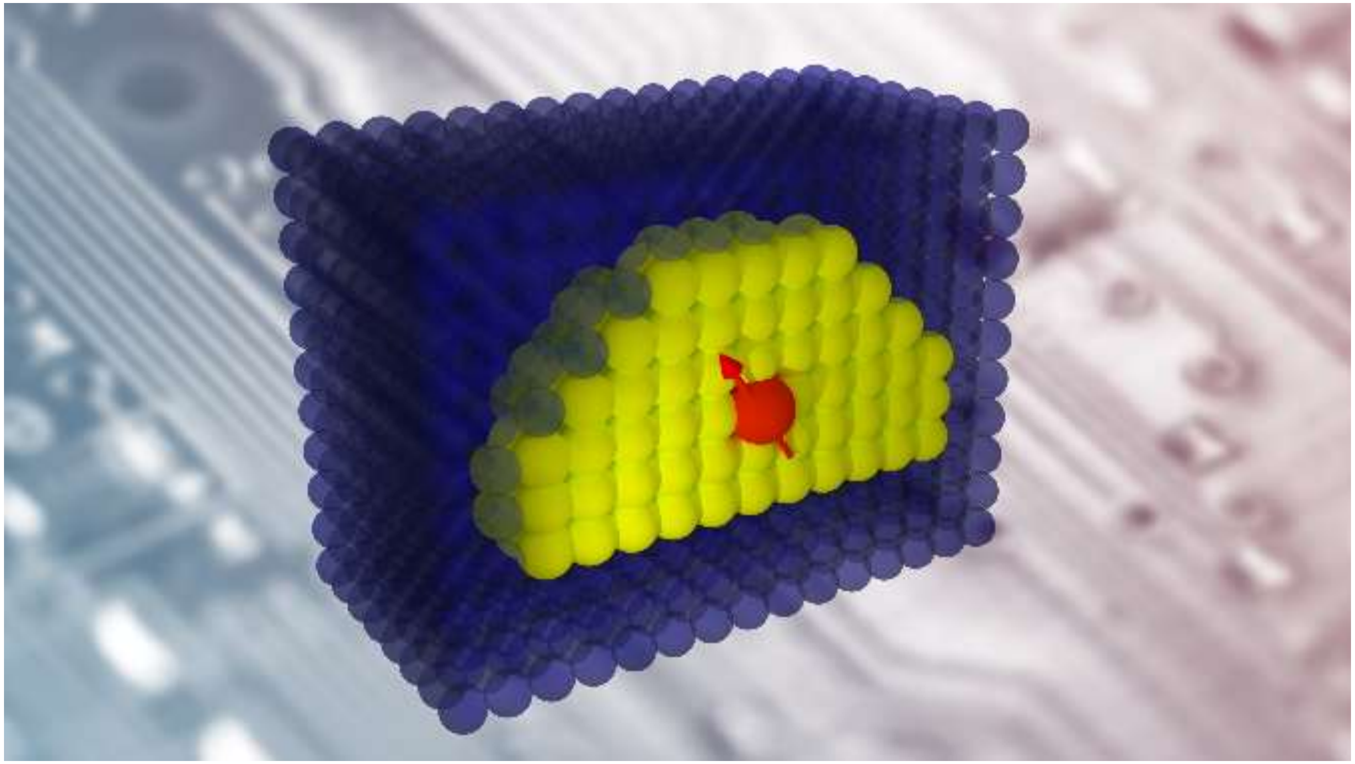
Solotronics - technology and science of single dopants

Wojciech Pacuski

University of Warsaw, Poland



Outline

Why single dopants?

Word „solotronics”

