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MINIWORKSHOP ON "*FRONTIERS IN MATERIALS SCIENCE*"
15 - 18 May 2001

301/1311-12

"Pushing the Limits of Electronic Structure Theory. Can We Design New Spintronic Materials?"

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Please note: These are preliminary notes intended for internal distribution only.

Pushing the limits of electronic structure theory

Can we design new spintronic materials?

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Acknowledgments

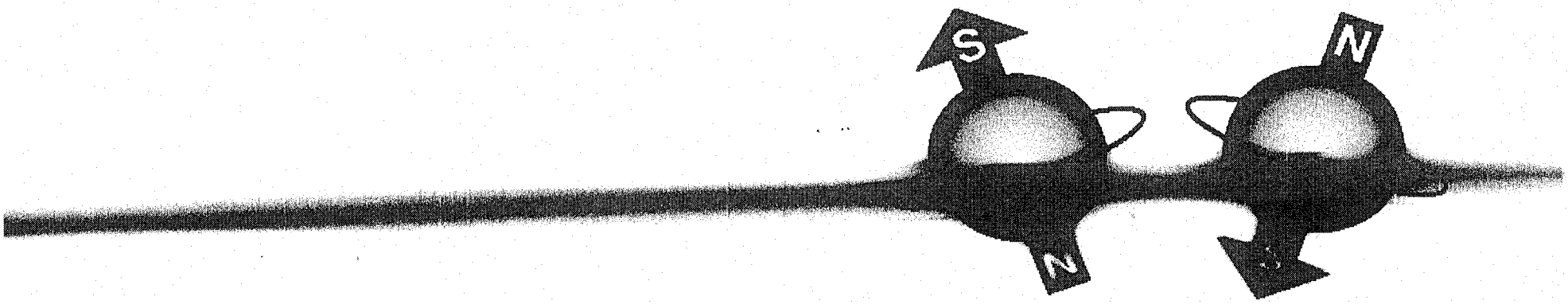
ONR
ACS / PRF
JNC + IISc Bangalore

Outline

- What is spintronics
- Theoretical techniques - successes + shortcomings
- Solutions! Spinor + Siesta
- Results for materials

What is Spintronics?

- **Spin** polarized electronics
- exploits the fact that electrons have spin as well as charge
- tunable/controllable by magnetic fields
- extra degree of freedom

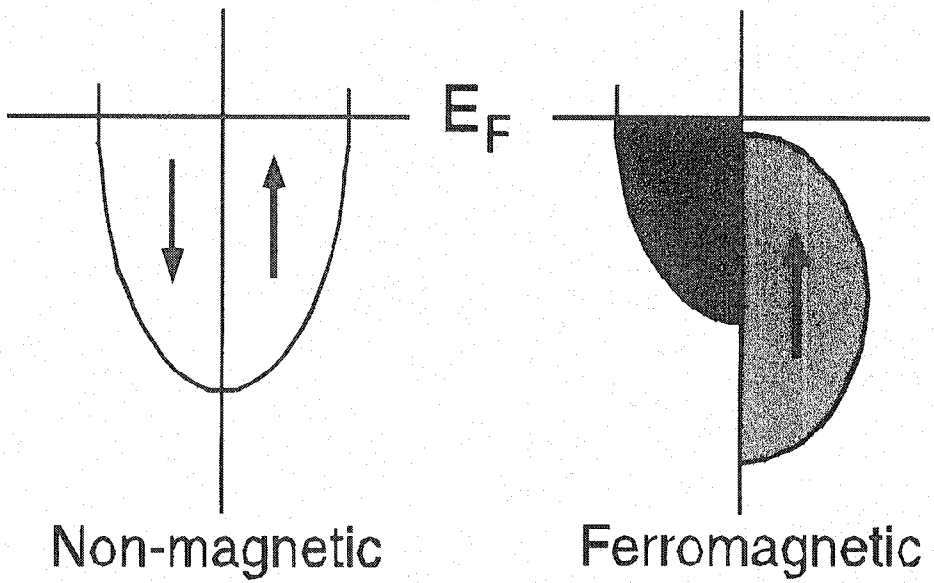


Application: Quantum computing!

- Fundamentally new mode of information processing
- Uses quantum **interference** and **entanglement**
- Requires stable, long-lived, **coherent** quantum states
- Good for cryptography, searching, factorization

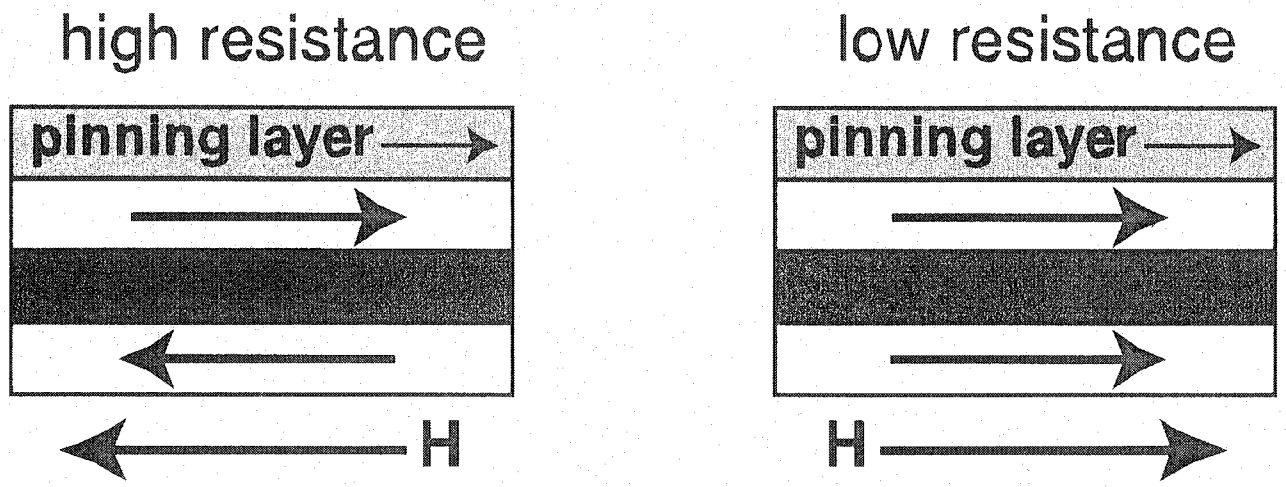
Spin-polarized transport

- imbalance of spin populations at Fermi level
- e.g. ferromagnetic metals
- Half-metallic ferromagnets!



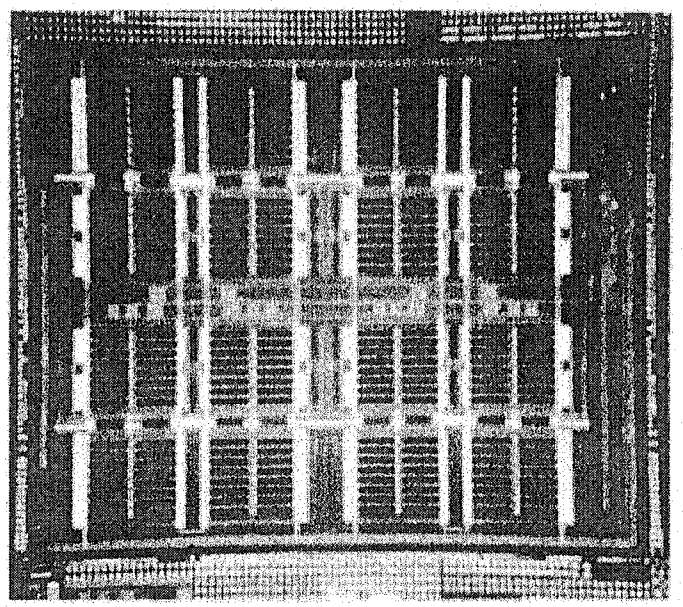
Applications

Spin valves



used in:

- magnetic field sensors
- recording heads
- MRAM



Technology-enabling material

Need:

- Room temperature ferromagnet
- Compatible with existing processing techniques
- Compatible interfaces with semiconductors

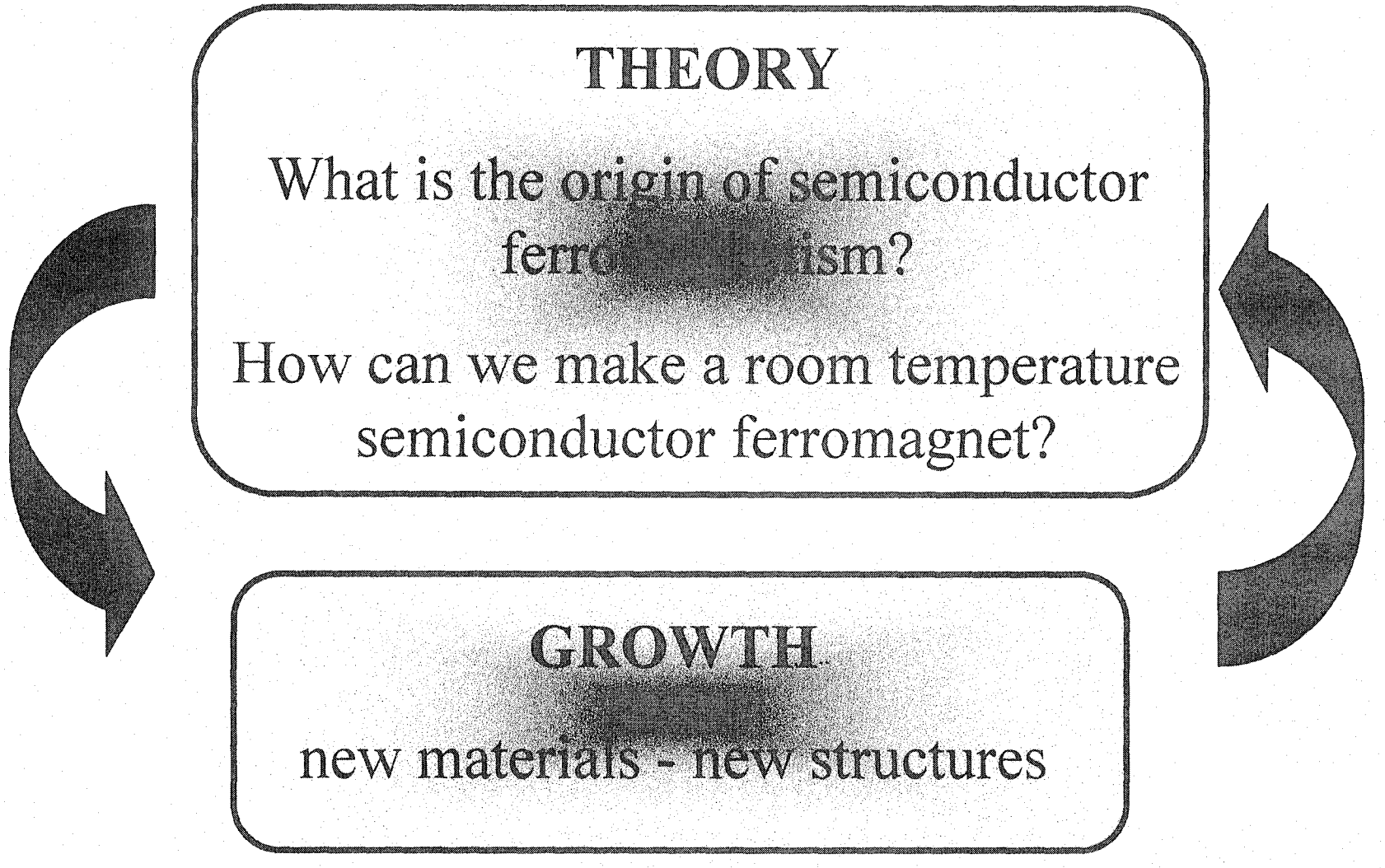
FERROMAGNETIC SEMICONDUCTOR!

