Theory of STM spectroscopy of Mn impurities on GaAs surfaces and subsurfaces

VETENSKAPSRÅDET
SWEDISH RESEARCH COUNCIL

Carlo M. Canali
T. Olof Strandberg
Linnaeus University, Kalmar, Sweden

Allan H. MacDonald
University of Texas at Austin

M. Reza Mahani

Fhokrul Islam

Linnaeus University, Kalmar

Paul M. Koenraad
Technical University of Eindhoven

Michael E. Flatté
University of Iowa

Cyrus Hirjibehedin
University College, London

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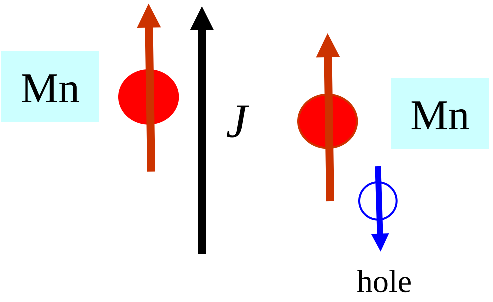
Nanospintronics
Theory & Simulations

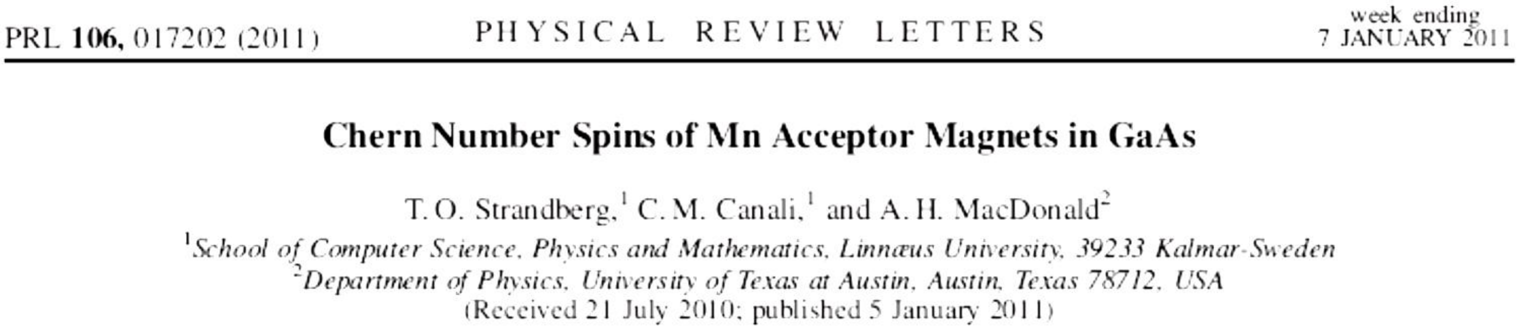
- Mn atoms substituting Ga atoms in GaAs provide both localized ***magnetic moments*** (S= 5/2) and itinerant ***acceptors*** (holes).

Ga: [Ar] $3d^{10}\ 4s^2p^1$

Mn: [Ar] $3\boldsymbol{d}^{\,5}\ 4s^2\boldsymbol{p}^{0}$

- New magnetic entities: **acceptor Mn nanomagnets**
- Can we assign an effective ``giant spin´´ *J* ?
- Orbital vs spin contributions
- Previous studies (ESR): *J* = 1 for Mn in bulk
- What about when Mn is on surface?
- What about when there two or more intereacting Mn?
- Can we derive an effective quantum Hamiltonian for *J*?




PRL 106, 017202 (2011) PHYSICAL REVIEW LETTERS week ending 7 JANUARY 2011

Chern Number Spins of Mn Acceptor Magnets in GaAs

T. O. Strandberg,[1] C. M. Canali,[1] and A. H. MacDonald[2]
[1]*School of Computer Science, Physics and Mathematics, Linnæus University, 39233 Kalmar-Sweden*
[2]*Department of Physics, University of Texas at Austin, Austin, Texas 78712, USA*
(Received 21 July 2010; published 5 January 2011)

Outline

- Motivation -- Review of recent STM experiments

- Theoretical modelling of magnetic impurities in semiconductors -- Mn in GaAs: electronic stucture of acceptor states

- Quantization of magnetic degrees of freedom of ***acceptor magnets***
  → - Chern number spins and spin Hamiltonians
  - Predictions and implications for experiments

- Conclusions and outlook

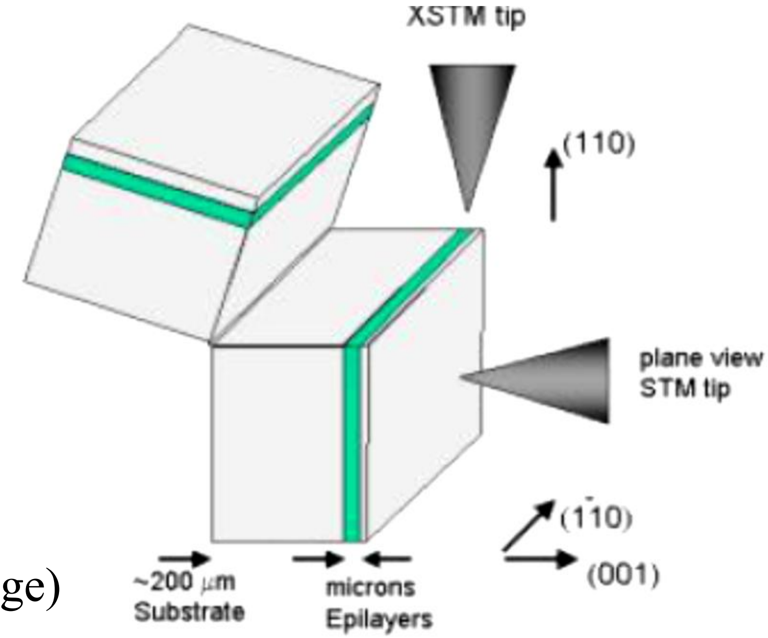
nature materials

REVIEW ARTICLE

PUBLISHED ONLINE: 24 JANUARY 2011 | DOI: 10.1038/NMAT2940

Single dopants in semiconductors

Paul M. Koenraad[1] and Michael E. Flatté[2]

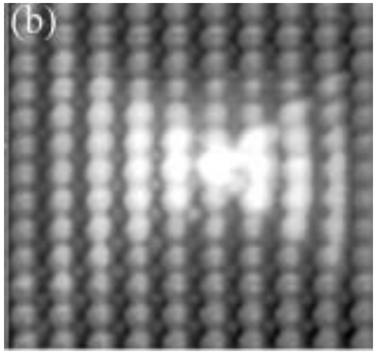


Fundamentals of
cross-sectional
STM (XSTM)
(Weber’s homepage)

”Recently, it has become possible to [….] identify the effects of a solitary dopant […] locally on the fundamental properties of a semiconductor.”

STM experiments on **magnetic** impurities in semiconductors: Mn in GaAs

- Yakunin et al., PRL **92** (2004)
- Yakunin et al., PRL **96** (2005)
- Kitchen et al., Nature **442** (2006)
- Marczinowski et al, PRL **99** (2007)
- Jancu et al., PRL **101**(2008)
- Garleff et al., PRB **78** (2008)
- Kitchen et al., PRB **80** (2009)
- Celebi et al., PRL **104** (2010)
- Garleff et al., PRB **82** (2010)
- Lee et al., Science **330** (2010)



STM image of acceptor wf. for neutral Mn on the (110) GaAs subsurface layer

Possible building blocks of **single-spin** devices in quantum information and nanospintronics

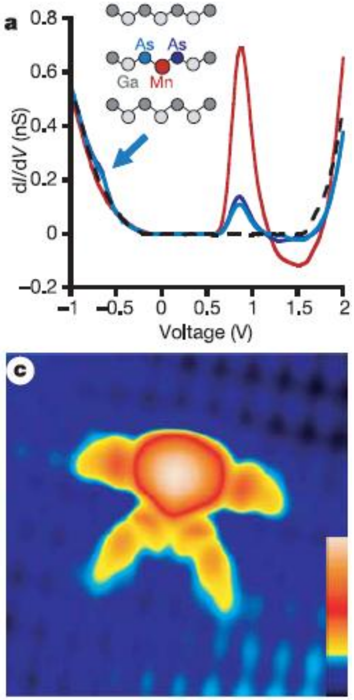
Mn atoms on GaAs (110) surface by STM: novel nanomagnets