Various methods of single dopant manipulation

Magnetic ions in semiconductors

Single magnetic ions in QDs

Speculation on TMD-solotronics

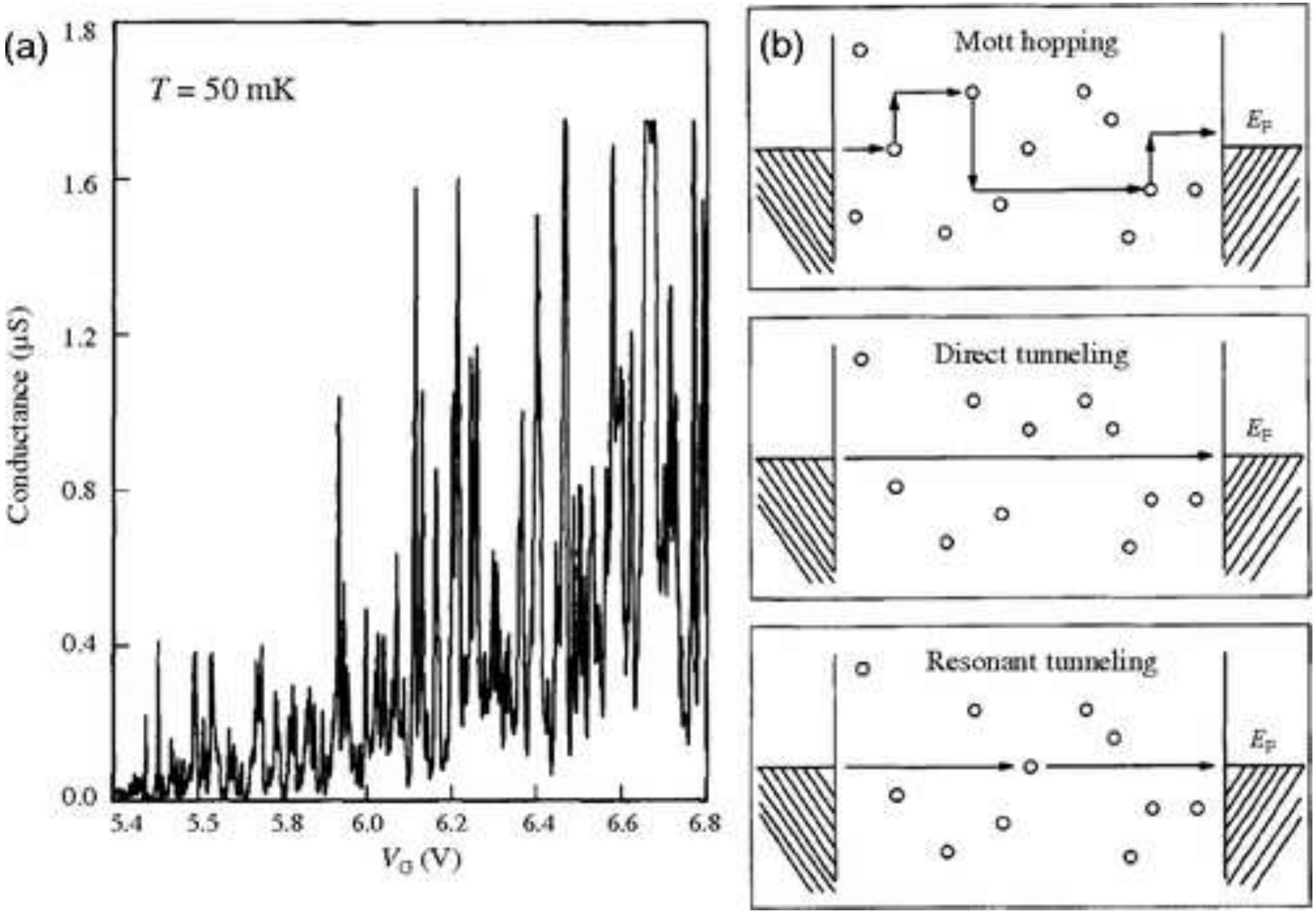
why single dopants?

- Properties of individual atoms are different than properties of ensembles of atoms (in particuar in nanostructures)

- No problem of inhomogeneous broadening – possibility of sensing very weak fields or interactions