Promising systems

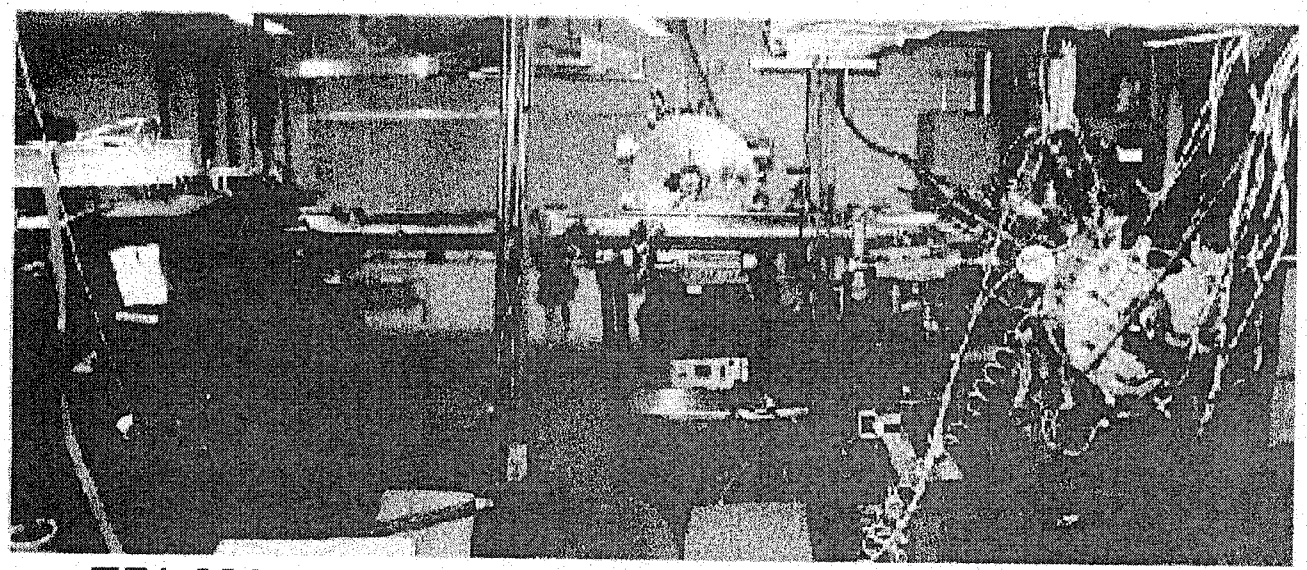
MnAs ⟺ (Ga,Mn)As

1) they can be grown on commonly used GaAs,
2) the interfaces with GaAs are thermodynamically stable,
3) the growth process is compatible with existing III-V MBE technology.
4) They can be ferromagnetic **BUT** Tc is only around 100K!

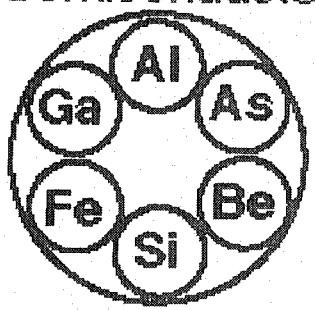
UCSB Research Effort



Spintronics MBE Laboratory

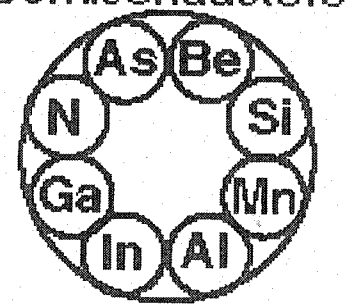


EPI-620
Ferromagnetic Metals
on Semiconductors

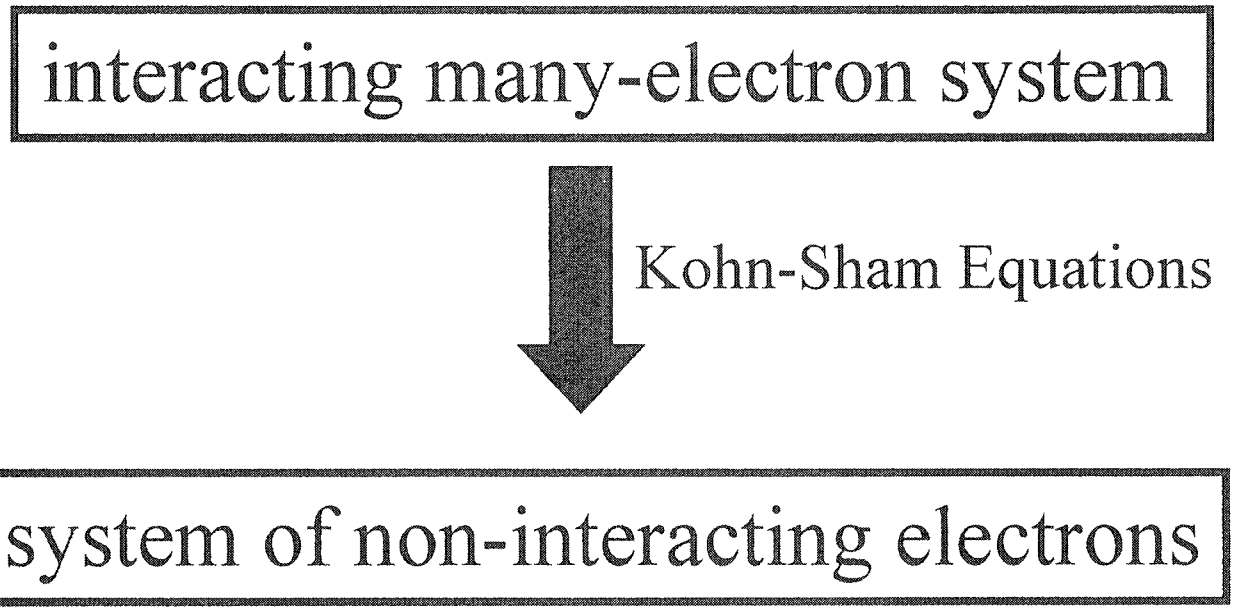


Analysis Chamber

Gen-II
Ferromagnetic
Semiconductors



Density Functional Theory



Hohenberg and Kohn (1964)
Kohn and Sham (1965)

The Kohn-Sham Equations

$$\{T+V_{ei}(\mathbf{r})+V_H(\mathbf{r})+V_{xc}(\mathbf{r})\}\phi_i(\mathbf{r}) = \varepsilon_i\phi_i(\mathbf{r})$$

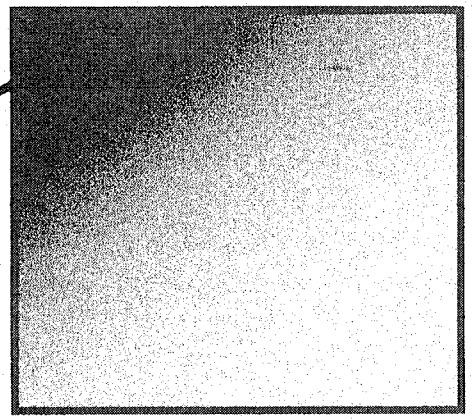
where both the Hartree potential, V_H, and the exchange correlation, V_{xc}, depend on the density

$$\rho(\mathbf{r}) = \Sigma\, \phi_i^*(\mathbf{r})\, \phi_i(\mathbf{r})$$

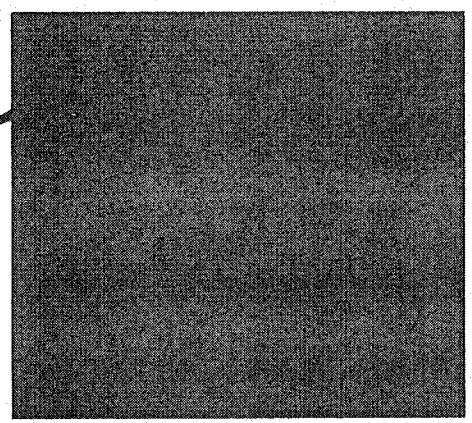
Local Density Approximation (LDA)

assumes that the exchange-correlation energy per electron at a point **r** in the electron gas is equal to the exchange-correlation energy per electron in a homogeneous electron gas that has the same density as the electron gas at point **r**.

$E_{xc}(\mathbf{r})$ (True)



$E_{xc}(\mathbf{r})$ (LDA)

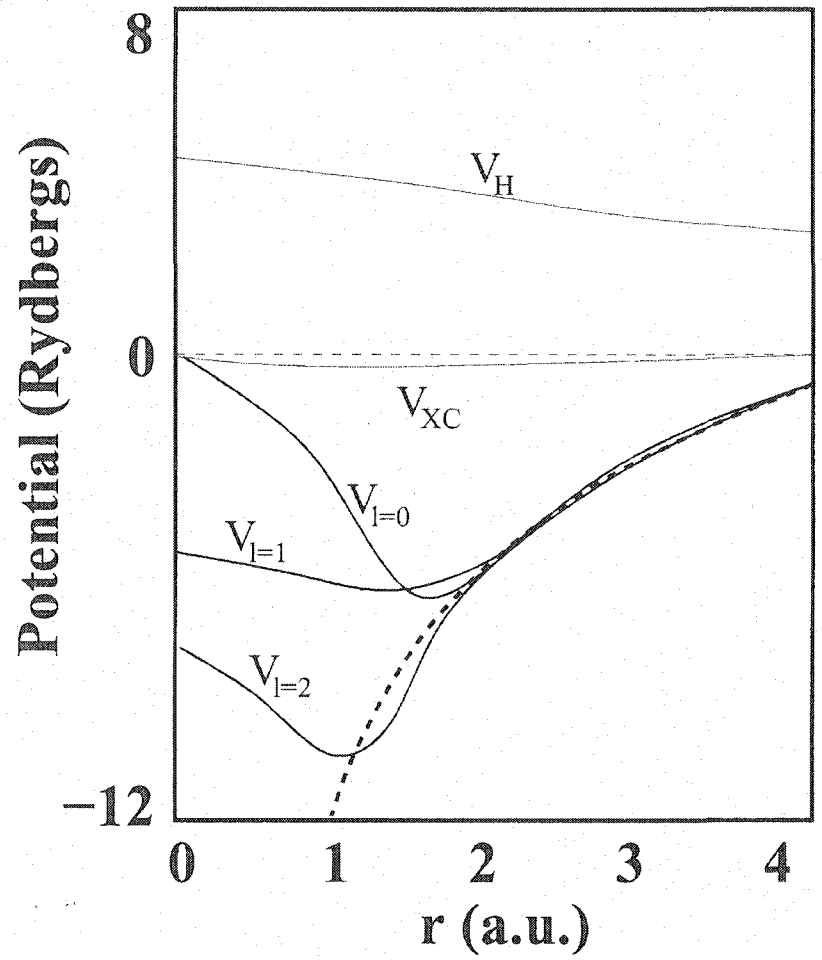


Pseudopotential Approximation

- Replacement:

$$V_{nuc} \rightarrow V_{ion}$$

- Treat only valence electrons
- Nodeless wave functions
- Plane waves are o.k.