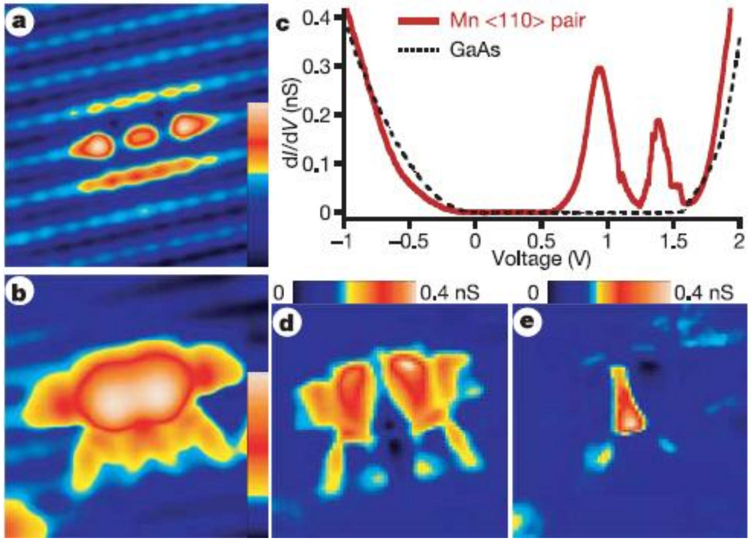
nature Vol 442|27 July 2006|doi:10.1038/nature04971

LETTERS

Atom-by-atom substitution of Mn in GaAs and visualization of their hole-mediated interactions

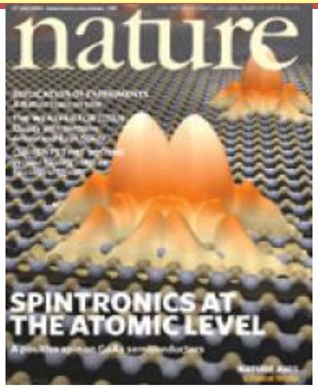
Dale Kitchen[1,2], Anthony Richardella[1,2], Jian-Ming Tang[3], Michael E. Flatté[3] & Ali Yazdani[1]





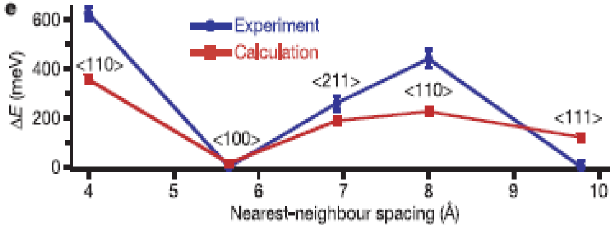
Acceptor levels for Mn pair

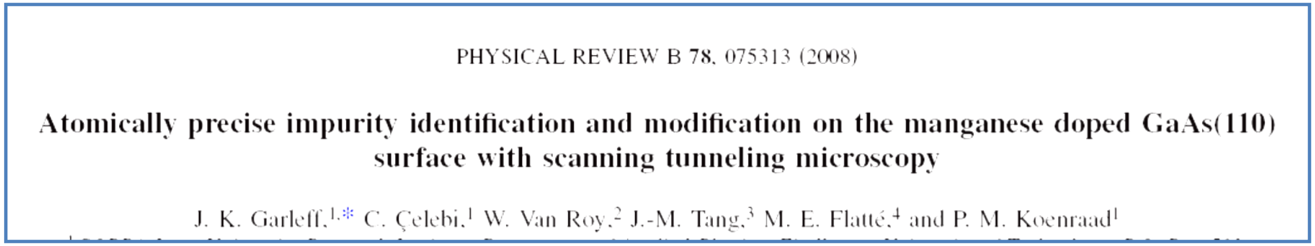
Acceptor level for Mn atom



Mn pair coupled ferromagnetically

- Anisotropic acceptor splitting
- Related to exchange energy ?

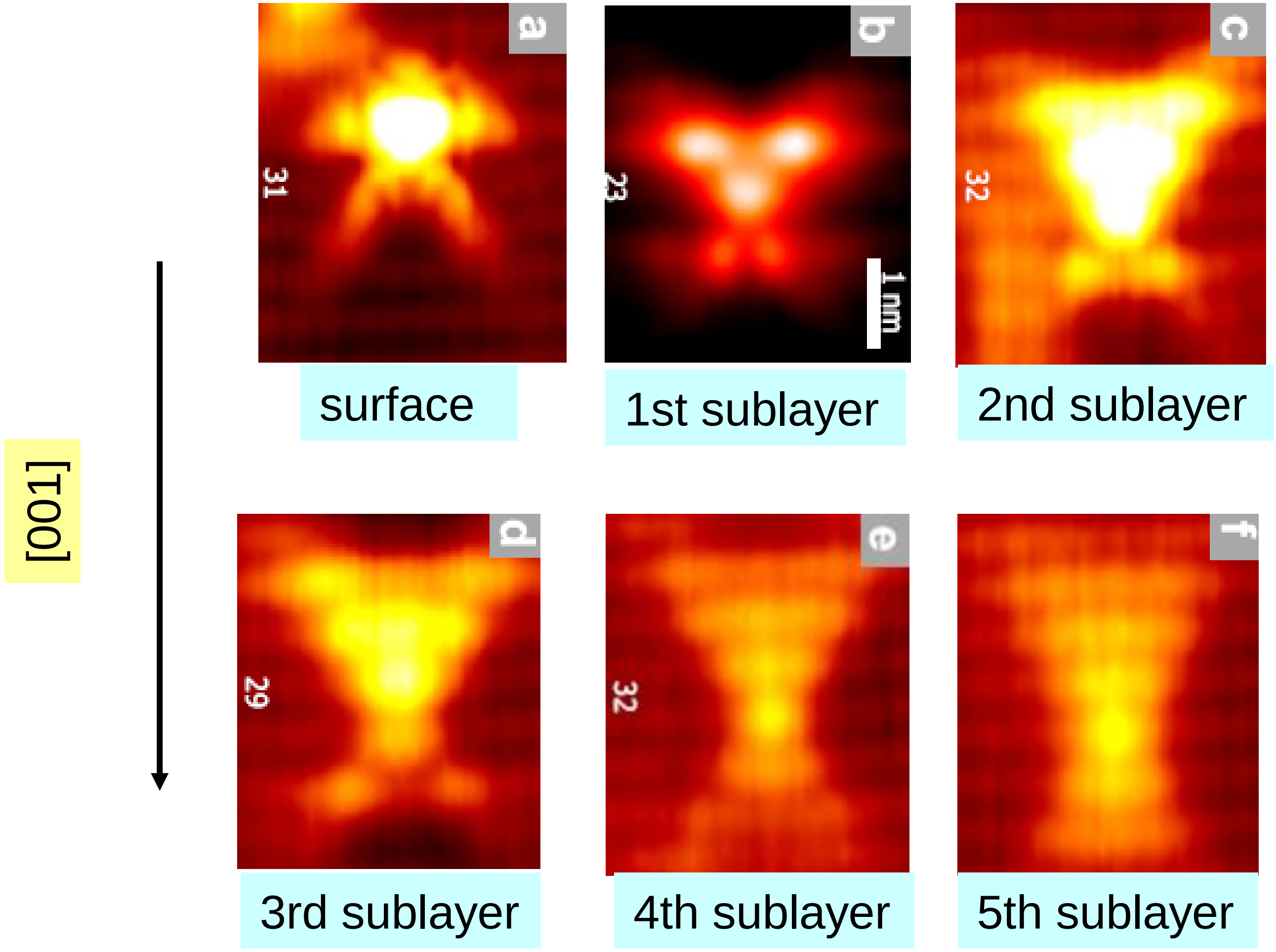




PHYSICAL REVIEW B 78, 075313 (2008)

Atomically precise impurity identification and modification on the manganese doped GaAs(110) surface with scanning tunneling microscopy

J. K. Garleff,[1,*] C. Çelebi,[1] W. Van Roy,[2] J.-M. Tang,[3] M. E. Flatté,[4] and P. M. Koenraad[1]



surface

1st sublayer

2nd sublayer

[001]

3rd sublayer

4th sublayer

5th sublayer

Theory of electronic states of Mn impurities on (110) GaAs surfaces and subsurfaces

T.O. Strandberg, CMC, A.H. MacDonald, 2009-2010

PRB **80**, 024425 (2009)

- 1 Mn in GaAs:
  - Tight-binding model + kinetic exchange
  - Magnetic anisotropy and LDOS

PRB, **81**, 054401 (2010)

