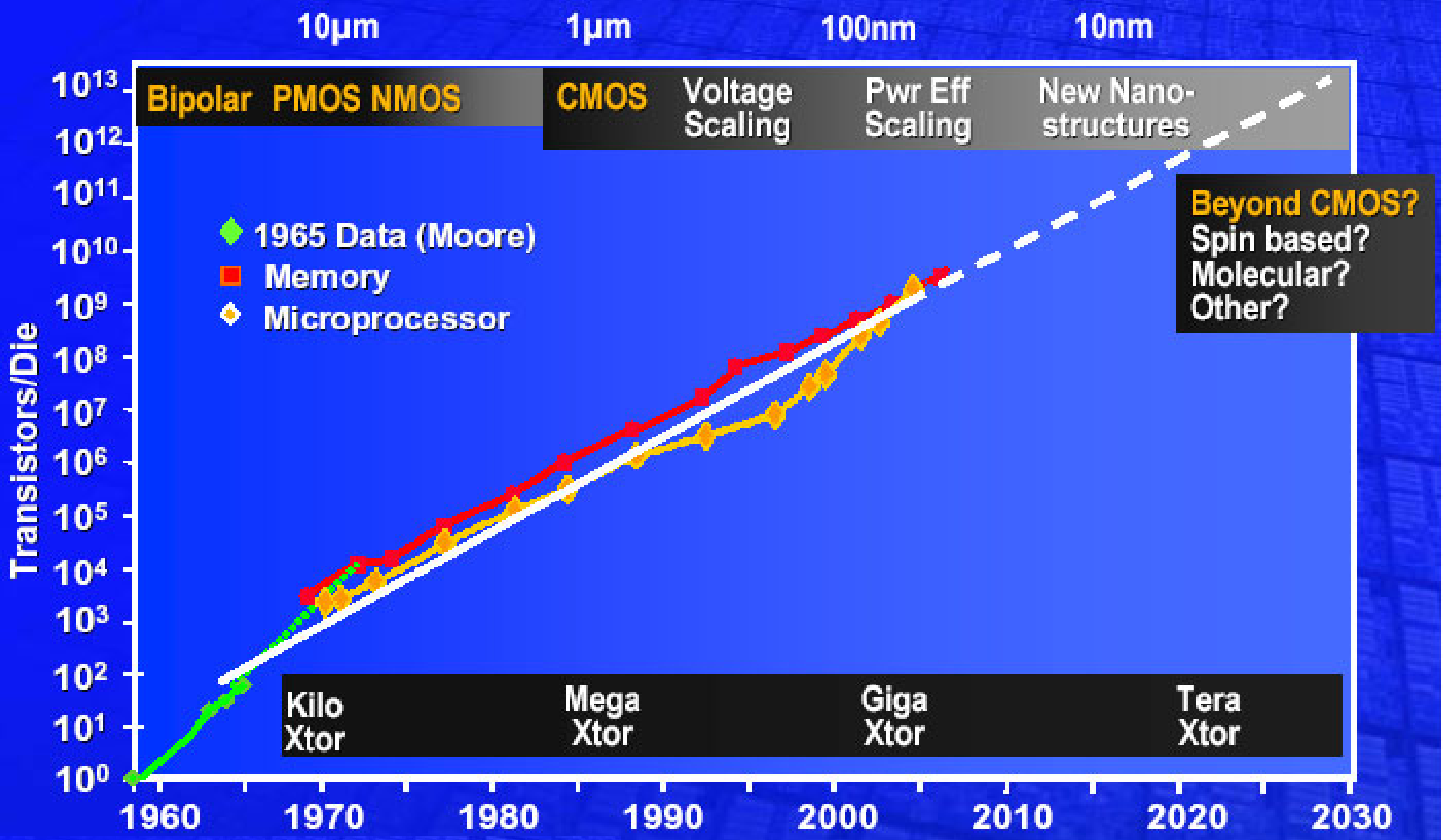


$I_{tot} = 0$

dissipation less currents

cf. John Schliemann

Moore's Law Will Outlive CMOS

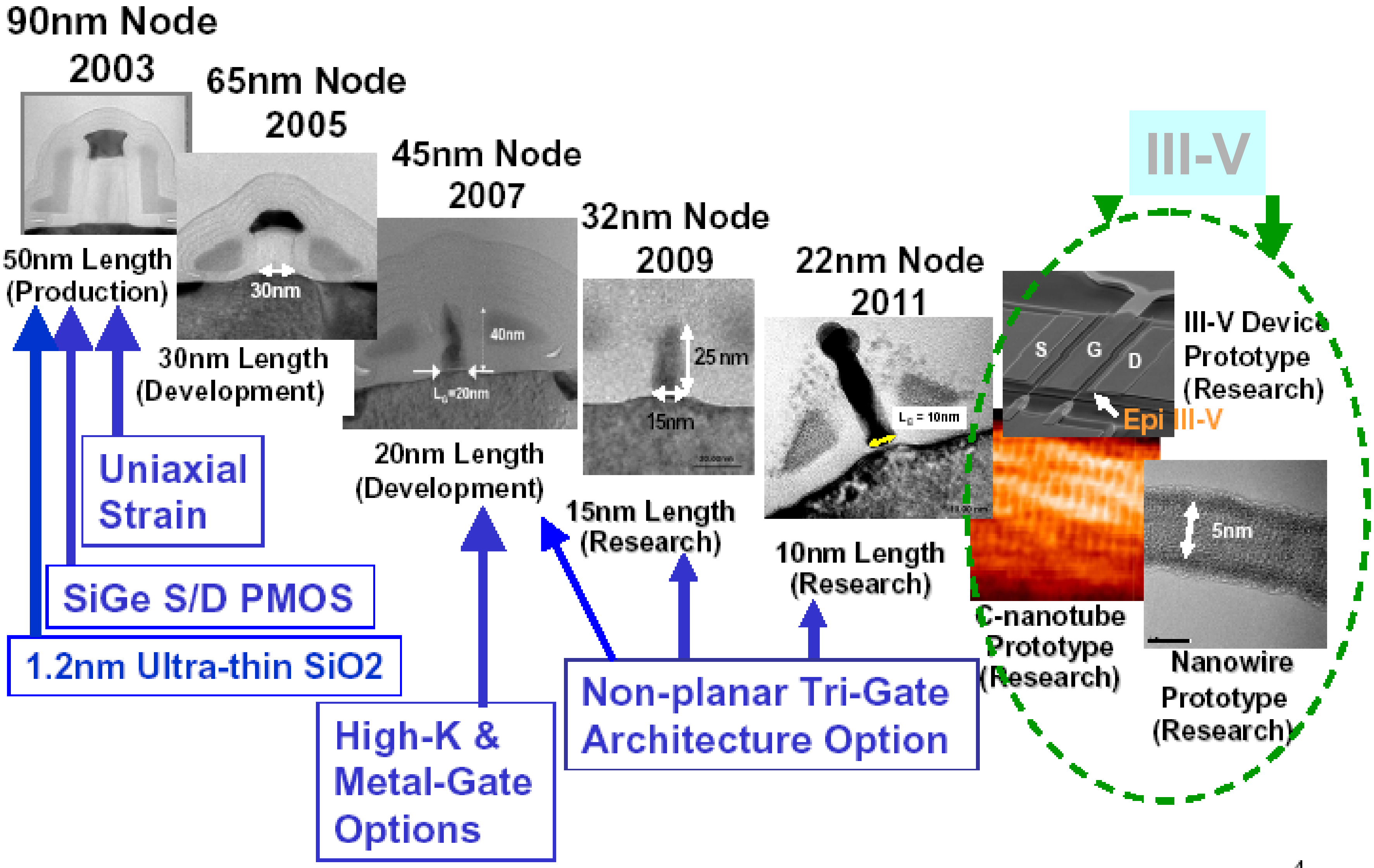


Sunlin Chou
Technology and Manufacturing Group
Intel Corporation

International Solid-State Circuits Conference
February 2005

Materials

strain → new oxides → new channels



90nm Node 2003

50nm Length (Production)

65nm Node 2005

30nm Length (Development)

45nm Node 2007

20nm Length (Development)

32nm Node 2009

15nm Length (Research)

22nm Node 2011

10nm Length (Research)

III-V

III-V Device Prototype (Research)

C-nanotube Prototype (Research)

Nanowire Prototype (Research)

Uniaxial Strain

SiGe S/D PMOS

1.2nm Ultra-thin SiO2

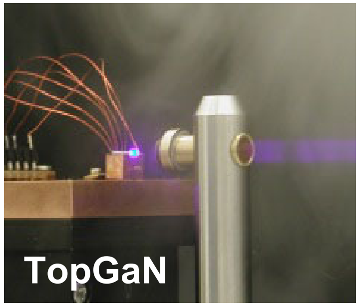
High-K & Metal-Gate Options

Non-planar Tri-Gate Architecture Option

Robert Chau, Intel, ICSICT 2004

Spintronics -- materials aspect

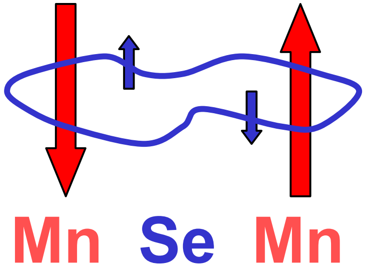
Why to do not combine complementary resources of ferromagnets and semiconductors?



- ferromagnetic metal / semiconductor hybrid structures
- ferromagnetic semiconductors – *multifunctional materials*

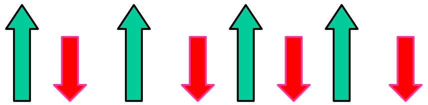
Search for ferromagnetic semiconductors

- *Antiferromagnetic* superexchange dominates in magnetic insulators and semiconductors
  → no spontaneous magnetisation
  NiO, MnSe, EuTe, …

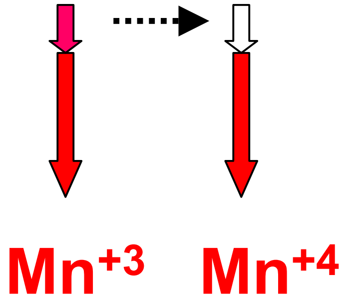


- **Exceptions**

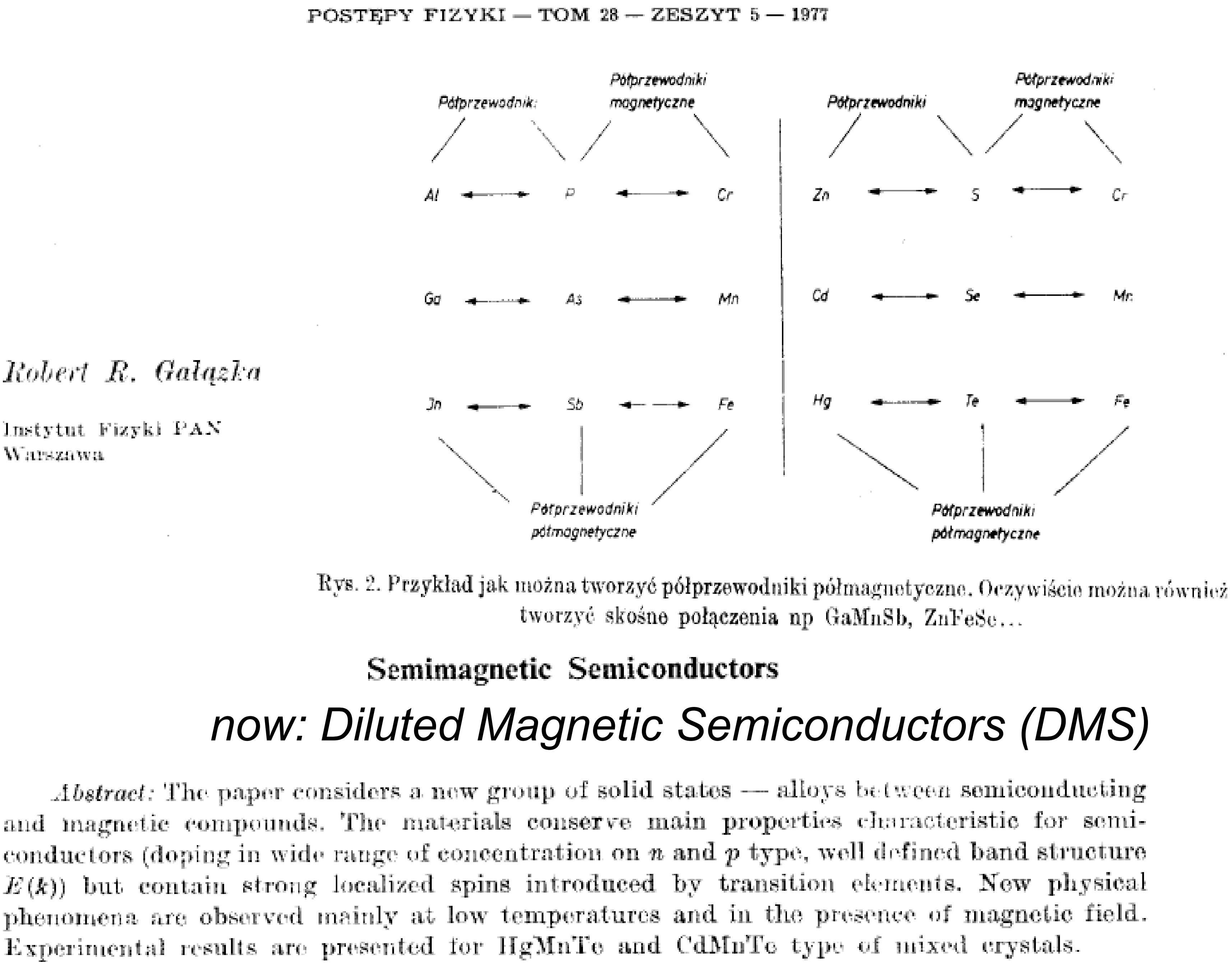
  -- **ferrimagnets (two ions or two spin states co-exist)**
  NiO(Fe_2O_3), Mn_4N, …



