Spintronics – material aspects

Why to do not combine complementary properties and functionalities of semiconductor and magnetic material systems?

- ***hybrid structures***

-- overlayers or inclusions of ferromagnetic metals => source of stray fields and spin-polarized carriers

-- soft ferromagnets => local field amplifiers

-- hard ferromagnets => local field generators

- ***ferromagnetic semiconductors***

MAGNETIC SEMICONDUCTORS

Tomasz DIETL

Institute of Physics, Polish Academy of Sciences, Warsaw

Collaboration: ***Grenoble (J. Cibert et al.), Sendai (H. Ohno et al.), Austin (a. MacDonald et al.), Regensburg (D. Weiss et al.), …***

1. **Families of magnetic semiconductors**
2. **Spin manipulations in ferromagnetic semiconductors**
3. **Magnetic impurities in semiconductors**
4. **sp-d exchange interactions**
5. **d-d exchange interactions**
6. **Outlook**
7. **Summary**

Support: EC: AMORE, FENIKS, ERATO (JST), A.V. Humboldt Foundation

Families of magnetic semiconductors

Magnetic semiconductors

- **magnetic semiconductors**

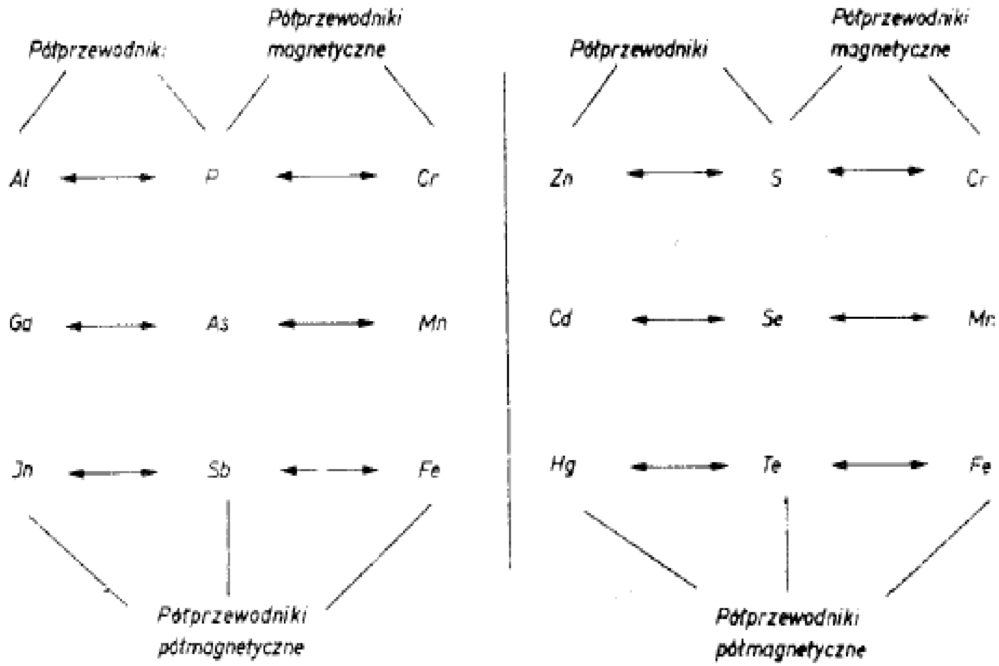
  short-range ferromagnetic super- or double exchange

  EuS, $ZnCr_2Se_4$, $La_{1-x}Sr_xMnO_3$, ...

  short-range antiferromagnetic superexchange

  $EuTe$, ...

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

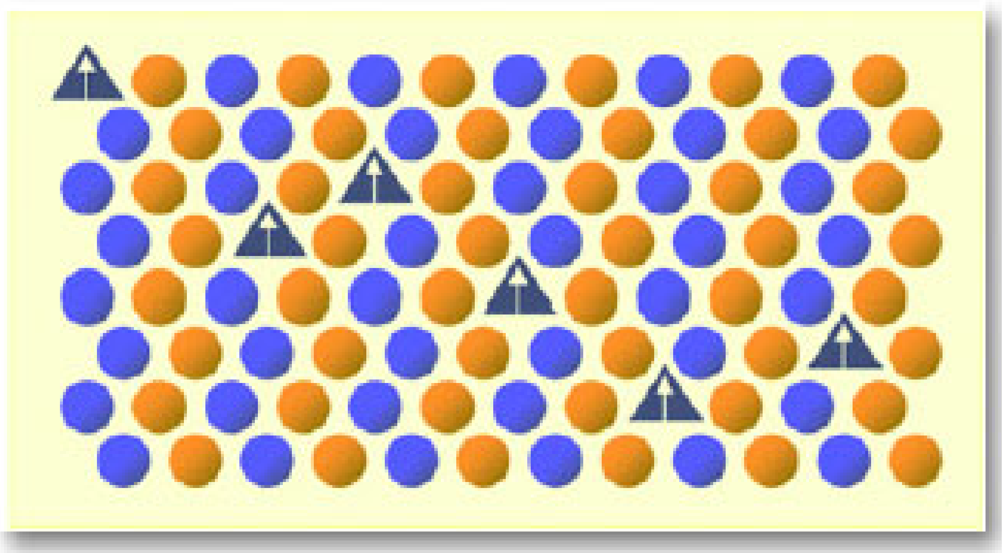
now: Diluted Magnetic Semiconductors (DMS)

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.

DMS: standard semiconductor + magnetic ions

- **Various magnetic ions:**
  - **mostly 3d transition metals: Sc, ..., Cu**
  - **rare earth (4f): Ce, ..., Tm**
  - **also actinides (5f), 4d TM, ...**
- **Various hosts:**
  - **II-VI:** $Cd_{1-x}Mn_xTe$, $Hg_{1-x}Fe_xSe$,...
  - **IV-VI:** $Sn_{1-x}Mn_xTe$, $Pb_{1-x}Eu_xS$
  - **III-V:** $In_{1-x}Mn_xSb$, $Ga_{1-x}Er_xN$, ...
  - **IV:** $Ge_{1-x}Mn_x$, $Si_{1-x}Ce_x$
  - **....**

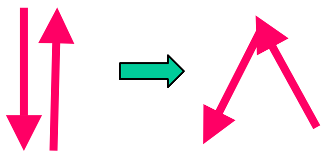
Most of DMS: random antiferromagnet



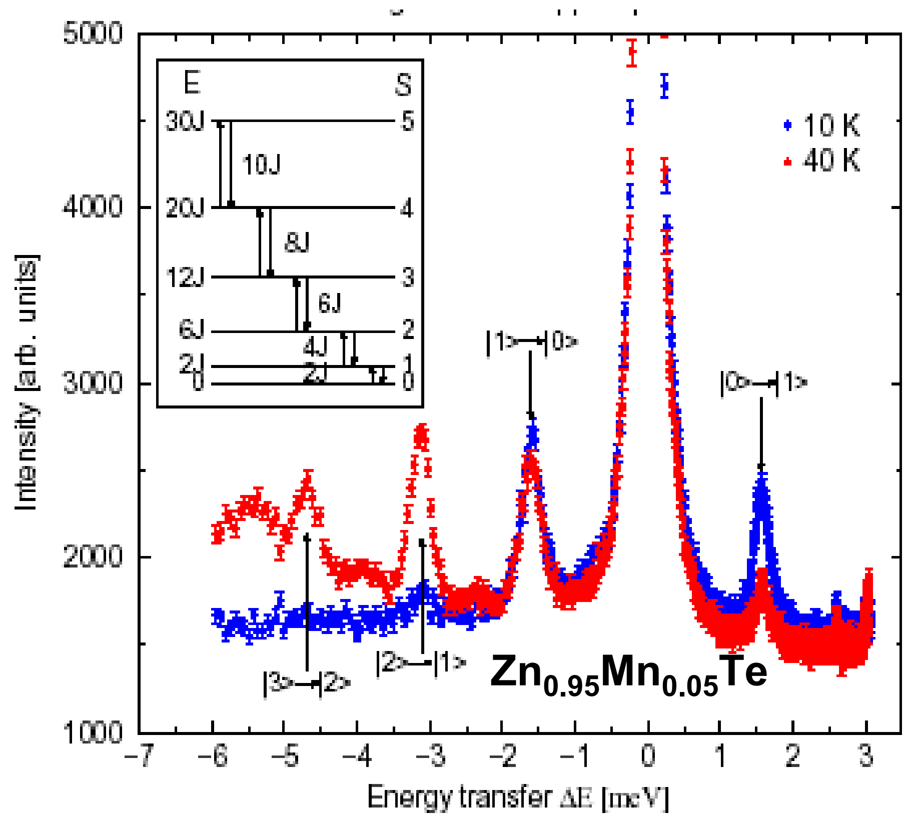
short range antiferromagnetic superexchange

Evidences for antiferromagnetic pairs

$$H_{12} = -2J\mathbf{S}_1\mathbf{S}_2$$



inelastic neutron scattering



T. Giebultowicz et al.
H. Kepa, …, T.D., PRL'03

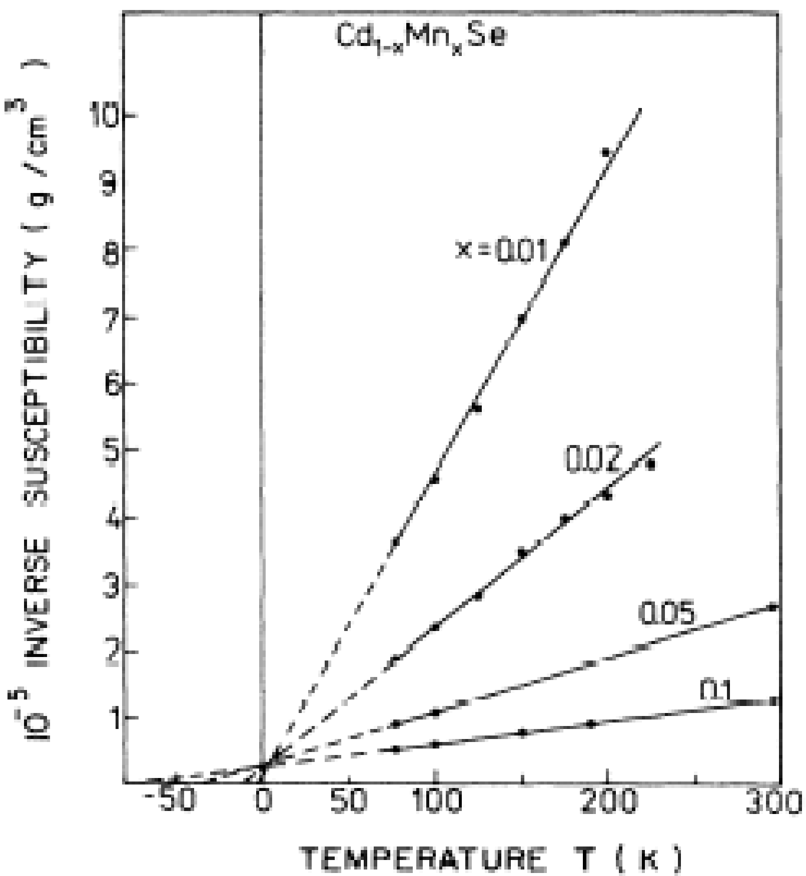
Evidences for antiferromagnetic interactions: magnetic susceptibility

Curie-Weiss law

$\chi = C/(T - \Theta)$

$C = g\mu_B S(S+1)xN_o/3k_B$

$\Theta < 0$ antiferro



A. Lewicki et al.

Magnetization of localized spins

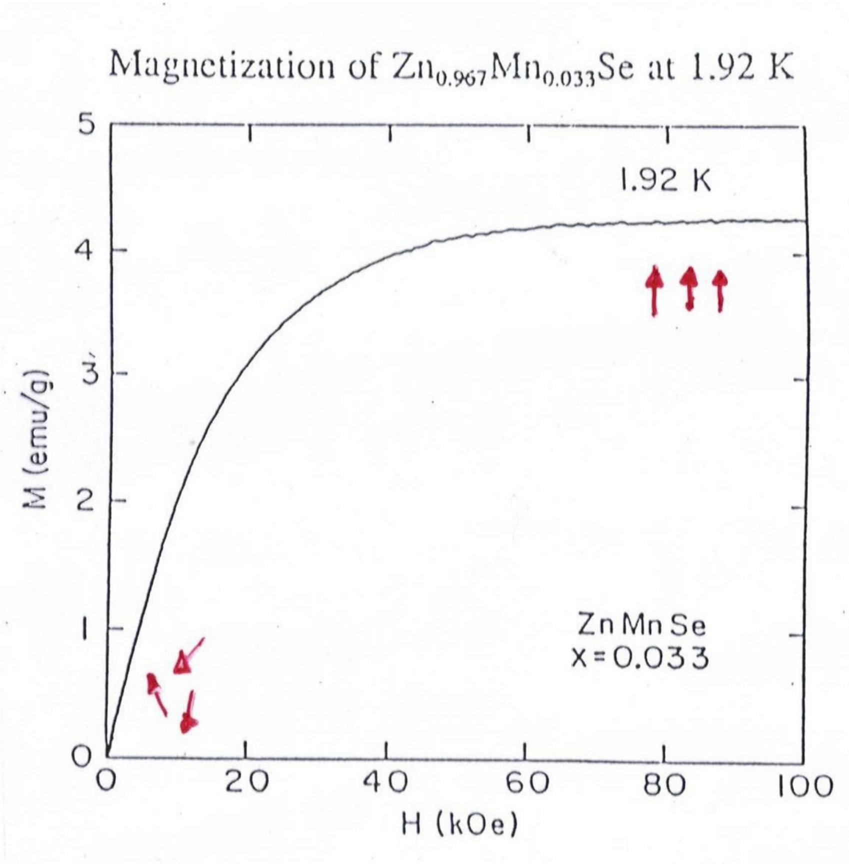
$M(T,H) =$
$g\mu_B S x_{eff} N_o B_S[g\mu_B H/k_B(T + T_{AF})$

antiferromagnetic interactions

$x_{eff} < x$

$T_{AF} > 0$

Modified Brillouin function



Y. Shapira et al.

Ferromagnetic DMS

long-range hole-mediated ferromagnetic exchange

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

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

$Ga_{1-x-}Mn_xAs$ *(Ohno et al.'96)* **$T_C \approx 100$ 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.'97, Kossacki et al.'99)

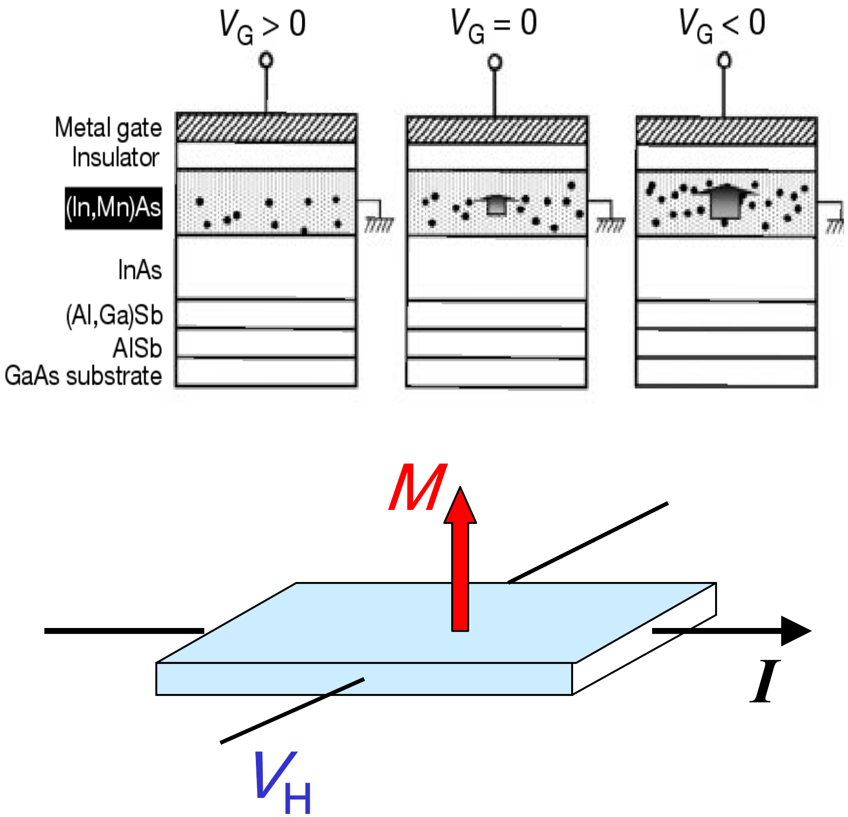
p-$Zn_{1-x}Mn_xTe$:N *(Ferrand et al.'99)*