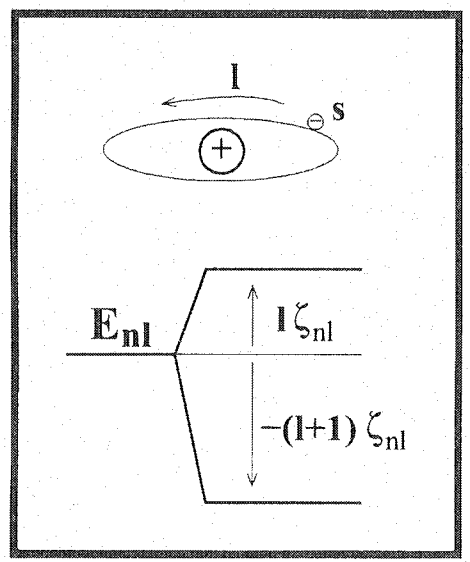
Pseudopotential Success Story

The *ab initio* pseudopotential method has been successfully employed in the prediction of structural and electronic properties for a wide range of materials, including:

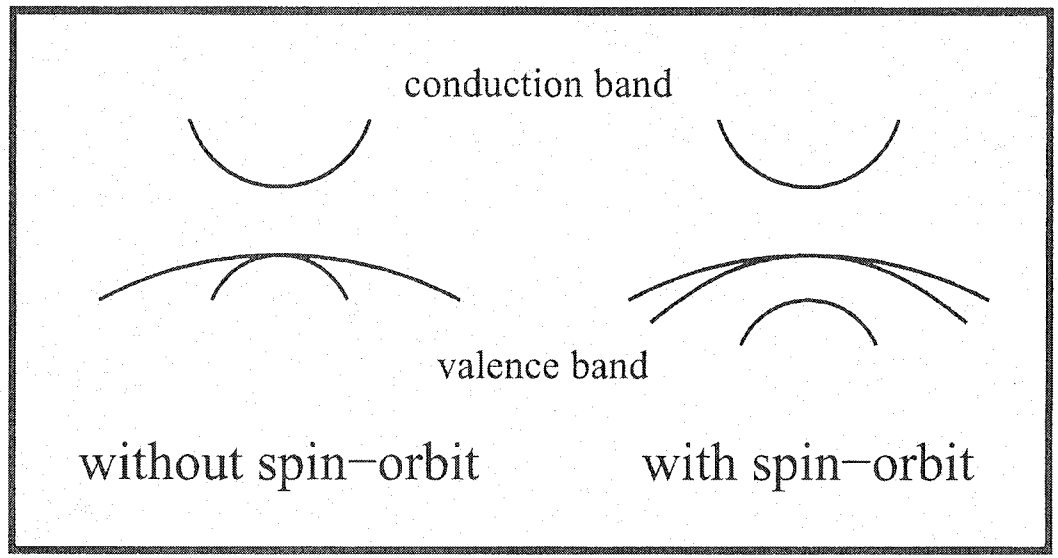
- Silica Frameworks
- Semiconductors
- Metals
- Transition metals
- Ferromagnetic Ferroelectrics !

What's missing?
Spin–Orbit Coupling

Atom:

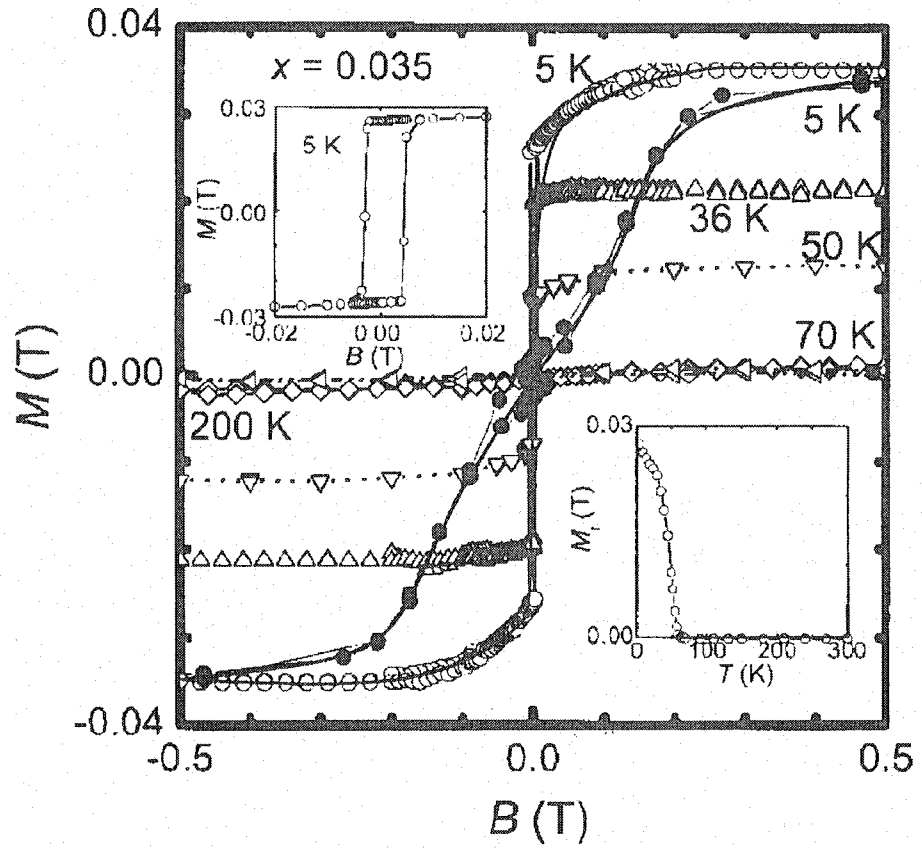


Semiconductor:



What's missing?
Magnetocrystalline Anisotropy

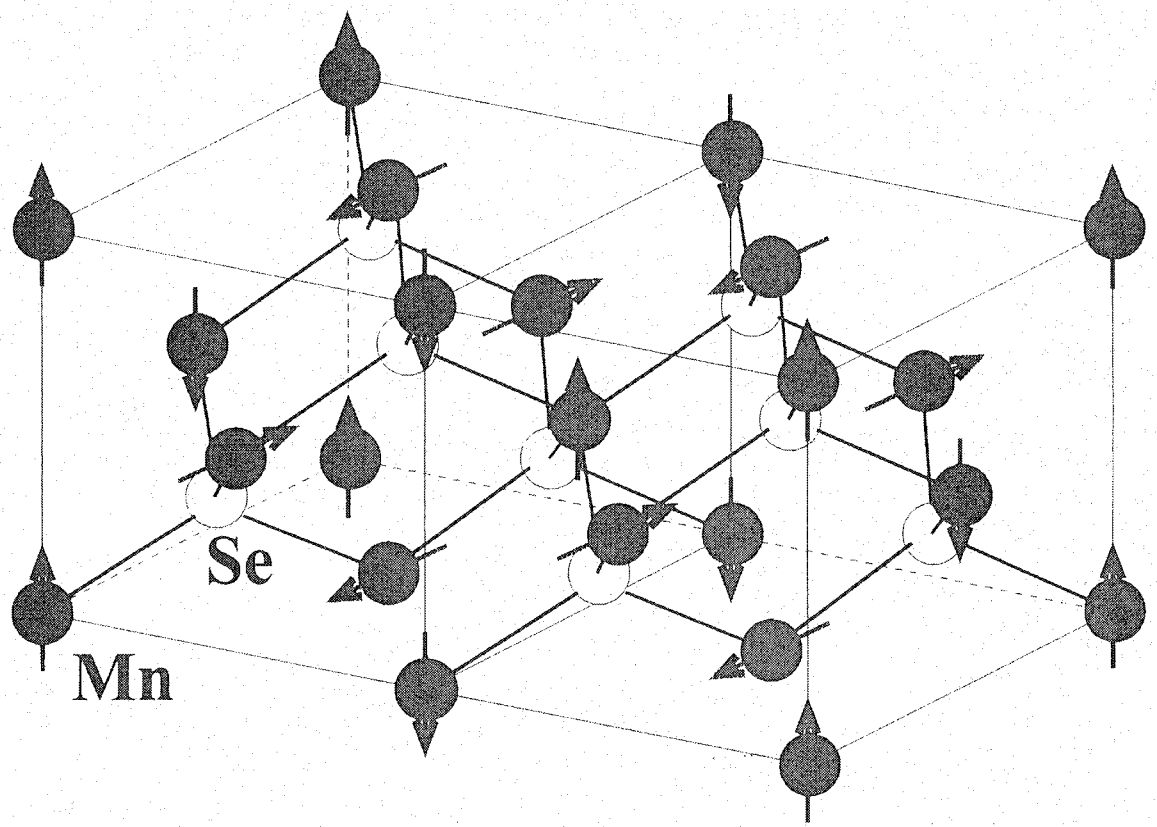
Easy & hard axis: (Ga,Mn)As



H. Ohno and F. Matsukura, Solid State Commun. **117**, 179 (2001)

What's missing?
Non–collinear Magnetism

Anisotropic superexchange (Dzyaloshinskii–Moriya): MnSe



How can we fix it?

- Wave functions become general spinors

$$\psi = \phi_{\uparrow}(r)|\uparrow\rangle + \phi_{\downarrow}(r)|\downarrow\rangle \ .$$

- Local density approximation needs to be generalized

$$\vec{b}_{xc}(\vec{r}) = \frac{\delta E_{xc}[n,\vec{m}]}{\delta \vec{m}(\vec{r})} = \frac{\delta E_{xc}[n,m]}{\delta m(\vec{r})}\hat{m}(\vec{r}) \ .$$

- Pseudopotential needs to include spin–orbit coupling.