  -- **double exchange (two charge states co-exist)**
  $LaMnO_3$ → $La_{1-x}Sr_xMnO_3$ (holes in d band)



  -- **ferromagnetic superexchange dominates**
  EuO, $ZnCr_2Se_4$, … $T_C \approx 100$ K *IBM, MIT, Tohoku, … '60-'70*



POSTĘPY FIZYKI — TOM 28 — ZESZYT 5 — 1977

Rys. 2. Przykład jak można tworzyć półprzewodniki półmagnetyczne. Oczywiście można również tworzyć skośne połączenia np GaMnSb, ZnFeSe...

Robert R. Gałązka

Instytut Fizyki PAN
Warszawa

Semimagnetic Semiconductors

now: Diluted Magnetic Semiconductors (DMS)

Abstract: The paper considers a new group of solid states — alloys between semiconducting and magnetic compounds. The materials conserve main properties characteristic for semiconductors (doping in wide range of concentration on n and p type, well defined band structure $E(k)$) but contain strong localized spins introduced by transition elements. New physical phenomena are observed mainly at low temperatures and in the presence of magnetic field. Experimental results are presented for HgMnTe and CdMnTe type of mixed crystals.

Diluted magnetic semiconductors (DMS)

III-V	II-VI
Al ↔ P ↔ Cr	Zn ↔ S ↔ Cr
Ga ↔ As ↔ Mn	Cd ↔ Se ↔ Mn
In ↔ Sb ↔ Fe	Hg ↔ Te ↔ Fe

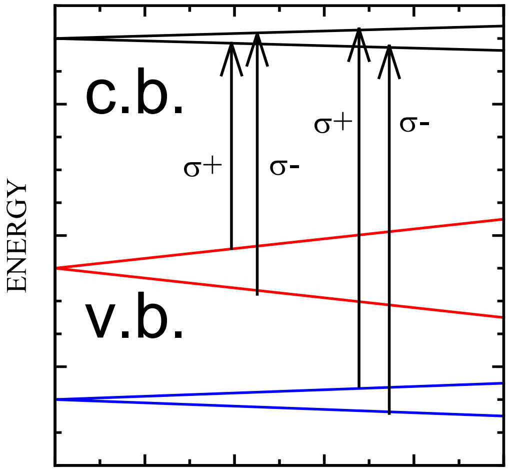
Gałązka (Warsaw) ICPS‘78

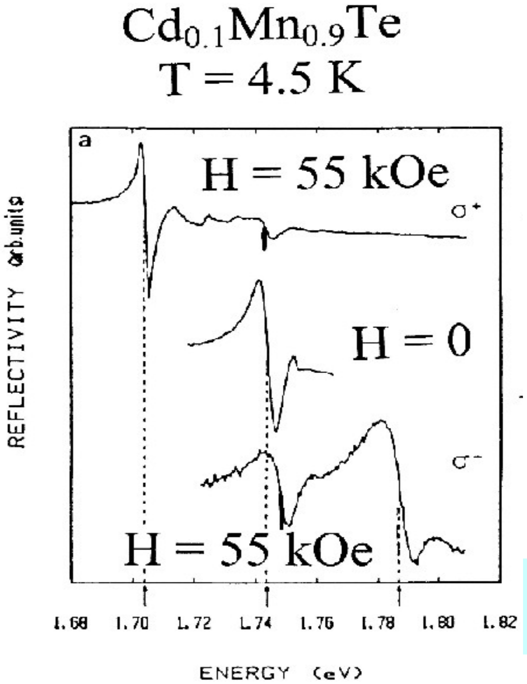
- Large solubility of Mn in II-VI’s
- AF superexchange in (II,Mn)VI

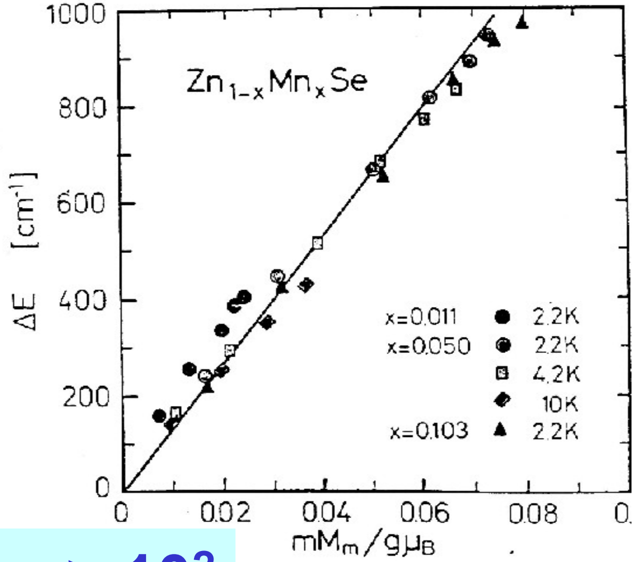
  ➔ random antiferromagnets

Determination of sp-d exchange integrals I - giant splitting of exciton states

$\Delta E \sim M \sim B_S(H)$







$g_{\mathrm{eff}} > 10^2$

Gaj et al.;Twardowski et al. (Warsaw)

-- p-d: $I_{pd} \equiv \beta N_o \approx -1.0$ eV

large *p-d* hybridization and large intra-site Hubbard *U* =>
kinetic p-d exchange *(T.D. '80, …, P. Kacman, SST'01)*

-- s-d: $I_{sd} \equiv \alpha N_o \approx 0.2$ eV

no s-d hybridization => potential s-d exchange

Hybrid optical isolators of DMS

- **absorption $\alpha(\sigma^+) > \alpha(\sigma^-)$ ➔ magnetic circular dichroism ➔ large Faraday rotation**