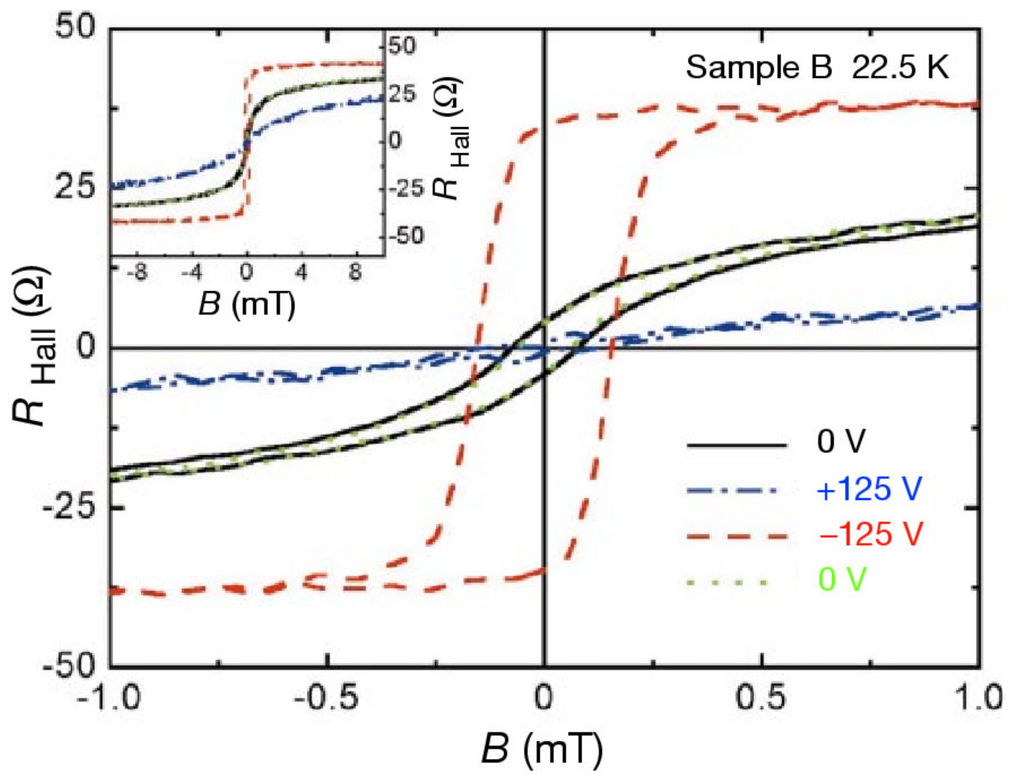
p-$Be_{1-x}Mn_xTe$:N *(Hansen et al.'01)*

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

Spin manipulations in ferromagnetic DMS

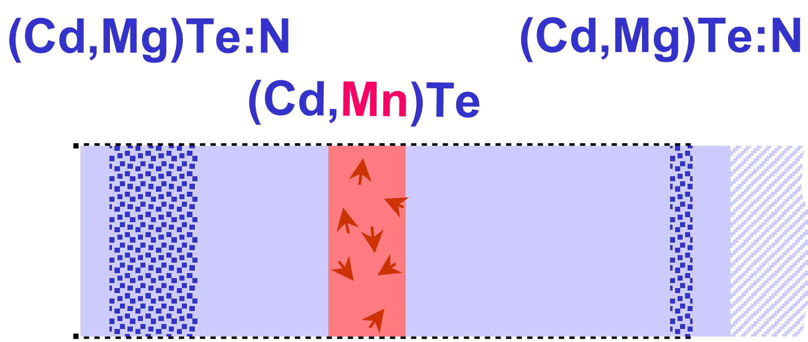
Tuning magnetic ordering by electric field (ferro-FET) (In,Mn)As

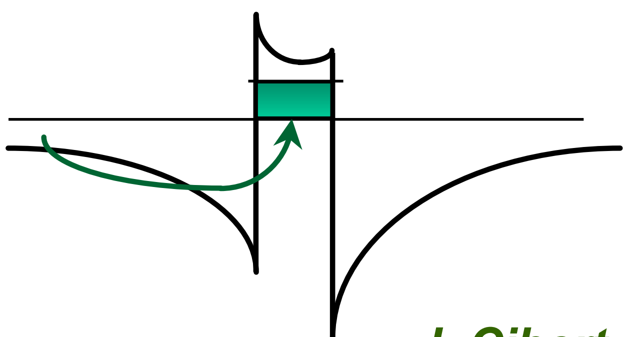


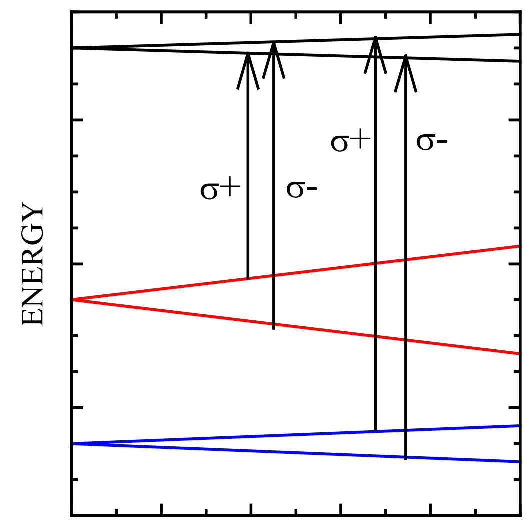


H. Ohno, .., T.D., ...Nature '00

Modulation-doped p-type magnetic QWs



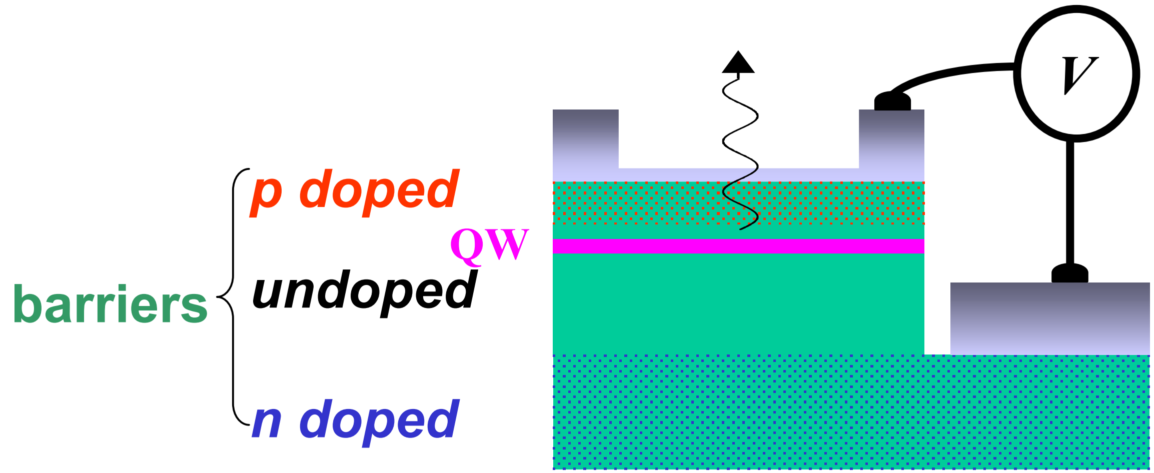




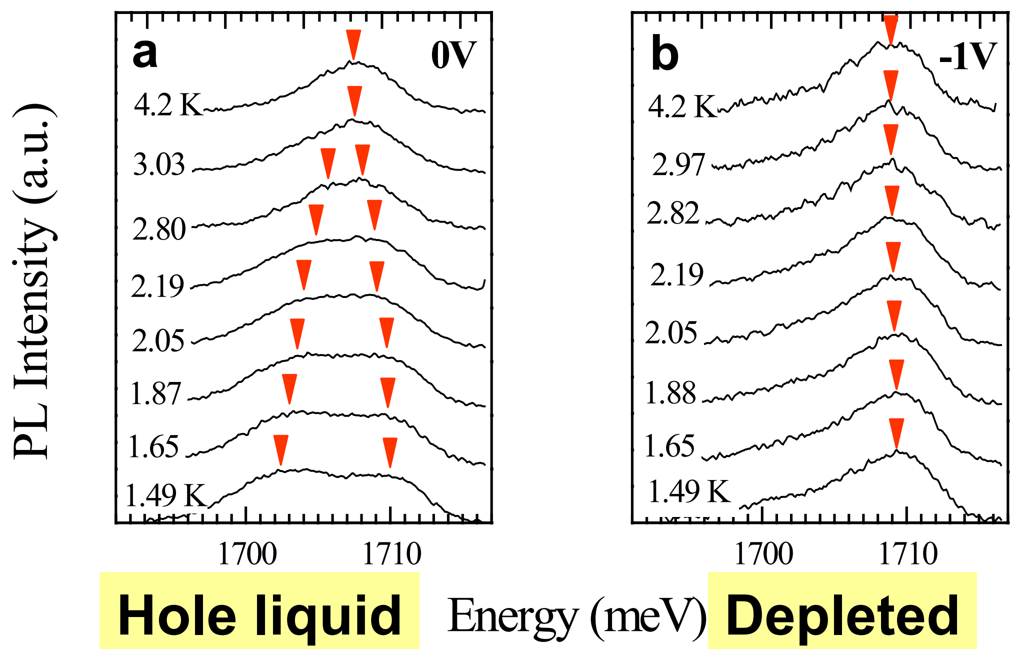
$\Delta E \sim M$

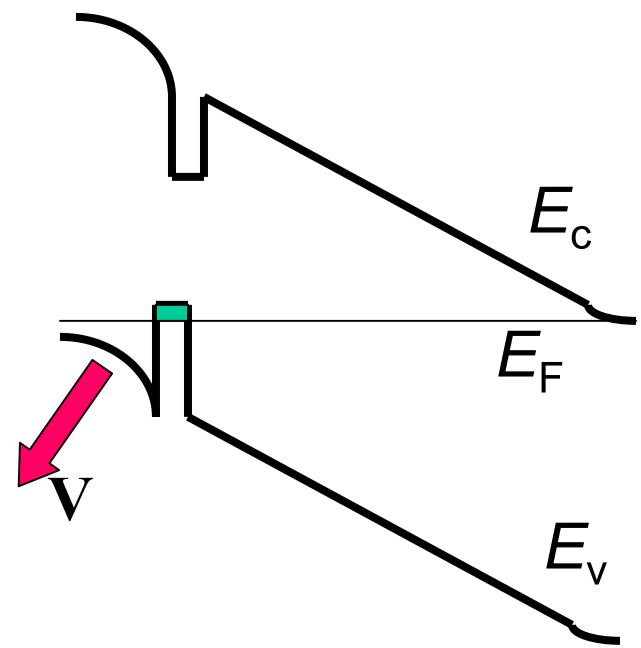
J. Cibert et al. (Grenoble)

Control of ferromagnetism by electric field in a *pin* diode – ferro-LED



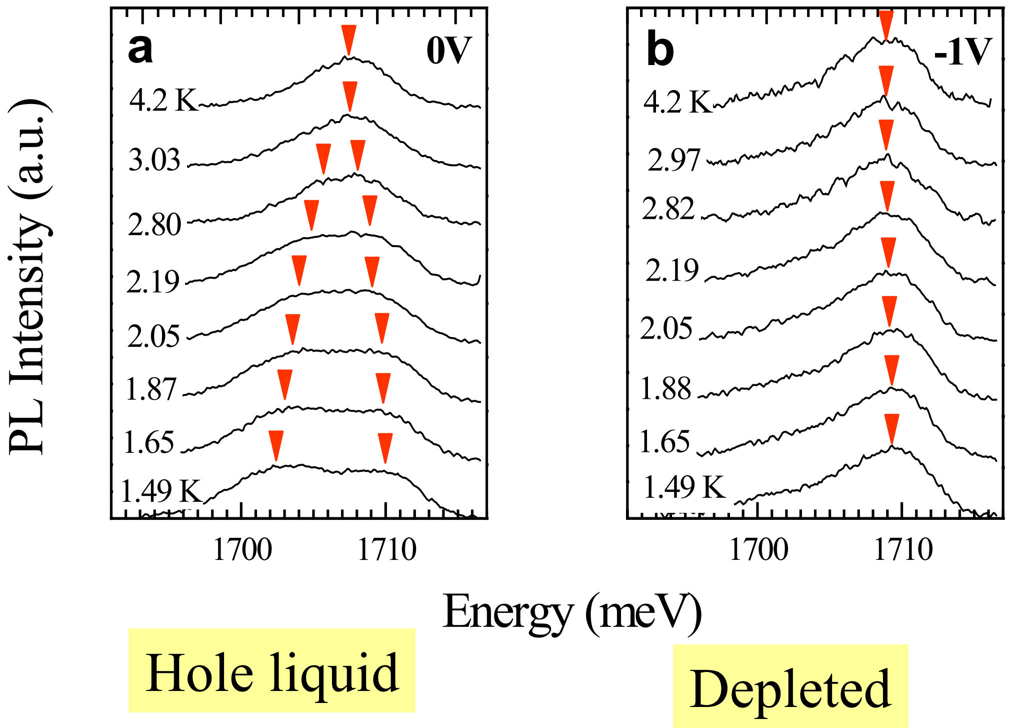
Photoluminescence

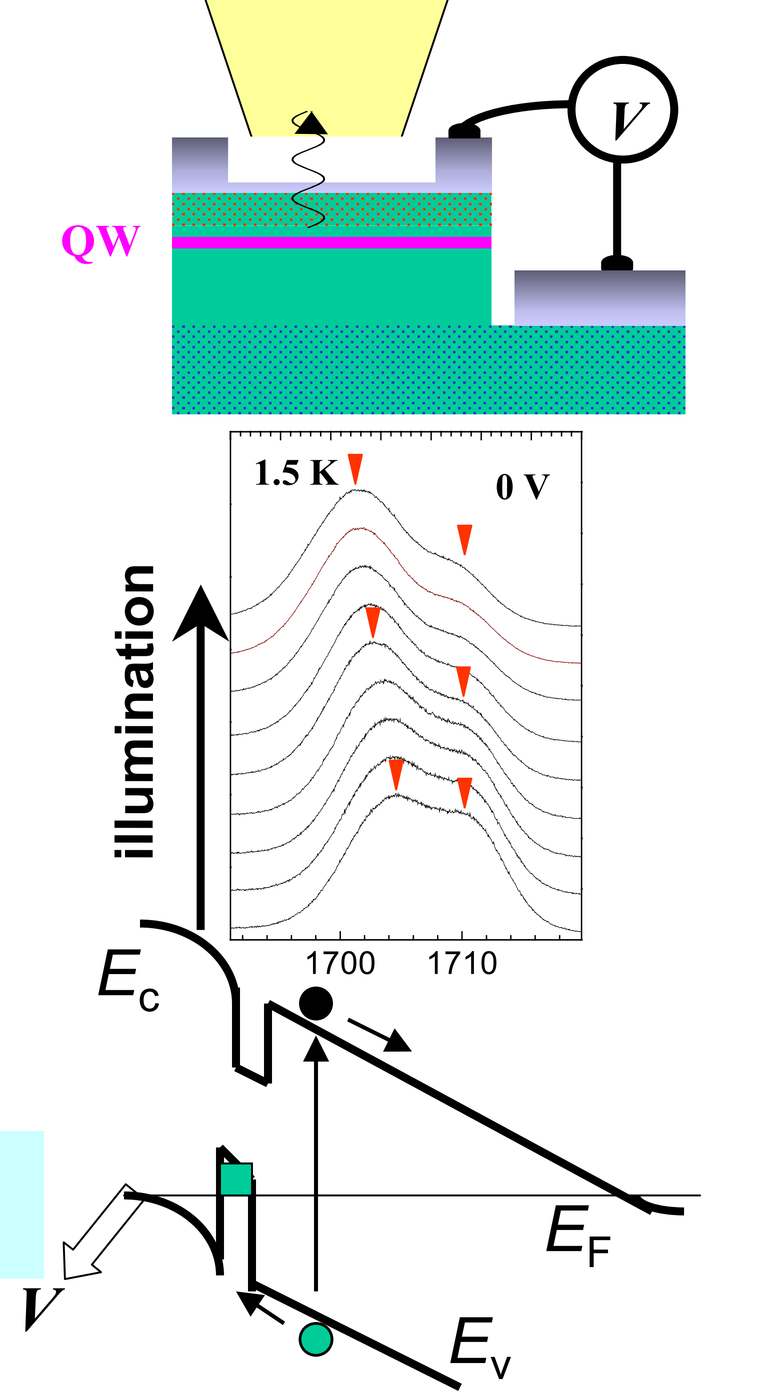




H. Boukari, …, T.D., PRL'02

Combined: electrostatic gate + illumination in *p-i-n* diode (ferro-LED)