- 2 Mn impurities in GaAs:
  - ”interacting” acceptors → FM double-exchange

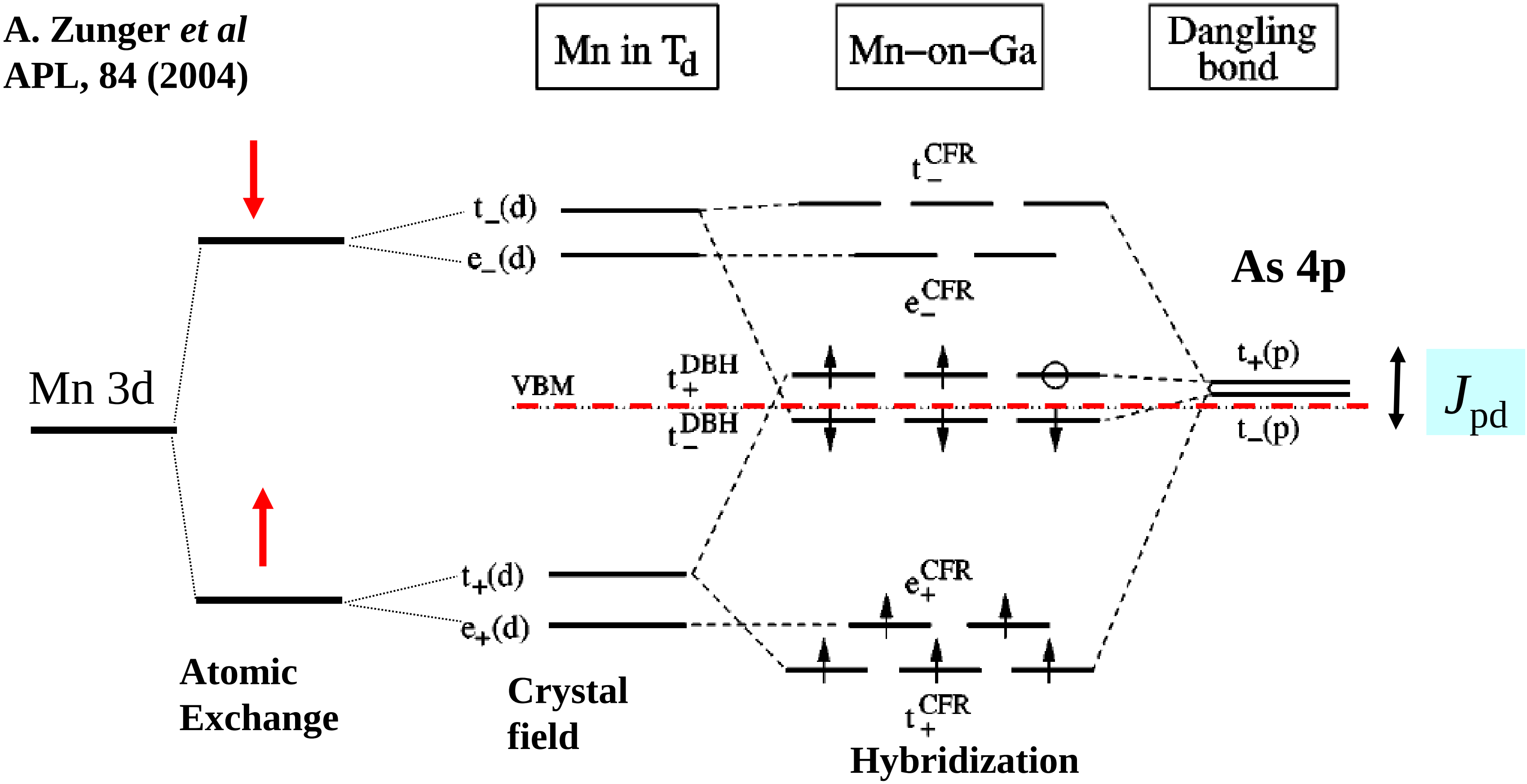
Previous work by
J.-M. Tang & M. Flatté
PRL **92**, 047201 (2004)
PRB **72**, 161315 (2005)
(mainly Mn **in bulk** GaAs)

- From bulk Mn impurites to **surface impurities**
- Quantization of Mn magnetic moment dynamics via Chern-number Berry phase theory

C.M.C, Cehovin & MacDonald, PRL **91** 46805 (2003)

1 Mn replacing 1 Ga in bulk GaAs: *pd* kinetic exchange

A. Zunger *et al*
APL, 84 (2004)



Direction of spin polarization on Mn site is ***opposite*** to spin polarization on nearest neighbor anion As sites → AFM coupling between Mn 3*d* and As *p* orbitals

Tight-binding model with kinetic exchange and spin-orbit interaction

$$\mathcal{H} = H_{Band} + H_{Exchange} + H_{SO} + H_{Coulomb}$$

Hopping and Onsite
Energies for GaAs Bulk [1]

$$= \sum_{ij} t_{ij} a_i^\dagger a_j$$

Mn **classical** spin vector S=5/2

Exchange on nearest neighbour
As p-electrons: *J* = 1.5 eV [2]

$$+J \sum_{m}^{N_{Mn}} \sum_{n\in\{N.N.\ to\ m\}} \langle \mathbf{s}_{n,\pi} \cdot \hat{\Omega}_m \rangle a_n^\dagger a_n$$

NN As p-spins

Spin-Orbit [1]

$$+ \sum_i \lambda_i \langle \mathbf{L} \cdot \mathbf{S} \rangle a_i^\dagger a_i$$

Long Range Coulomb

$$+ \frac{e^2}{4\pi\varepsilon\varepsilon_0} \sum_{m}^{N_{Mn}} \sum_i \frac{1}{|\mathbf{R}_m - \mathbf{R}_i|} a_i^\dagger a_i + H_{Coul.Corr.}$$

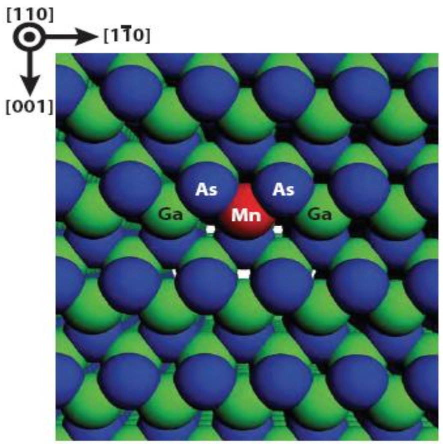
Dielectric Screening:
reduced at surface!

On (Mn) and Offsite (NN As) **Coulomb corrections:**
Off-site sets bulk acceptor @ 113 meV

[1] **D.J. Chadi**, PRB V19, p2074 (1979)

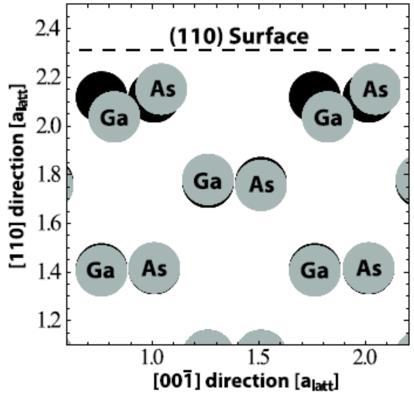
[2] Timm , MacDonald PRB 71, 155206 (2005)

Tight-binding calculations on clusters of 3200 atoms (20 x 20 x 32 atomic layers) – Strandberg et al prb 2009



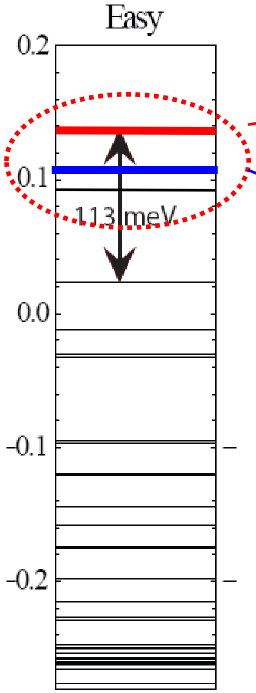
Bulk: - one Mn replacing a Ga in the center of cluster
- periodic boundary conditions in all directions

cut exposing (110) surface



Surface: - one Mn replacing a Ga on the (110) surface
- periodic BC in 2 directions
- relaxation of (110) surface and subsurface
[see Chadi PRB **19**, 2074, (1979)]

Single Mn in ‘bulk’ GaAs



Level structure inside the gap

”LUMO”

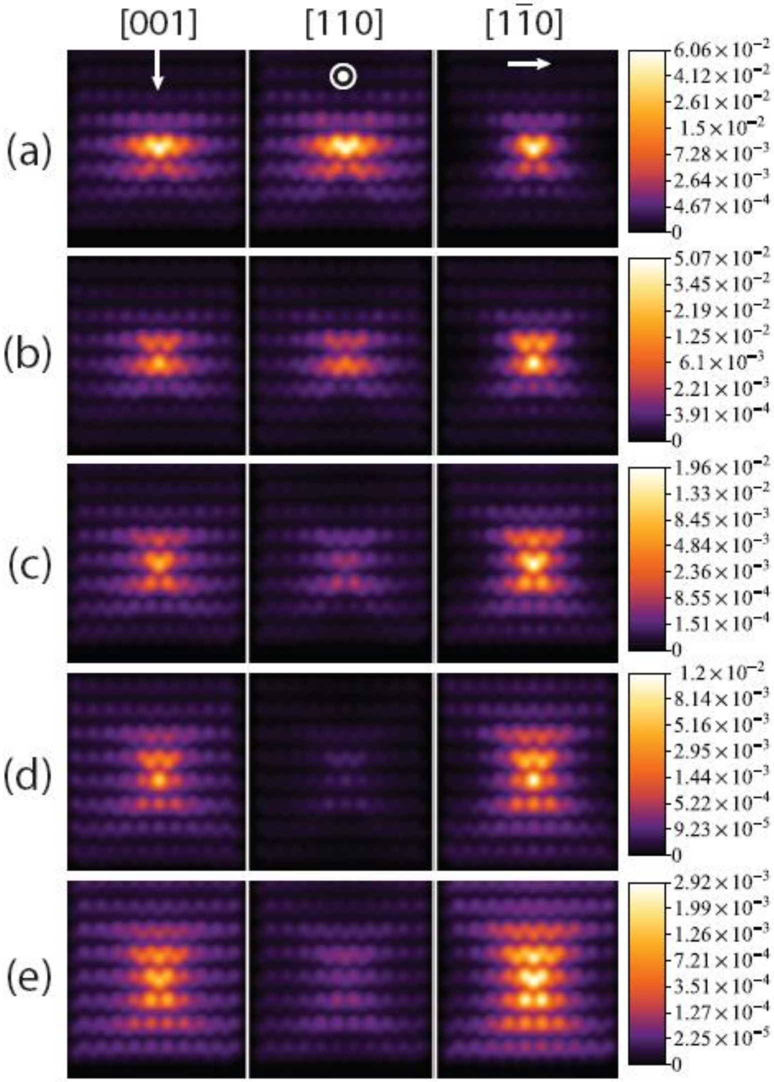
”Fermi level”