Gaj et al. (Warsaw) SSC'78

- **optical isolators:**

$$\Theta_F = \pi/4$$

Puremat (A. Mycielski) – world-wide monopole on pure Mn

Making DMS ferromagnetic

long-range ***carrier*-**mediated ferromagnetic exchange

IV-VI: p-$Pb_{1-x-y}Mn_xSn_yTe$ ***Story et al. (Warsaw) PRL'86***

III-V: $In_{1-x-}Mn_xAs$ ***Ohno et al. (IBM) PRL'92***

$Ga_{1-x-}Mn_xAs$ ***Ohno et al. (Tohoku) APL'96***

T_C ≈ 100 K for x = 0.05

II-VI: p-$Cd_{1-x}Mn_xTe/Cd_{1-x-y}Zn_xMg_yTe$:N QW

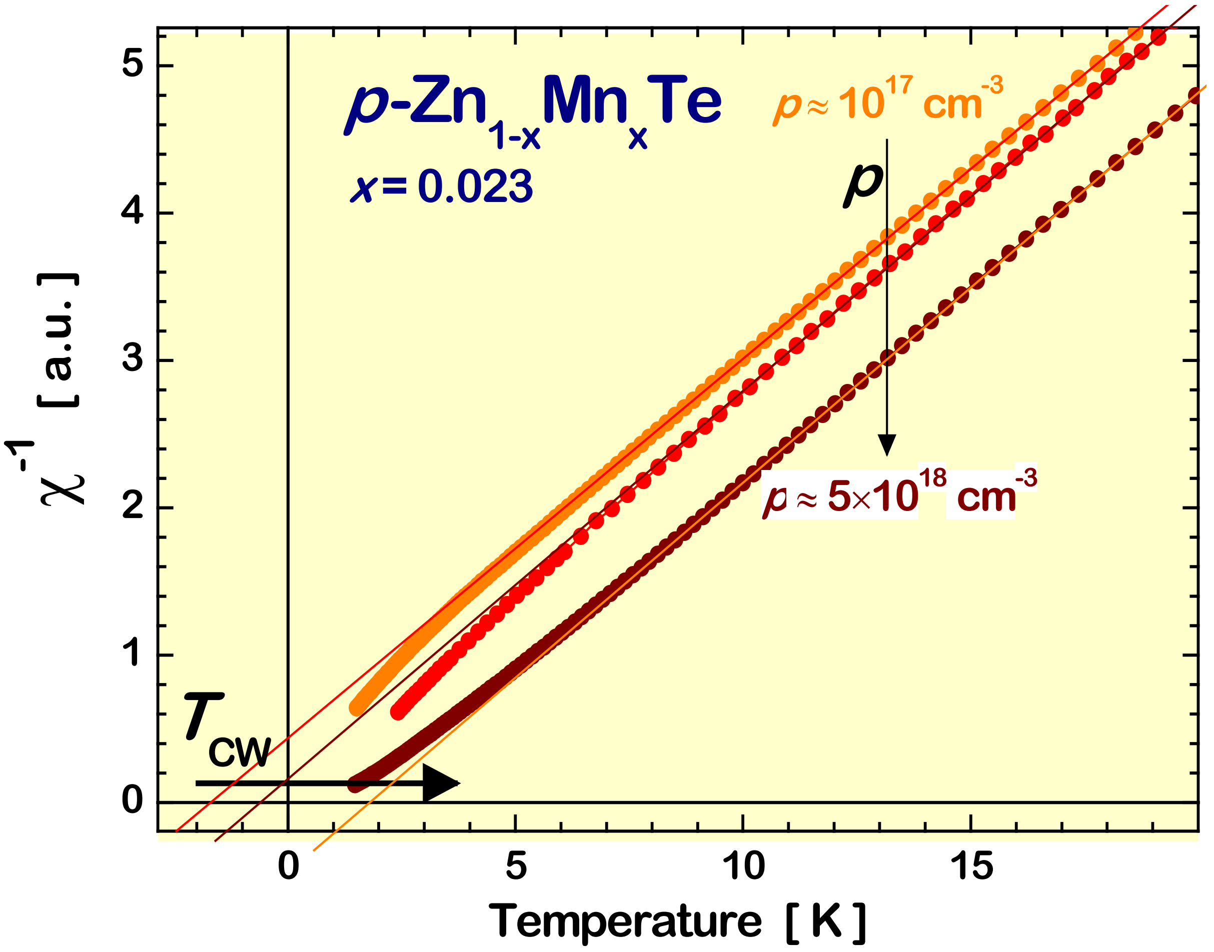
Haury et al. (Grenoble, Warsaw) PRL'97

p-$Zn_{1-x}Mn_xTe$:N ***Ferrand et al. (Grenoble, Warsaw) PRB'01***

p-$Be_{1-x}Mn_xTe$:N ***Hansen et al. (Wuerzburg, Warsaw) APL'01)***

III-V and II-VI DMS:
quantum nanostructures and ferromagnetism combine

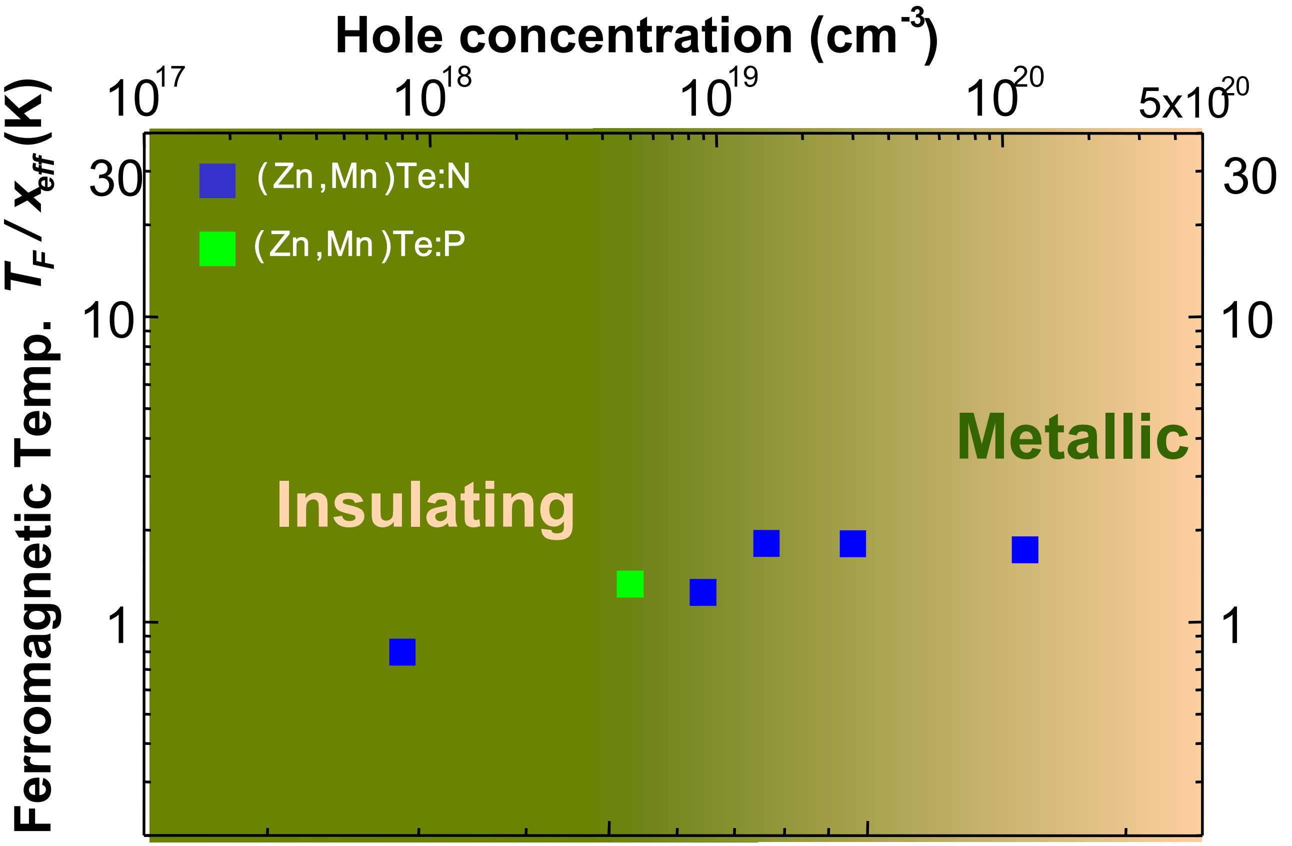
Effect of acceptor doping on magnetic susceptibility in $Zn_{1-x}Mn_xTe:P$



χ^{-1} vs. T

Sawicki et al. (Warsaw) pss'02
Kępa et al. (Warsaw, Oregon) PRL'03

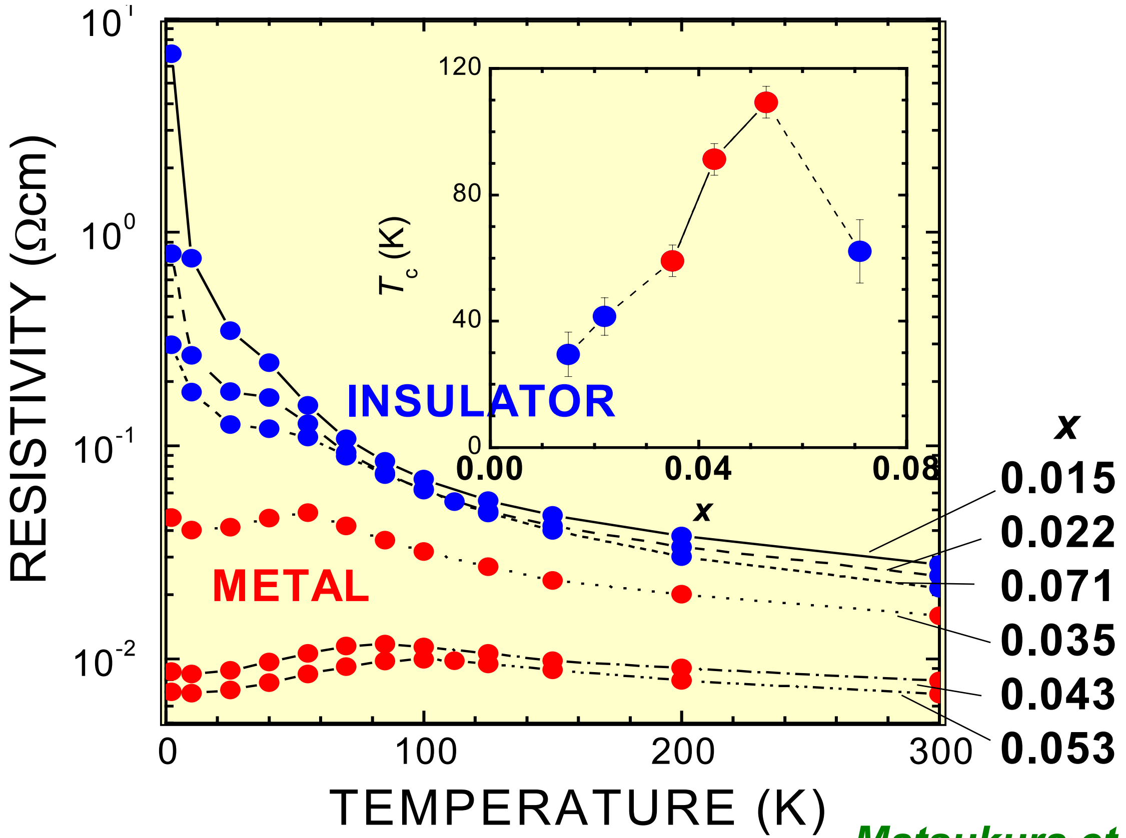
Ferromagnetic temperature in p-(Zn,Mn)Te



- ferromagnetism disappears in the absence of holes
- ferromagnetism on both sides of metal-insulator transition

Ferrand et al. (Grenoble, Warsaw) PRB'01
Sawicki et al. (Warsaw) pss'02

$Ga_{1-x}Mn_xAs$: resistance vs. temperature and Curie temperature vs. x



Matsukura et al. (Tohoku) PRB'98

- **ferromagnetism on both sides of metal-insulator transitions**
- **ferromagnetism disappears in the absence of holes**

Carrier-induced ferromagnetism in DMS

- ferromagnetism on both sides of metal-insulator transitions
- coexistence of physics of:
  - -- strongly correlated metals
  - -- disordered magnetic insulators
  - -- highly doped semiconductors (Andersona-Mott localization, self-compensation)

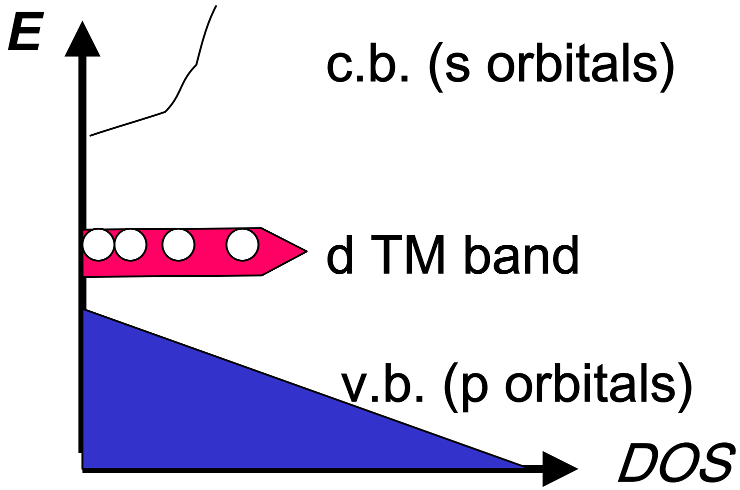
A number of theoretical proposals ….

Where do Mn d levels and holes reside?

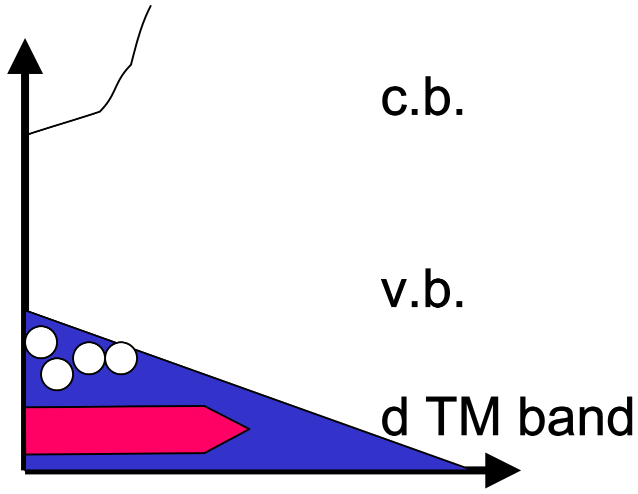
Where do Mn d levels and holes reside?

Two possibilities:

-- Mott-Hubbard insulator
[manganides $La_{1-x}Sr_xMnO_3$]

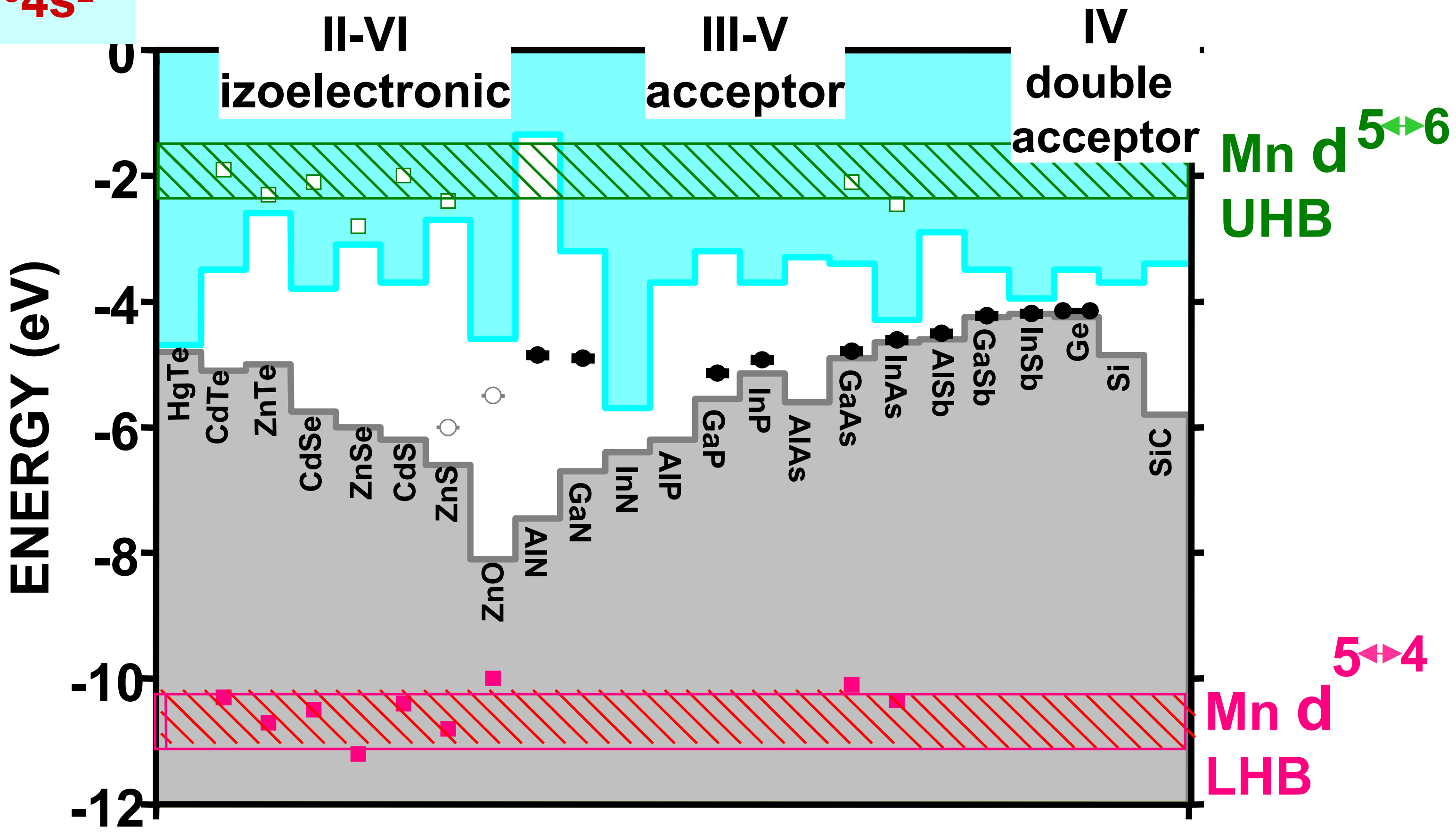


-- charge transfer insulator
[cuprates $La_{2-x}Sr_xCuO_4$]