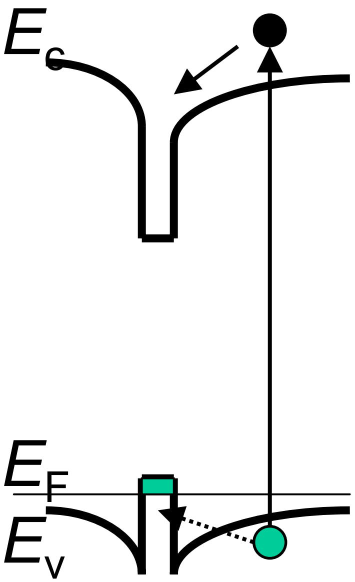




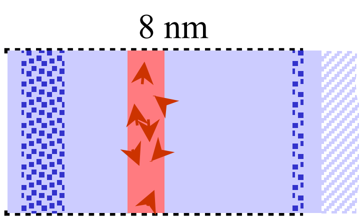
***Ferro-* diode:**
electric field and light tuned ferromagnetism

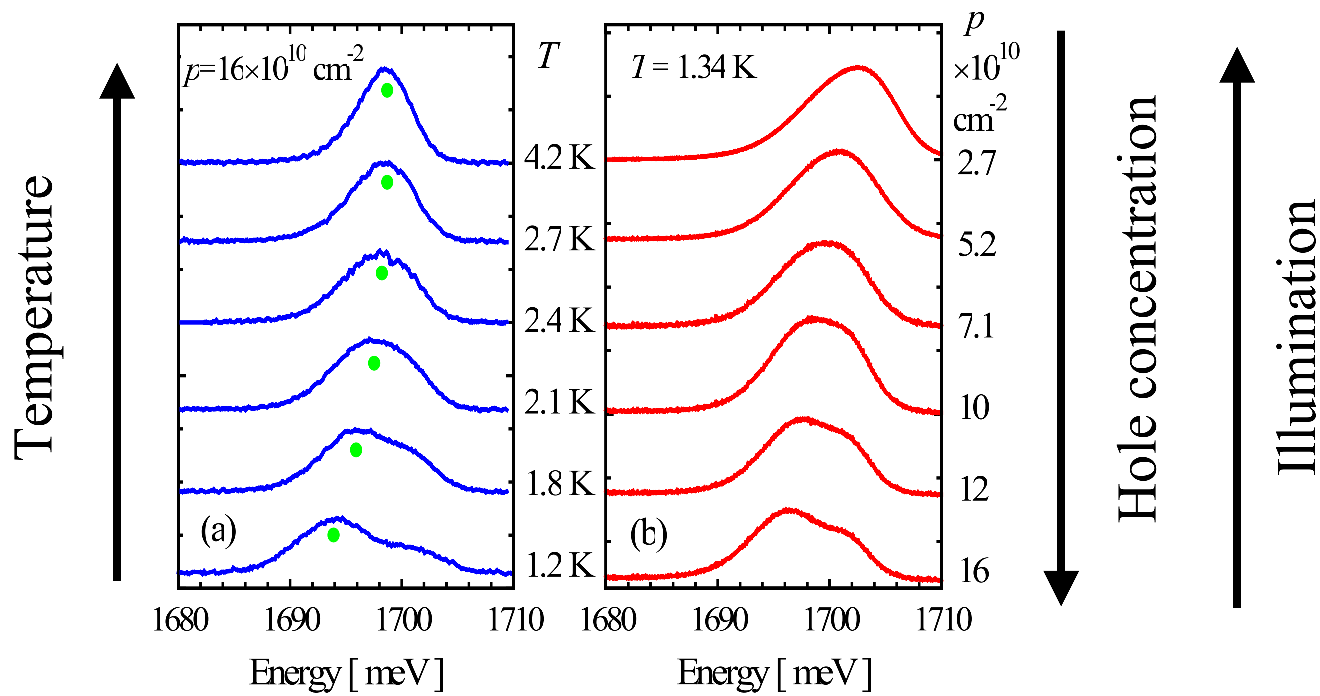
Optical tuning of magnetization – *p-i-p* diode

paramagnetic



CdMnTe QW





p = const

ferromagnetic

T = const

***pip* diode: light destroys ferromagnetism**

Magnetic ions in semiconductors

- **position of d levels, *U***
- **charge and spin states**
- **intra ion excitation energies d → d***
- **coupling to band states:**

  -- spin dependent: *sp-d exchange interactions*

  -- spin independent: *band offsets*

  -- *crystal-field effects*

Transition metals – free atoms

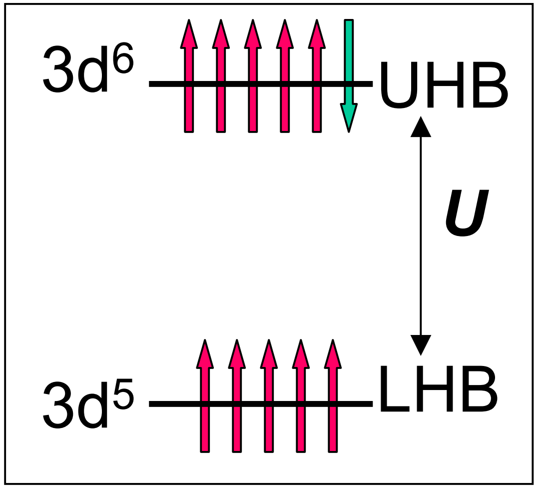
- Electronic configuration of TM atoms: $3d^n4s^2$

  $1 \leq n \leq 10$: Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

- Important role of electron correlation for open d shells

  - intra site correlation energy $U = E_{n+1} - E_n$

    for n =5, $U \approx 15$ eV



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- **Important role of electron correlation for open d shells**

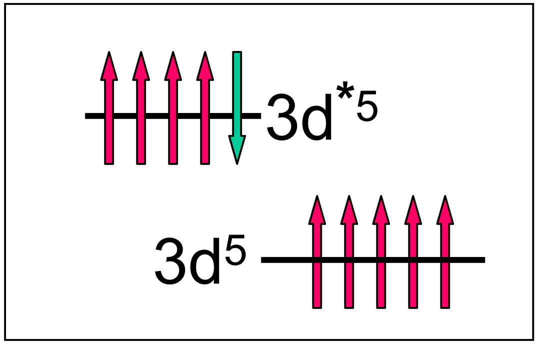
  - intra site correlation energy $U = E_{n+1} - E_n$

  for n =5, $U \approx 15$ eV

  - intra-site exchange interaction: *ferromagnetic*

  Hund's rule: S the highest possible

  for n = 5, $E_{S=3/2} - E_{S=5/2} \approx 2$ eV



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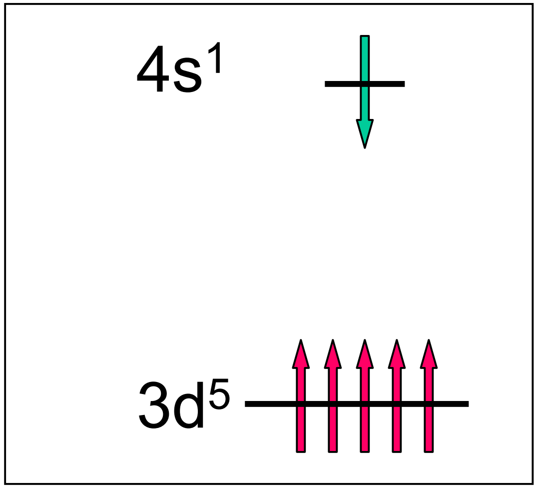
  - intra-site exchange interaction: *ferromagnetic*

    Hund's rule: S the highest possible

    for $n = 5$, $E_{S=3/2} - E_{S=5/2} \approx 2$ eV

  - TM atoms, $3d^n 4s^1$, e.g., Mn:

    $E_{S=2} - E_{S=3} \approx 1.2$ eV ➔ $J_{s\text{-}d} \approx 0.4$ eV *ferromagnetic*



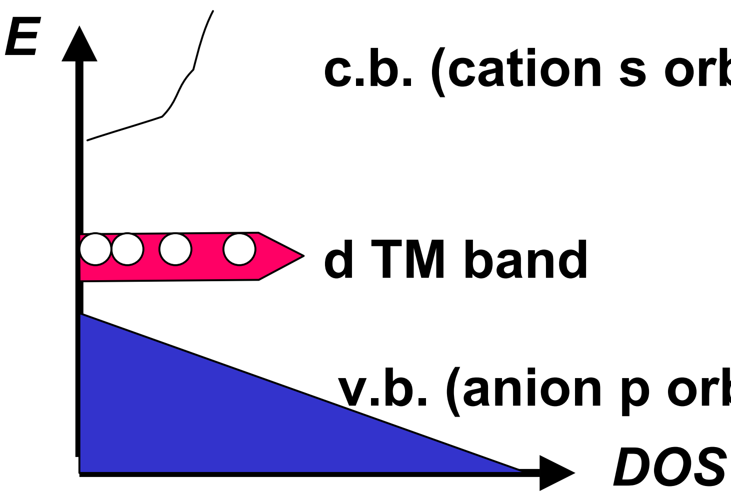
despite of screening and hybridization these effects survive in solids

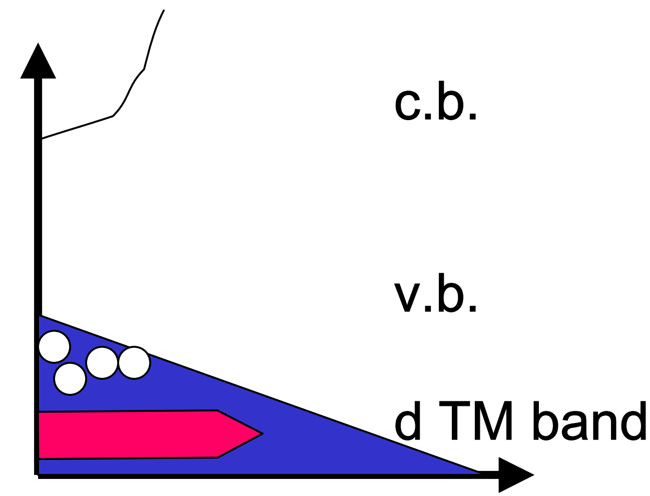
Where d levels and carriers reside in DMS?

Possibilities:

-- manganides $La_{1-x}Sr_xMnO_3$
Mott-Hubbard AF insulator for x → 0

-- cuprates $La_{2-x}Sr_xCuO_4$
charge transfer AF insulator for x → 0

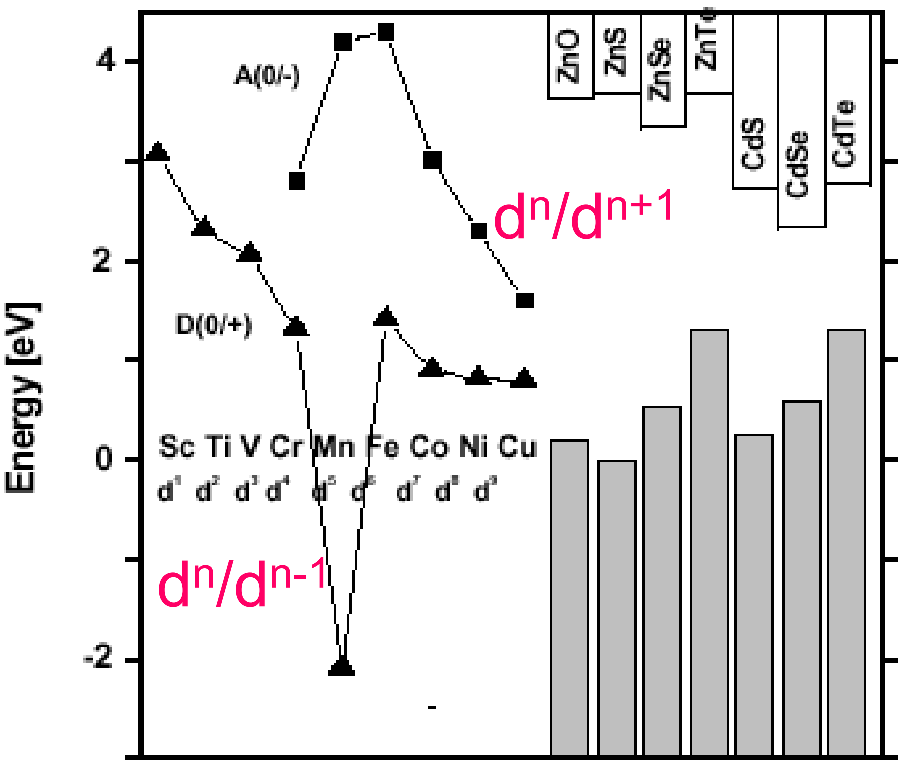




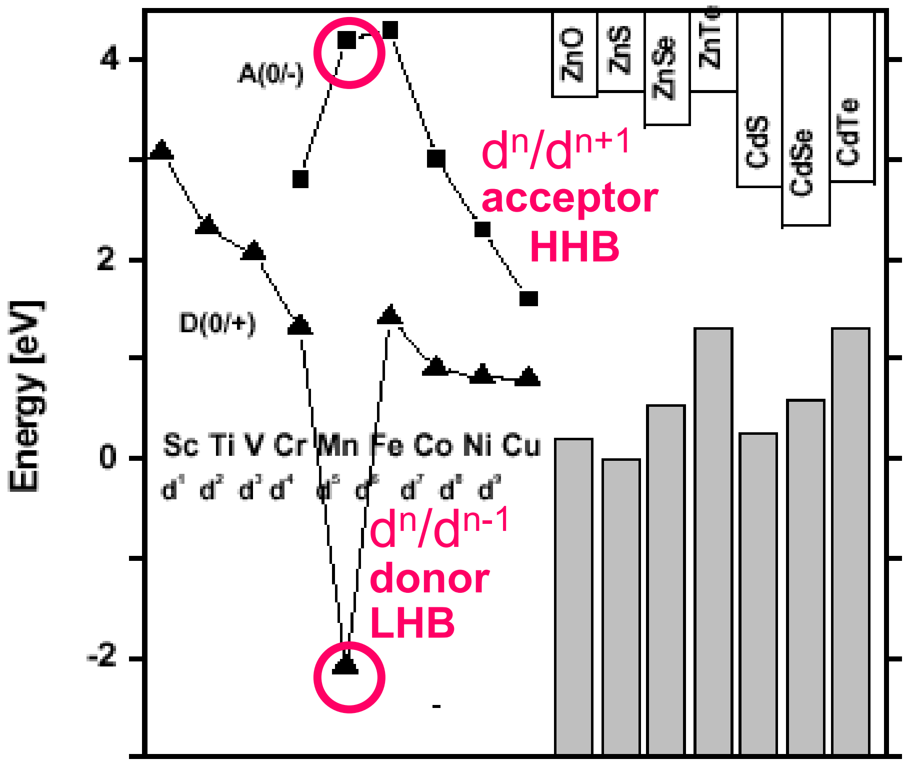
Experimental guide: impurity limit (EPR, d –> d*, …)

TM impurities in II-VI compounds

- TM atoms: $3d^n4s^2$ ➔
- TM impurity (d^n) neutral since:
  - -- donor level d^n/d^{n-1} resides below c.b.
  - -- acceptor level d^n/d^{n+1} resides above v.b.
- Exceptions (charged TM)
  - -- Sc in CdSe

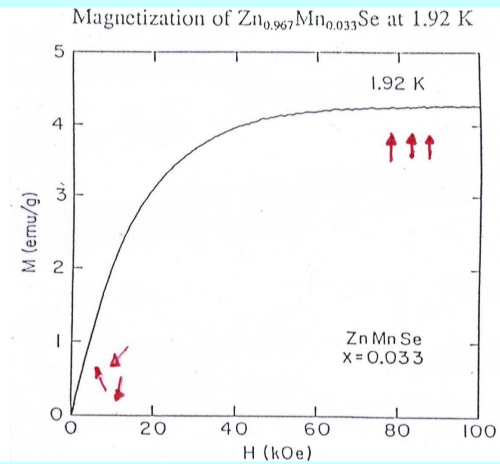


d-levels of TM ($3d^n4s^2$) impurities in II-VI's



A.Zunger, J.Baranowski, P.Vogl, J.Langer, A.Fujimori, ...