LDOS of acceptor state
on parallel (110) planes:

- extended + anisotropic LDOS
- 20% spectral weight in core
- strong dependence on moment direction

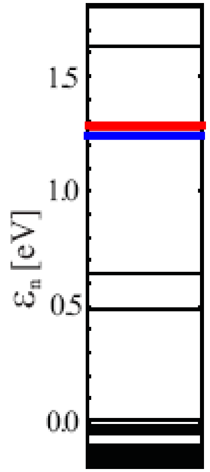
Agreement with Tang & Flatté

easy   hard directions



Substitutional Mn on (110) GaAs Surface

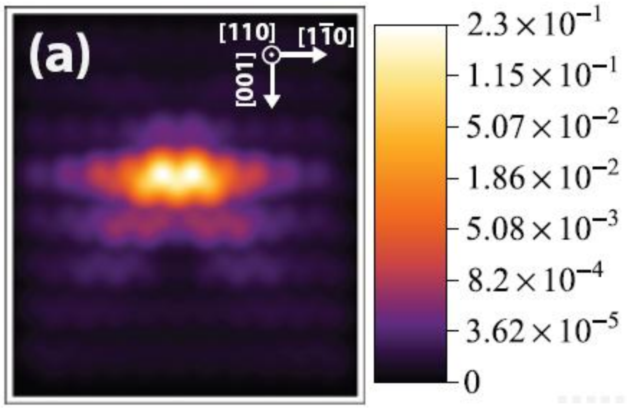
- **Deep acceptor!**: 0.8-1.2 eV
  - Sensitive to off-site Coulomb repulsion
- Highly Localized hole WF: 60% in core (too much?)

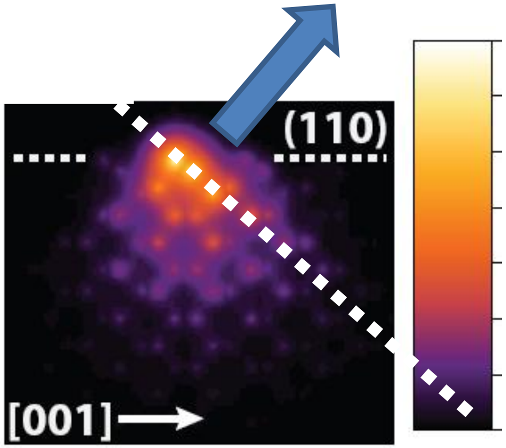


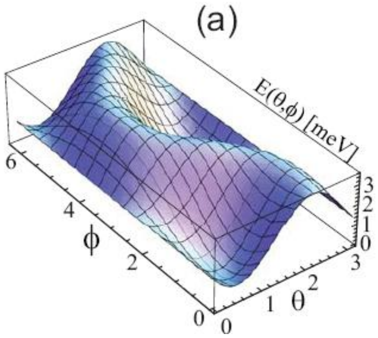
Level structure inside the gap with bulk parameters in the Hamiltonian

Anisotropy energy ~ 2 meV

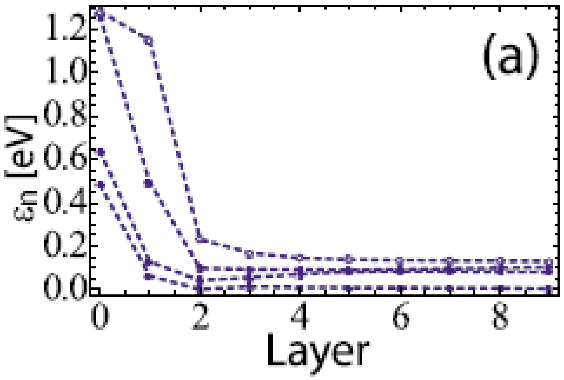
Easy axis

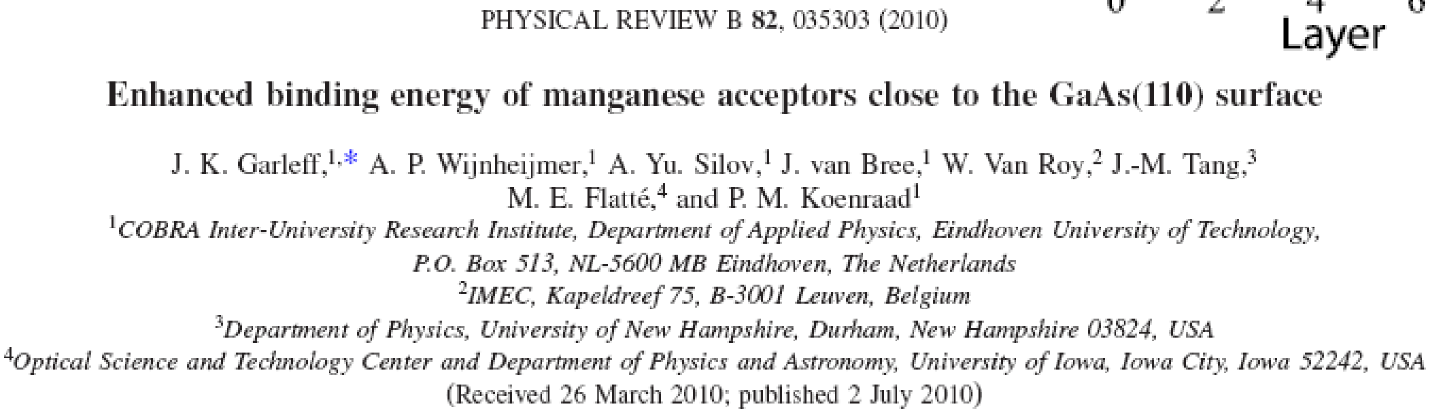






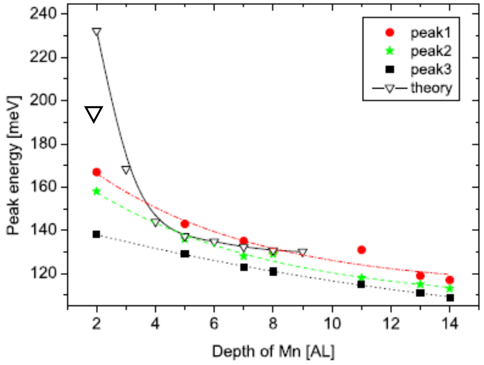
Acceptor binding energy is enhanced near the surface but approaches v.b. quickly with layer depth




PHYSICAL REVIEW B **82**, 035303 (2010)

Enhanced binding energy of manganese acceptors close to the GaAs(110) surface

J. K. Garleff,[1,*] A. P. Wijnheijmer,[1] A. Yu. Silov,[1] J. van Bree,[1] W. Van Roy,[2] J.-M. Tang,[3]
M. E. Flatté,[4] and P. M. Koenraad[1]
[1]*COBRA Inter-University Research Institute, Department of Applied Physics, Eindhoven University of Technology,*
P.O. Box 513, NL-5600 MB Eindhoven, The Netherlands
[2]*IMEC, Kapeldreef 75, B-3001 Leuven, Belgium*
[3]*Department of Physics, University of New Hampshire, Durham, New Hampshire 03824, USA*
[4]*Optical Science and Technology Center and Department of Physics and Astronomy, University of Iowa, Iowa City, Iowa 52242, USA*
(Received 26 March 2010; published 2 July 2010)



See also:

Lee and Gupta, Science, **330** (2010)

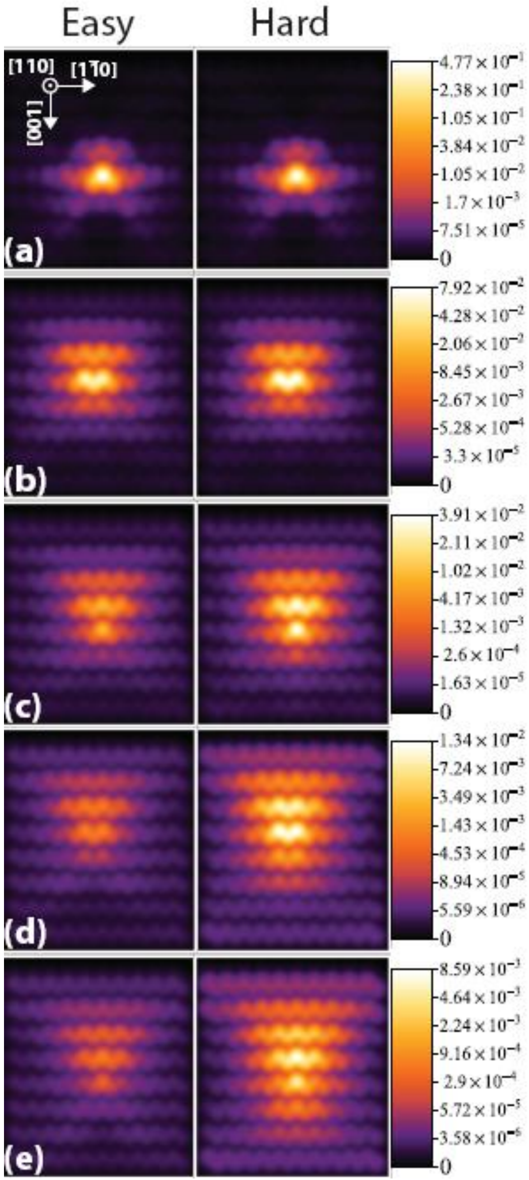
Can manipulate the binding energy with As vacancies!