Mn-derived states in semiconductors

Mn: $3d^5 4s^2$



Photoemission: *Fujimori et al. (Tokyo), PRB'02, PRB'04*

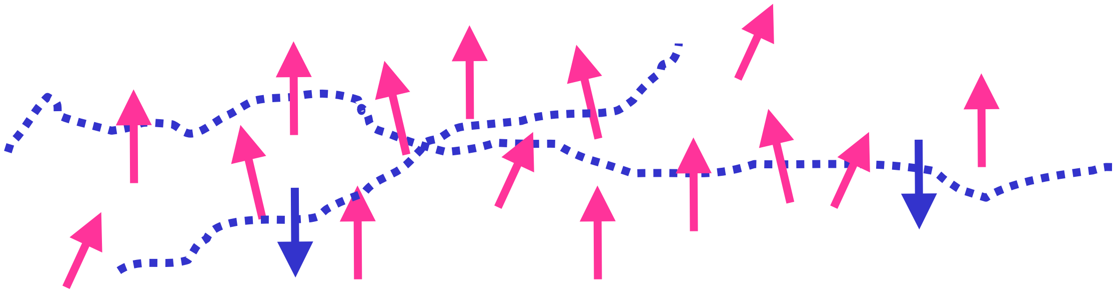
Band edges compile by: *Van de Walle (UCSB) Neugebauer (Dusseldorf), Nature'04*

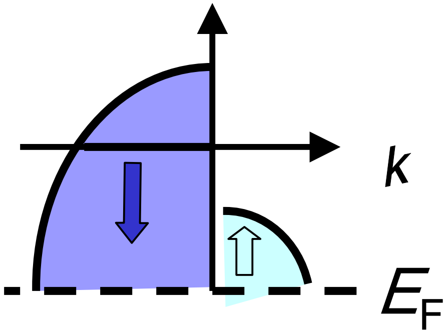
Band-gap states compile by: *T.D. et al.*, PRB'02 *cf. Paul Koenraad*

Contradicts LSDA → SIC, LSDA +U, ...

Modelling of carrier-controlled ferromagnetism in DMS

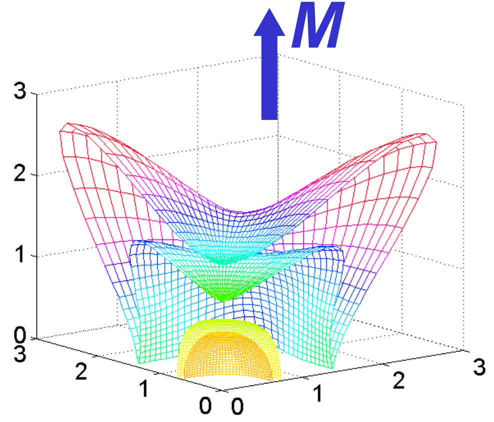
Mean-field Zener/RKKY model of hole-controlled ferromagnetism in DMS





Driving force:

lowering of the hole energy due to redistribution between hole spin subbands split by p-d exchange interaction



Essential ingredient:

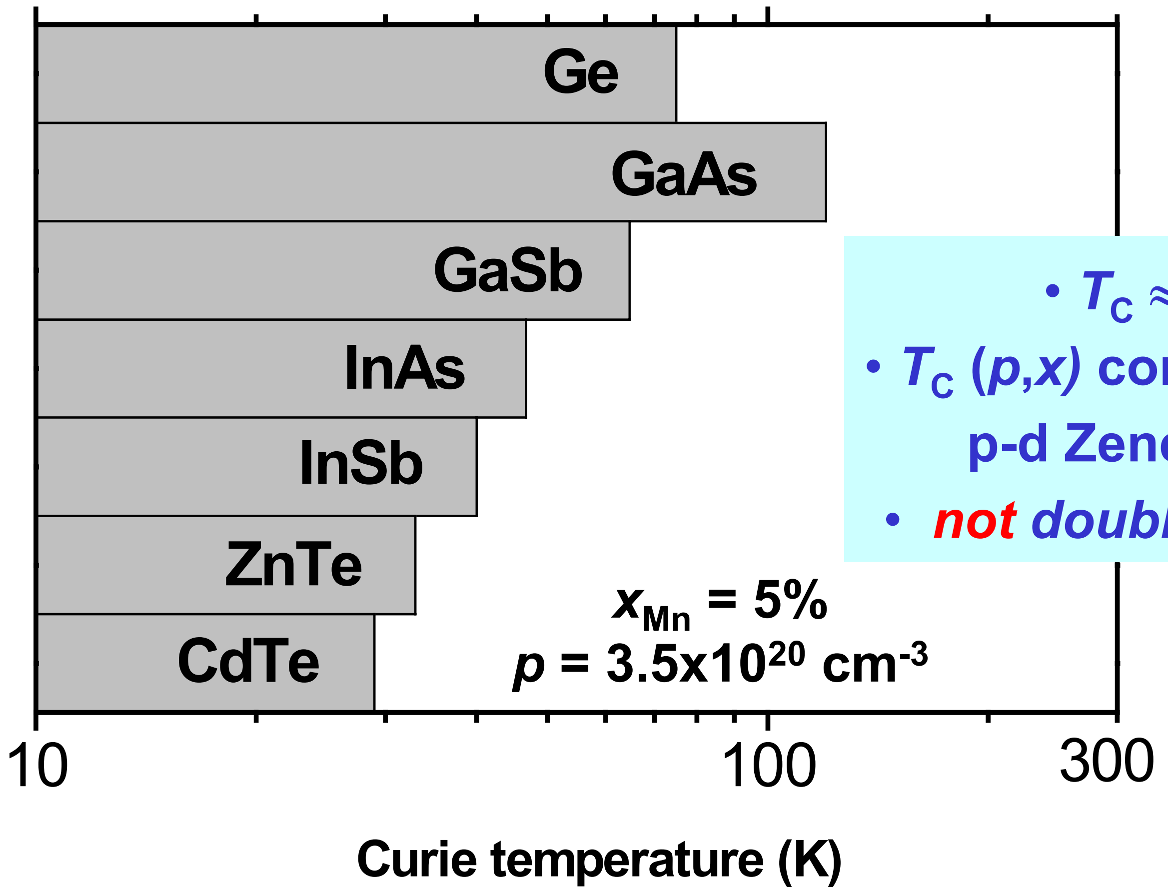
Complexity of the valence band structure has to be taken into account

No adjustable parameters

$T_C = T_F - T_{AF}$; $T_F \sim I_{pd}^2 \rho^{(s)}_{DOS}$

T.D. et al.,'97-
MacDonald et al. (Austin) '99-

Mn-based p-type DMS to which p-d Zener model has been found to apply



- $T_C \approx \Theta_{CW}$
- T_C (p,x) consistent with p-d Zener model
- ***not** double exchange*

Theory: *T. D et al. (Warsaw, Tohoku, Grenoble) Science'00, PRB'01*
Jungwirth et al. (Austin, Prague, PRB'02), also UCSD, NRL, …
Support *LSDA+U, LSDA+SIC (Osaka, Juelich, Uppsala, Prague, Golden , Oak Ridge ....)*
Expl.: *Tohoku, Kanagawa, Tokyo, Grenoble, PSU, NRL, Notre Dame, UCSB, Nottingham, …*

p-d Zener model for p-type DMS

- ***the model explains/predicted:***

-- $T_C(x, p, n)$, spin polarization, *M(T,H), magnetic anisotropy*

-- magnetic stiffness (domain width, spin wave spectrum)

-- anomalous Hall effect

-- a.c. conductivity and magnetic circular dichroism

-- magnetoresistance (WLR) and anisotropic magnetoresistance

cf. Carsten Timm

-- …

T.D. et al.,'97-
A.H. MacDonald et al. '99-

- **(Ga,Mn)As, p-(Cd,Mn)Te, … emerge as model ferromagnets**
- **basis for magnetisation manipulation**

cf. Hideo Ohno

Examples of effects of nanoscale fluctuations in ferromagnetic DMS

- (III,Mn)V
  electrostatic disorder caused by ionised Mn acceptors and compensating donors