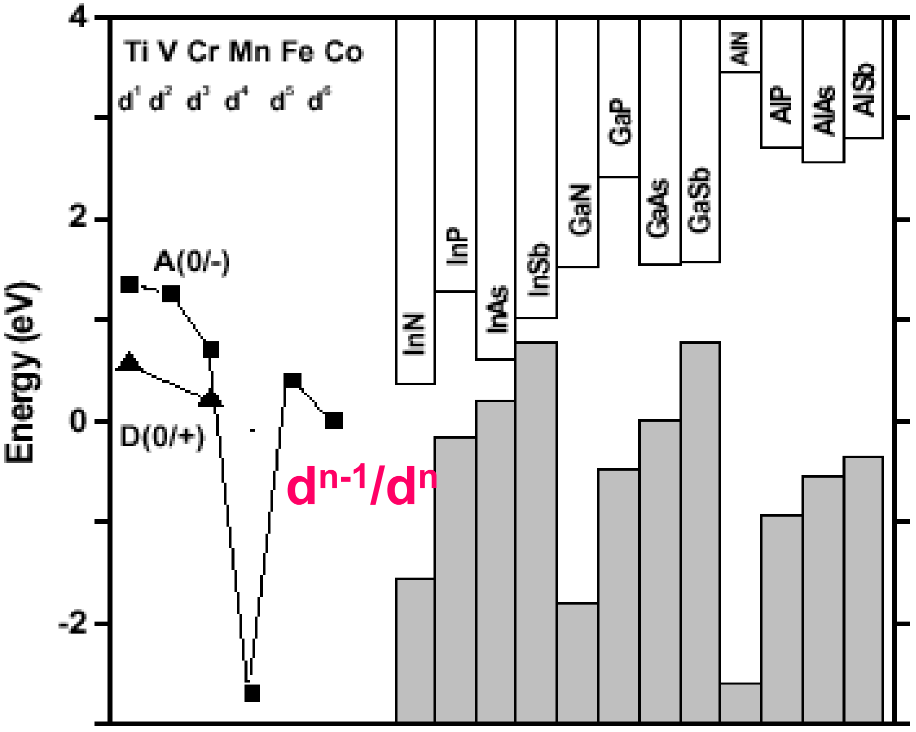
- Mn^{2+} (d^5, S = 5/2)
- AF superexchannge (random AF)



- no d levels at E_F
- independent control of Mn and carrier densities (doping, light)
- strong sp-d exchange $H = -IsS$

TM impurities in III-V compounds

- TM atoms: $3d^n4s^2$ ➔
- TM impurity (d^{n-1}) neutral if
  - -- donor level d^{n-1}/d^{n-2} resides below c.b.
  - -- acceptor level d^{n-1}/d^n resides above v.b.
- Mn in III-V: resonant + hydrogenic acceptor



sp-d exchange interactions in DMS

Potential s-d exchange interaction

Spin part of Coulomb energy for s and d electrons

$$E_{sd} = -J_{sd}(\mathbf{S} + \mathbf{s})^2 = -J_{sd}\mathbf{S}^2 - J_{sd}\mathbf{s}^2 - 2J_{sd}\mathbf{Ss} = C - 2J_{sd}\mathbf{Ss}$$
$$= C - \alpha N_o \mathbf{Ss}$$

for Mn atom $\alpha N_o = 0.4$ eV

interaction of magnetic moments: $E_{dipole\text{-}dipole} \approx 0.004$ eV

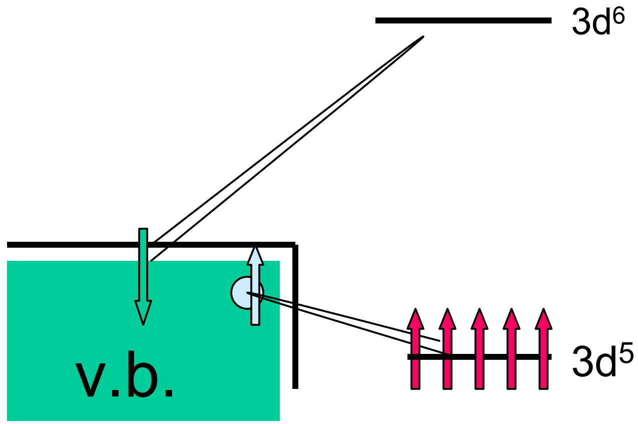
in semiconductor compounds αN_o reduced by

- screening
- admixture of s-type anion wave function

Spin dependent interaction between valence band holes and Mn spins

Gain of energy due to symmetry allowed hybridization

- quantum hopping of electrons from the v.b. to the d level
- quantum hopping of electrons from the d level to the empty v.b states
- $H_i = -\beta N_o \boldsymbol{s}\boldsymbol{S}_i$ *(Schriffer-Wolff)*
  ➔ kinetic pd exchange



Contribution to the *kp* hamiltonian due to the presence of a magnetic ion

- $H_j = U_o(\mathbf{r} - \mathbf{R}_j)$ - sites with no magnetic ion
- $H_i = U(\mathbf{r} - \mathbf{R}_i) - J(\mathbf{r}-\mathbf{R}_i)\mathbf{s}\mathbf{S}_i$ - sites with the magnetic ion
- ***kp*** model: non-vanishing matrix elements:

$V = \langle S|U-U_o|S\rangle$, $W = \langle X|U - U_o|X\rangle$ - *conduction and valence band offset integrals*

$\alpha = \langle S|U|S\rangle$, $\beta = \langle X|U|X\rangle$ - *s-d and p-d exchange integrals*

$S\rangle$, $X\rangle$ - Bloch wave functions

Energies: VN_o etc.

Virtual crystal and molecular-field approximations

- The translation symmetry restored by introducing an average potential, the same for each site:

  $H_n = (1 - x)\, U_o\, (\mathbf{r} - \mathbf{R}_n) + xU(\mathbf{r} - \mathbf{R}_n) - xJ(\mathbf{r} - \mathbf{R}_n)\mathbf{s}\mathbf{S}_n$

  $E_g = x(VN_o - WN_o)$

- replacing spin-operators in a volume *v* by a classical field:

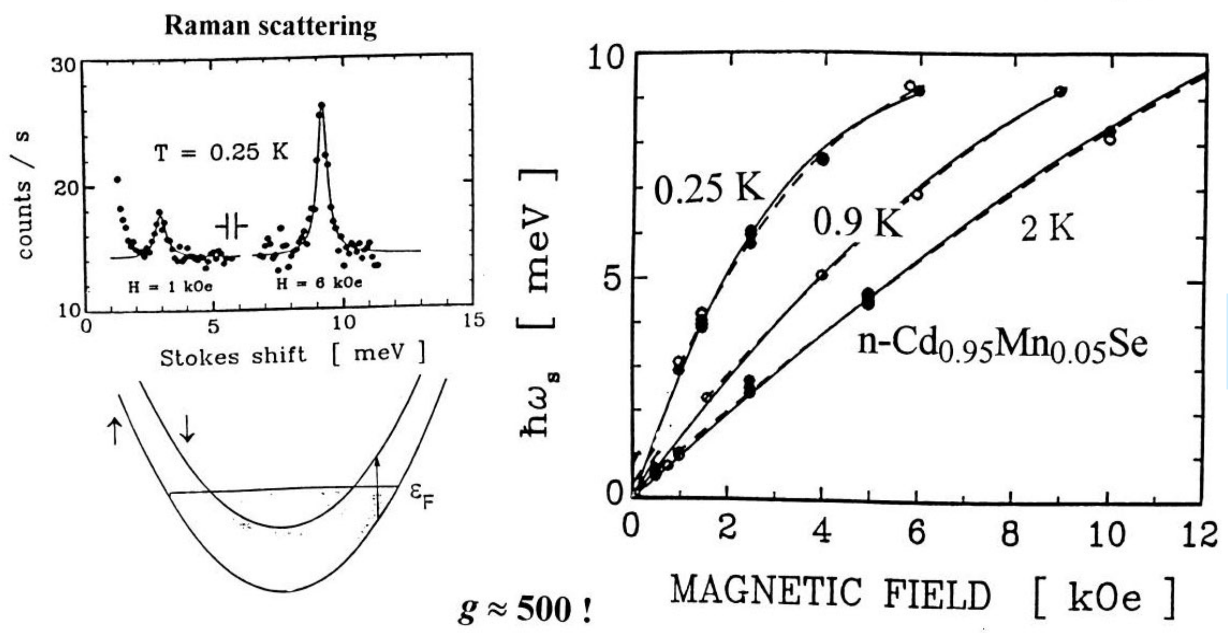
  $x \Sigma_n \mathbf{S}_n$ --> $\mathbf{M}(\mathbf{r})/g\mu_B$

  $H_{spin} = J\mathbf{s}\, \mathbf{M}(\mathbf{r})/g\, \mu_B$ *new contribution to spin splitting*

- Difference between real and VCA/MFA hamiltonians ➔ scattering (alloy and spin-disorder scattering)

Effects of exchange interaction and determination of exchange integrals

DMS: giant spin-splitting of bands, $\omega_s \approx \alpha M(T,H)$
spin-disorder scattering, $1/\tau_s \approx \alpha^2 T\chi(T,H)$

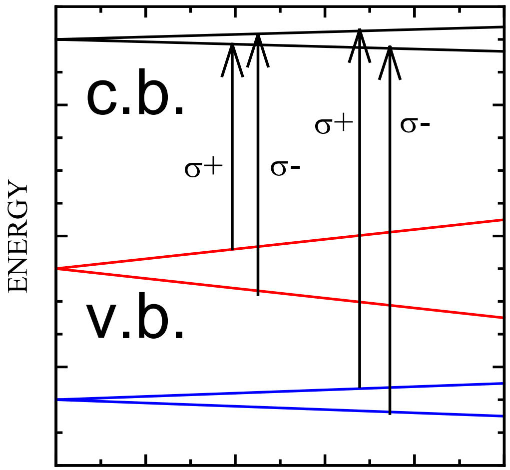


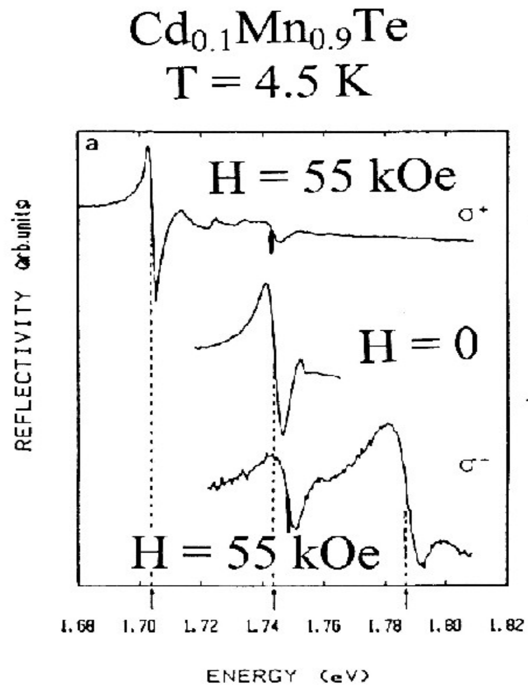
αN_o = 0.25 eV

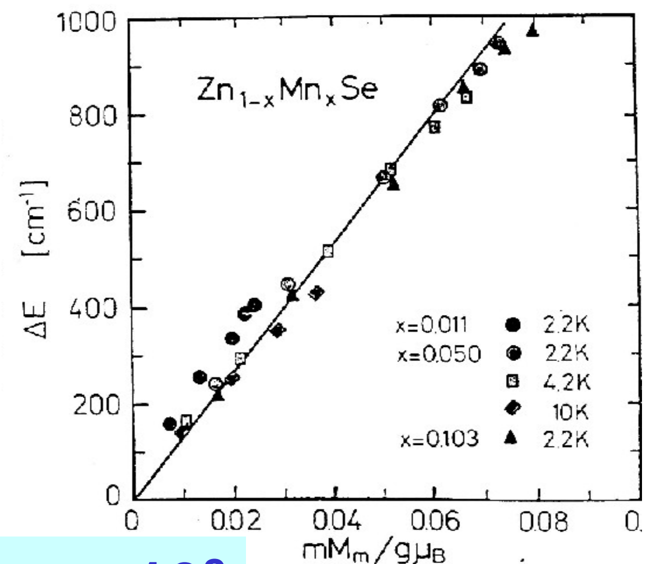
T. D. et al.

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

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







$g_{eff} > 10^2$

J. Gaj et al.
A. Twardowski et al.

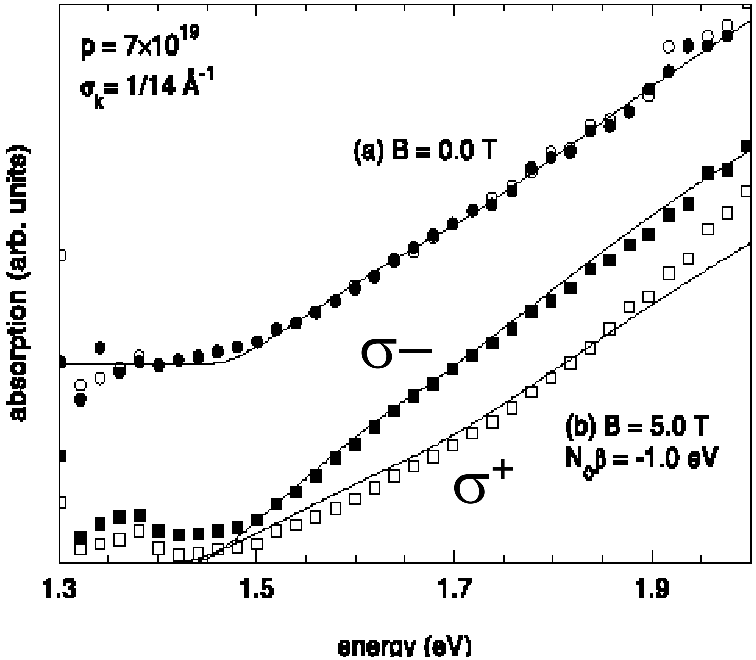
-- p-d: $I_{pd} \equiv \beta N_o \approx -1.0$ eV

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

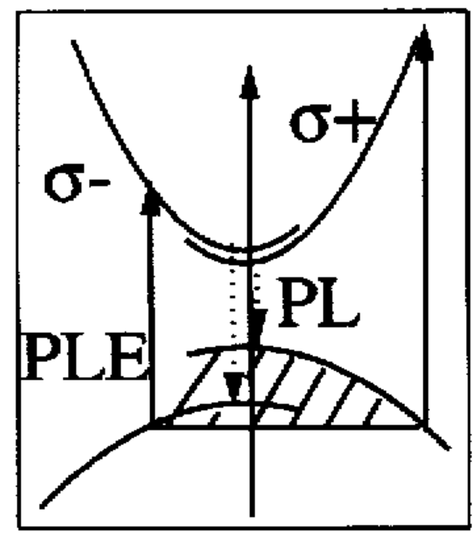
-- s-d: $I_{sd} \equiv \alpha N_o \approx 0.2$ eV

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

Magnetoabsorption -- determination of exchange integrals



Szczytko et al.

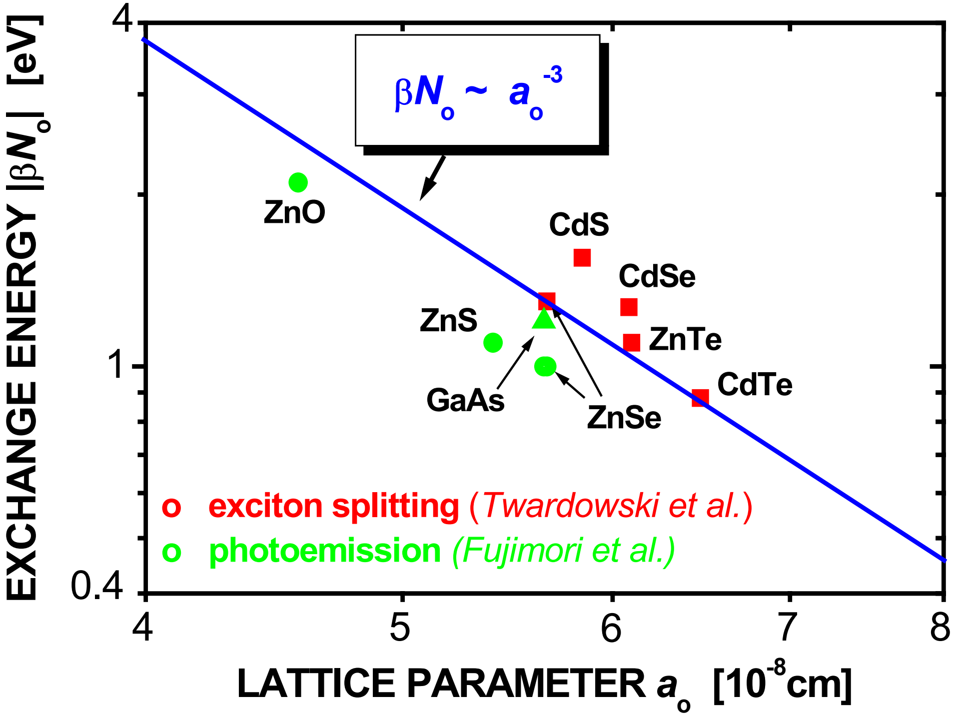


Haury et al., Kossacki et al.
Szczytko et al..