Fully Separable j–dependent Pseudopotentials

$$V_{pp}^{KB} = V_{loc} + \sum_{l,j,m_j} \frac{|\delta V_{l,j}\phi_{l,j,m_j}\rangle\langle\phi_{l,j,m_j}\delta V_{l,j}|}{\langle\phi_{l,j,m_j}|\delta V_{l,j}|\phi_{l,j,m_j}\rangle}$$

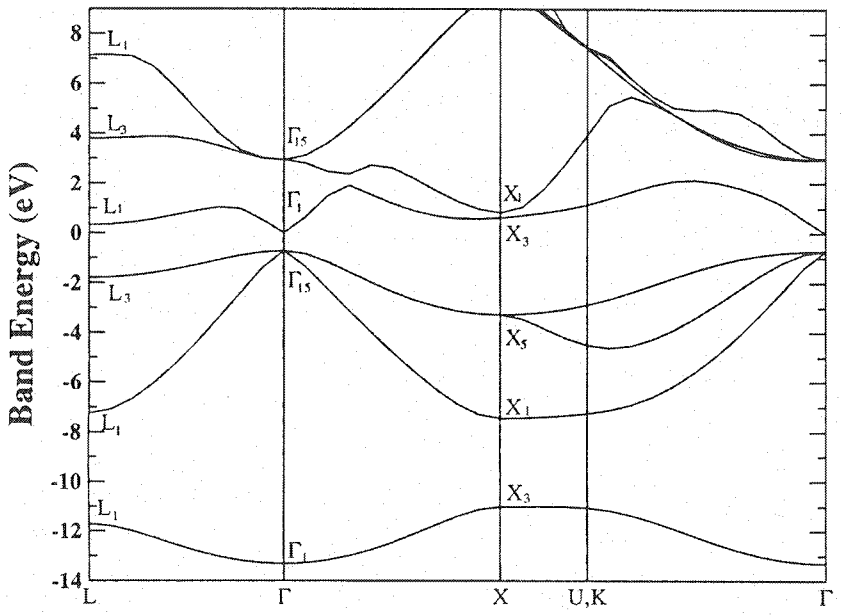
Pseudo wave function: $|\phi_{l,j,m_j}^{i_s,i_a}\rangle = |R_{l,j}^{i_s,i_a}\rangle|\Phi_{m_j}^{l,j}\rangle$

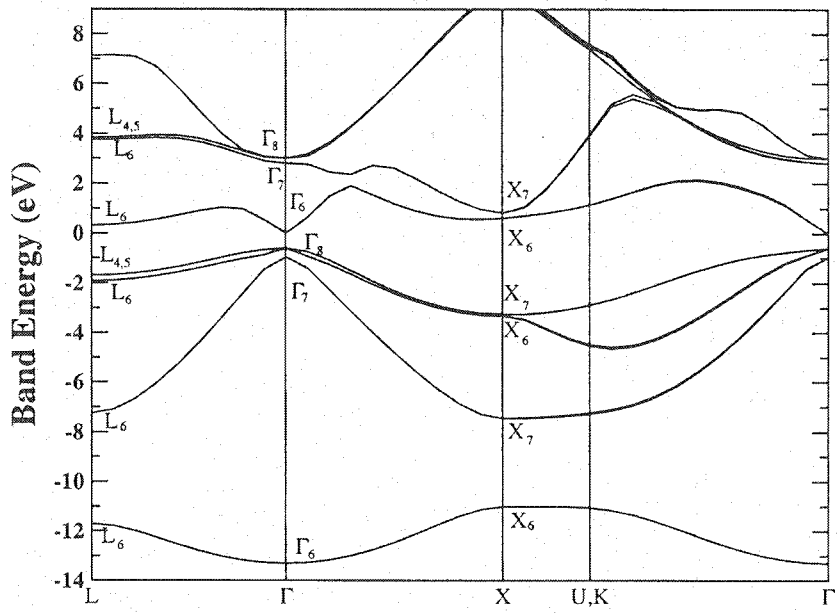
for $j = l + \frac{1}{2}$: $$|\Phi_{m_j}^{l,j}\rangle = \left(\frac{l+m+1}{2l+1}\right)^{\frac{1}{2}} |Y_l^m\rangle|\uparrow\rangle + \left(\frac{l-m}{2l+1}\right)^{\frac{1}{2}} |Y_l^{m+1}\rangle|\downarrow\rangle$$

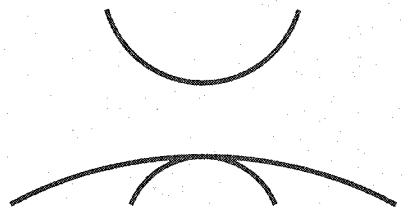
for $j = l - \frac{1}{2}$: $$|\Phi_{m_j}^{l,j}\rangle = \left(\frac{l-m+1}{2l+1}\right)^{\frac{1}{2}} |Y_l^{m-1}\rangle|\uparrow\rangle - \left(\frac{l+m}{2l+1}\right)^{\frac{1}{2}} |Y_l^m\rangle|\downarrow\rangle$$

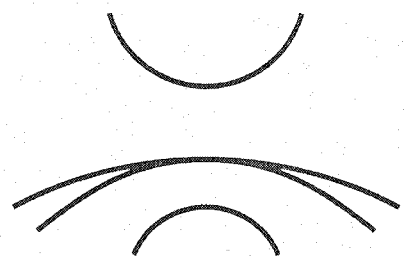
http://www.mrl.ucsb.edu/~theurich/Spinor

GaAs: scalar vs. fully relativistic

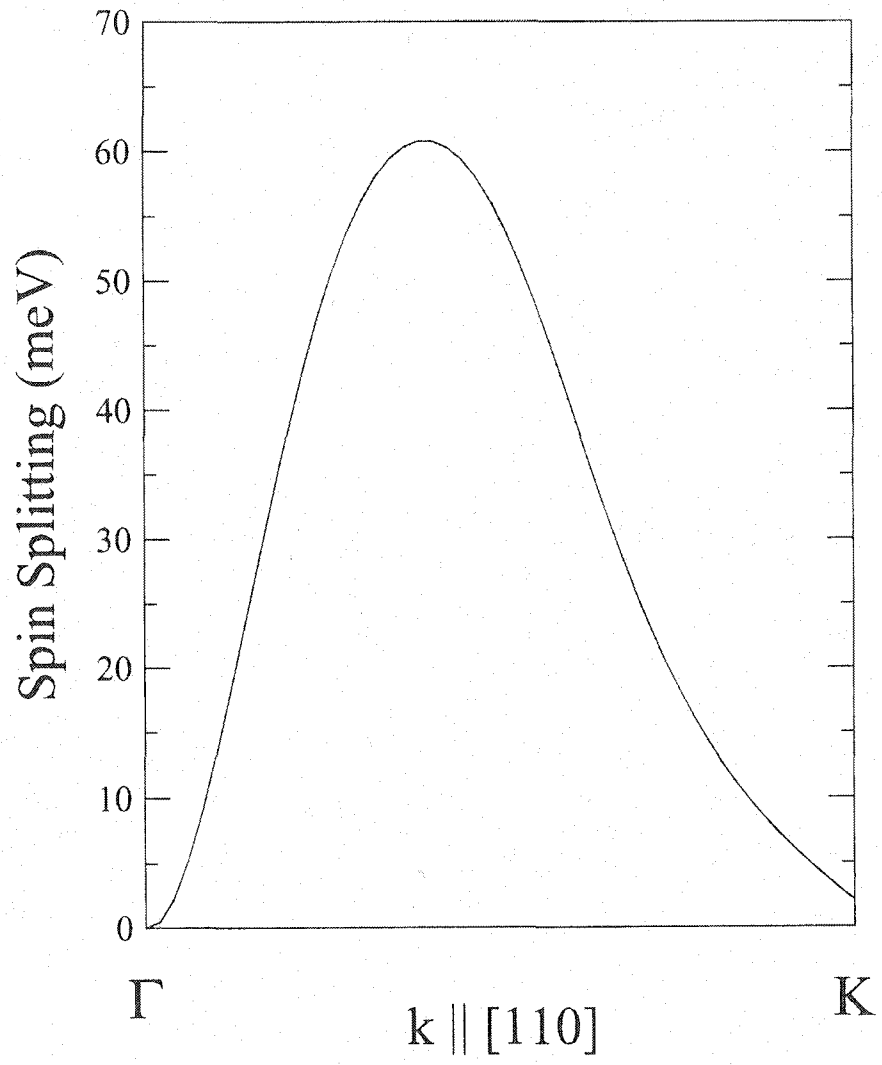








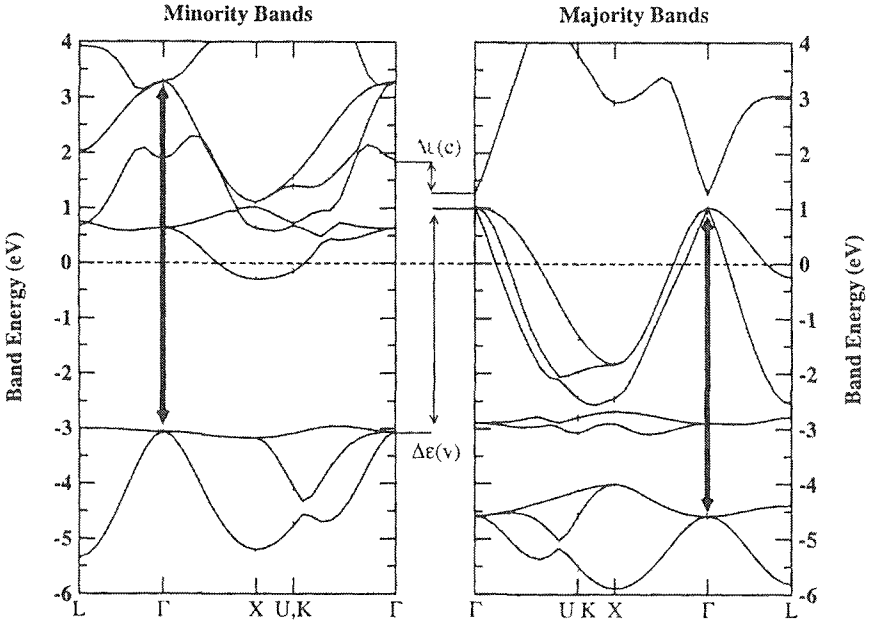
Spin–splitting in GaAs



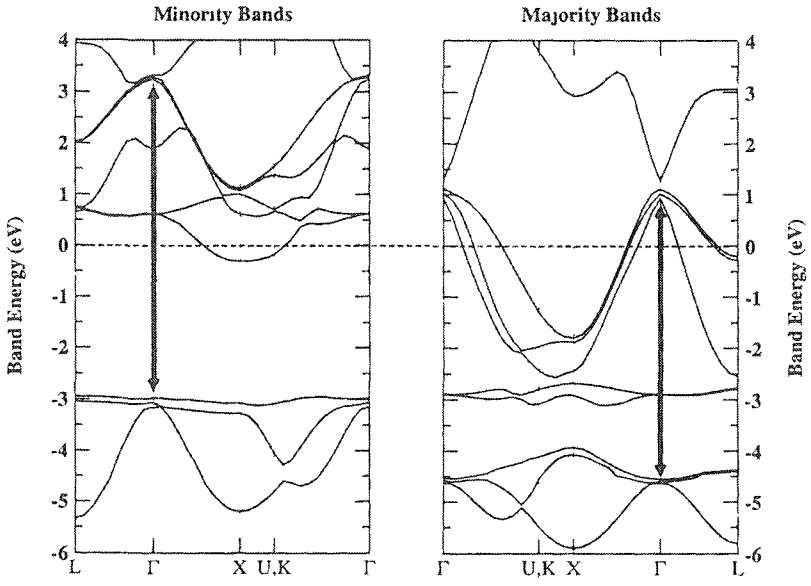
- Zincblende inversion asymmetry allows spin splitting
- Spin splitting is k dependent
- Spin splitting causes spin relaxation

