Mn in GaAs: from a single impurity to ferromagnetic layers

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Outline

✓ Introduction
✓ Single impurities
✓ Symmetry breaking
✓ Coupled impurities
✓ Delta doping layers
Mn-Doping Atoms
Electronic Structure

**Magnetic Doping:** A part of the atoms in the crystal is replaced by magnetic transition metal impurities.

- **Ga-atom GaAs:**
  - 4sp 4sp 4sp 4sp
  - 3d↑↓ 3d↑↓ 3d↑↓ 3d↑↓ 3d↑↓

- **Mn-atom GaAs:**
  - 4sp 4sp 4sp
  - 3d↑ 3d↑ 3d↑ 3d↑ 3d↑

**p-d Interaction:** Results in anti-ferromagnetic alignment.

**Mn on Ga-site in GaAs:**

- (3d⁵+h)
- Mn
- 3d⁶
- h↓
Electronic Structure

Mn-atom in GaAs

3d↑ 3d↑ 3d↑ 3d↑ 3d↑

Impurity band resonant with the valence band

3d-states split by cubic crystal symmetry

\[ \Gamma_{15} \]

Triplet

\[ T_2 \]

Doublet

\[ \Gamma_{12} \]

The p-d coupling is strongest for d-states with \( \Gamma_{15} \) symmetry

Anti-bonding (bound acceptor state)

Valence band states GaAs

4sp 4sp 4sp 4sp

States with \( \Gamma_{15} \) symmetry split due to SO interaction

113 meV ground state populated at \( T=0 \) when in neutral condition

Tang en Flatté
PRL 92, 047201 (2004)
Assessment at the Atomic Scale by Cross-Sectional STM

9 nm * 8 nm

15 nm * 30 nm

InAs self-assembled quantum dot in GaAs

Two Si impurities in GaAs

110-surface cleaved III/V sample

UHV (10^{-11} torr)
Impurity Imaging

Iso-electronic impurities

InGaAs-wetting layer

30 nm * 30 nm

Counting demonstrated up to 40%

Charged impurities

Si:InP

100 nm * 100 nm

sharp (surface Si-atoms)
diffuse (sub-surface Si-ions)
Scanning Tunneling Microscopy on Semiconductors
Scanning Tunneling Microscopy on Semiconductors

Positive sample voltage

(empty states)

Negative sample voltage

(filled states)

Depletion, accumulation, inversion
$A^-$ and $A^0$ Charge States of Mn

**Ionized** Mn $A^-$

$(V=-1.1 \, \text{V})$

**Neutral** Mn $A^0$:

$(V=+1.1 \, \text{V})$

Contrast depends on depth of Mn-atom below cleaved surface.

$3 \times 10^{18}/\text{cm}^3$

Grown by J. De Boeck et al., IMEC, Belgium

Same position is imaged at both voltages.
Manipulation of the Charge State by STM tip

**Ionized Mn acceptor**

- $E_c$
- $E_F$
- $E_V$
- $I_{TUNNEL}$
- Tip
- $p$-type sample

**Neutral Mn acceptor**

- $E_c$
- $E_F$
- $E_V$
- $I_{TUNNEL}$
- Tip
- $p$-type sample

Negative sample voltage

Positive sample voltage
$A^-$ and $A^0$ Charge States of Mn

**Ionized** $\text{Mn } A^-\ (V=-0.9\ \text{V})$

**Neutral** $\text{Mn } A^0:(\text{ion } + \text{ hole})\ (V=+0.7\ \text{V})$

Contrast is due to Coulomb field

Tunneling to the bound hole
($\text{Mn in } \sim 3^{rd}\ \text{sublayer}$)
Spectroscopic Signature of Mn

Current map at +1.2 V

-0.02 0.00 0.02 0.04

Current (nA)

200x200 points

E_v E_f

 Binding energy Mn 113 meV

-0.8 -0.4 0.0 0.4 0.8 1.2 1.6

Bias (V)