Moss-Burstein shift => positive sign of MCD
Fermi liquid also in insulator => positive sign of MCD

Exchange energy βN_o

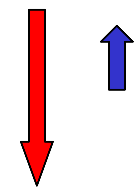
- Antiferromagnetic (Kondo-like)
- Magnitude increases with decreasing lattice constant



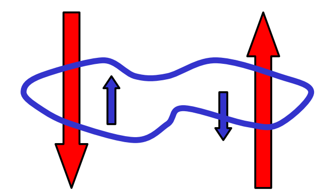
Origin of d-d exchange interactions in DMS

Mechanisms of couplings between localized spins

Origin of the coupling: exchange interaction between the localized spins and band electrons, $-\beta N_o \mathbf{S}\mathbf{s}$



- **INSULATORS**
  spin polarization of orbitals



magnetic orbitals involved:

Kramers and Anderson superexchange **Mn As Mn**

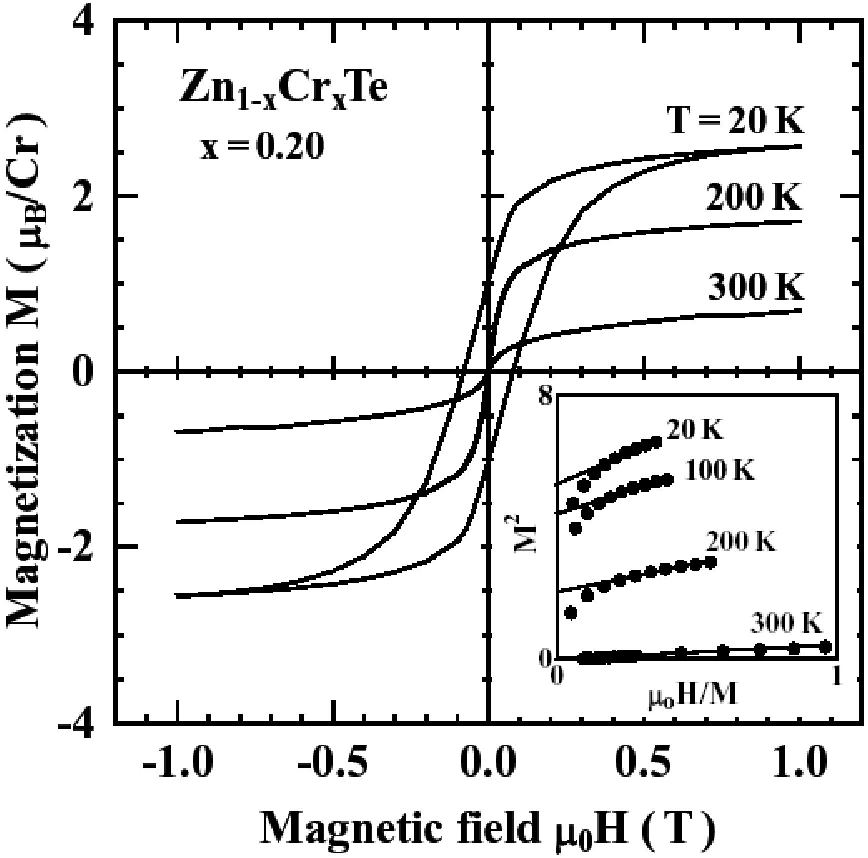
non-magnetic orbitals involved:

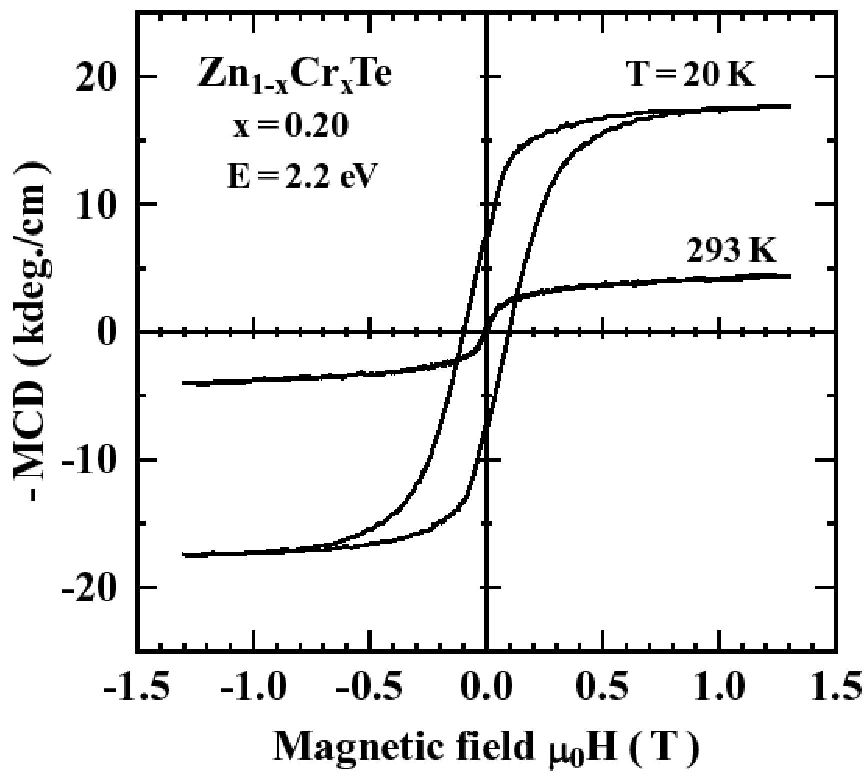
Bloembergen-Rowland mechanism

short-range, accounts for antiferromagnetic interactions in DMS … exceptions found

Ferromagnetic superexchange (?)

Theoretical prediction: (II,Cr,V)VI *J. Blinowski et al., PRB'96*

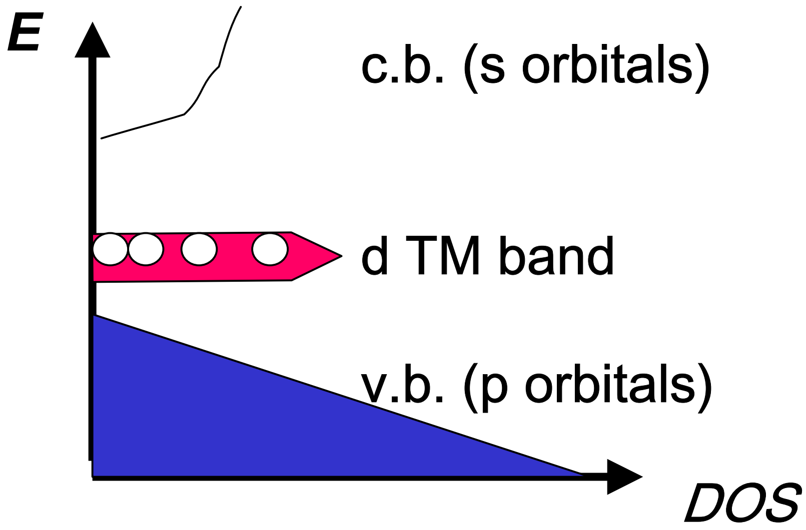




K. Ando et al., PRL'03

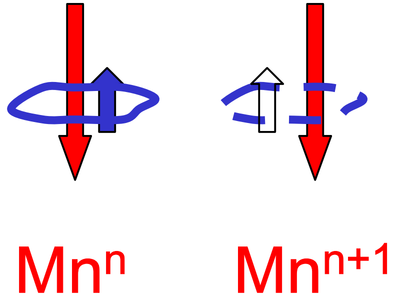
Doped materials

- **MIXED VALENCE MATERIALS**



- **Zener double exchange**

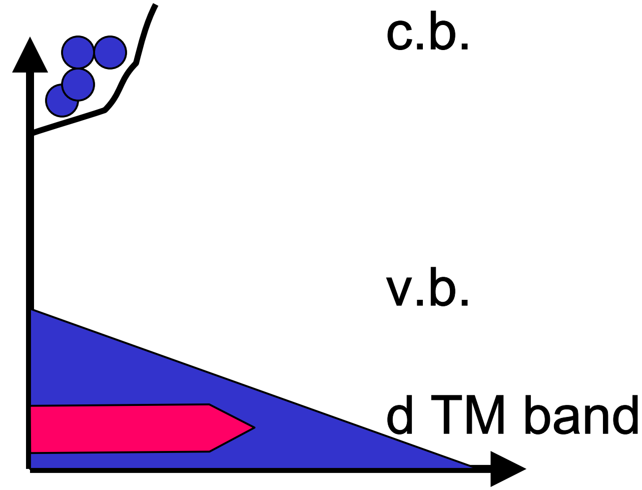
  possibility of hopping lowers energy



short range, ferromagnetic, e.g. **(La,Sr)MnO$_3$**

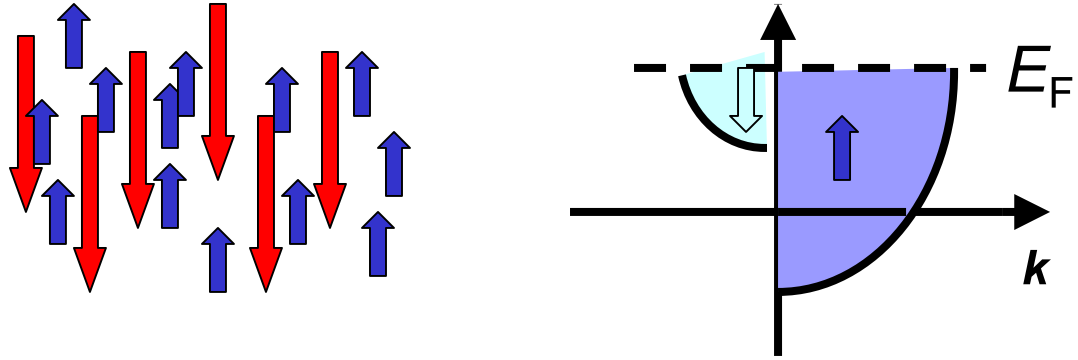
- METALS

(heavily doped semiconductors)



Zener exchange mediated by free carriers

redistribution of carriers between spin subbands lowers energy



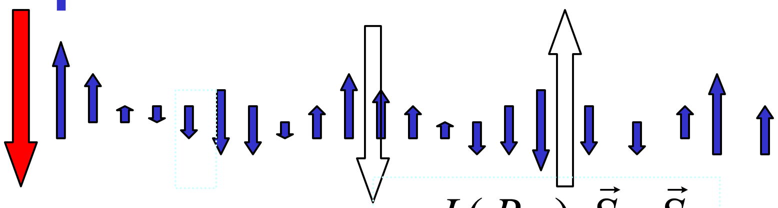
$\hbar\omega_s = \beta N_o \langle S \rangle$

long range, ferromagnetic

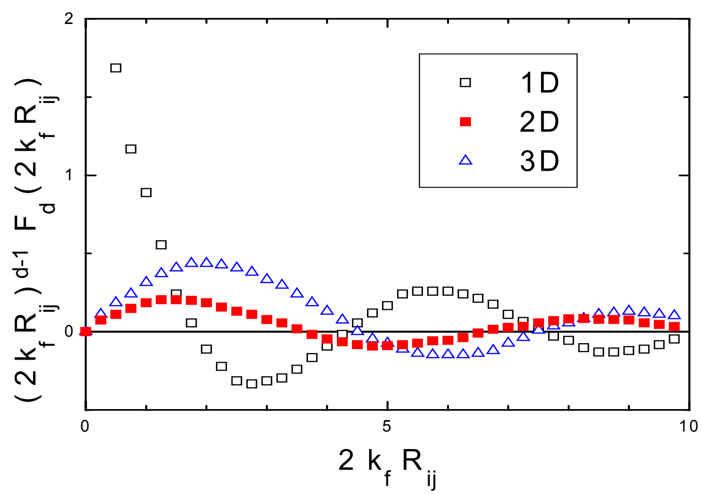
- METALS

Ruderman-Kittel-Kasuya-Yosida interaction

Spin polarization of free carriers induced by a single spin:



$$-J(R_{ij})\,\vec{S}_i\,.\,\vec{S}_j$$



long range, sign of the interaction depends on $k_F R_{ij}$

Making (II,Mn)VI DMSs ferromagnetic: Zener/RKKY MF model of doped DMS

$$T_{\mathrm{C}} = T_{CW} = T_{\mathrm{F}} - T_{\mathrm{AF}}$$ ⟸ **superexchange**

$$T_F = S(S+1)x_{eff}N_oA_{\mathrm{F}}\rho^{(\mathrm{s})}(E_{\mathrm{F}})\,\beta^2/12L_{\mathrm{c}}^{d-3}$$

$A_{\mathrm{F}} > 1$ Stoner enhancement factor

(A_{F}= 1 if no carrier-carrier interaction)

$\rho^{(\mathrm{s})}(E_{\mathrm{F}}) = m^*k_{\mathrm{F}}^{d-2}$ (if no spin-orbit coupling)

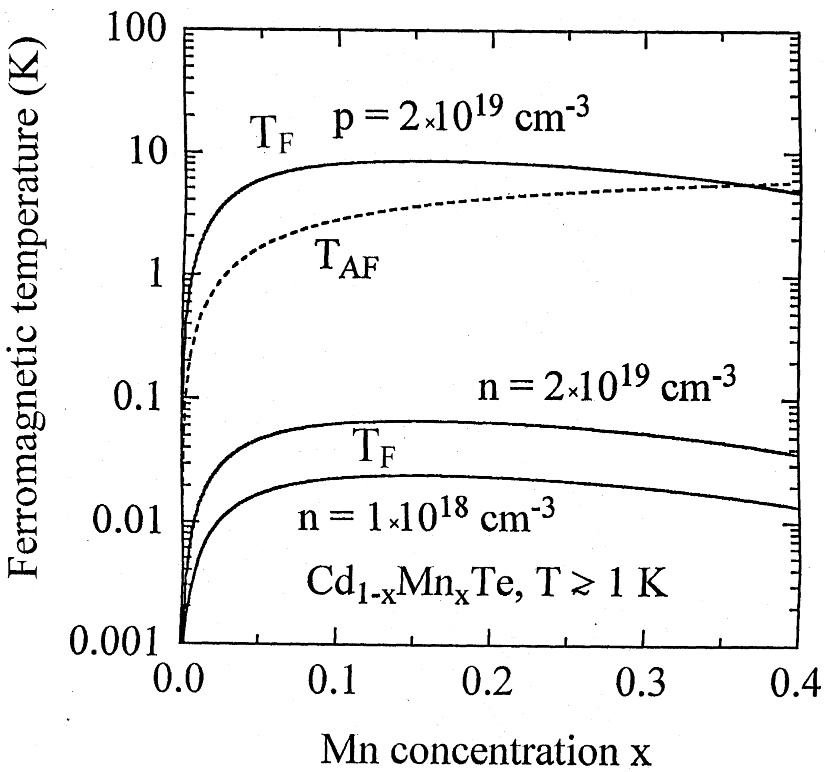
=> T_{C} ~ 50 times greater for the holes