[001] FM zincblende MnSe

Scalar–Relativistic



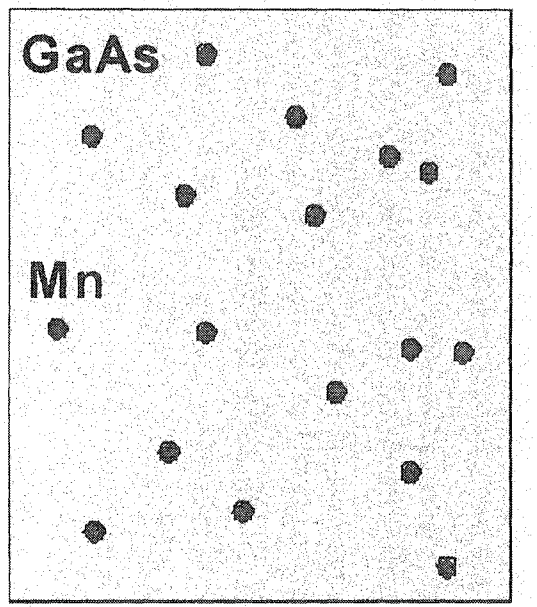
Fully Relativistic



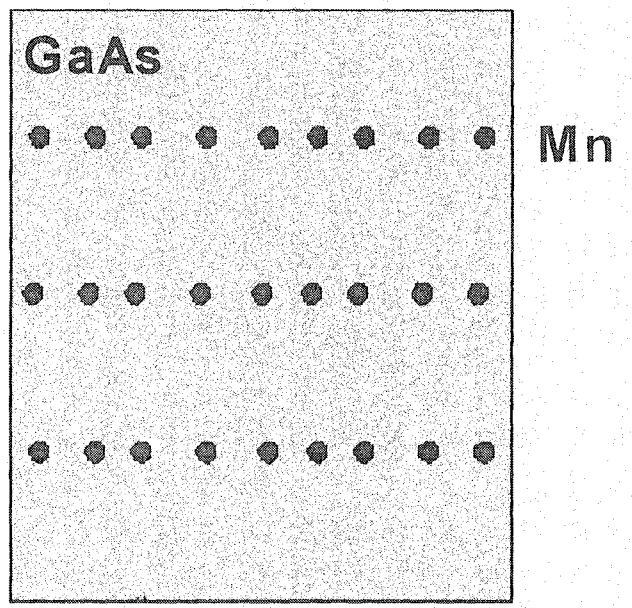
		M (μ_B)	$N\alpha$(eV)	$N\beta$(eV)
theory	Fully Relativistic	4.41	0.28	-1.86
theory	Scalar–Relativistic	4.42	0.28	-1.85
experiment	$Zn_{1-x}Mn_xSe$ (Twardowski et al., 1984)	-	0.26	-1.31

New materials and structures

Random Alloy



"DFH"



Theoretical Techniques

Density functional theory within the LSDA. Details:

MnAs

"SPINOR"

http://www.mrl.ucsb.edu/~theurich/Spinor

- Plane-wave basis (cutoff energy 70 Ryd) [2]
- Optimized Pseudopotentials
- Small unit cells
- non-collinear magnetism and spin-orbit coupling

(Ga,Mn)As

"SIESTA"

D. Sanchez-Portal et al., Int. J. Quant. Chem. **65**, 453 (1997).

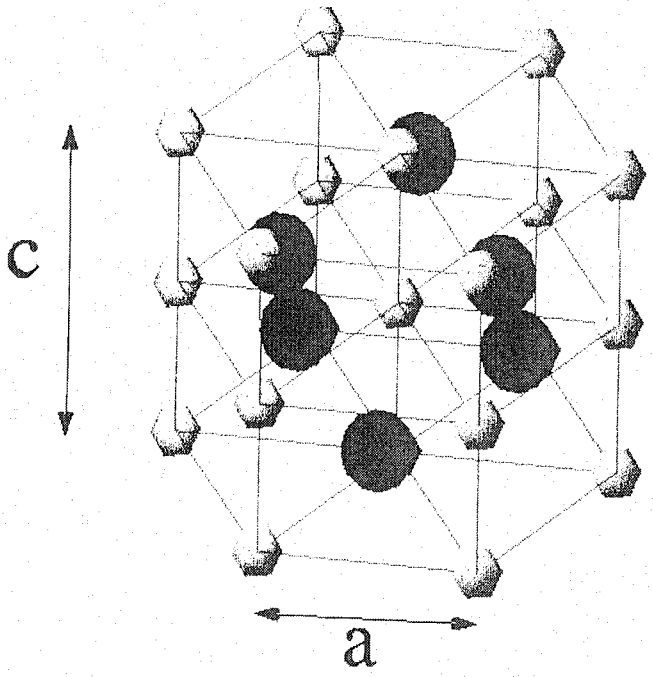
- Localized multiple-ζ Pseudo-atomic orbital basis
- Troullier-Martin Pseudopotentials
- Super-cells with up to 100 atoms

QUESTIONS WE'D LIKE TO ANSWER:-

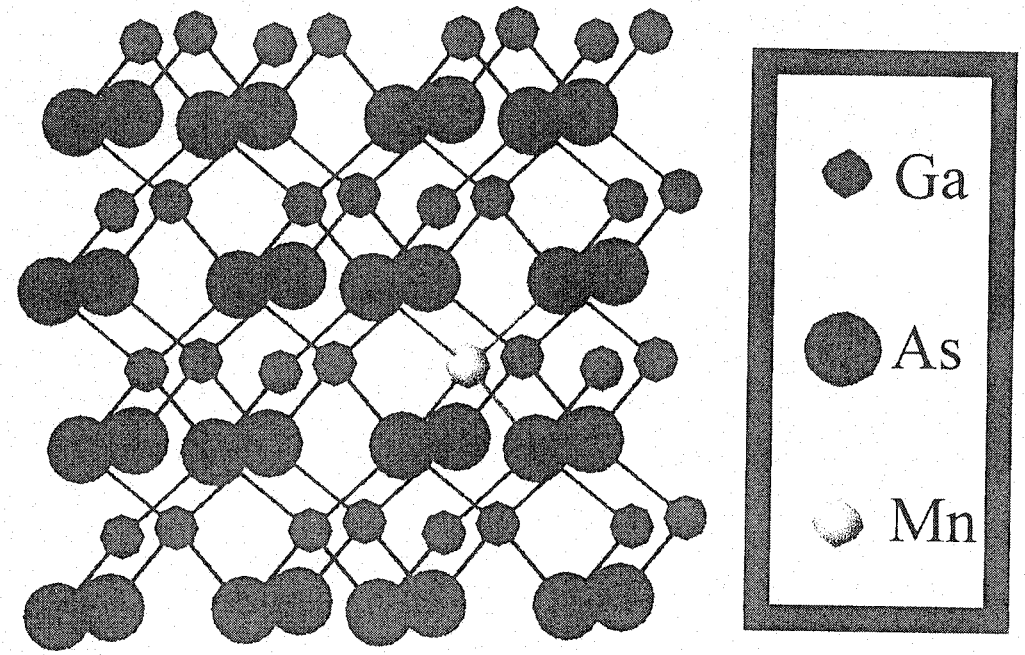
- Can we grow thicker MnAs layers (and do we want to?)
- Where does the ferromagnetism come from?
- Can we increase T_c?
- Smaller is Better. How will quantum confinement affect exchange interactions?

Design of new (and better!) spintronic materials.

MnAs: two crystalline phases



NiAs-type



Zincblende (Ga,Mn)As

1) Bulk MnAs has NiAs-type structure

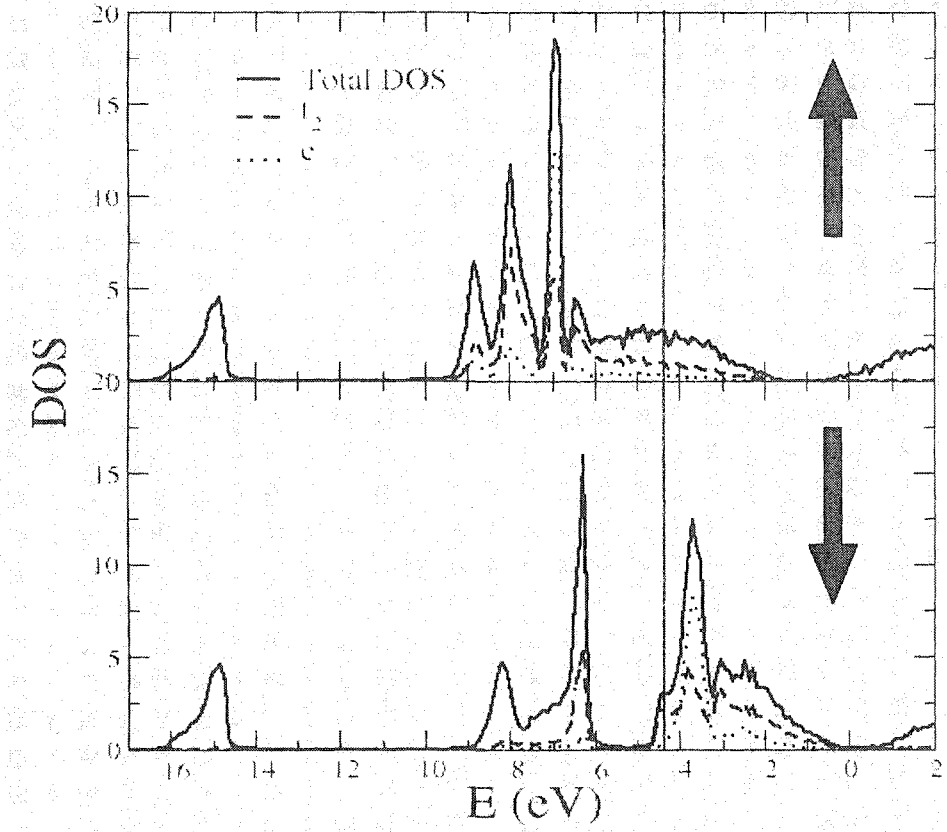
2) ZB MnAs can be MBE-grown up to 1 monolayer