~100 meV

Mn

200 * 200 I(V)-curves taken around impurity

Mn^0

E_c

E_v

p-type sample

tip
Contrast Mechanism

**Ionized acceptor**

`p-type sample`

Around charged acceptor bands bend upwards this increases current (height STM tip)

**Screened acceptor**

`p-type sample`

Around screened acceptor weak band bending. Due to impurity LDOS increase of current (height STM tip)
Modeling of Impurity States in Semiconductors
Effective Mass Donor

\[ \psi (1S_{1/2}) = R_0(r)Y_{0,0}(\theta, \varphi) \]

http://www.orbitals.com/orb/index.html

\[
\frac{\hbar^2 k}{2m^*} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi_{n,l,m} + \frac{1}{\varepsilon_0 \varepsilon_r r} \psi_{n,l,m} = \varepsilon_{n,l,m} \psi_{n,l,m}
\]

\[ \varepsilon_e = \frac{\hbar^2}{2m^*} (k_x^2 + k_y^2 + k_z^2) \]
Luttinger Hamiltonian

\[ H_{\text{Lut}}(k_x, k_y, k_z)\psi_i + V(r)\psi_i = \varepsilon_i\psi_i \]

**Luttinger Hamiltonian**

\[
H_{\text{Lut}}(k_x, k_y, k_z) = \frac{\hbar^2}{2m_o} \begin{bmatrix}
H_{hh} & c & -b & 0 \\
c^+ & H_{lh} & 0 & b \\
-b^+ & 0 & H_{lh} & c \\
0 & b^+ & c^+ & H_{hh}
\end{bmatrix}
\]

- \( H_{hh} = \left(k_x^2 + k_y^2\right)(\gamma_1 + \gamma_2) + k_z^2(\gamma_1 - 2\gamma_2) \)
- \( H_{lh} = \left(k_x^2 + k_y^2\right)(\gamma_1 - \gamma_2) + k_z^2(\gamma_1 + 2\gamma_2) \)
- \( b = 2\sqrt{3}\gamma_3(k_x - ik_y)k_z \)
- \( c = -\sqrt{3}\left[\gamma_2(k_x^2 - k_y^2) - 2i\gamma_3 k_x k_y\right] \)

\( \psi_i = \begin{pmatrix}
\varphi_1 \cdot \left|\frac{3}{2}, +\frac{3}{2}\right> \\
\varphi_2 \cdot \left|\frac{3}{2}, +\frac{1}{2}\right> \\
\varphi_3 \cdot \left|\frac{3}{2}, -\frac{1}{2}\right> \\
\varphi_4 \cdot \left|\frac{3}{2}, -\frac{3}{2}\right>
\end{pmatrix} \)

**4-vector representation based on spin-projection**

**Spin-orbit coupling mixes the light and heavy hole bands in confined states**

\( \gamma_1, \gamma_2 \) and \( \gamma_3 \) Luttinger parameters

\( \gamma_2 = \gamma_3 \) isotropic dispersion
Effective Mass Acceptor

\[ H_{Lut} \psi_{n,l,m} + \frac{1}{\epsilon_o \epsilon_r r} \psi_{n,l,m} = \epsilon_{n,l,m} \psi_{n,l,m} \]

**Isotropic dispersion**

**Ground state components**

\[ \psi_{3/2} = R_0 \begin{pmatrix} Y_{0,0} \\ 0 \\ 0 \end{pmatrix} + \beta \cdot R_2 \begin{pmatrix} \sqrt{2}Y_{2,0} \\ -2Y_{2,1} \\ 2Y_{2,2} \end{pmatrix} \]

\[ \psi_{1/2} = R_0 \begin{pmatrix} 0 \\ Y_{0,0} \\ 0 \end{pmatrix} + \beta \cdot R_2 \begin{pmatrix} 2Y_{2,-1} \\ -\sqrt{2}Y_{2,0} \\ 2Y_{2,2} \end{pmatrix} \]

\[ Y_{lm} \text{ spherical harmonics} \]

\[ R_l \text{ radial distribution} \]