large m*

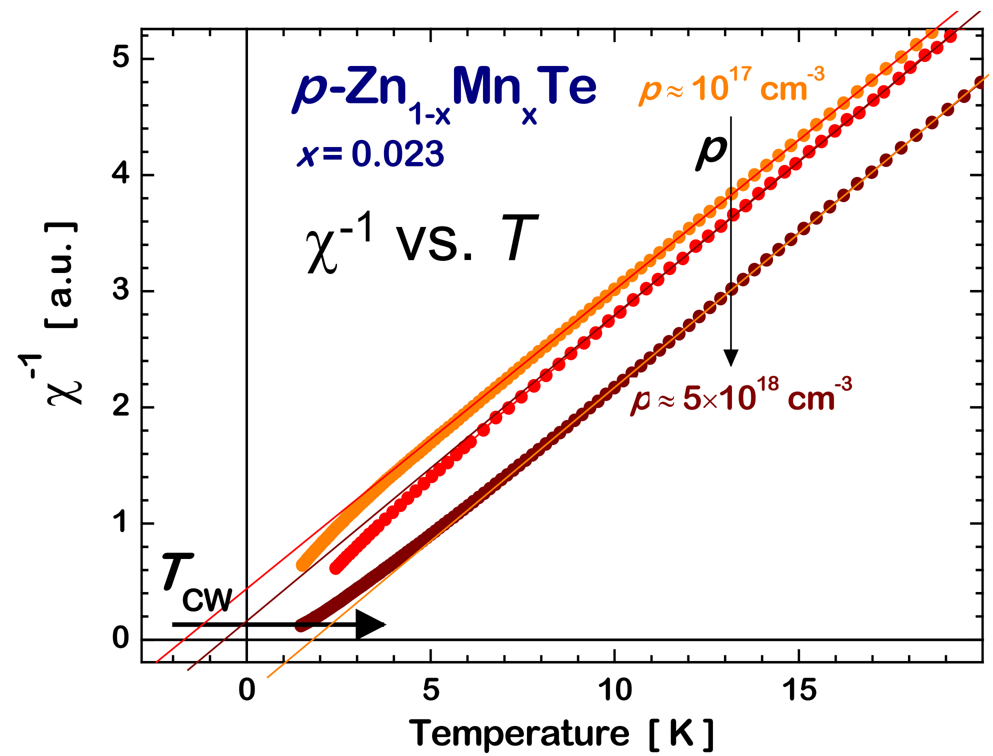
large β

T.D. et al. PRB'97,'01,'02, Science '00

Effect of doping



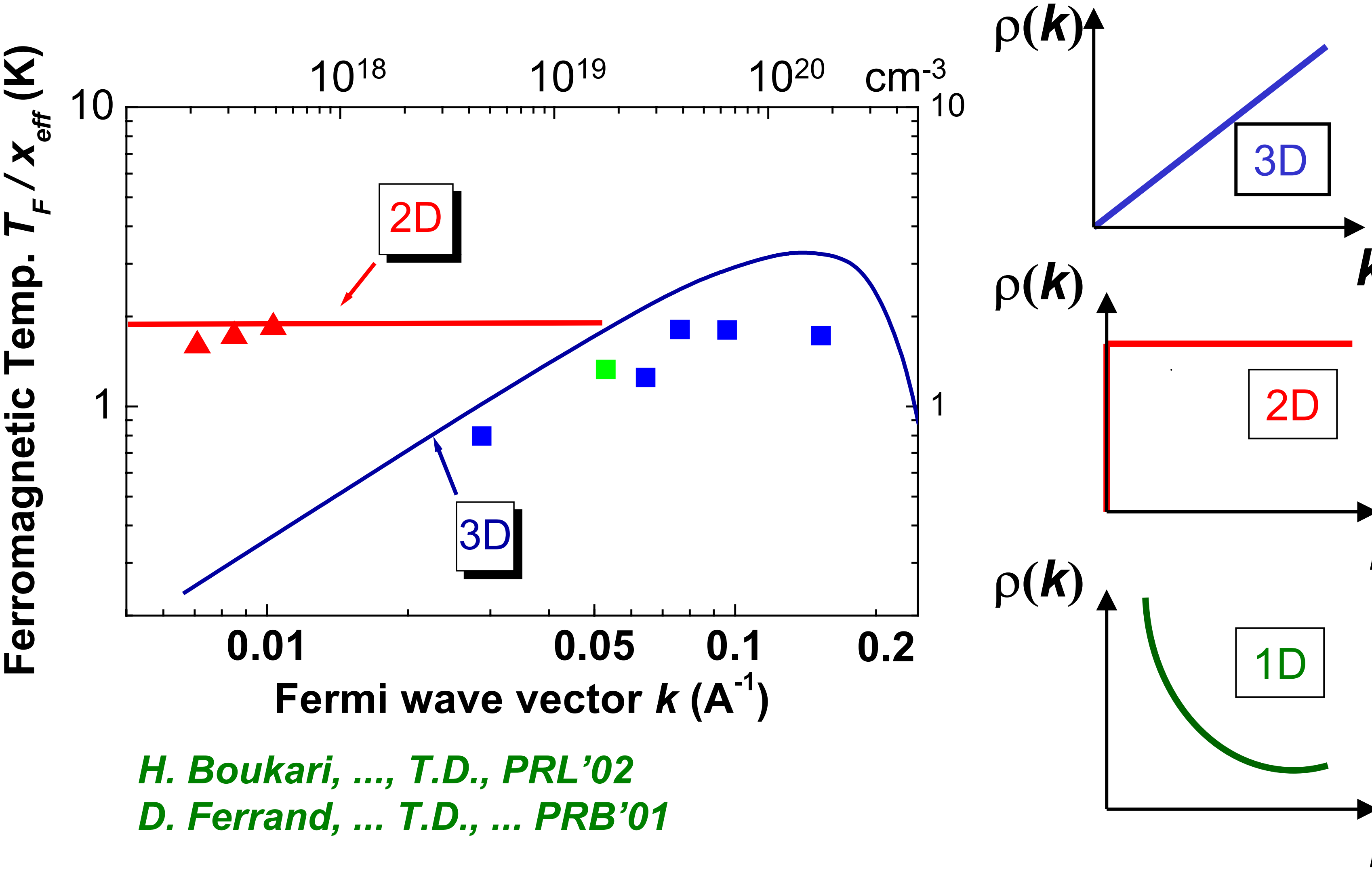
T.D. et al. PRB'97



D.Ferrand,…,T.D. PRB'01
M.Sawicki,…,T.D., pss'02

MIT at $p \approx 10^{19}$ cm^{-3}

Ferromagnetic temperature in 2D p-$Cd_{1-x}Mn_xTe$ QW and 3D $Zn_{1-x}Mn_xTe$:N

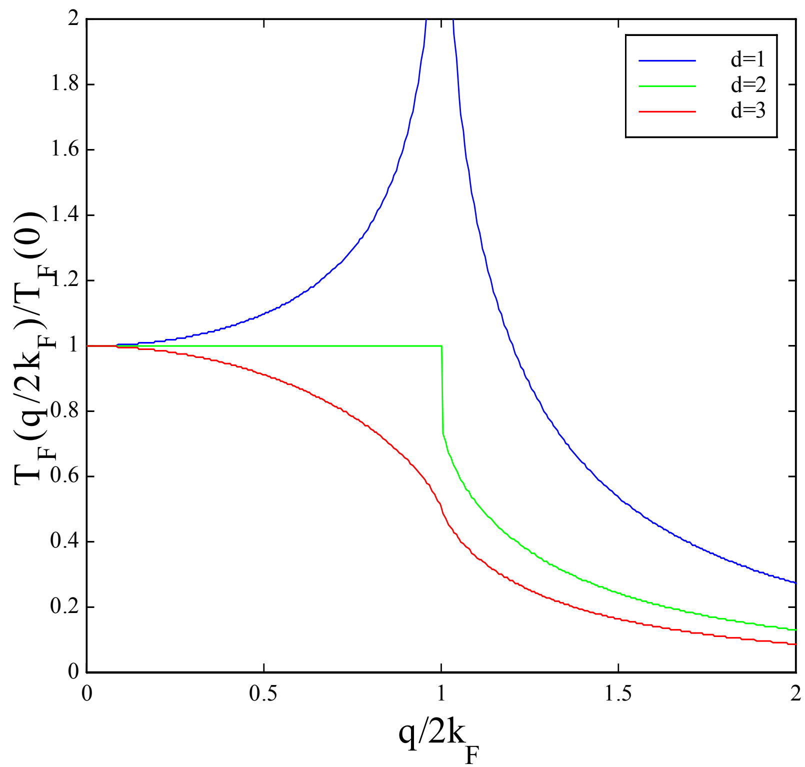


H. Boukari, ..., T.D., PRL'02

D. Ferrand, ... T.D., ... PRB'01

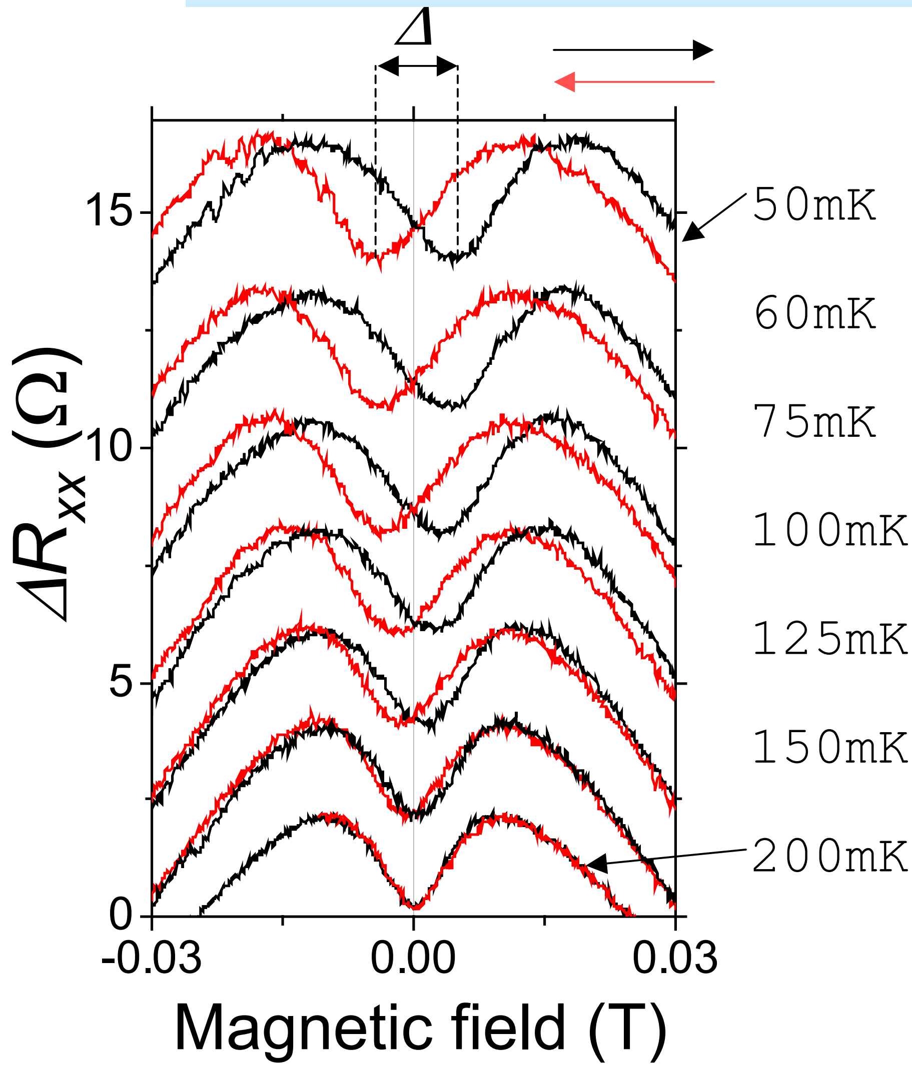
Effects of confinement magnetic quantum wires - expectations

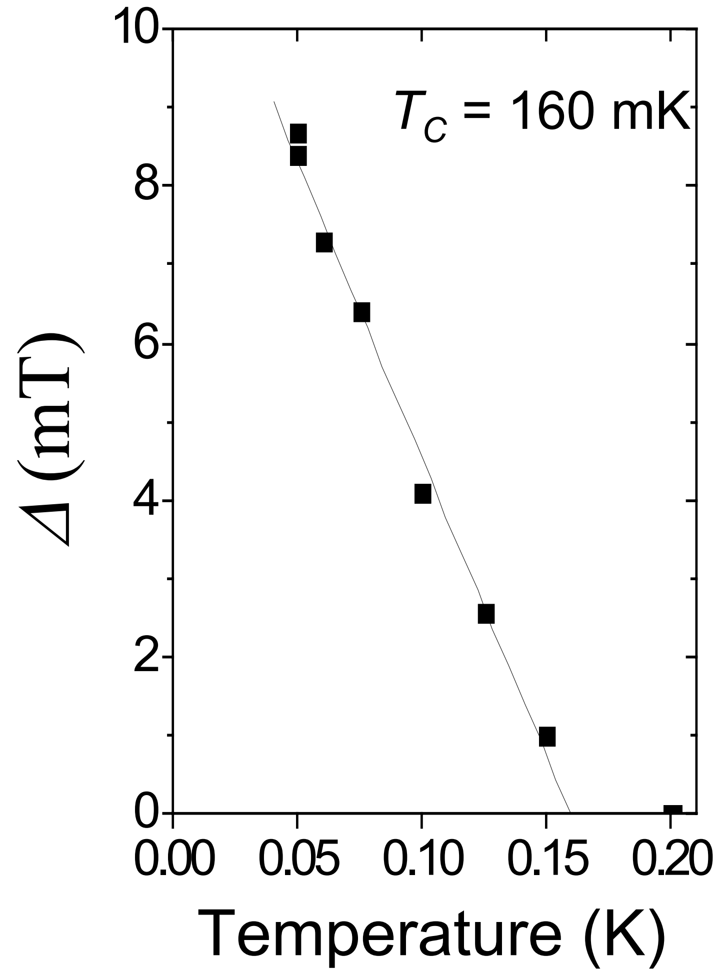
1D: T_F(q) has maximum at 2k_F
➔ spin-Peierls instability ➔ SDW



T_F(q)/T_F (0) **for s-electrons neglecting e-e interactions and disorder**

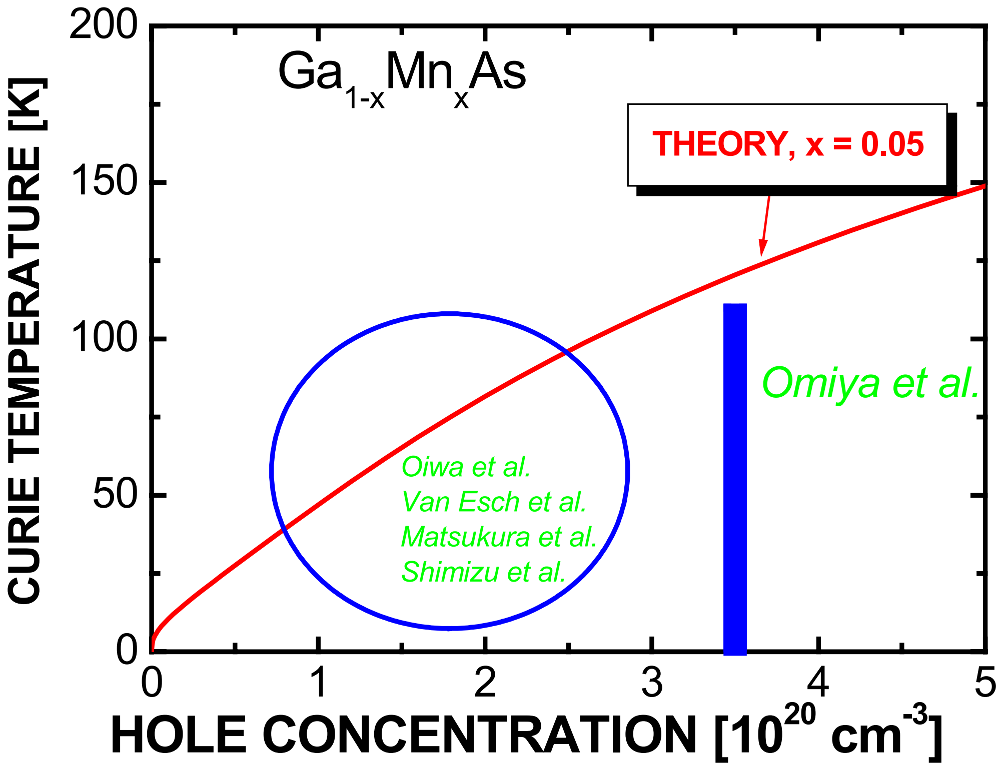
Magnetoresistance hysteresis
n-$Zn_{1-x}Mn_xO$:Al, x = 0.03