3) ZB MnAs important to understand the Mn-Mn exchange coupling in (Ga,Mn)As

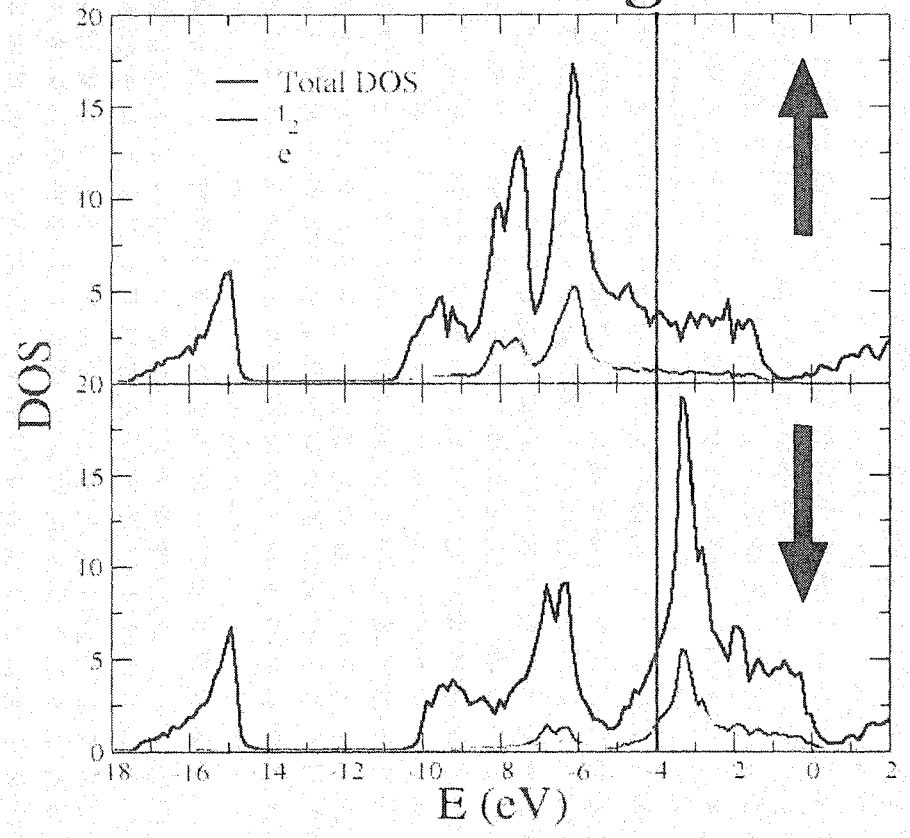
4) Experimentally (Ga,Mn)As **Mn < 7%**

MnAs: ZB vs Hexagonal

LDOS Zincblende

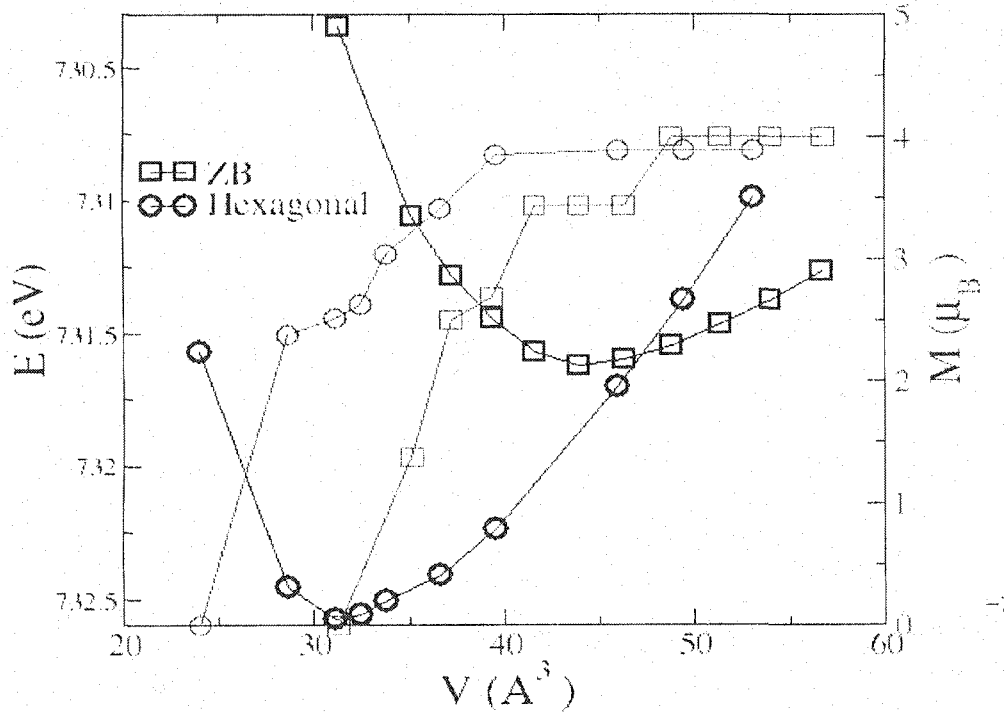


LDOS Hexagonal



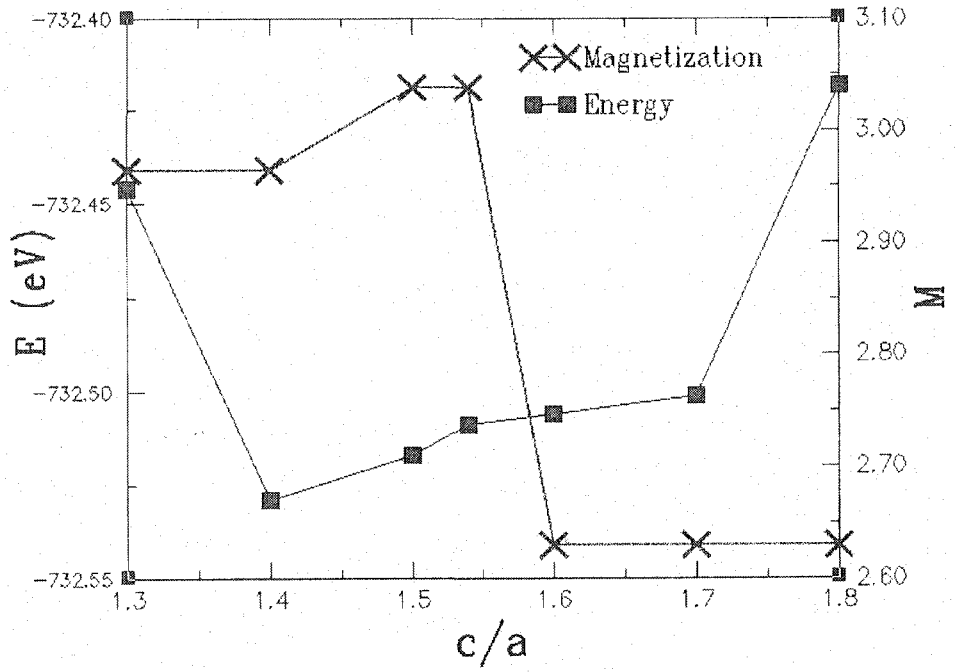
- In the minority band of ZB MnAs the Fermi Energy cuts through a dispersionless d-band. For large lattice spacing it is **Half Metallic**

MnAs: ZB vs Hexagonal



- NiAs-type is more stable with smaller unit cell volume
- Crossover volume for large stress

- NiAs-type MnAs can accommodate large distortions
- **ZB MnAs difficult to stabilize**



Mulliken Analysis for ZB MnAs

Mülliken Population analysis confirms the **antiferromagnetic coupling** between Mn-d and As-p states in MnAs:

$$n(\mathrm{Mn-d}\uparrow) - n(\mathrm{Mn-d}\downarrow) = 3.787$$

$$n(\mathrm{As-p}\uparrow) - n(\mathrm{As-p}\downarrow) \equiv -0.285$$

Conclude - FM is mediated by As-p based holes

MnAs: Conclusion

- ZB MnAs presents half-metal behavior and large spin polarization: ideal conditions for spintronics applications

but

- NiAs-type is more stable with smaller unit cell volume. It can also accommodate large distortions

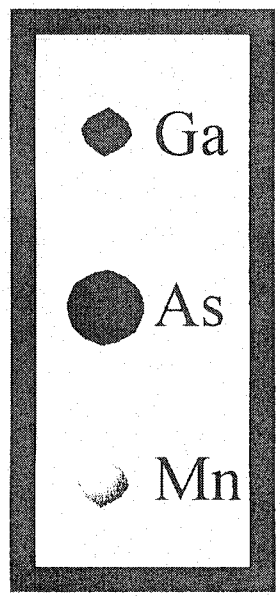
- band spin split and Mulliken population analy...

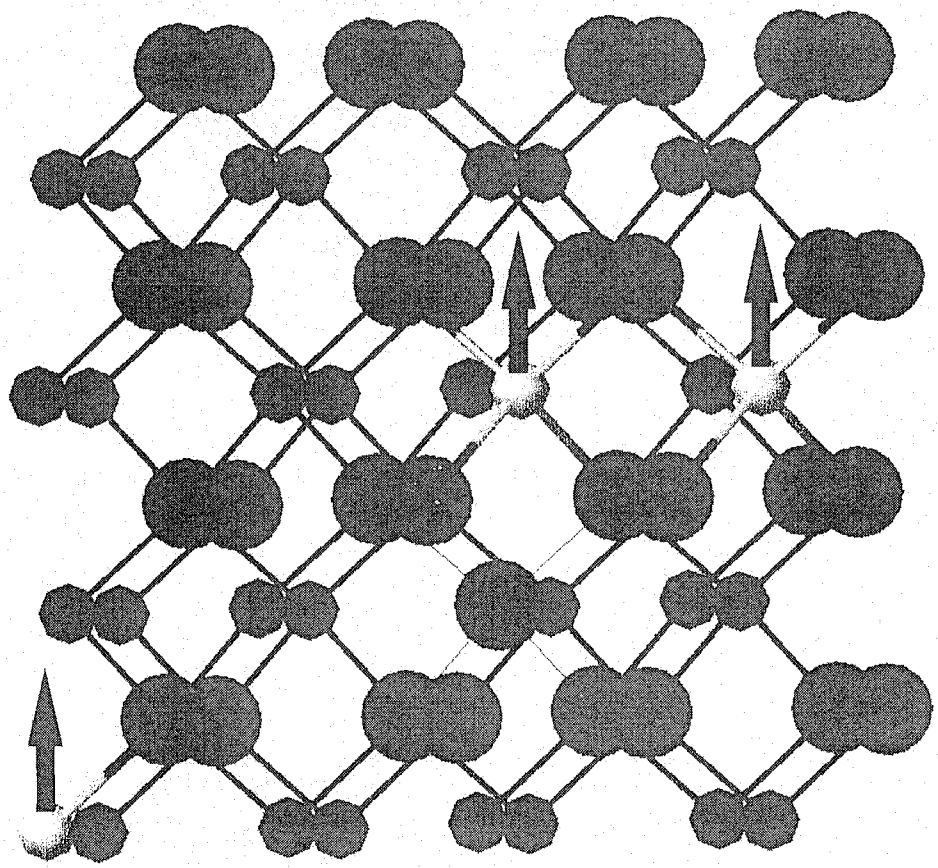
p-d coupling is
ANTIFERROMAGNETIC
and drives the ferromagnetism

(Ga,Mn)As

- Grown by low temperature MBE, with random or digital arrangement of Mn ions.
- Inclusion of As antisites is unavoidable
- Study effect of As antisites on magnetic properties. Each As antisite is a double donor, so for a Mn density twice as large as the As antisite density compensation is expected
- Study effect of Mn arrangement (random versus DFHs).