Linnæus University

1 Mn in (110) subsurface layers

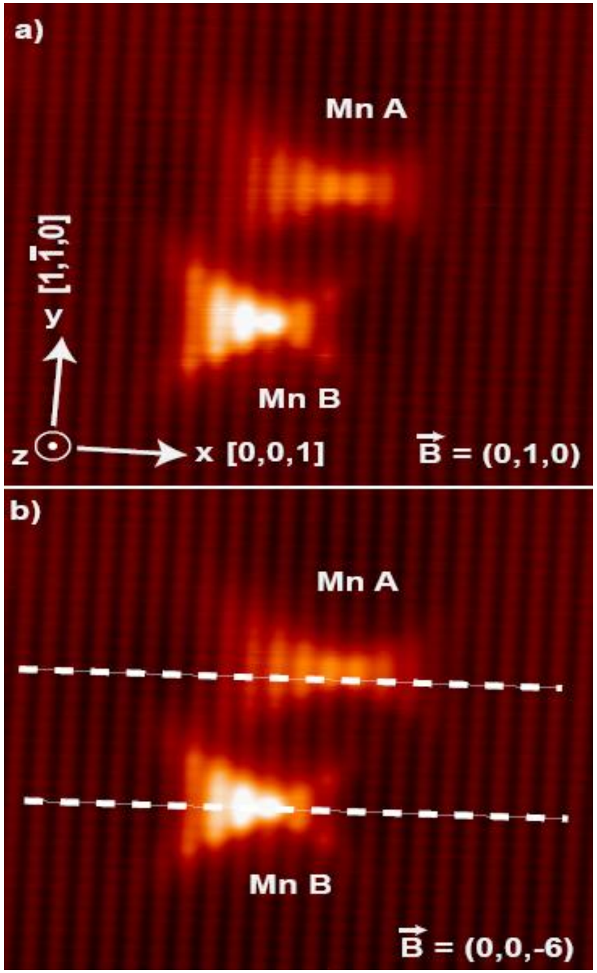
- Acceptor WF extends with depth
- Characteristic bow-tie shape
  → **Koenraad’s group experiments**
- Strong dependence on Mn direction

Can we control tunneling current by steering the Mn moment with an external magnetic field?

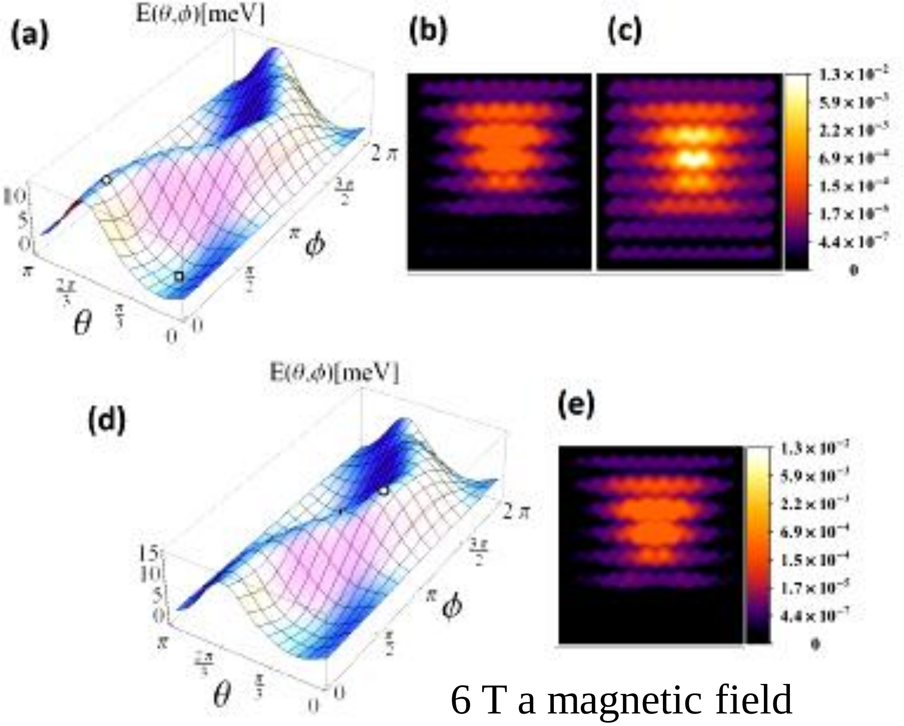


Magnetic Anisotropy of Single Mn Acceptors in GaAs in a magnetic field

M. Bozkurt,[1,*] M.R.K. Mahani,[2] P. Studer,[3,4] S.R. Schofield,[3,5] N.J. Curson,[3,4]
M.E Flatté,[6] A.Y. Silov,[1] C.F. Hirjibehedin,[3,5,7] C. Canali,[2] and P.M. Koenraad[1]

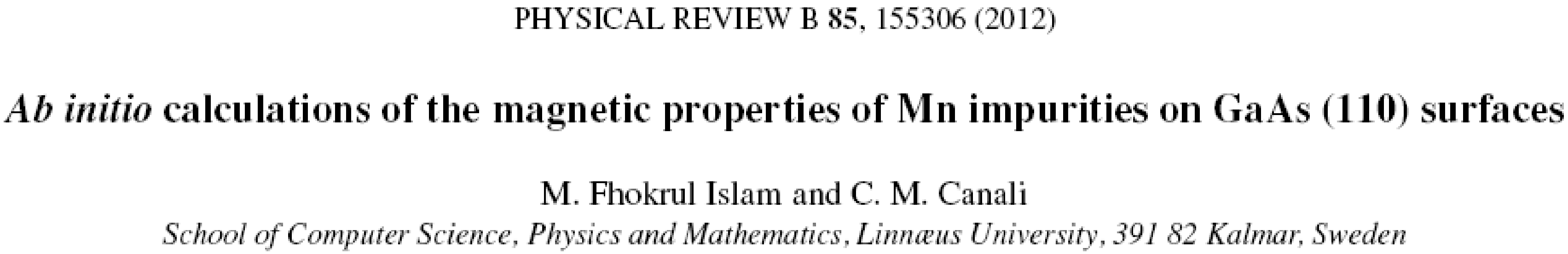


no magnetic field



6 T a magnetic field

6 T magnetic field not strong enough to overcome anisotroy barrier



PHYSICAL REVIEW B **85**, 155306 (2012)

Ab initio calculations of the magnetic properties of Mn impurities on GaAs (110) surfaces

M. Fhokrul Islam and C. M. Canali

School of Computer Science, Physics and Mathematics, Linnæus University, 391 82 Kalmar, Sweden

Magnetic anisotropy energy consistent
with tight-binding calculations

Can provide microscopic parameters for TB models

Mn pairs in bulk GaAs and on (110) GaAs surface

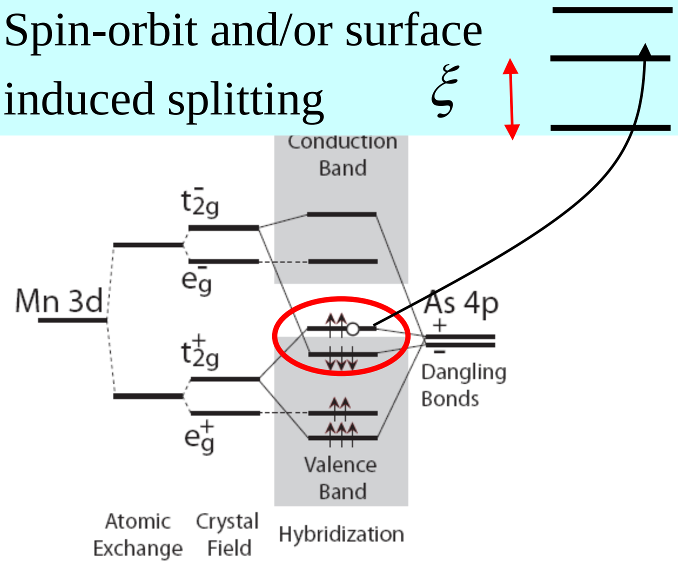
T.O. Strandberg, CMC, A.H. MacDonald, PRB, 2010