M. Sawicki, ..., M. Kawasaki, T.D., ICPS'00

Curie temperature in p-$Ga_{1-x}Mn_xAs$
theory vs. experiment

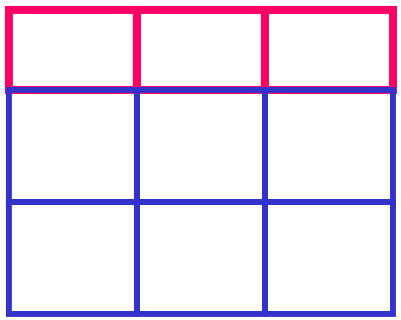


T.D. et al., PRB'01

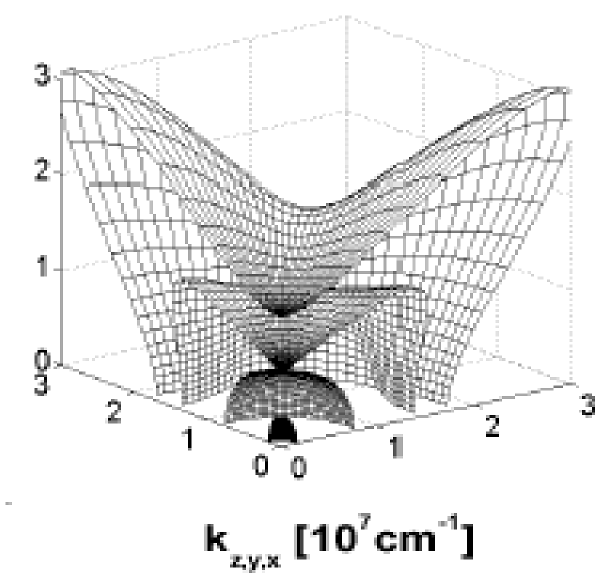
- **Anomalous Hall effect ➔ *p* uncertain**
- **Omiya et al.: 27 T, 50 mK**
- ***Theory:* T_C > 300 K for x > 0.1 and large *p***
- **2003: T_C up to 170 K (Sendai, Notre Dame, Pen State, Nottingham, Tokyo…)**

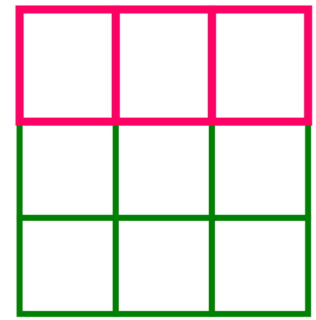
cf. first principles studies: **Shirai, Katayama-Yosida, Sanvito, Dederichs, ...**

Strain engineering

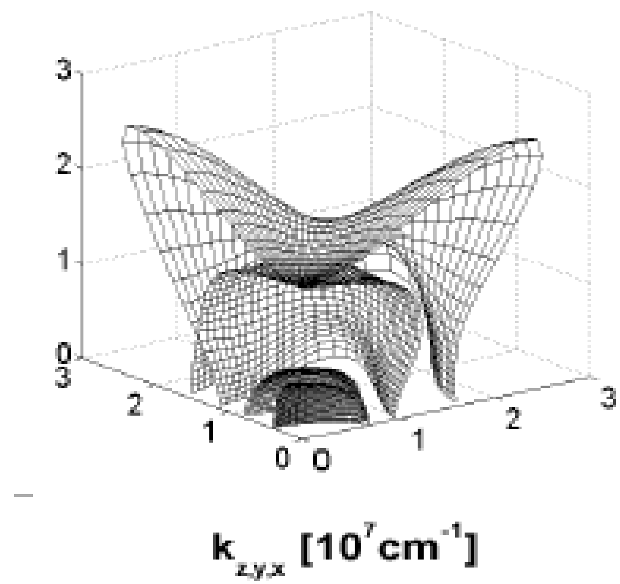


Tensile strain
e.g (Ga,Mn)As/InAs

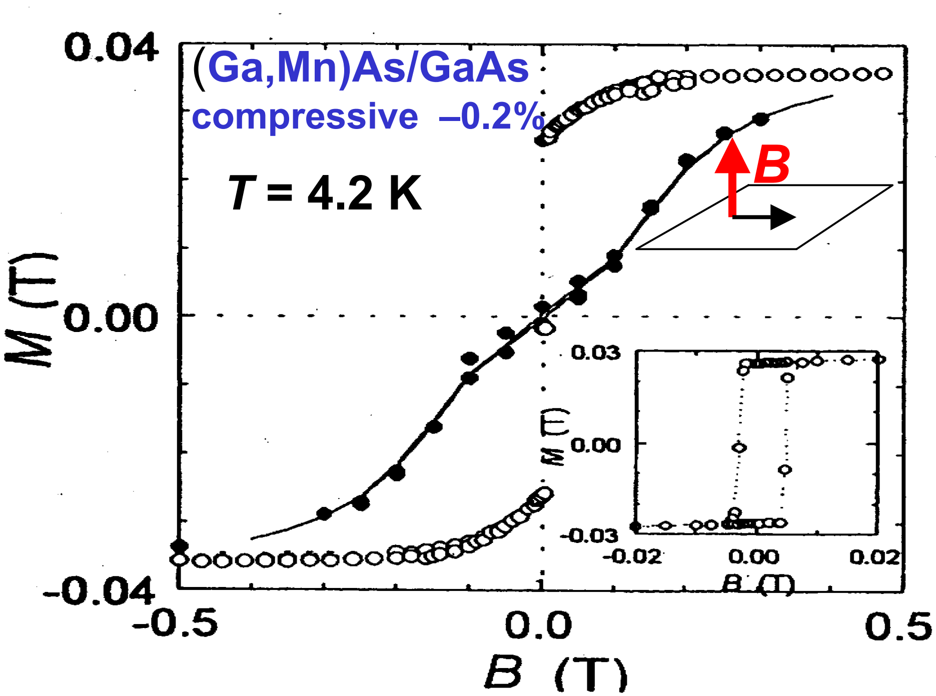




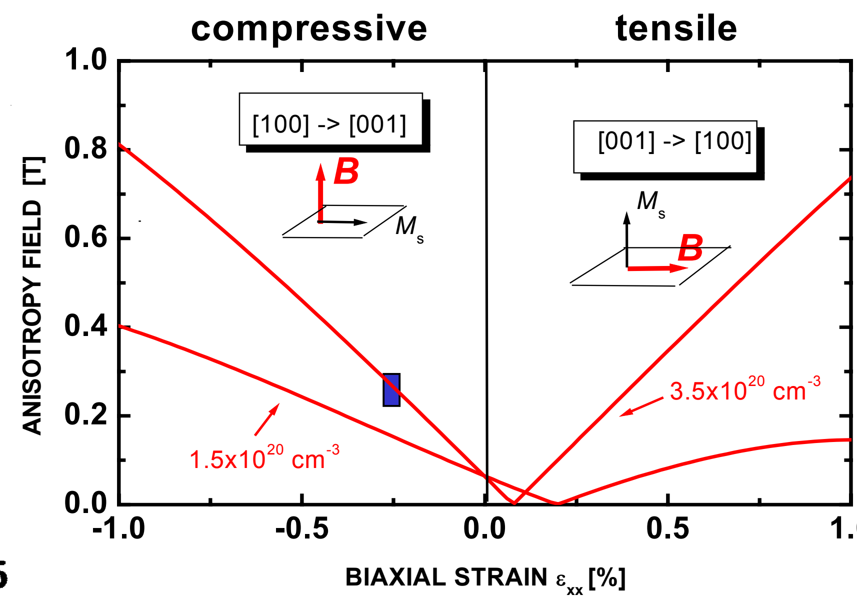
Compressive strain
e.g (Ga,Mn)As/GaAs



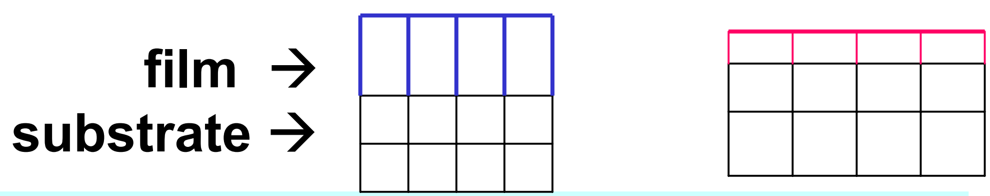
Effect of strain on easy axis and anisotropy field (Ga,Mn)As



F. Matsukura et al.



T.D. et al., PRB ‘01

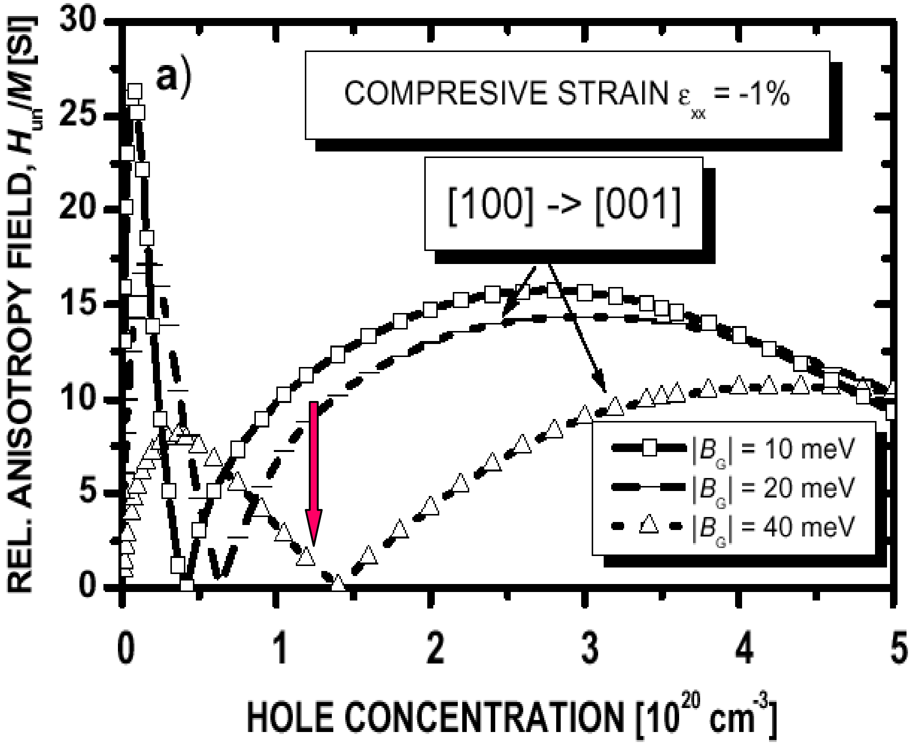


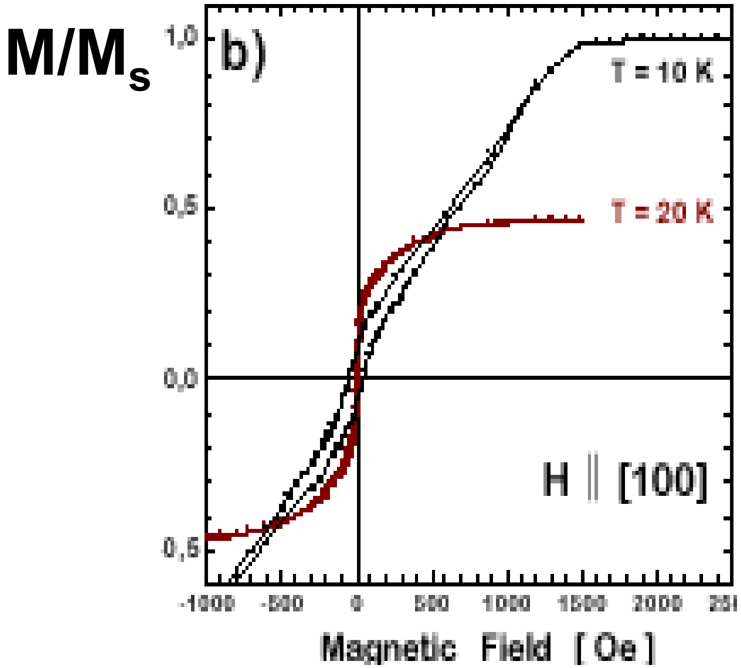
- (Ga,Mn)As/GaAs compressive strain => easy axis in plane
- (Ga,Mn)As/(Ga,In)As tensile strain => easy axis out of plane

Temperature dependent anisotropy (Ga,Mn)As

compressive strain
easy axis flips from [001]→ [100]