**and their Kramers conjugates** \[ \psi_{3/2} \] and \[ \psi_{3/2} \]

Bir, Pikus in "Symmetry and strain-induced effects in semiconductors"

**the ground state has a mixed s + d character**
Effective Mass Acceptor

\[ H_{L\mu} \psi_{n,l,m} + \frac{1}{\varepsilon_o \varepsilon_r r} \psi_{n,l,m} = \varepsilon_{n,l,m} \psi_{n,l,m} \]

\[ \psi_{3/2}^{3/2} = R_0 \begin{pmatrix} Y_{0,0} \\ 0 \\ 0 \\ 0 \end{pmatrix} + \beta T_2 \cdot R_2 \begin{pmatrix} 0 \\ 2Y_{2,1} \\ Y_{2,2} - Y_{2,-2} \\ 0 \end{pmatrix} + \beta E \cdot R_2 \begin{pmatrix} \sqrt{2}Y_{2,0} \\ 0 \\ Y_{2,2} + Y_{2,-2} \\ 0 \end{pmatrix} \]

Cubic symmetry of crystal selects d-components

\( T_2 \)

\( E \)
Effect of Crystal Anisotropy

η = 1 corresponds with isotropic dispersion

η = 0 corresponds with a pure $T_2$ symmetry

$\eta = \frac{\beta_E}{\beta_{T_2}}$

Cut at 6 monolayer's trough impurity state along a 110 plane

Effective mass model

110 plane

8 nm * 8 nm
Electronic Structure of Mn-acceptor

Experiment

Grown by J. De Boeck et al., IMEC, Belgium

Yakunin et al. PRL 92, 216806 (2004)

Tight Binding

J.-M. Tang M. Flatté, Iowa, US

Effective mass model
**Experiment**

*Mn in ~ 4\textsuperscript{th} sublayer*

**Effective mass model**

\[
\eta = \beta E / \beta T_2 = 0
\]

**Tight-binding model**

*(M. Flatté, University of Iowa)*

\[
\eta = \beta E / \beta T_2 \approx 0
\]

**Real Space**

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
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**Fourier Space**

<table>
<thead>
<tr>
<th>(c)</th>
<th>(d)</th>
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<table>
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<tr>
<th>(e)</th>
<th>(f)</th>
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</table>

*12 nm *12 nm  0.8 nm\(^{-1}\) * 0.8 nm\(^{-1}\)

Yakunin et al. PRL 92, 216806 (2004)
Improved Effective Mass Model

Inclusion of anisotropy ($\gamma_2 \neq \gamma_3$) in the dispersion

A. Monakhov & N. Averkiev, Ioffe Institute
Symmetry Breaking
by crystal symmetry
Broken Symmetry

Mn:GaAs

Yakunin et al. PRL 92, 216806 (2004)

Zn:GaAs

110-surface

1-10-surface

Mathieu et al. PRL 94, 026407 (2005)
Inversion Asymmetry

Figure: S. Loth, Goettingen

Mathieu et al.
PRL 94, 026407 (2005)
Inversion Asymmetry

\[
\begin{align*}
&\text{110-surface} \\
&\text{1-10-surface}
\end{align*}
\]

\[\text{Fig. 1(a)} : 19.5\text{nm} \times 19.5\text{nm} \quad U_{\text{zmp}} = +1.7V\]

\[\text{Fig. 1(b)} : 13.5\text{nm} \times 13.5\text{nm} \quad U_{\text{zmp}} = +1.7V\]

Figure: S. Loth, Goettingen

\[\text{Ga} \quad \text{As} \quad \text{impurity}\]
Symmetry Breaking
by strain
Stacked Quantum Dots

55 nm * 55 nm

current image

Grown by M. Hopkinson, Sheffield (UK)