2 interacting Mn:

Mahadevan, Zunger, Sarma, PRL, 2004

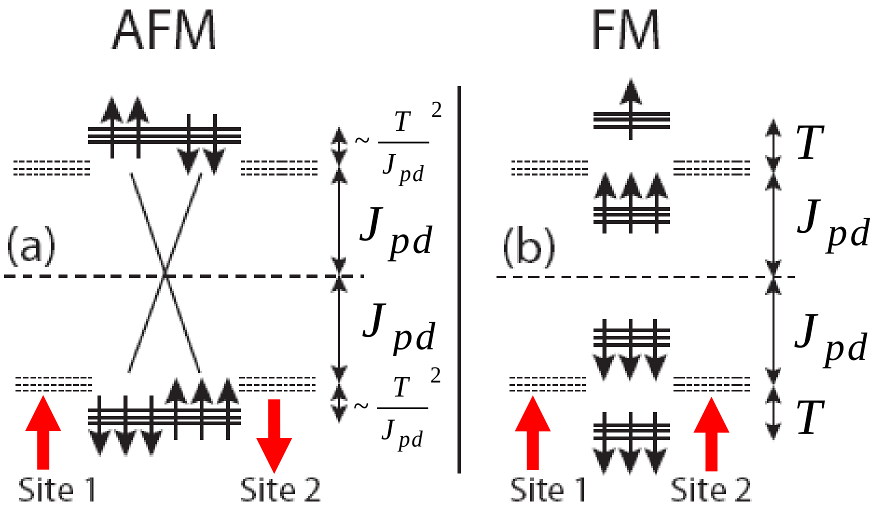
Flatté, (private communication), 2006

Spin-orbit and/or surface induced splitting ξ



- Two sets of doubly degenerate levels
- NO acceptor splitting

- Bonding vs antibonding
- Acceptor level splitting



- Compare E_{AFM} and E_{FM}
- For 10 electrons FM stable for large parameter space (J_{pd}, ξ , T)