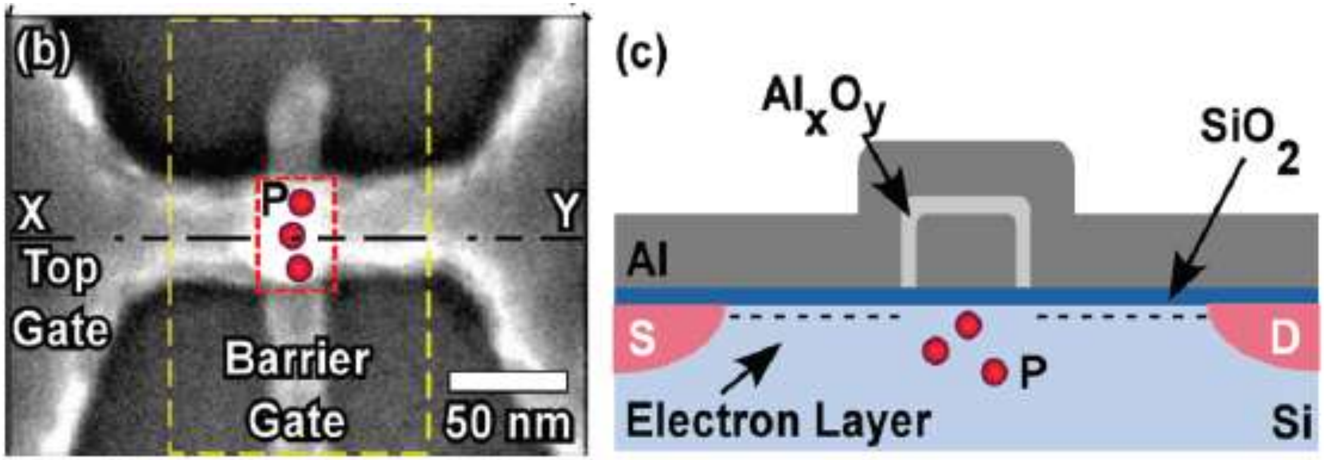
- Miniaturization of electronics reaches limit related to atomic structure of matter

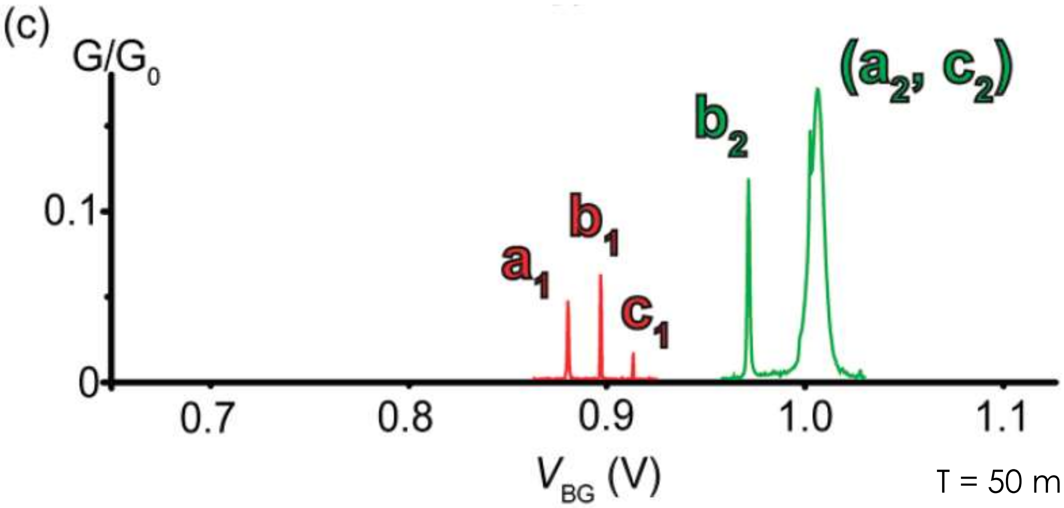
Low nubmer of impurities in a small transistor



Fowler, A. B., J. J. Wainer, and R. A. Webb, IBM J. Res. Dev. 32, 372 (1988).