(Ga,Mn)As





=FM

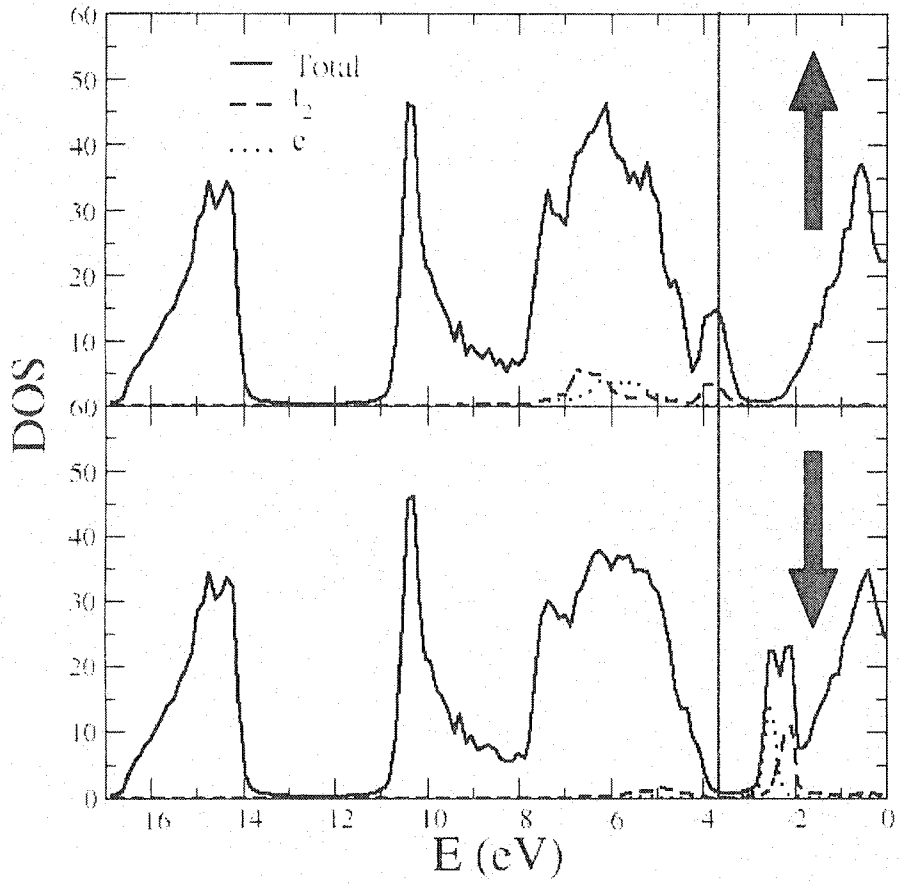
=AF

1) Effects of <u>As antisites</u> on the ferromagnetism

exp: [Mn] > ρ

2) Effects of the Mn distribution on the ferromagnetism

GaAs:Mn Local DOS



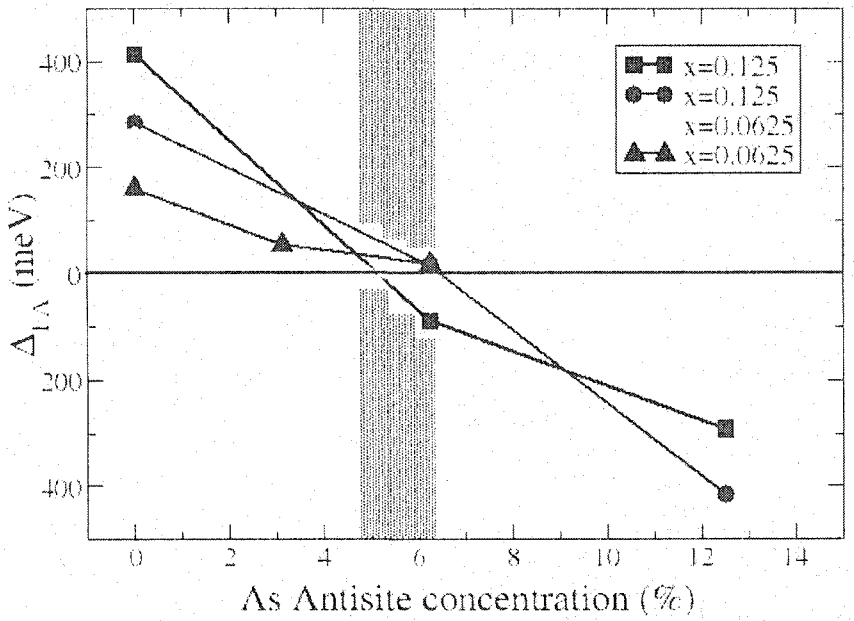
32 atom unit cell with 1 Mn impurity

- Large spin-splitting of Mn-d orbitals
- The Fermi energy cuts through the Mn-d impurity band in the majority spin band
- Almost no-occupation of the Mn-d orbitals in the minority band
- Mn impurity band strongly hybridized with the As-p orbitals of the nearest neighbors

(Ga,Mn)As and As antisites

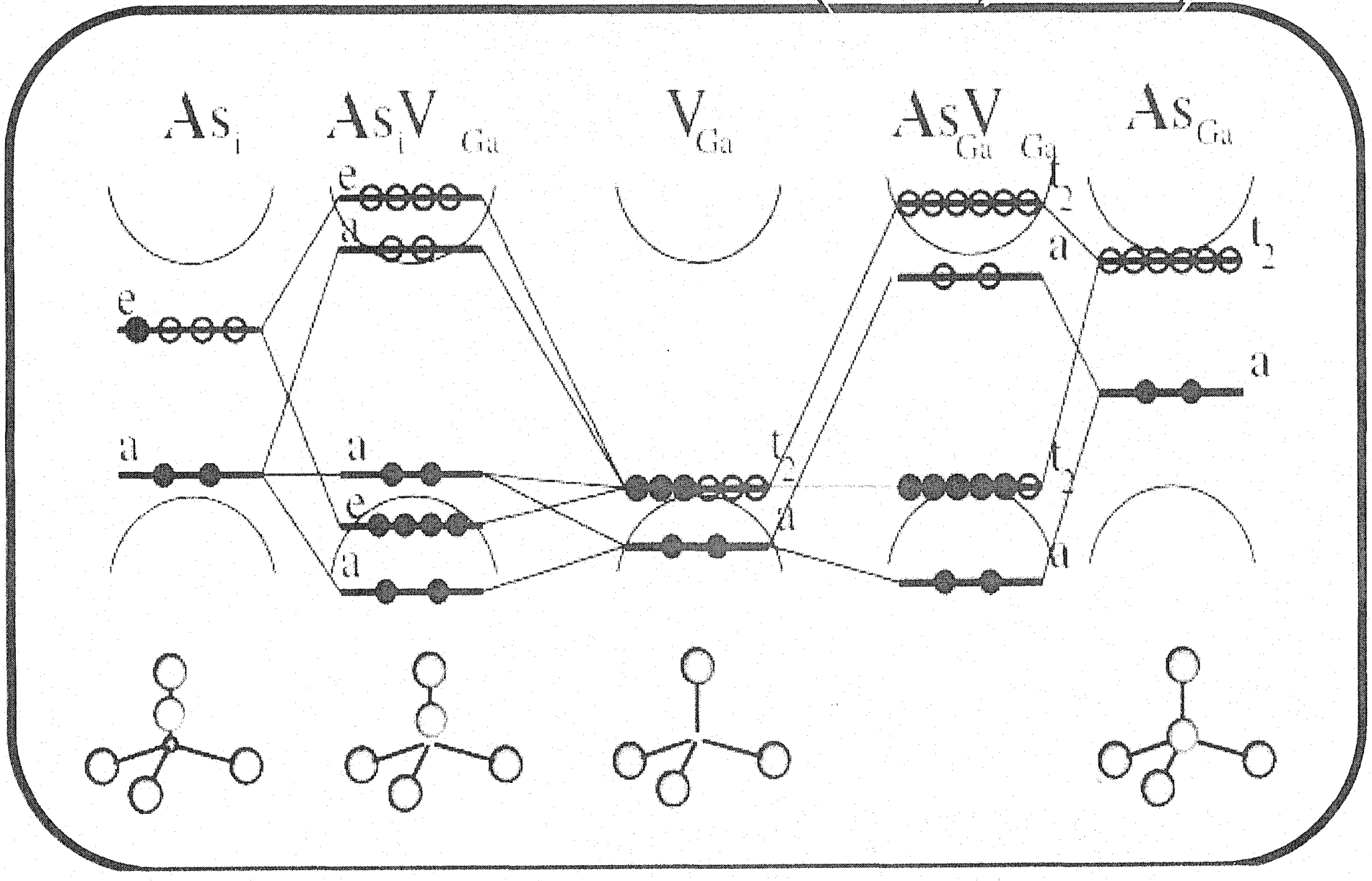
Do As antisites weaken the ferromagnetism in (Ga,Mn)As? We consider the energy split Δ between the ferromagnetic and antiferromagnetic alignment of Mn ions in a large GaAs cell

$$\Delta_{FA} = E_{FM} - E_{AF}$$



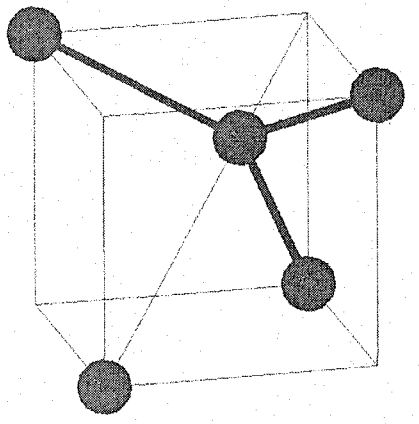
- No As antisites = strong FM order
- Presence of As antisites weakens FM alignment
- Picture of Zener exchange model not strictly valid since ferromagnetic order at compensation
- Also short range AF contribution to ferromagnetism

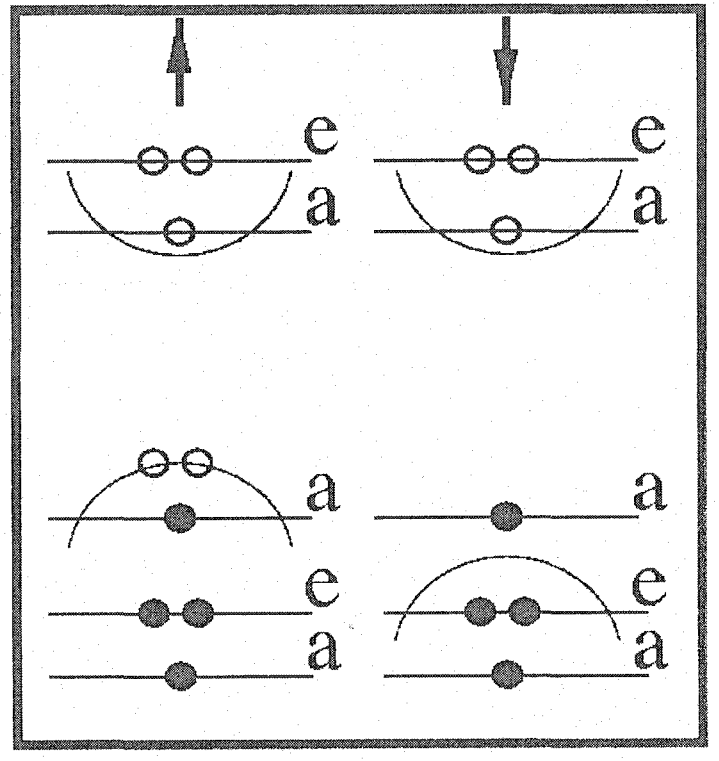
Other defects in (Ga,Mn)As



As interstitial/Ga-vacancy pair

- **No suppression** of the FM coupling $\Delta_{AF} \cong 120\,\text{meV}$
- Polarization similar to the defect-free case $P_{\text{Mn}} = 0.723$
- No extra-carrier
- Metastable-state from As antisite