Bruls et al. APL 82, 3758 (2003)
Lattice Constant Profile

InAs/GaAs dot

Growth direction

Grown by K. Pierz, PTB-Braunschweig, Germany

22 nm * 22 nm
Strained Mn impurity

Grown by J. De Boeck et al., IMEC, Belgium
Strained Mn impurity

Unstrained

60 nm * 60 nm

Mn$_1$

m$_1$

m$_2$

Mn$_2$

60 nm * 60 nm

[001]

[1-10]

Distance along [1-10] direction, nm

Measured height, nm

m$_1$

m$_2$

GaAs host

QD (InAs)

Mn$_1$

Mn$_2$

-4 -2 0 2 4

0,00,10,20,30
Strained Mn impurity

Unstrained

Strained

EMA

TBM

[001] [110]
Symmetry Breaking

Shallow Impurities
Broken Symmetry Shallow Impurities

Co-doped GaAs:Be,Mn

30 nm * 30 nm
Shallow & Deep Acceptor states

C:GaAs  
$E_B = 26$ meV  
Reusch et al.  
Univ. Of Gottingen

Be:GaAs  
$E_B = 28$ meV  
Mahieu et al.  
PRL 94, 026407 (2005)

Zn:GaAs  
$E_B = 31$ meV  
Zheng et al.  
APL 64, 1836 (1994)

Cd:GaAs  
$E_B = 35$ meV  
vан der Wielen et al.  
PRB 63, 125336 (2001)

Mn  
113 meV

Co  
150 meV

C  
26 meV  
Be  
28 meV  
Zn  
30 meV  
Cd  
35 meV

Valence band

Shallow & Deep Acceptor states

Mn:GaAs  
$E_B = 113$ meV  
Yakunin et al.  
PRL 92, 216806 (2004)
Interaction with Surface

Broken symmetry

Shallow

Deep

Effective localization radius of a neutral acceptor

\[ a_0 = \sqrt{\frac{\hbar^2}{2m^*E_b}} \]
Spin-orbit Interaction
Spin-orbit Interaction

Acceptor with $E_b = 113$ meV at 6 monolayers below surface

$\text{Spin-orbit Interaction}$

$\text{Split-off Energy (eV)}$

$\text{N}^7 - \text{P}^{15} - \text{As}^{33} - \text{Sb}^{51}$

$\text{Al}^{13}, \text{Ga}^{31}, \text{In}^{49}$

$\text{Cd}, \text{Zn}, \text{Mn}$

$8 \text{ nm} \times 8 \text{ nm}$
Spatial Structure of Zn in GaP(110)

*Bulk GaP intentionally doped with Zn (~2x10$^{18}$ cm$^{-3}$)*
Anisotropy & Spin-orbit Interaction

η=1 corresponds with isotropic dispersion

η=0 corresponds with a pure T$_2$ symmetry

Acceptor with $E_b = 113$ meV at 6 monolayers below surface

Crystal anisotropy dominates see also Yakunin et al. PRL 92, 216806 (2004)
Missing link

Zn in GaAs
$E_b(Zn) = 30\text{meV}$
$a_0 = 1.8\text{nm}$

Zn in GaP
$E_b(Zn) = 70\text{meV}$
$a_0 = \sim 0.6\text{nm}$

Mn in GaAs
$E_b(Mn) = 110\text{meV}$
$a_0 = 1\text{nm}$
Symmetry of Impurities

Mn in GaAs

Zn in GaP

Zn in GaAs

$O_8$

$T_d$

Effective mass
Tight binding
Ab-initio modelling

Yakunin et al. PRL 92, 216806 (2004)

S. Loth et al. PRL 96, 066403 (2005)
Mathieu et al. PRL 94, 026407 (2005)
Pairs of magnetic impurities
Mn-delta Doped Layers

Intentional Mn concentration
\[ N = 3 \times 10^{13} \text{ cm}^{-2} \]