- (II,Mn)VI
  magnetic disorder caused by competing AF and FM interactions

cf. Georges and Richard Bouzerar

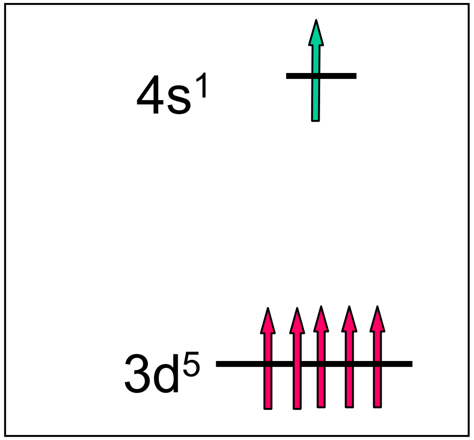
Electrostatic disorder

s-d exchange energy αN_o in (III,Mn)V

Experimental values of s-d exchange energy

-- **Mn^{+1} free ion: $\alpha N_o = 396$ meV**

-- **in (II,Mn)VI: $\alpha N_o = 220 \pm 50$ meV**



Experimental values in (III,V)Mn

-- **n-$Ga_{1-x}Mn_xN$**

$\alpha N_o = |14 \pm 4|$ meV $0.01\% < x < 0.2\%$

EPR- Korringa ***Wolos et al. (Warsaw) APL'03***

-- **$Ga_{1-x}Mn_xAs$**

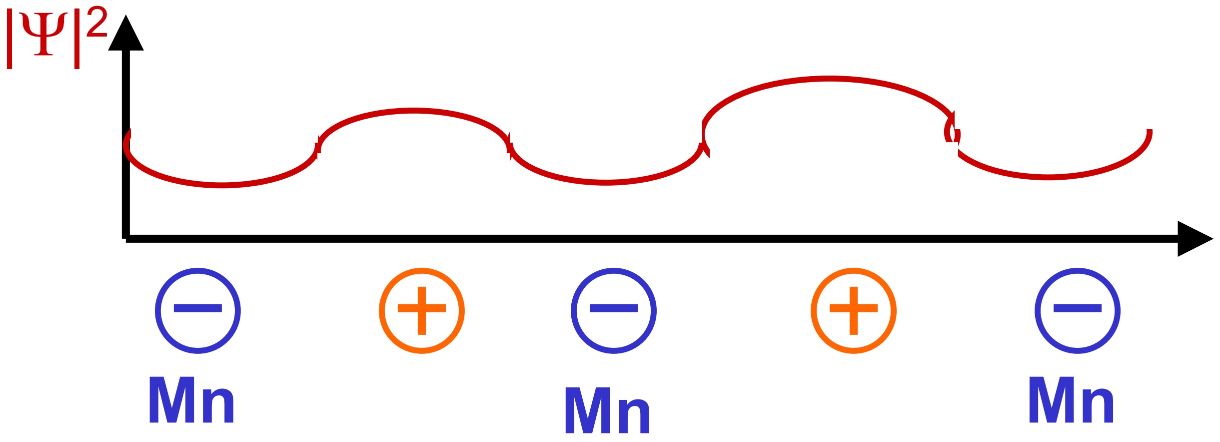
$\alpha N_o = 23$ meV $x = 0.1\%$

SFRS ***Heimbrodt et al. (Marburg) Physica E'01***

$\alpha N_o = -90 \pm 30$ meV $x < 0.03\%$

Time-resolved Kerr ***Myers et al. (St. Barbara) cond-mat/0502115***

Model for *apparent* s-d exchange energy αN_o in (III,Mn)V



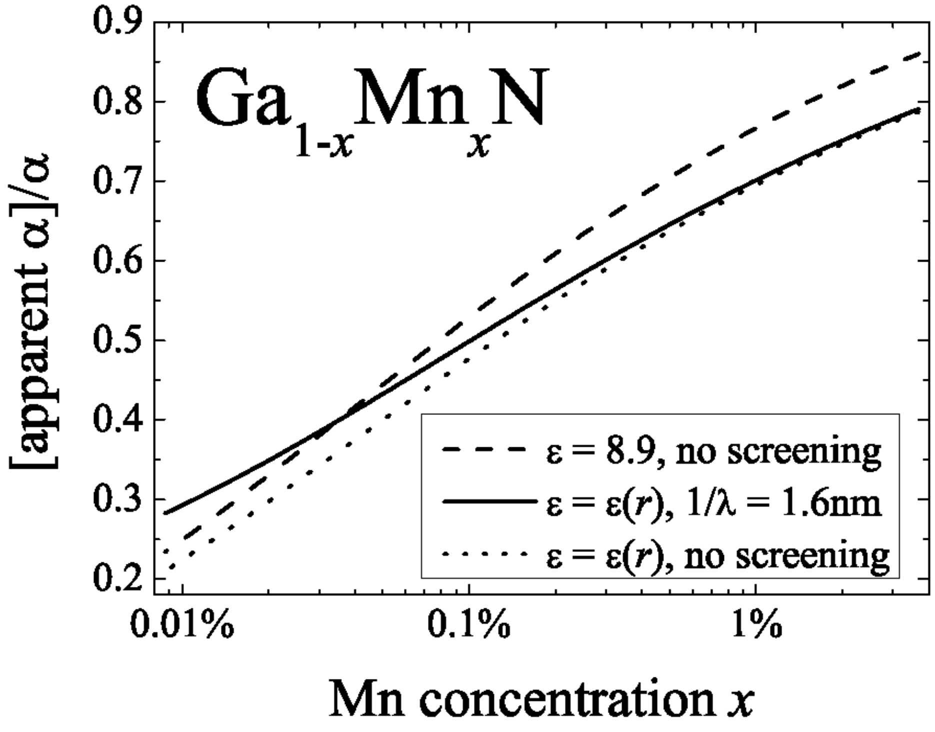
Electron repulsion by Mn acceptors and attraction by donors:

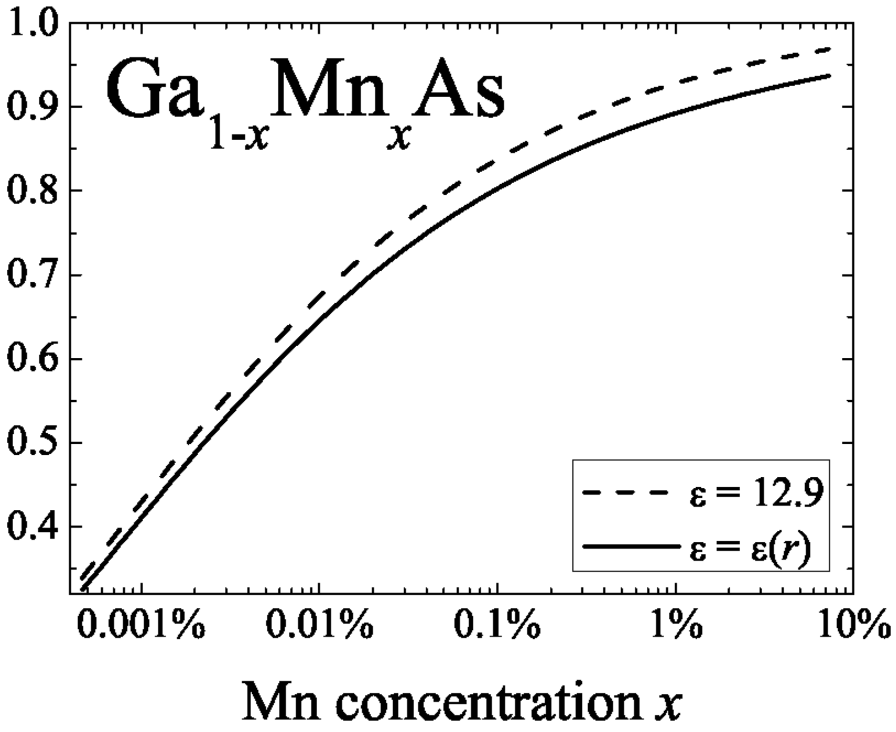
→ **reduces: $|\Psi|^2$ at Mn → spin-splitting → apparent αN_o**

→ **effect large at small x**

C. Śliwa, T.D. (Warsaw) cond-mat/0505126

Reduction of *apparent* αN_o taking into account Coulomb repulsion by Mn acceptors

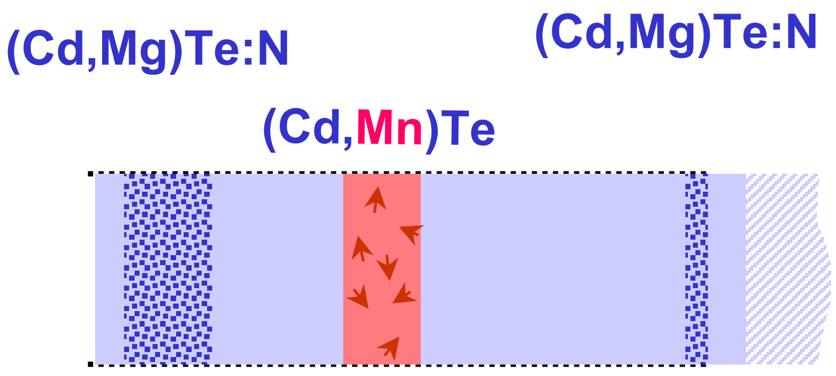




C. Śliwa, T.D. (Warsaw) cond-mat/0505126

Magnetic disorder

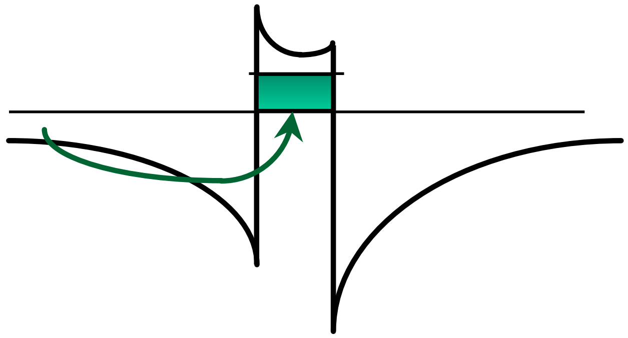
Modulation-doped (Cd,Mn)Te quantum wells

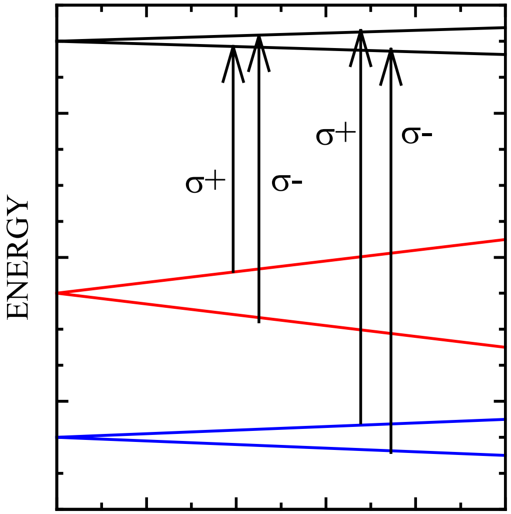


(Cd,Mg)Te:N

(Cd,Mg)Te:N

(Cd,**Mn**)Te



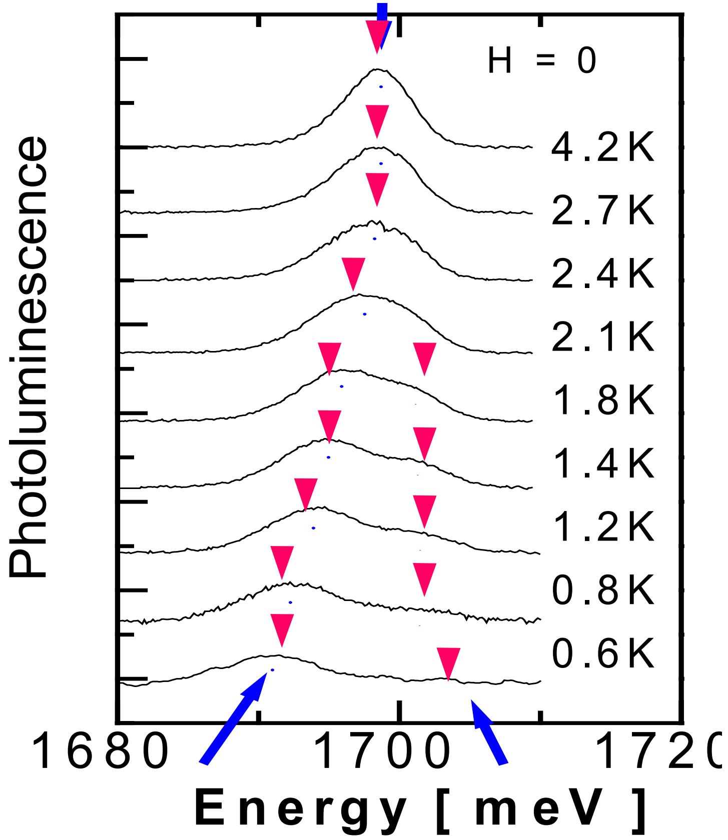


$\Delta E \sim M$

- **weak disorder**
- **Ising system**

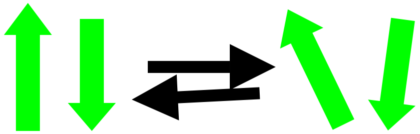
cf. Joël Cibert

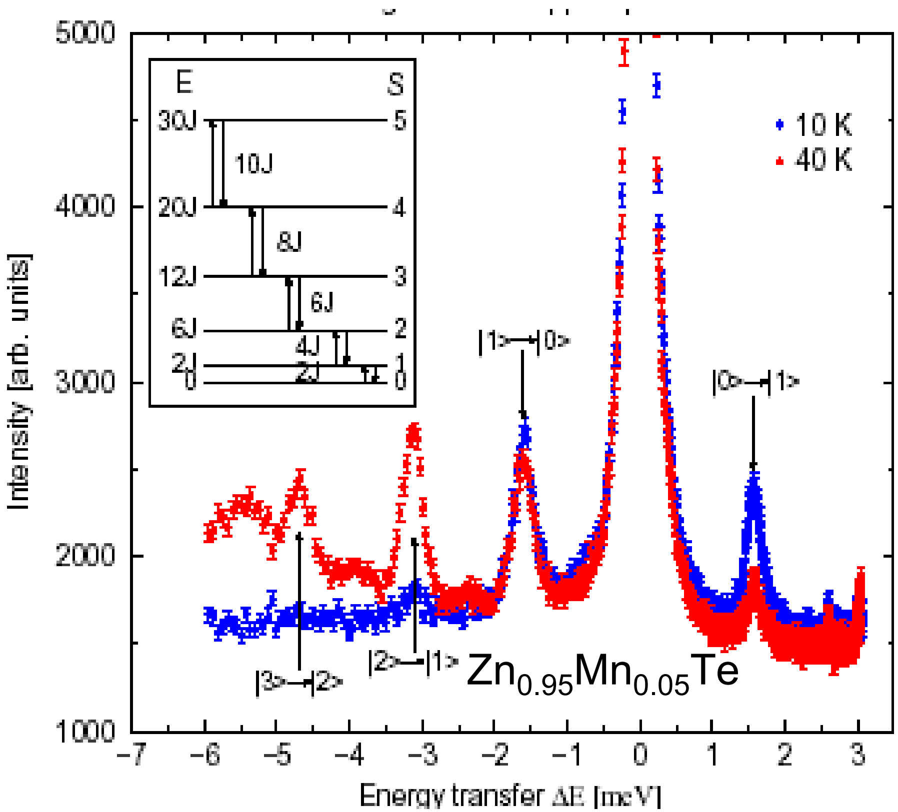
Spontaneous splitting of PL line in p-(Cd,Mn)Te QW



Kossacki et al. (Warsaw, Grenoble) Physica E'00

Probing competing AF and FM interactions by inelastic neutron scattering in p-(Zn,Mn)Te