The formation of this complex from As antisite strongly enhances the ferromagnetic order of (Ga,Mn)As. This metastable configuration can be induced optically

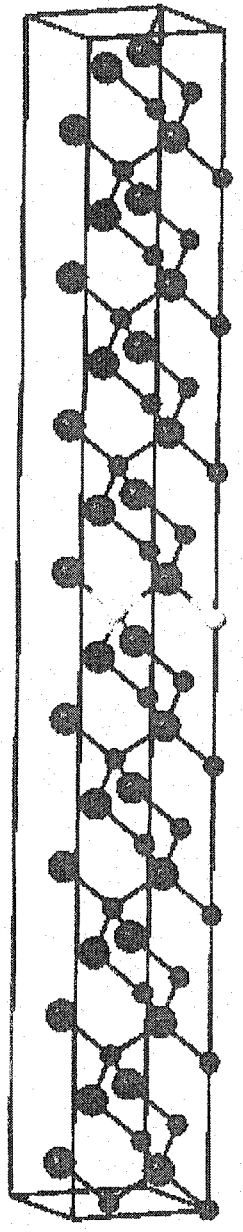
(Ga,Mn)As Predictions

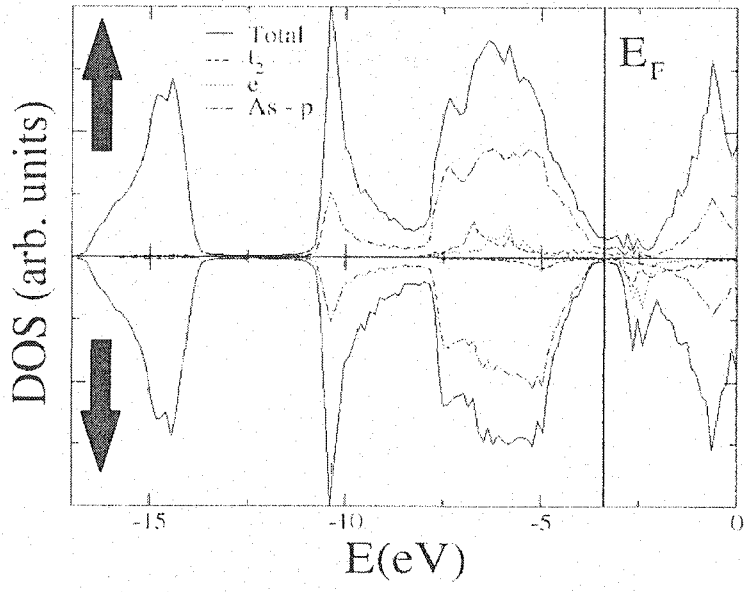
- Conversion of As antisites into As interstitial - Ga vacancy pairs will strongly enhance the ferromagnetism.

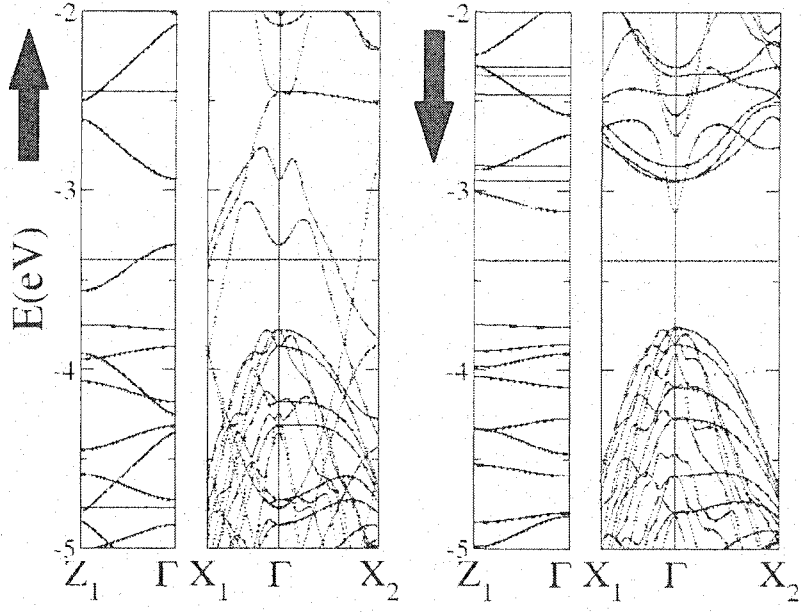
- Such a conversion can be achieved by photoexcitation [Scheffler et al.]

- PHOTOEXCITATION will increase the ferromagnetic Curie temperature in (Ga,Mn)As.

Digital Magnetic Structures





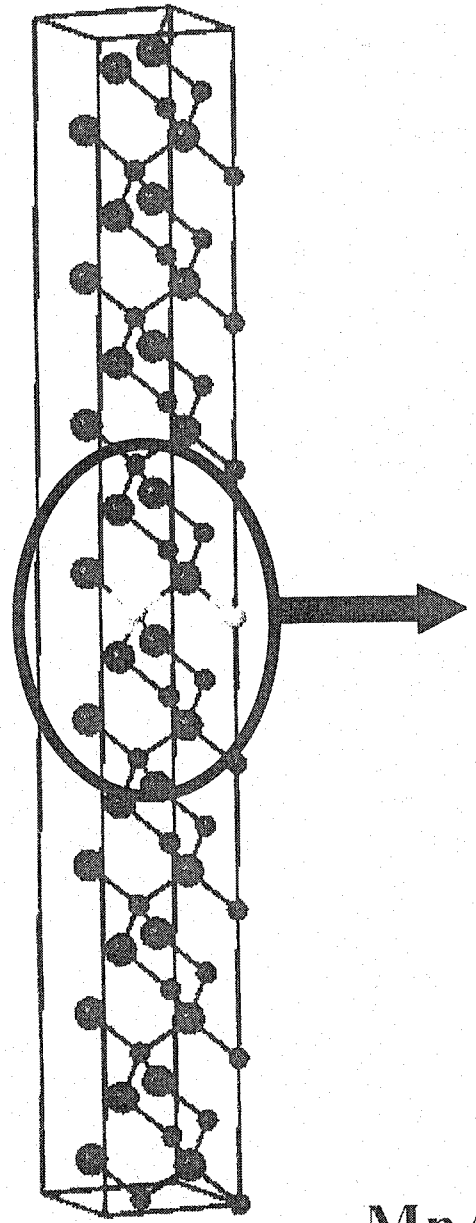


Half-metal

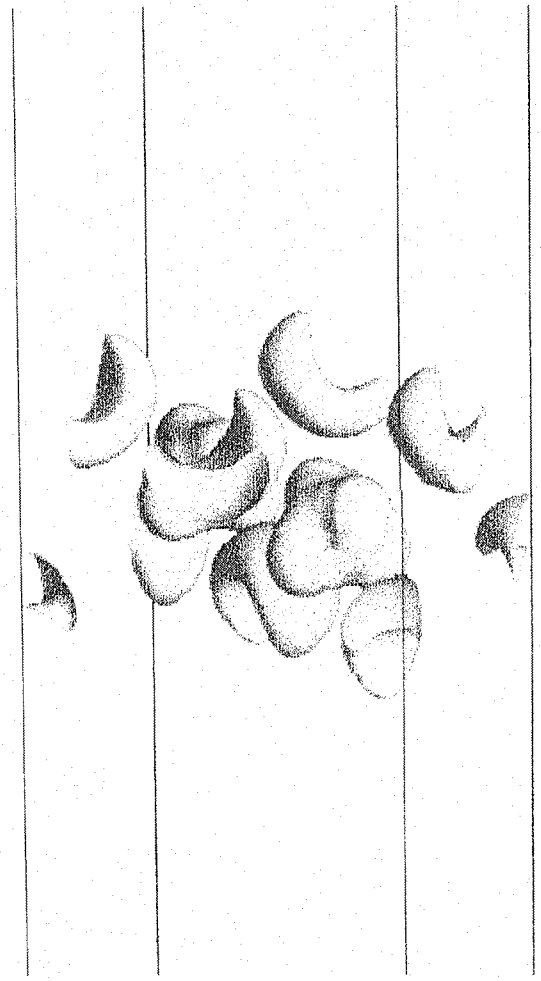
The DOS is similar to the random alloy but small at the Fermi energy

Large dispersion parallel to MnAs plane

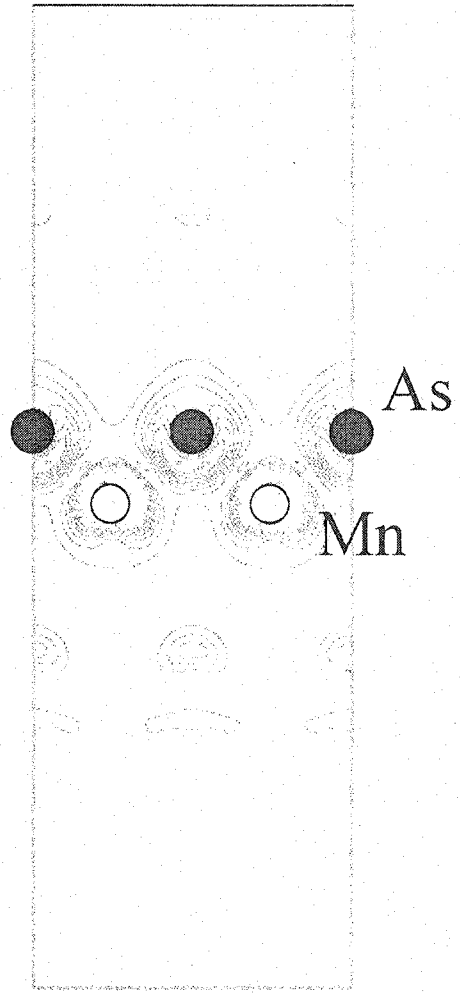
Small dispersion perpendicular to MnAs plane



Isosurface



Contour plot

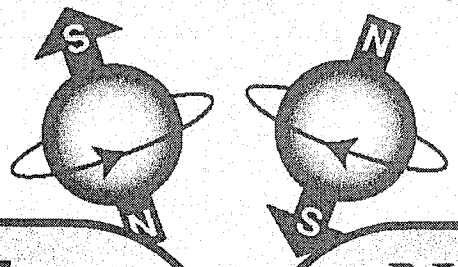


MnAs monolayers embedded into GaAs behave like two-dimensional half-metals

(Ga,Mn)As Conclusion

- The atomic configuration of Mn in GaAs is compatible with both d^5 and d^6 electron densities
- The Mn-d band is **ANTIFERROMAGNETICALLY** coupled with the As-p band
- In the absence of As antisites (Ga,Mn)As is found to be ferromagnetic
- The arrangement of the Mn ions influences the strength of the ferromagnetic ordering
- As antisites weaken the ferromagnetism and a transition to an antiferromagnetic alignment is possible
- The positions of the antisites also affect the strength of the exchange interactions.

Future work



New Materials

Mn-doped GaN - stronger p-d hybridization

Mn-doped ZnO - ferromagnetic and piezoelectric!?

New Techniques

Spin-orbit coupling versus p-d hybridization

Non-collinear magnetism