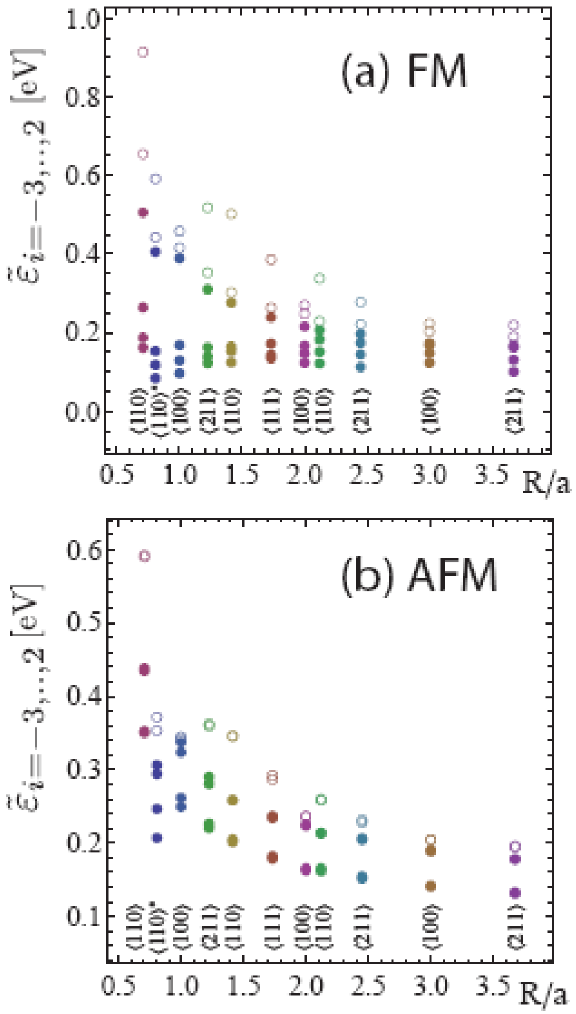
Super-exchange favors AFM

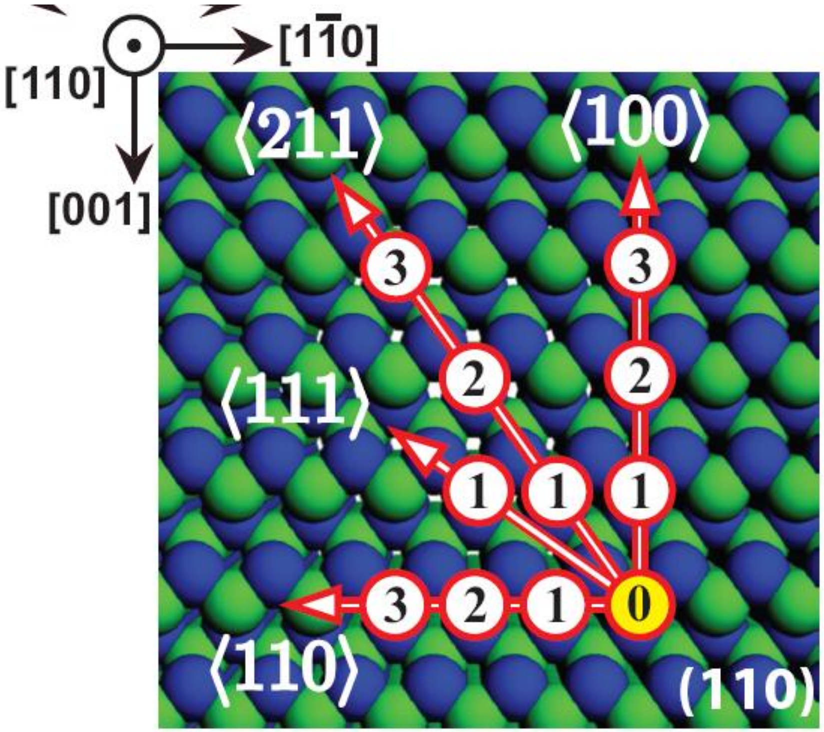
Double-exchange favors FM

Mn pairs in bulk GaAs: acceptor splitting

○ hole

● electron

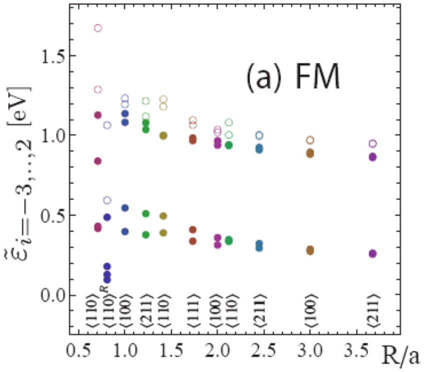


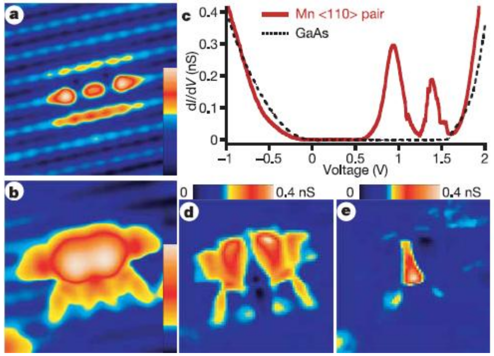


No splitting of 2 acceptors

Mn pairs in on (110) surface: FM configuration

Very localized wave functions



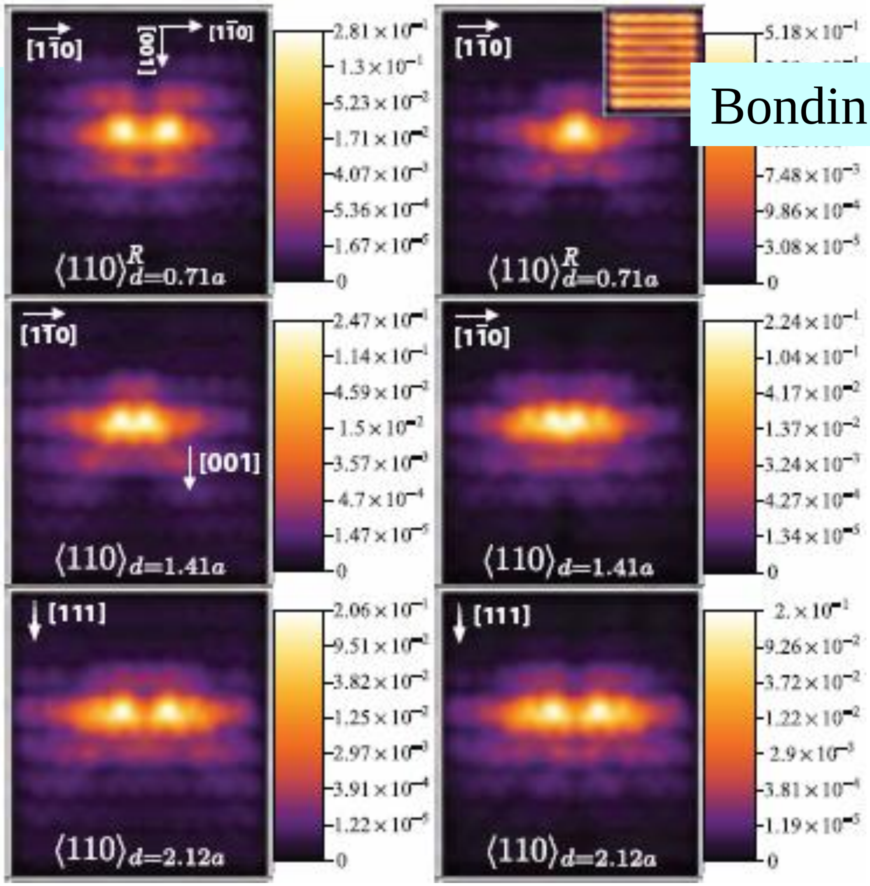


Lower acceptor

Higher acceptor

Anti-bonding

Bonding

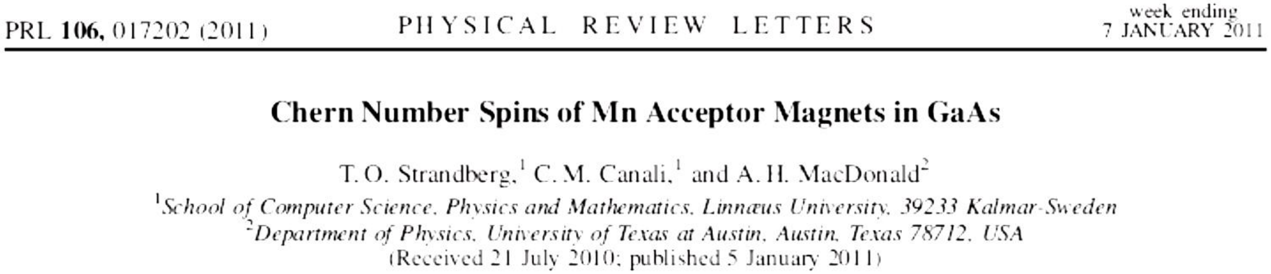


Both acceptor splitting (and exchange *J)* decay very rapidly with Mn separation

Quantum spin dynamics of Mn acceptor magnets

How to quantize the Mn magnetic moment and include

spin & orbital contributions of acceptor states?



PRL **106,** 017202 (2011) PHYSICAL REVIEW LETTERS week ending 7 JANUARY 2011

Chern Number Spins of Mn Acceptor Magnets in GaAs

T. O. Strandberg,[1] C. M. Canali,[1] and A. H. MacDonald[2]

[1]*School of Computer Science, Physics and Mathematics, Linnæus University, 39233 Kalmar-Sweden*

[2]*Department of Physics, University of Texas at Austin, Austin, Texas 78712, USA*

(Received 21 July 2010; published 5 January 2011)

Chern Numbers for Spin Models of Transition Metal Nanomagnets

C.M.C., A. Cehovin & A. H. MacDonald, PRL **91** 46805 (2003)

Implemented in TM magnetic clusters by DFT
- Strandberg et al., Nat. Mat. **6**, 648 (2007)
- Strandberg et al., PRB **77**, 174416 (2008)

Quantum action for the coherent magnetization-orientation direction $\hat{n}(\tau)$

orientation of Mn moments

$$S[\hat{n}] \equiv \int d\tau \left[\langle \Psi[\hat{n}] | \vec{\nabla}_{\hat{n}} \Psi[\hat{n}] \rangle \cdot \frac{\partial \hat{n}}{\partial \tau} + E[\hat{n}] \right]$$

Berry Phase

GS Energy

$$S_{\text{Berry}}[\hat{n}] = \oint d\hat{n} \cdot \langle \Psi | \vec{\nabla}_{\hat{n}} \Psi \rangle = \int \vec{\nabla}_{\hat{n}} \times \langle \Psi | \vec{\nabla}_{\hat{n}} \Psi \rangle \cdot \hat{n}\, da$$

$$\vec{C}[\hat{n}] = \sum_i^{\text{occ}} \vec{C}_i[\hat{n}]$$

$$C[\hat{n}] \equiv i\, \vec{\nabla}_{\hat{n}} \times \langle \Psi[\hat{n}] | \vec{\nabla}_{\hat{n}} \Psi[\hat{n}] \rangle \cdot \hat{n}$$

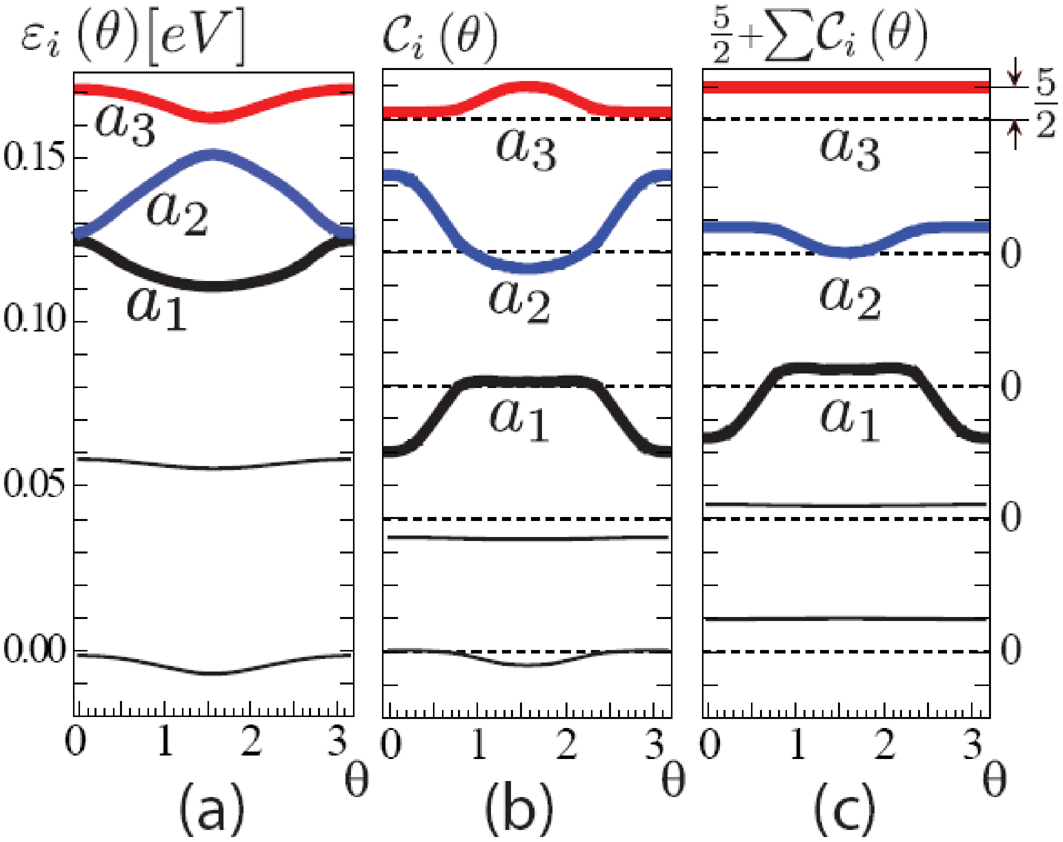
Berry curvature

No spin-orbit → $= \sum_i^{\text{occ}} \pm \frac{1}{2} = S$

spin-orbit → $C_i = \vec{C}_i[\hat{n}] \cdot \hat{n}$

vary with $\hat{n}$ and can differ from + -1/2

Example: one Mn in GaAs



Berry curvatures near level crossing diverge

$$C_i \propto \sum_n (E_i - E_n)^{-2}$$

All fluctuations below the Fermi level cancel out in the comulative curvature

$$\sum_i^{\text{valence}} C_i(\theta) = 0$$

Berry Curvature Chern Numbers

$$J = \frac{1}{4\pi} \int_{S^2} \vec{C}[\hat{n}] \cdot \hat{n} \, dA,$$

J is always half of an integer → Chern number

- J is a topological invariant
- J can change only when level crossing at E_F occurs

$$j_i = \frac{1}{4\pi} \int_{S^2} \vec{C}_i[\hat{n}] \cdot \hat{n} \, dA,$$

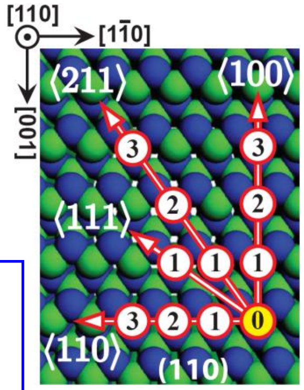
$$J = \sum_i^{\mathrm{occ}} j_i + \frac{5}{2} N_{\mathrm{Mn}}$$

Why do we care about the Chern number *J*?