Low nubmer of impurities in a small transistor

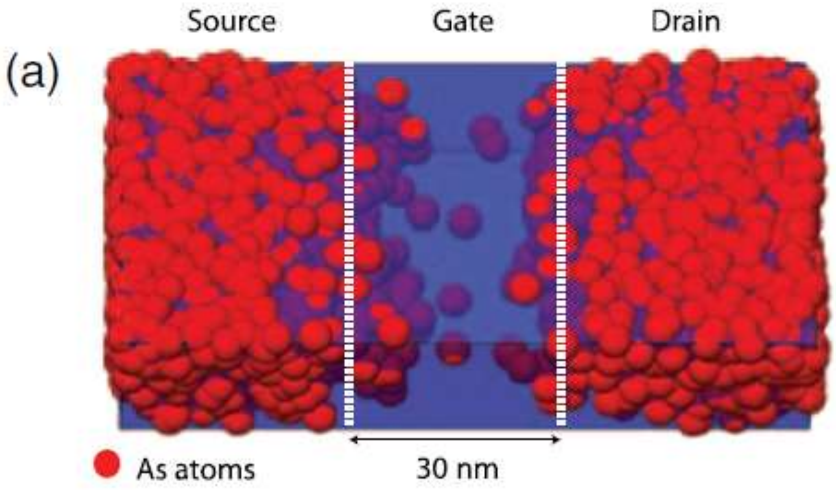




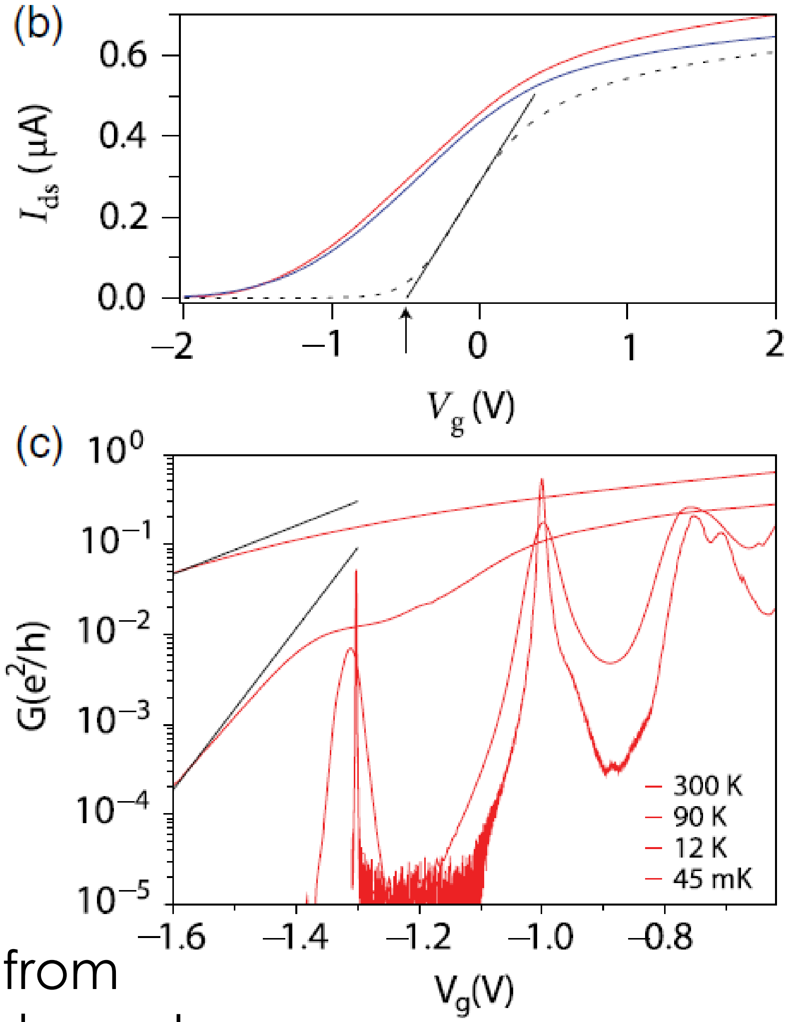
T = 50 mk

Kuan Yen Tan et al., Nano Lett. 10, 11 (2010).
Floris A. Zwanenburg et al., Reviews of modern physics 85, 961 (2013).