Grown by J. De Boeck et al., IMEC, Belgium
Interacting Impurities

5th sub-surface layer

Separation 0.8 nm

6 nm * 6 nm

Separation 1.38 nm

12 nm * 10 nm

A. Yakunin et al. PRL 95, 256402 (2005)

Grown by J. De Boeck et al., IMEC, Belgium
J.-M. Tang M. Flatté
Iowa, US

Experimental

0.8 nm  1.4 nm

TBM Simulation

0.8 nm  1.4 nm

6 nm * 6 nm  12 nm * 10 nm

anti-parallel spin

6 nm * 6 nm  12 nm * 10 nm

J.-M. Tang M. Flatté
Iowa, US

A. Yakunin PRL 95, 256402 (2005)
Delta layers
Impurity-Impurity Interaction

Mn-Mn pair (70 nm)

Mn-Mn pair (1.4 nm)

Mn-As$_{Ga}$ pair

140 nm * 140 nm

60 nm * 80 nm

12 nm * 10 nm
Directional Dependence Mn-overlap

Calculated overlap

\[ d \text{-character dominates far from impurity} \]

\[ \text{EMA [001]} \]
\[ \text{EMA [011]} \]
\[ \text{EMA [111]} \]

\[ r \text{ (nm)} \]

\[ 23\% \]
\[ 34\% \]

\[ \text{EMA [001]} \]
\[ \text{EMA [011]} \]
\[ \text{EMA [111]} \]
Directional Dependence Mn-overlap

Calculated overlap

$TBM [001]$

$TBM [011]$

$TBM [111]$

$d$-character dominates far from impurity
Directional Dependence Mn-overlap

Calculated overlap vs Mn-Mn separation r (nm)

- TBM [001]
- TBM [011]
- TBM [111]
- EMA [001]
- EMA [011]
- EMA [111]

- d-character dominates far from impurity

- 23% for [001]
- 43% for [011]
- 34% for [111]
- 34% for EMA [001]
- 56% for EMA [111]
Directional Dependence Mn-overlap

Bohr radius 0.9 nm

d-character dominates far from impurity
Directional Dependence Mn-overlap

- Normalized Overlap, a.u.
- Direction: [111] → [011]
- Separation (nm): 0.5, 1, 2, 3, 4, 5
- Bohr radius: 0.9 nm
- d-character dominates far from impurity
Overlap Expectation on [i,j,k] Plane

<table>
<thead>
<tr>
<th>$r$ (Å)</th>
<th>$N$</th>
<th>$\Omega^{(001)}$</th>
<th>$\Omega^{(110)}$</th>
<th>$\Omega^{(111)}$</th>
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<tbody>
<tr>
<td>5</td>
<td>0.654</td>
<td>0.986</td>
<td>0.990</td>
<td>0.992</td>
</tr>
<tr>
<td>10</td>
<td>0.438</td>
<td>0.963</td>
<td>0.976</td>
<td>0.980</td>
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<tr>
<td>20</td>
<td>0.216</td>
<td>0.912</td>
<td>0.941</td>
<td>0.952</td>
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<tr>
<td>30</td>
<td>0.112</td>
<td>0.870</td>
<td>0.913</td>
<td>0.929</td>
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<tr>
<td>40</td>
<td>0.060</td>
<td>0.837</td>
<td>0.892</td>
<td>0.912</td>
</tr>
<tr>
<td>50</td>
<td>0.033</td>
<td>0.812</td>
<td>0.875</td>
<td>0.898</td>
</tr>
</tbody>
</table>

4*10^{14} \text{ cm}^{-2} (100\%)

4*10^{12} \text{ cm}^{-2} (1\%)

Highest $T_{\text{curie}}$ on the [111] doping plane?

[001] doping plane

[011] doping plane

[111] doping plane
High Concentration Mn Delta Layers

Ga$_{0.8}$Mn$_{0.2}$As delta layers ($1 \times 10^{14}$ cm$^{-2}$)

Mn in ionized state

Local bonds
surface Mn

Local Coulomb potential

Grown at PDI, Berlin, Germany

35 nm * 35 nm

-3 V

-2 V

-1.2 V
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