- It turns out that *J* plays the role of an effective ``giant spin´´ for the Mn acceptor magnet!
- Important result

$$\boxed{J = \sum_{i}^{\mathrm{occ}} j_i + \frac{5}{2} N_{\mathrm{Mn}} = \sum_{i}^{\mathrm{valence}} j_i + \frac{5}{2} N_{\mathrm{Mn}} = (0 - j_{\mathrm{acc}}) + \frac{5}{2} N_{\mathrm{Mn}}}$$

Chern Number → Effective ``**Giant Spin**´´ *J* for Mn acceptor magnets



Agreement with

ESR studies by Schneider et al, PRB 1987

Infrared spectroscopy by Linnarson er al, PRB 1997

1 Mn

Bulk

J = 1 =
5/2(Mn) – 3/2(h hole)

$$j_{\mathrm{acc}} = \frac{3}{2}$$

l=1, *s* = 1/2

		j_1	j_2
$\langle 110\rangle_{d=0.7a,1.4a,2.1a}$	4	1/2	1/2
$\langle 110\rangle^{*}_{d=0.7a}$	3	3/2	1/2
$\langle 100\rangle_{d=a}$	3	1/2	3/2
$\langle 100\rangle_{d=2a,3a}$	4	−1/2	3/2
$\langle 211\rangle_{d=1.2a}$	4	1/2	1/2
$\langle 211\rangle_{d=2.4a,d=3.7a}$	3	3/2	1/2
$\langle 111\rangle_{d=1.7a}$	3	3/2	1/2

Bulk

(Sub-)Surface

$$j_{\mathrm{acc}} = \frac{1}{2}$$

J = 2 =
5/2(Mn) – 1/2(h hole)

Hole looses orbital contribution?

J = 4 = 2 +2
always!

(Sub-)Surface

Experimental implications

Can we see any evidence of the value of *J* and its change near the surface?

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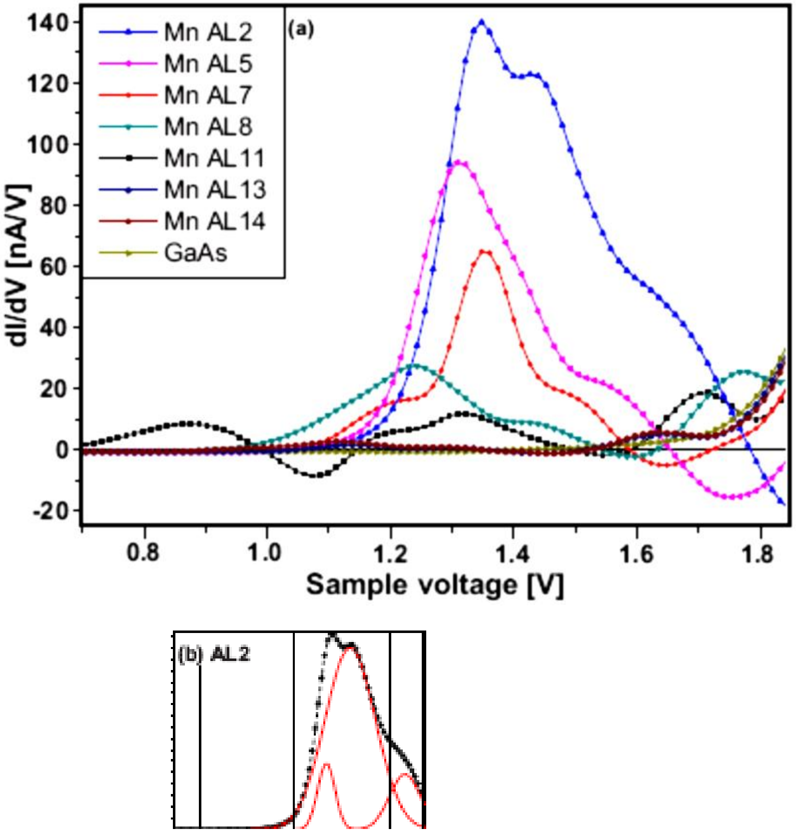
Enhanced binding energy of manganese acceptors close to the GaAs(110) surface

J. K. Garleff,[1,*] A. P. Wijnheijmer,[1] A. Yu. Silov,[1] J. van Bree,[1] W. Van Roy,[2] J.-M. Tang,[3]
M. E. Flatté,[4] and P. M. Koenraad[1]



The acceptor resonance has structure

It seems to split intro three peaks

(see Gaussian fitting for layer 2)

Is this an indication of a spin multiplet

J = 1??

It could still be *J*=2 (as predicted from Chern number theory) if some of the levels are quasi-degenerate

Effective Giant ``Spin´´ *J* Hamiltonian

Change variables: $\hat{n}(\theta,\phi) \Rightarrow \hat{n}'(\theta',\phi')$

$$C[\hat{n}] \Rightarrow C'[\hat{n}'] = J \text{ (Chern number)}$$

The (real time) action $\vec{A}_J = J\hat{\phi}'(1-\cos\theta')/\sin\theta'$

$$\mathcal{S}^{(J)}_{\rm spin}[\hat{n}'] \equiv \int_0^t dt'\left[i\vec{A}_J \cdot \frac{d\hat{n}'}{dt'} - E\{\hat{n}[\hat{n}'(t')]\}\right],$$

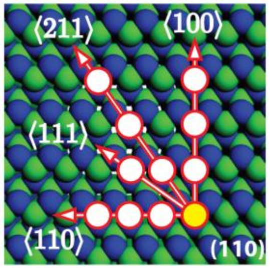
quantum action for an effective total ”spin” *J*

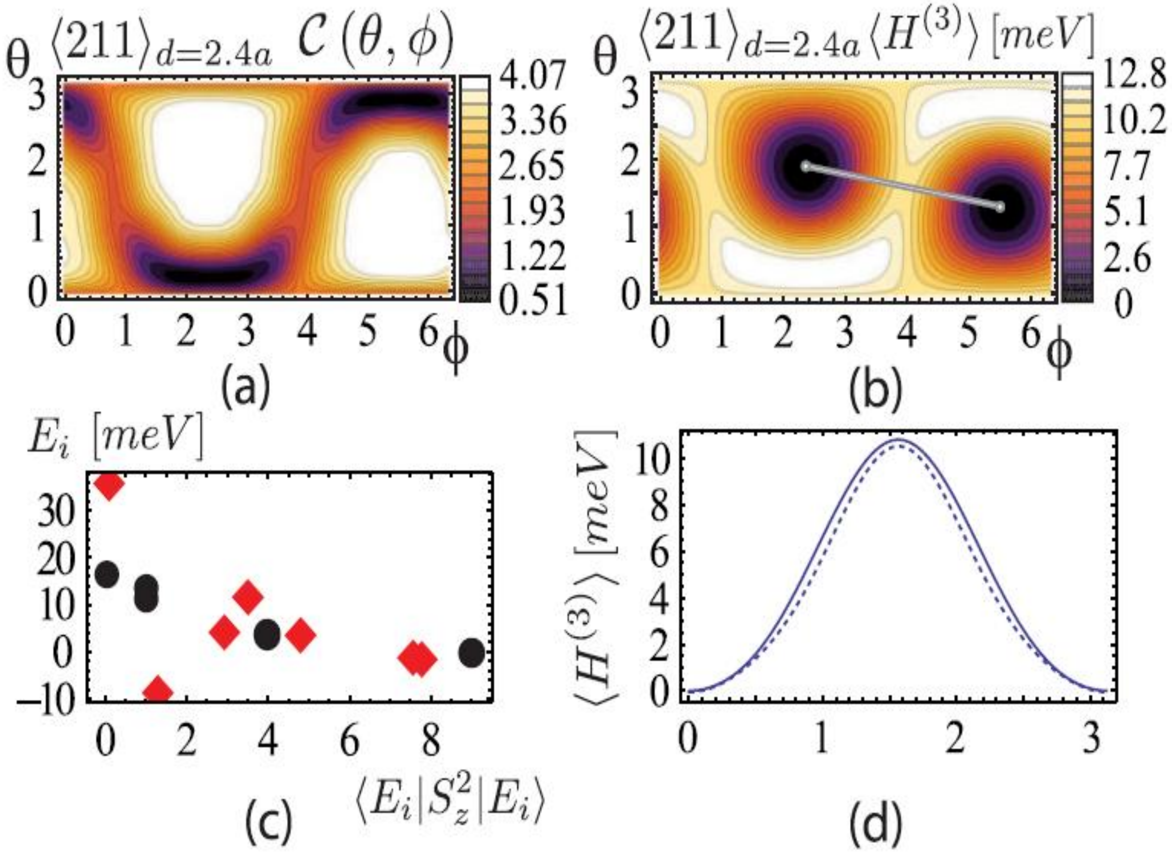
Semiclassical Hamiltonian

$$\tilde{E}(\hat{n}') = E\{\hat{n}[\hat{n}']\} = \langle J,\hat{n}'|\boxed{\tilde{\mathcal{H}}}|J,\hat{n}'\rangle$$

Quantum Spin Hamiltonian for *J*

Example: $<211>_{d=2.4a}$ pair





Quantum spectrum & effective anisotropy barrier are modified by Berry phase corrections!

Conclusions:

- New STM experiments in magnetic impurities in semiconductors

- Microscopic quantum theories are helping to elucidate basic mechanisms

- Mn impurities in GaAs surfaces lead to **deep acceptors**
  but treating **surface is HARD!**

- Mn impurities + acceptors: **novel molecular magnets**
  Prediction for effective ``spin´´ *J* (Chern number) perhaps visible in STM