Low nubmer of impurities in a small transistor



Monte Carlo simulation
of the doping profile



Deviation of characteristic from
avarage due to individual dopants

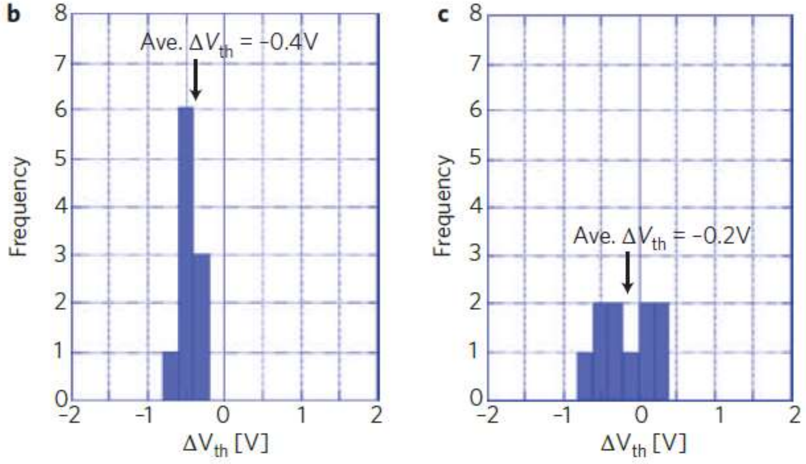
M. Pierre et al., Nat. Nanotechnol. 5, 133 (2010).

Low nubmer of impurities in a small transistor

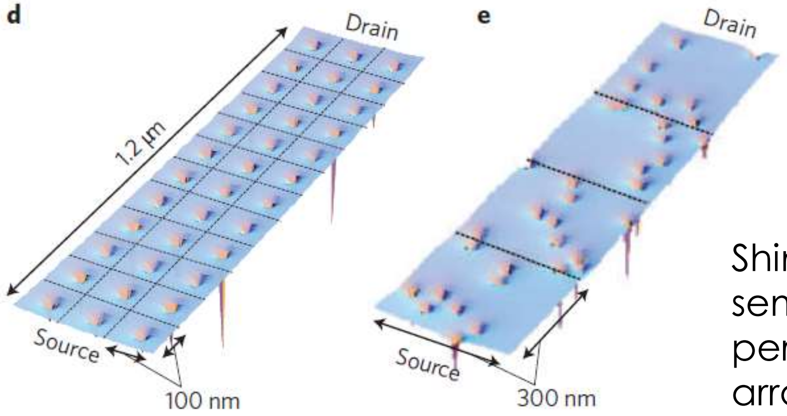
dopant distribution

ordered random

experiment:



simulation:



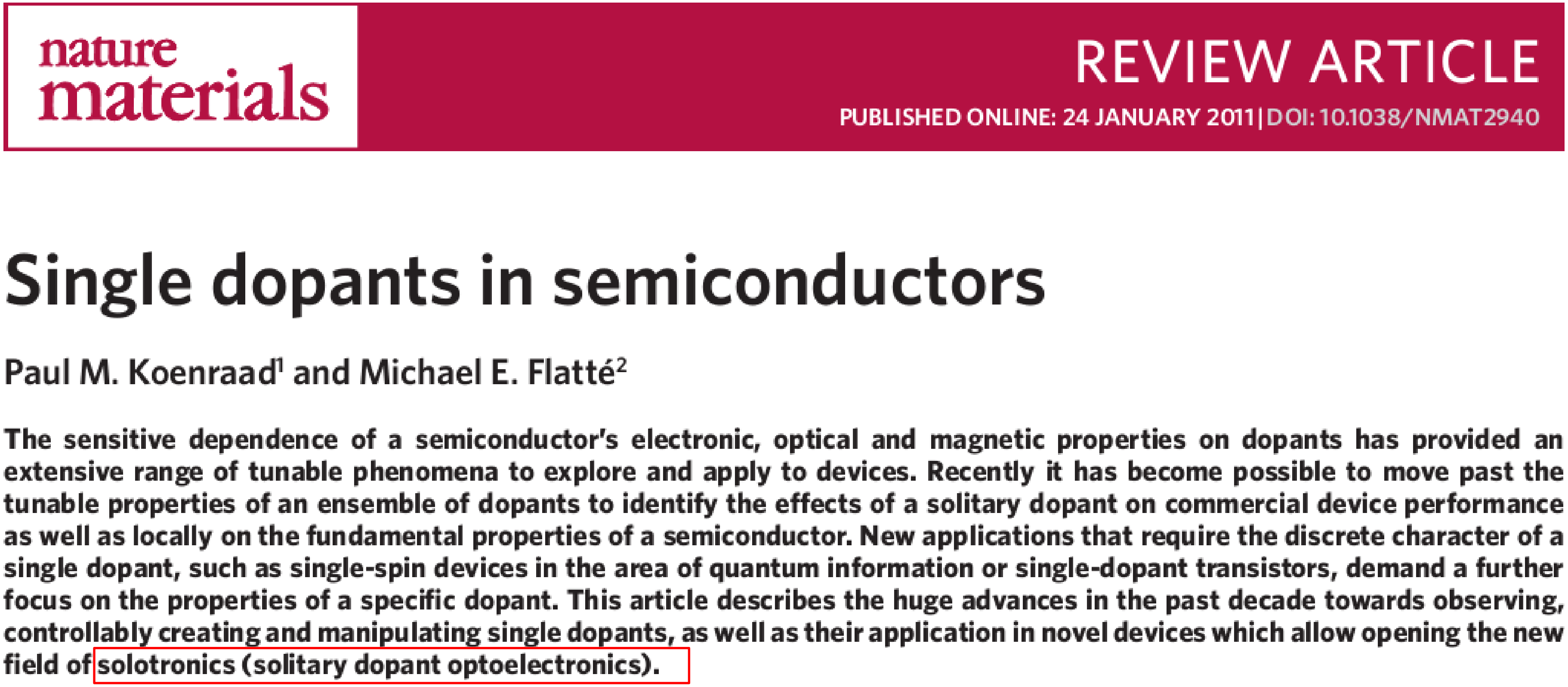
Shinada et al., Enhancing semiconductor device performance using ordered dopant arrays, Nature 437, 1128 (2005).