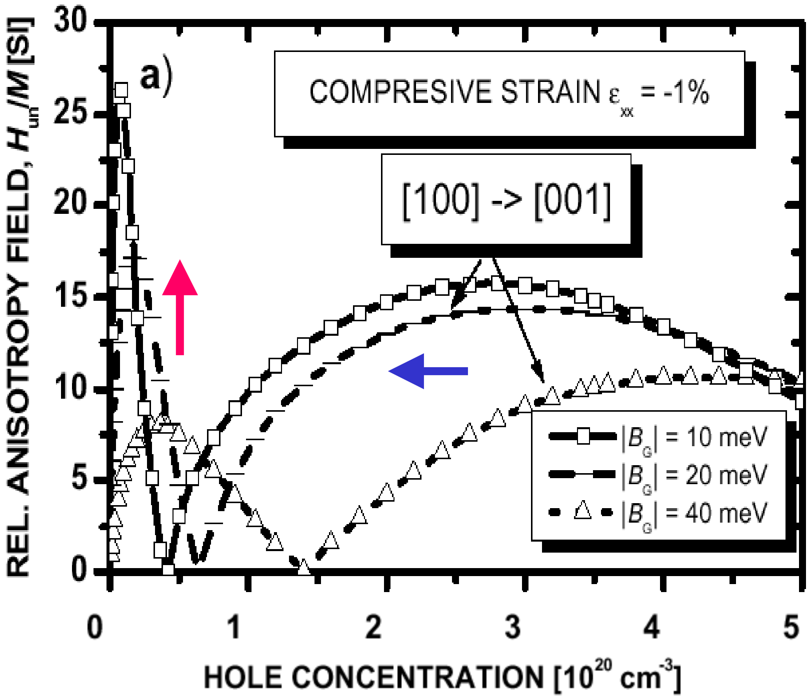
T.D. et al., Science ’00, PRB’01





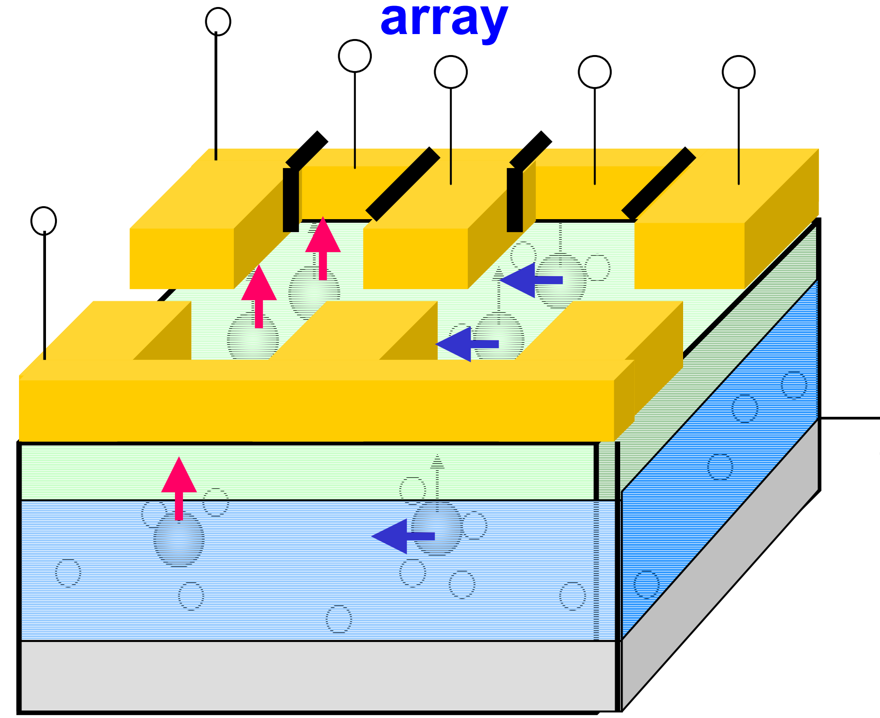
M. Sawicki et al., cond-mat/0212511

Controlling quantum magnetic dots



GATE VOLTAGE

Ferromagnetic quantum dot array



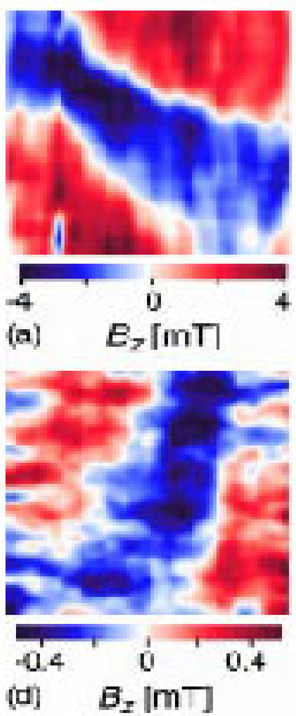
to be demonstrated

Stripe domains in (Ga,Mn)As perpendicular films

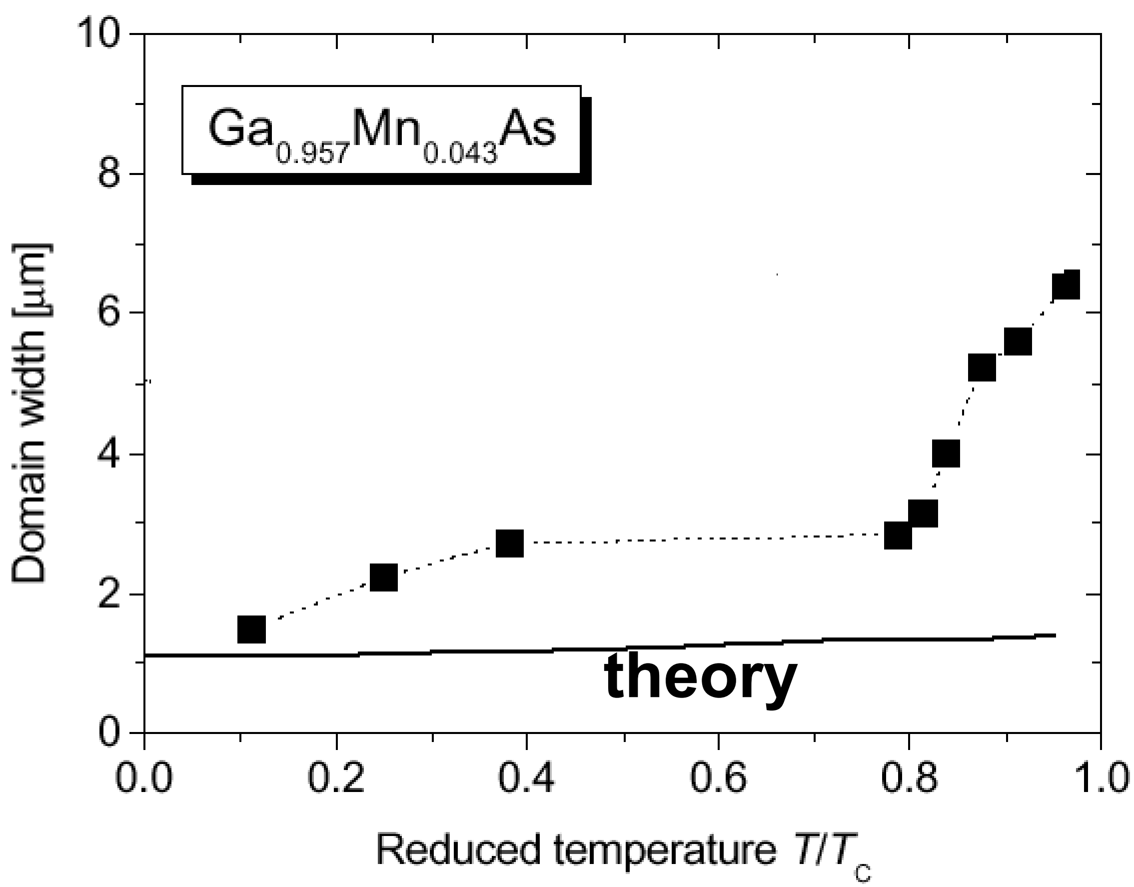
domain walls
[110] → [100]

9 K

65 K

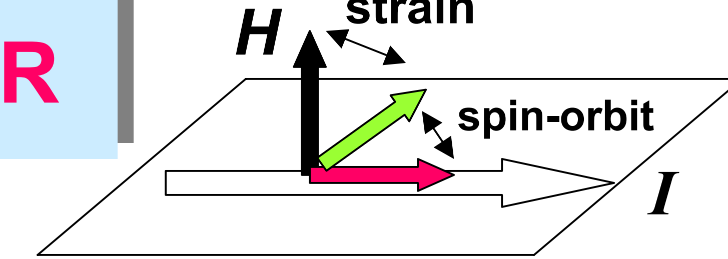


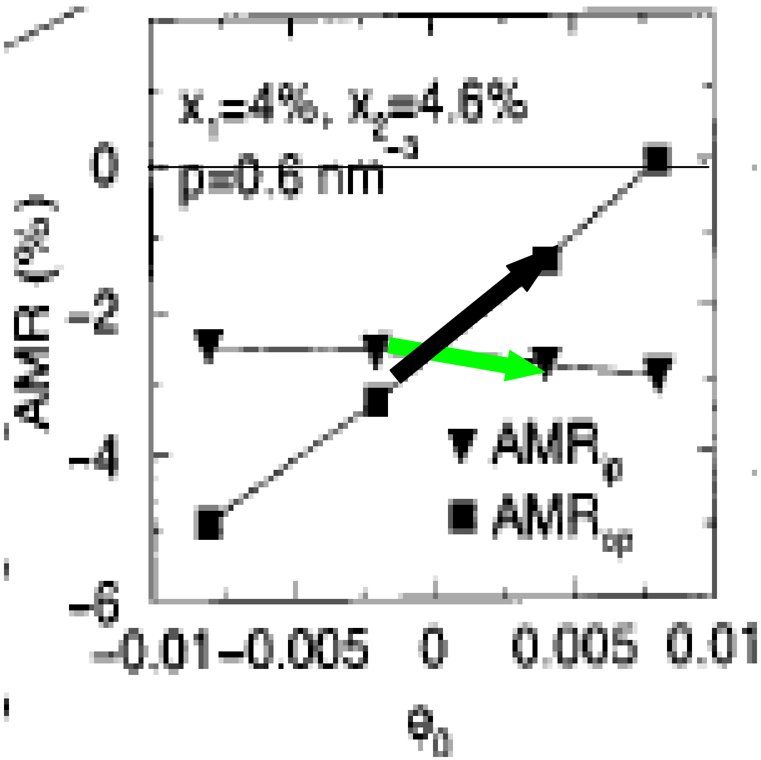
Shono et al.



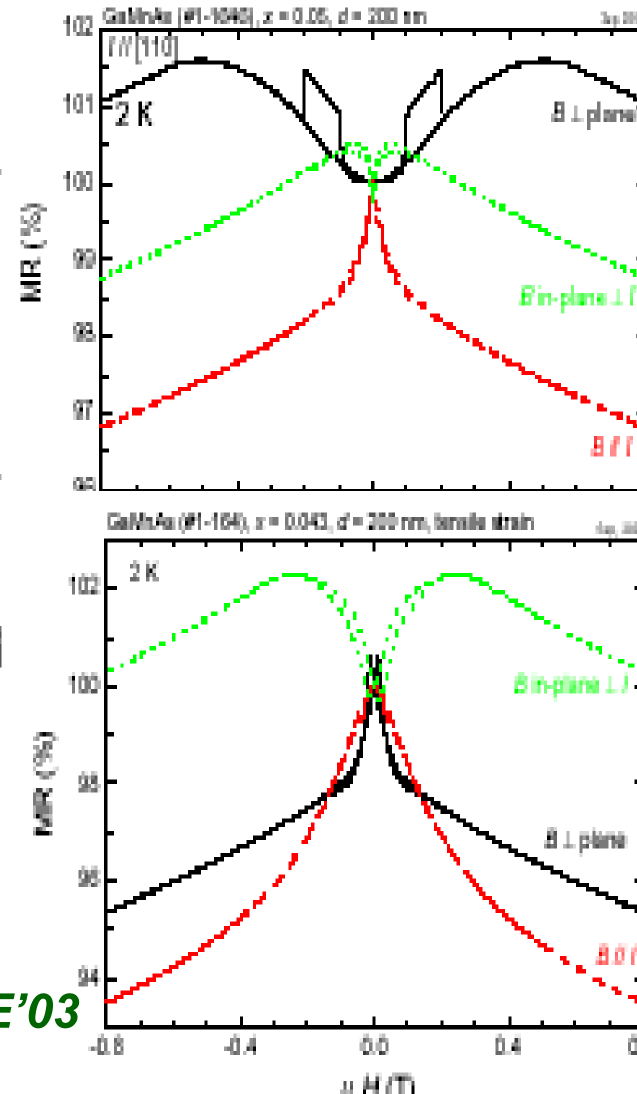
T.D. et al., PRB'01

Transport properties: AMR





$AMR = (\rho_{//} - \rho_{\perp})/\rho_{//}$



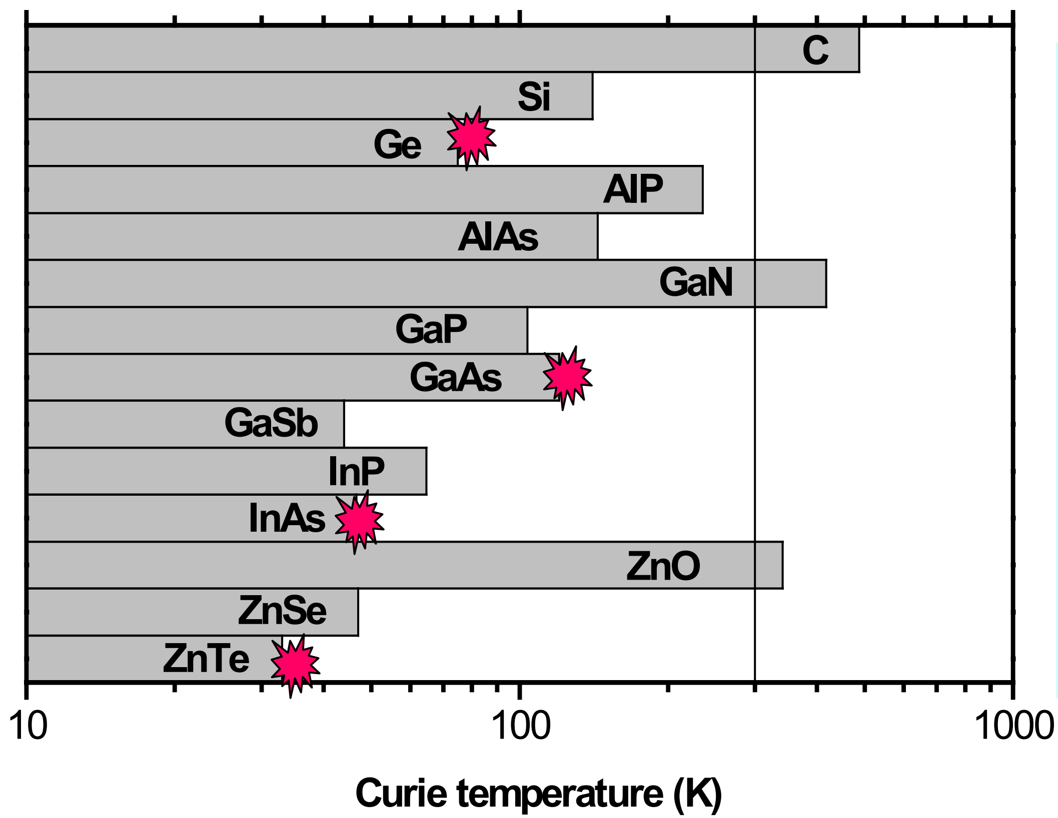
x = 0.05
compressive
$\varepsilon \approx -0.002$

x = 0.043
tensile
$\varepsilon \approx 0.002$

T. Jungwirth et al., APL'02

F.Matsukura, …, T.D., Physica E'03

Chemical trends – hole driven ferromagnetism
$x_{Mn} = 0.05$, $p = 3.5 \times 10^{20}$ cm^{-3}



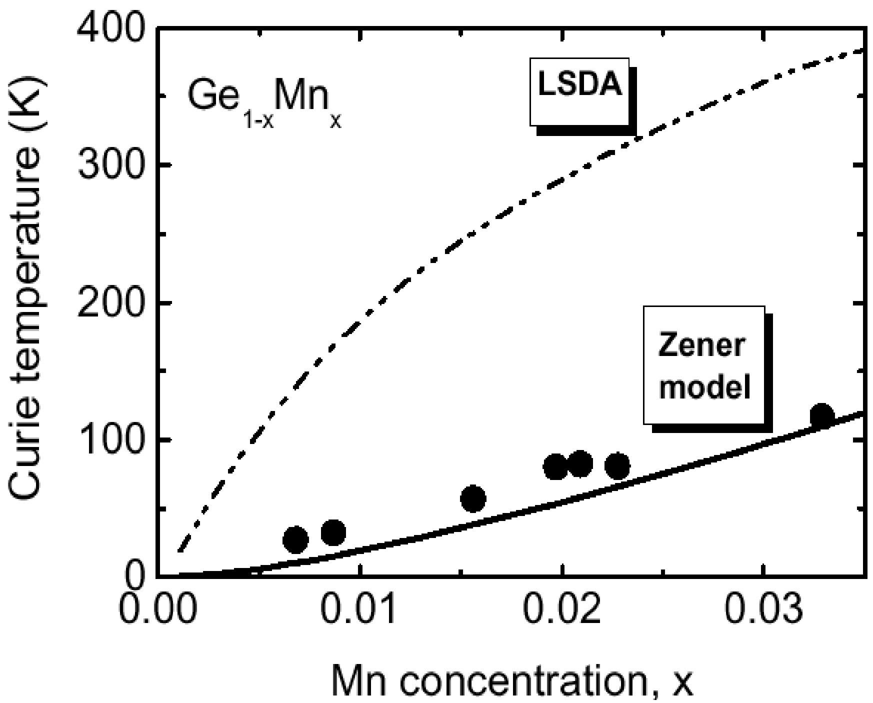
Materials of light elements*:*

- **large p-d hybridization**
- **small spin-orbit interaction**

T.D. et al., Science '00

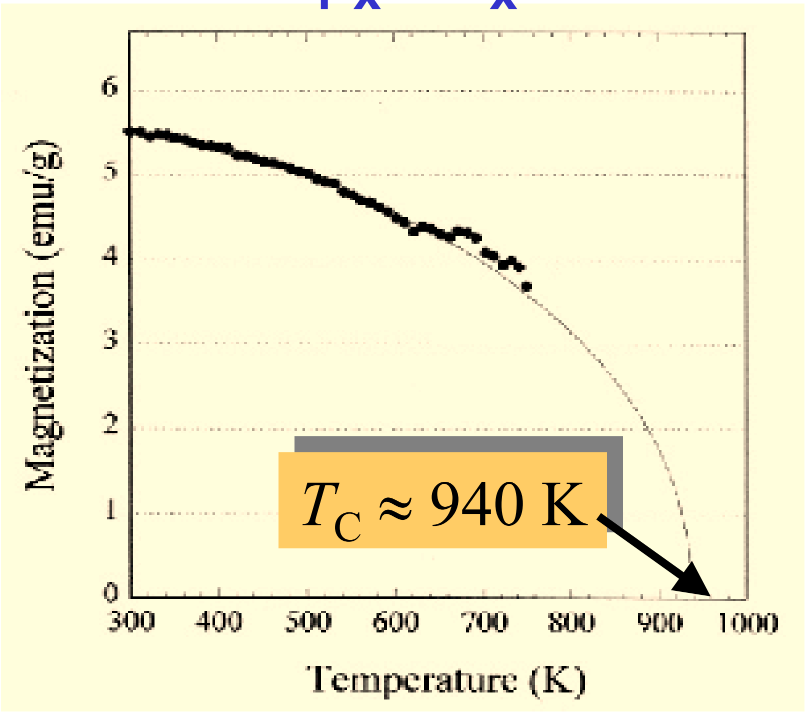
Chasing for functional ferromagnetic semiconductors

$Ge_{1-x}Mn_x$



Expl., LSDA, Park et al, Science '02

$Ga_{1-x}Mn_xN$



Sonoda et al., J. Cryst. Growth'02

Warning: precipitates and inclusions possible

Summary
III-V and II-VI ferromagnetic DMS

- **Spin manipulations**

-- spin injection ***(cf. H. Jaffres)***
-- GMR, TMR
-- ferro-FET, ferro-LED (electric field and light)
-- dimensionality
-- strain engineering

at low temperatures ➔ quantum information devices

- **Theory**

-- T_c**,** $M(T,H)$**, magnetic anisotropy, domains,** *MCD, AHE, AMR…*

- **Open issue:**

-- interplay between Stoner and Zener magnetism near MIT

- **Prospects for high** T_C**:** ***more materials science***

Summary, spin-spin interactions in DMS

➔ DMS with no carriers: **merely antiferro superexchange**

➔ DMS with carriers: **ferro Zener/RKKY**

- strong for holes
- weak for electrons

Literature

➔ DMS

TD, in: Handbook on Semiconductors, vol. 3B ed. T.S. Moss (Elsevier, Amsterdam 1994) p. 1251.

➔ ferromagnetic DMS

- ***F. Matsukura, H. Ohno, TD, in: Handbook of Magnetic Materials, vol. 14, Ed. K.H.J. Buschow, (Elsevier, Amsterdam 2002) p. 1***
- ***TD, Semicond. Sci. Technol. 17, 377 (2002)***