Kępa et al. (Warsaw, Oregon) PRL’03

inelastic neutron scattering of n.n. Mn pairs

large single crystals of $Zn_{0.95}Mn_{0.05}Te:P$

$p = 5 \times 10^{18}$ cm^{-3}, $T_{CW} = 2$ K

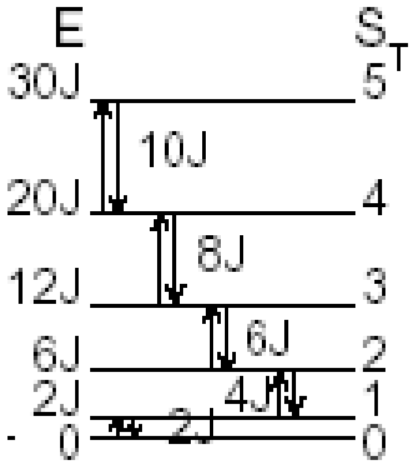
Insulator side of the MIT

$$H_{int} = -2(J_{AF} + J_h)S_iS_j$$

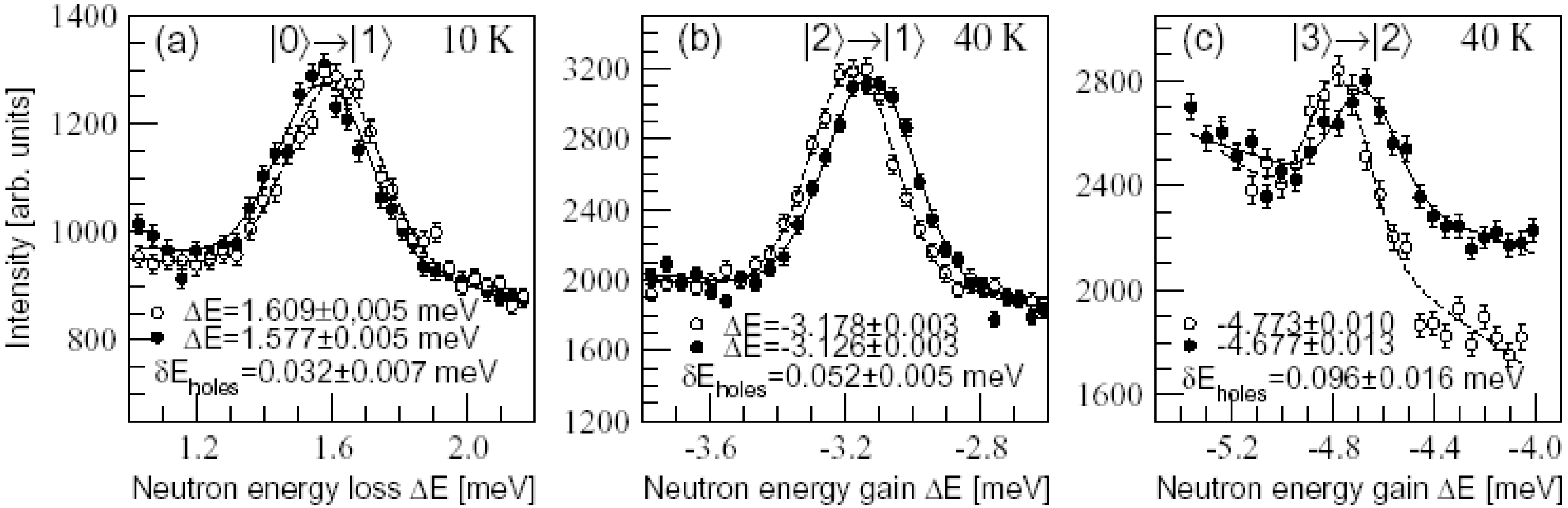
$J_{AF} < 0$ super-exchange

$J_h > 0$ hole-induced

Hole induced contribution



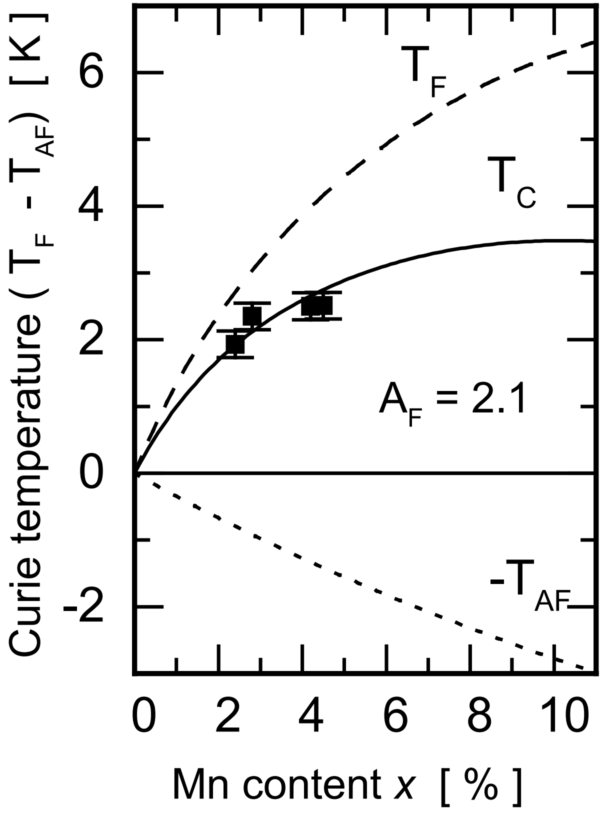
empty dots - no holes, full dots – with holes

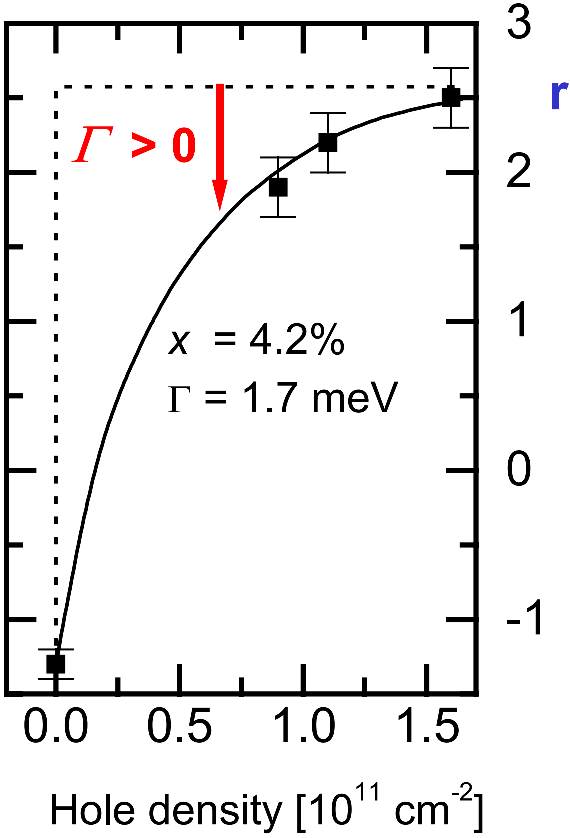


$\delta E = 2J_h = 0.03 \pm 0.006$ meV

$2J_h^{RKKY} = 0.020$ meV

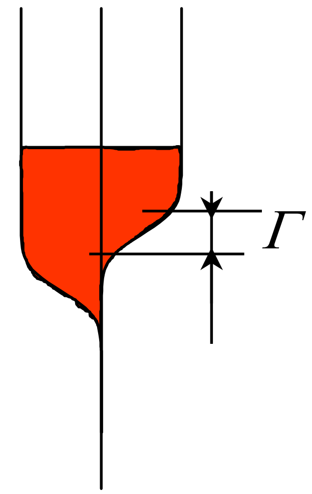
Mean field $T_C = T_F - T_{AF}$ vs. x and p in $p\text{-}Cd_{1-x}Mn_xTe$ QW





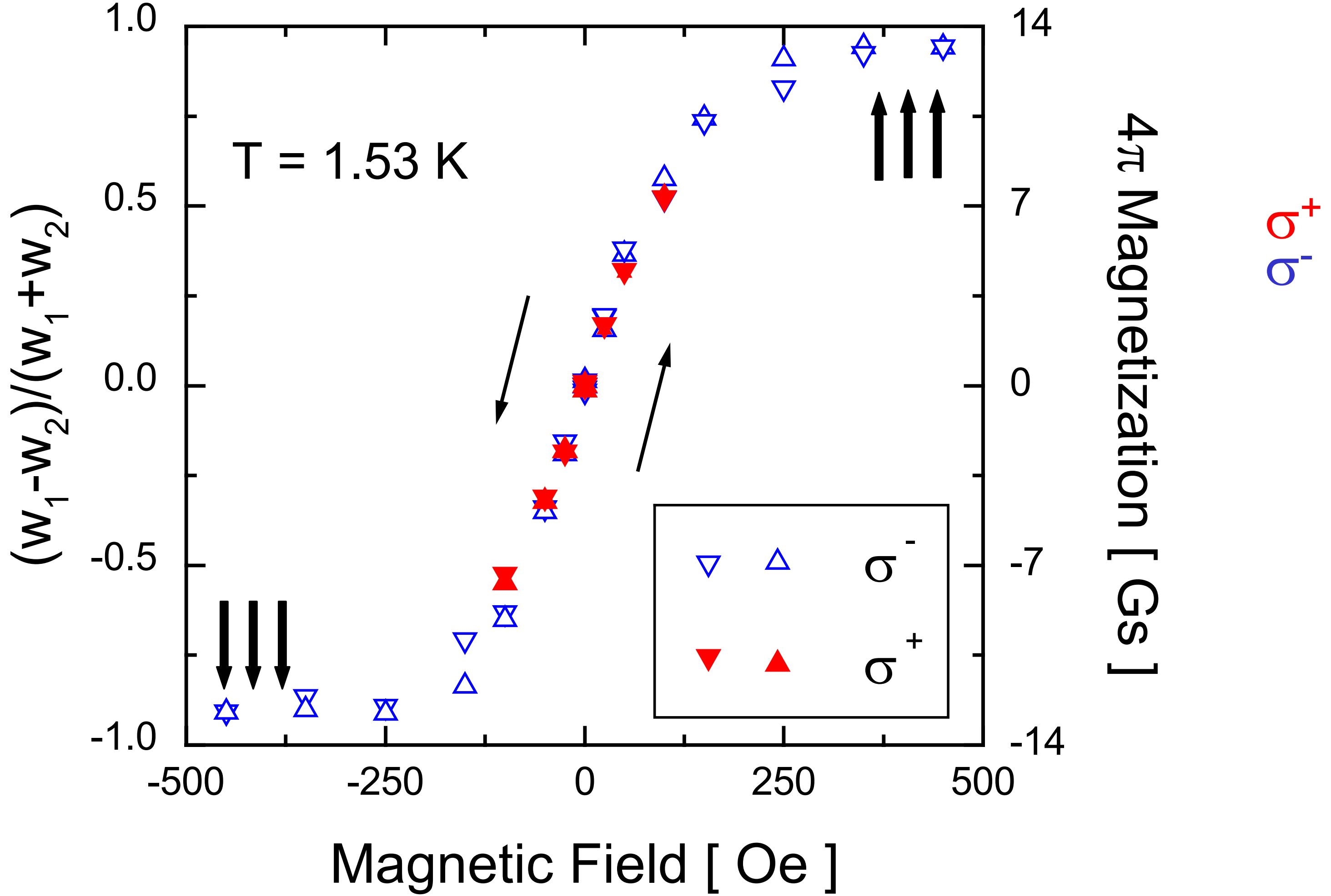
Boukari et al. (Grenoble, Warsaw) PRL'02

role of disorder:



MFA describes T_C but ….

Optically determined *M*(*H*) for *H* along easy axis

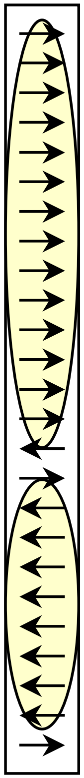


Kossacki et al. (Warsaw, Grenoble)
Physica E'02

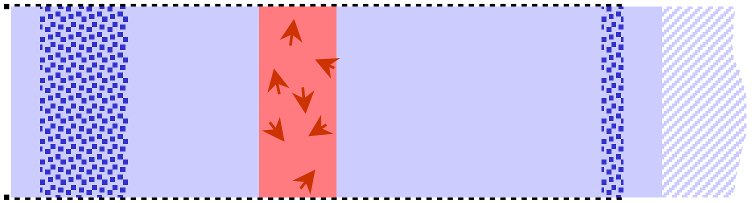
- **no hysteresis**
- **large saturation field**

Model and approach

Competing long-range FM and short-range AF produces nanoscale 180° domains



Monte Carlo simulations of coupled hole and Mn spin systems in (Cd,Mn)Te QW

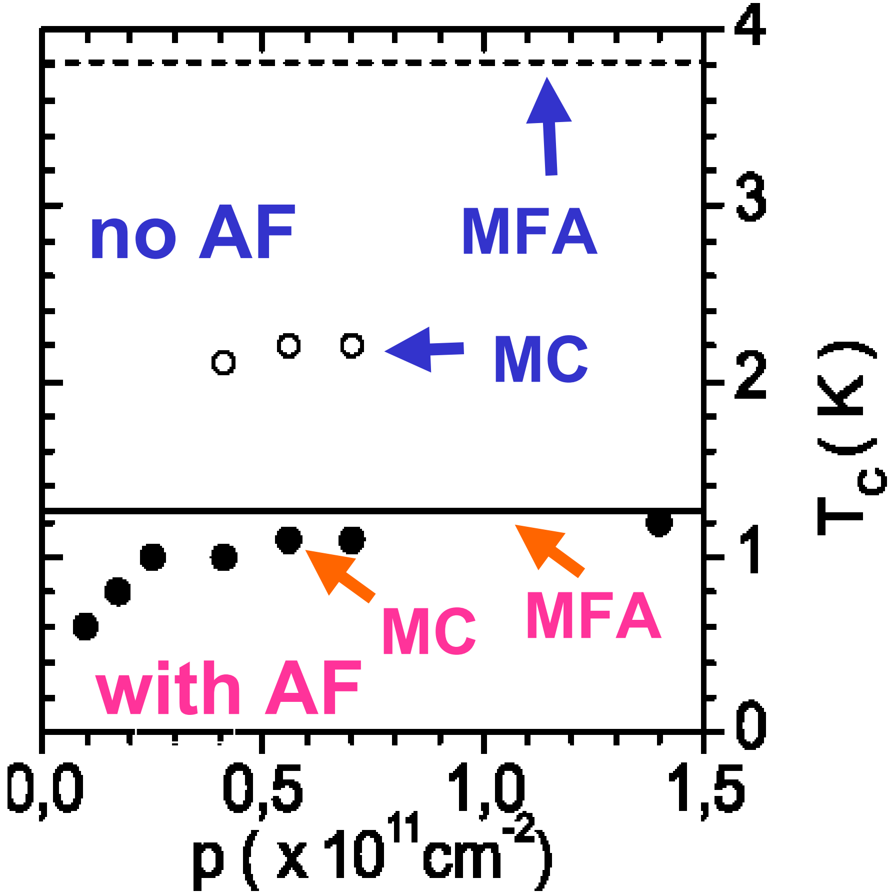


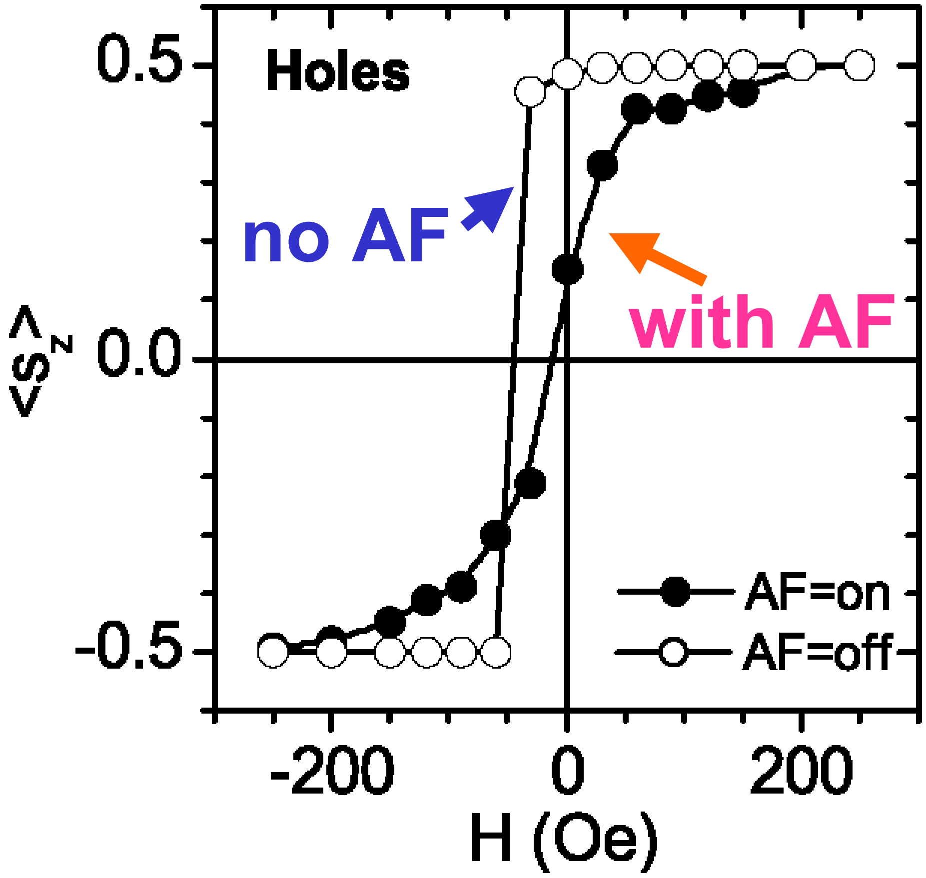
- *hole energies calculated at each Monte Carlo sweep*
- *AF interactions taken into account*

Dechrakos et al. (Athenes, Warsaw) PRL’05

previous MC simulations of DMS:
J. Schliemann et al., E. Dagotto et al., L. Brey et al., …

Comparison of MFA and Monte Carlo results with AF and with no AF interactions





Dechrakos et al. (Athenes, Warsaw) PRL'05

- **ordering temperature $T_C > T_F - T_{FA}$**
- **macroscopic spontaneous magnetisation reduced**

Nanoscale fluctuations - summary

- (III,Mn)V
  electrostatic disorder caused by ionised Mn acceptors and compensating donors reduces *apparent* s-d and enhances *apparent* p-d exchange integral at low *x*

- (II,Mn)VI
  magnetic disorder caused by competing AF and FM interactions increases $T_C = T_F - T_{FA}$ and diminishes spontaneous magnetisation

Nanoscale phase separation
Can we push T_c higher?

Strategies

- **Two strategies for increasing T_C**

  -- increasing p and/or x in existing ferromagnetic DMS

  -- searching for DMS with greater coupling constant $\beta^2\rho(E_F)$

T.D. et al. (Warsaw, Tohoku, Grenoble) Science'00

Strategies

- **Two strategies for increasing T_C**

  -- increasing p and/or x in existing ferromagnetic DMS

  -- searching for DMS with greater coupling constant $\beta^2\rho(E_F)$

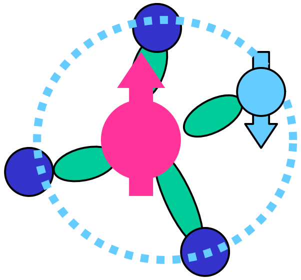
  ➔ *nitrides and oxides*

- **Obstacles**

  -- self-compensation

  -- solubility limits

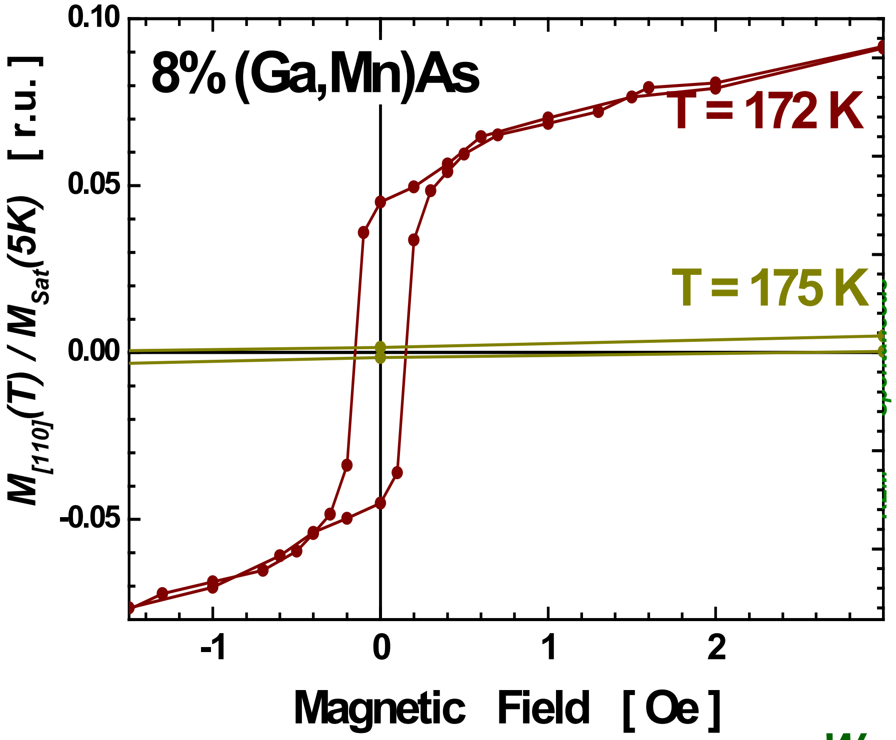
  -- tight binding of holes by TM ions (Zhang-Rice polaron)



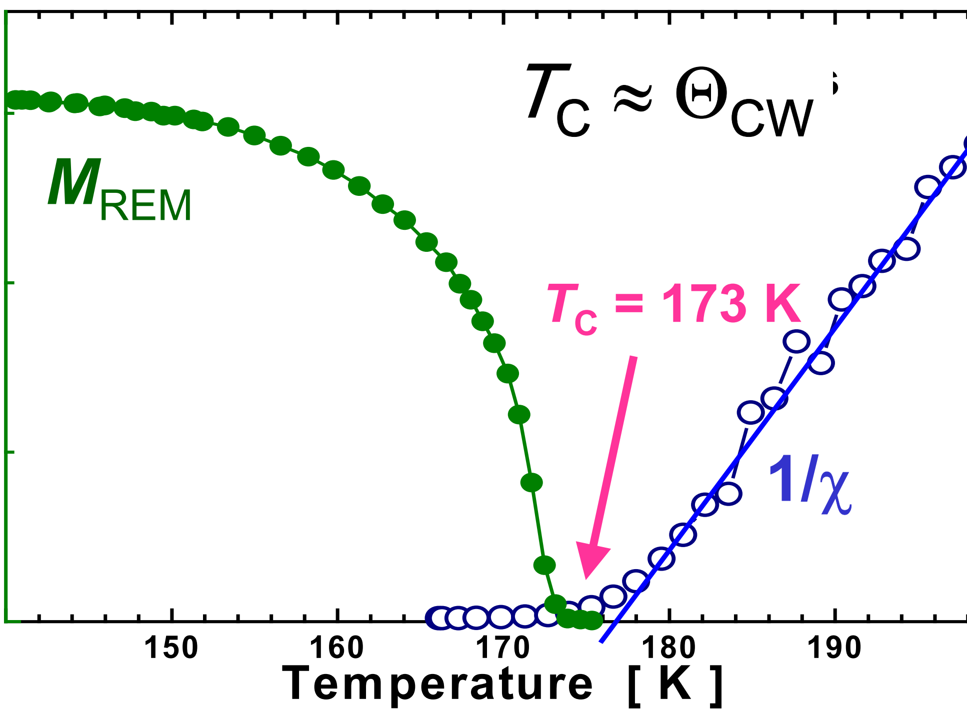
T.D. et al. (Warsaw, Tohoku, Grenoble) Science'00

Where do we stand?

hysteresis loops



remanent magnetisation and $1/\chi$ vs. T

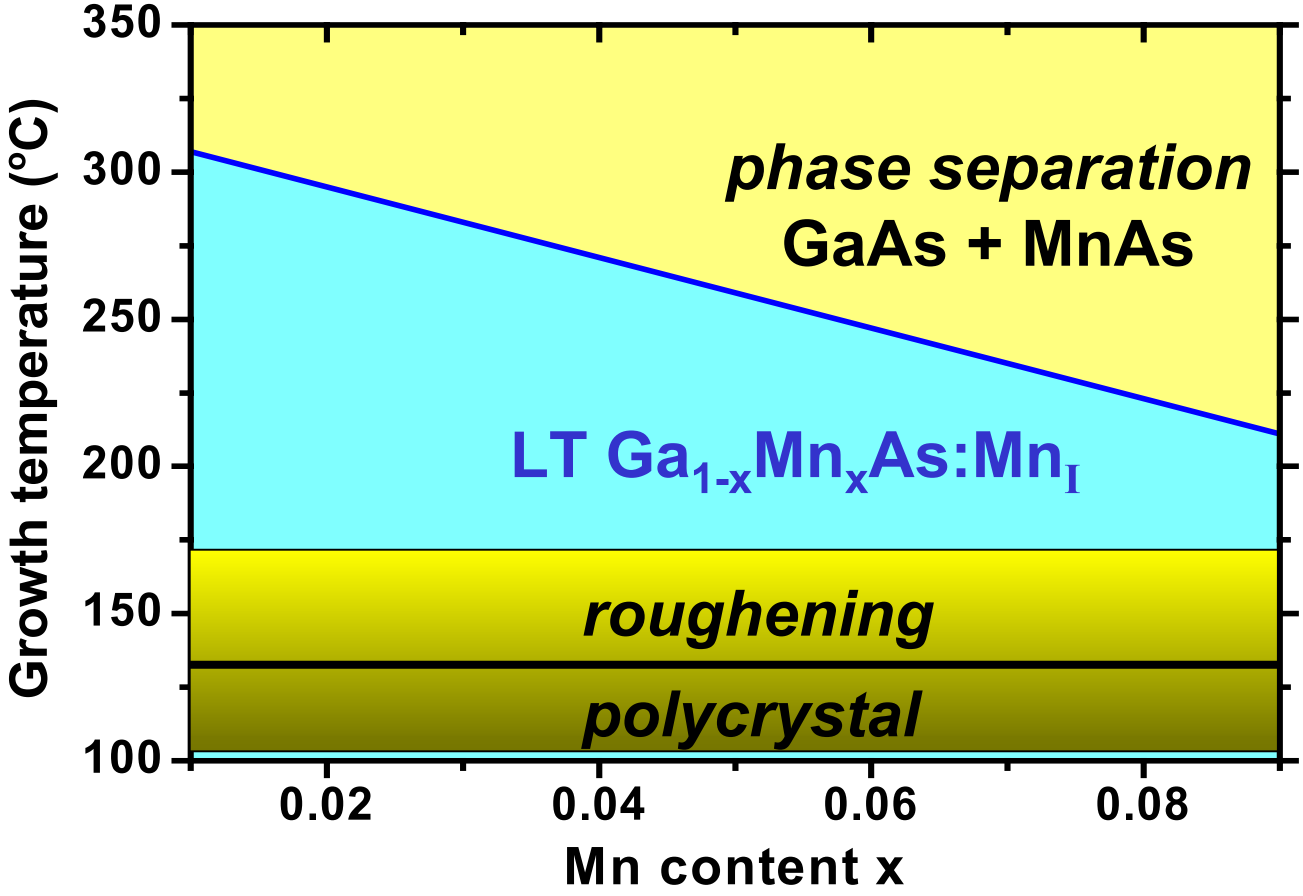


Wang et al. (Nottingham, Warsaw)

Progress due to control over self-compensation

cf. Nitin Samarth

(Ga,Mn)As – growth phase diagram

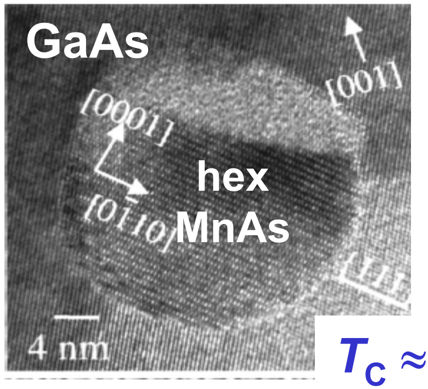


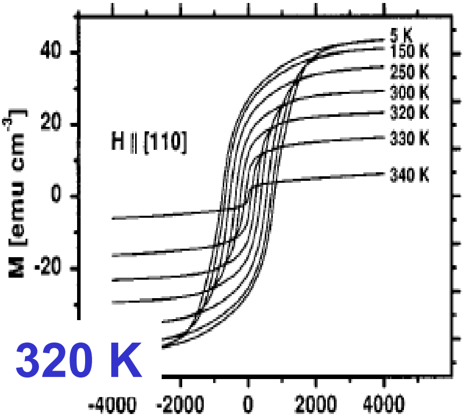
after Matsukura and Ohno (Tohoku)

GaAs + MnAs precipitates

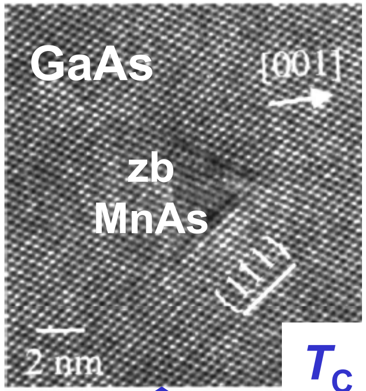
- size and structure determined by growth conditions
- control magnetic properties

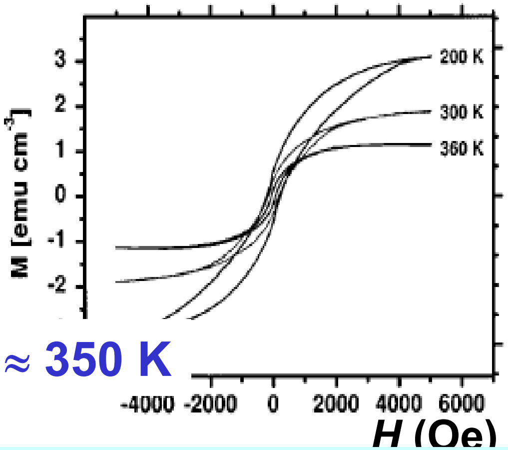
De Boeck et al. (IMEC) APL'96





$T_C \approx 320$ K





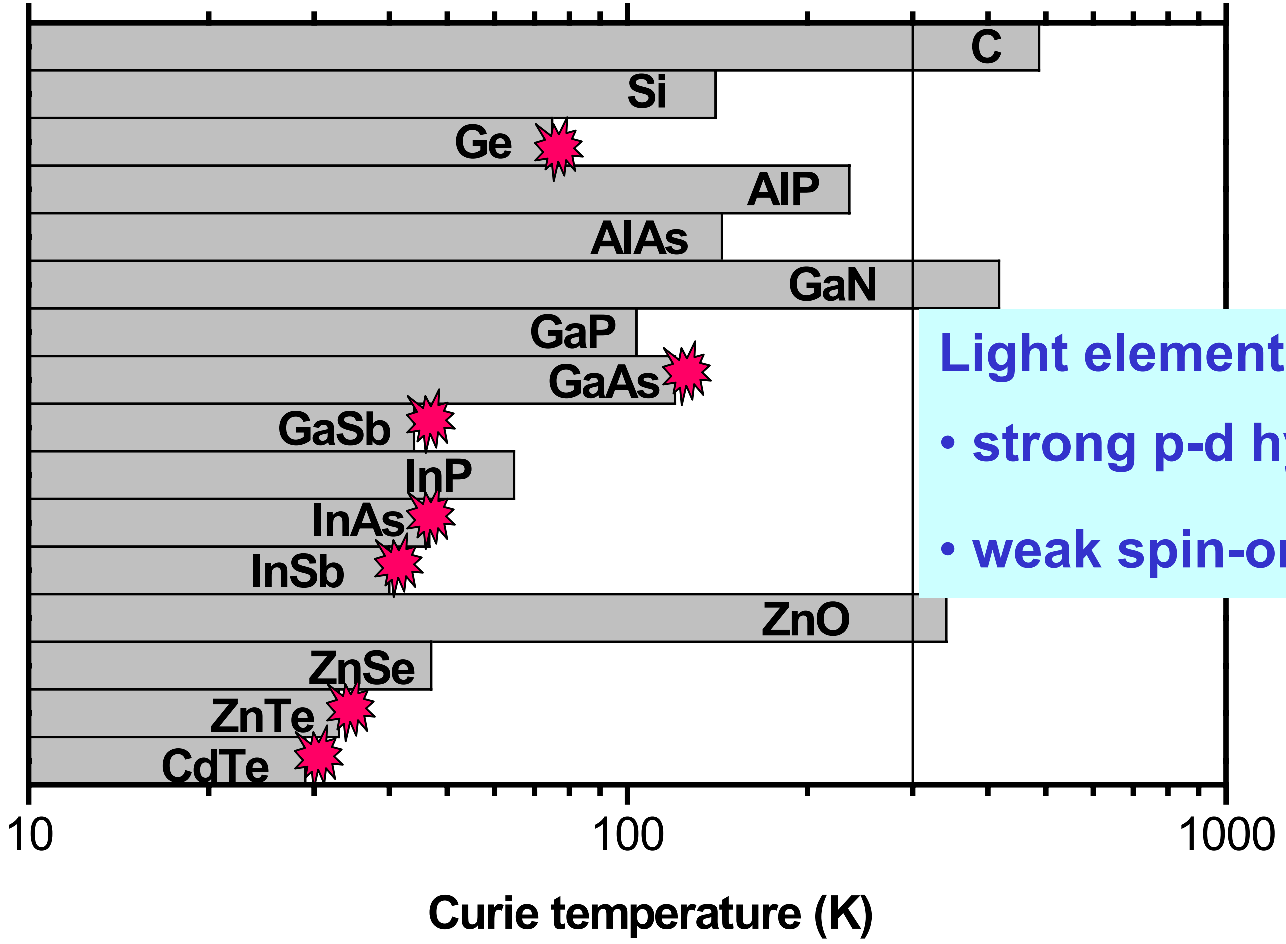
$T_C \approx 350$ K

Moreno et al. (Berlin) JAP'02

- spinodal decomposition
- superparamagnetic limit not reached

Other systems

Zener model prediction of T_C for semiconductors containing 5% Mn d^5, $p = 3.5\times10^{20}$ cm^{-3}



Light elements:

- strong p-d hybridisation
- weak spin-orbit interaction

T. D. et al. (Warsaw, Tohoku, Grenoble) Science'00, PRB'01

Semiconductor materials showing hysteresis and spontaneous magnetisation at 300 K

wz-c-(Ga,Mn)N, (In,Mn)N, (Al,Mn)N, (Ga,Cr)N, (Al,Cr)N, (Ga,Gd)N,

cf. Klaus Ploog

(Ga,Mn)As, (In,Mn)As, (Ga,Mn)Sb, (Ga,Mn)P:C

(Zn,Mn)O, (Zn,Ni)O, (Zn,Co)O, (Zn,V)O, (Zn,Fe,Cu)O

(Zn,Cr)Te

$\mathrm{(Ti,Co)O_2}$, $\mathrm{(Ti,V)O_2}$, $\mathrm{(Sn,Co)O_2}$, $\mathrm{(Sn,Fe)O_2}$, $\mathrm{(Hf,Co)O_2}$

$\mathrm{(Cd,Ge,Mn)P_2}$, $\mathrm{(Zn,Ge,Mn)P_2}$, $\mathrm{(Cd,Ge,Mn)As_2}$, $\mathrm{(Zn,Sn,Mn)As_2}$

(Ge,Mn), (Ge,Mn,Fe)

$\mathrm{(La,Ca)B_6}$, C, $\mathrm{C_{60}}$, $\mathrm{HfO_2}$, …

In many cases high T_C consistent with *ab initio* computations within LSDA

High T_C ferromagnetic semiconductors

- **Growth phase diagrams unknown**
- **Microscopic mechanism underlying ferromagnetic response unknown**

  LSDA largely overestimates tendency towards ferromagnetism

- **Each system brings new challenges**

-- new uniform ferromagnetic semiconductor?

  - long-range ferromagnetic coupling with no band carriers?

-- nanoscale phase separation?

  - structural: **precipitates of known or new ferro/ferrimagnets?**

  - atomic: **magnetic atom segregation (spinodal decomposition)?**

  ***- electronic*?**

  - magnetic?

-- role of defects and contamination?

CONCLUSIONS AND OUTLOOK

- (Ga,Mn)As, p-(Cd,Mn)Te, … emerge as the best understood model ferromagnets
- Beginning of the road for high temperature ferromagnetic semiconducting systems
  - nanoscale phase separations?
- Is high temperature ferromagnetism without magnetic ions possible? (low T_C: QHFM, organic materials)
  - defects bands, zinc-blende metals (CaAs, …), …?