Nanostructures with impurities

- ordered
  - additional degrees of freedom
- randomly distributed
  - every structure is different

solotronics

2011, Nature, the first use of „solotronics” - solitary dopant optoelectronics



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]

The sensitive dependence of a semiconductor's electronic, optical and magnetic properties on dopants has provided an extensive range of tunable phenomena to explore and apply to devices. Recently it has become possible to move past the tunable properties of an ensemble of dopants to identify the effects of a solitary dopant on commercial device performance as well as locally on the fundamental properties of a semiconductor. New applications that require the discrete character of a single dopant, such as single-spin devices in the area of quantum information or single-dopant transistors, demand a further focus on the properties of a specific dopant. This article describes the huge advances in the past decade towards observing, controllably creating and manipulating single dopants, as well as their application in novel devices which allow opening the new field of solotronics (solitary dopant optoelectronics).

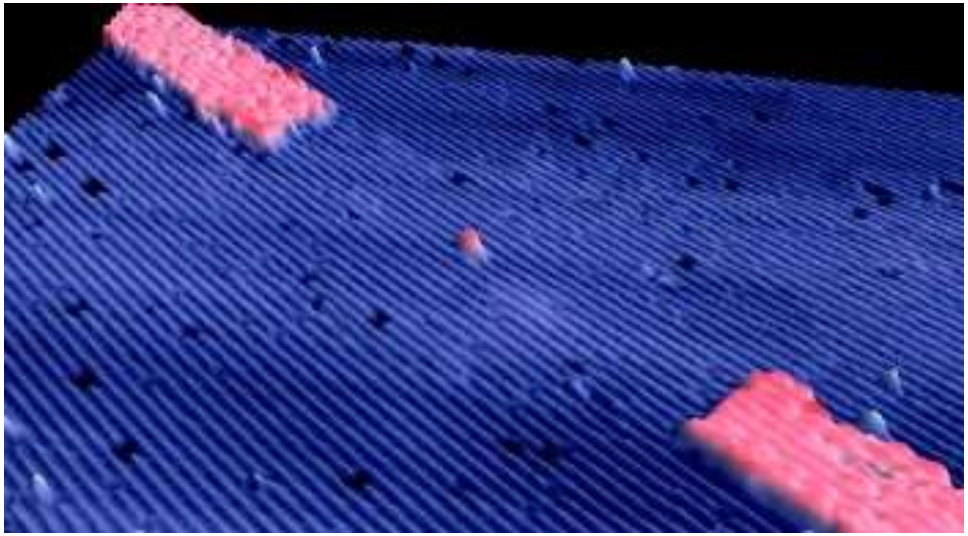
Solotronics- electronics based on solitary dopants

Objectives:
Initialize, store, operate, and read-out information
with individual ions or defects

Control of
- electrical
- optical
- magnetic

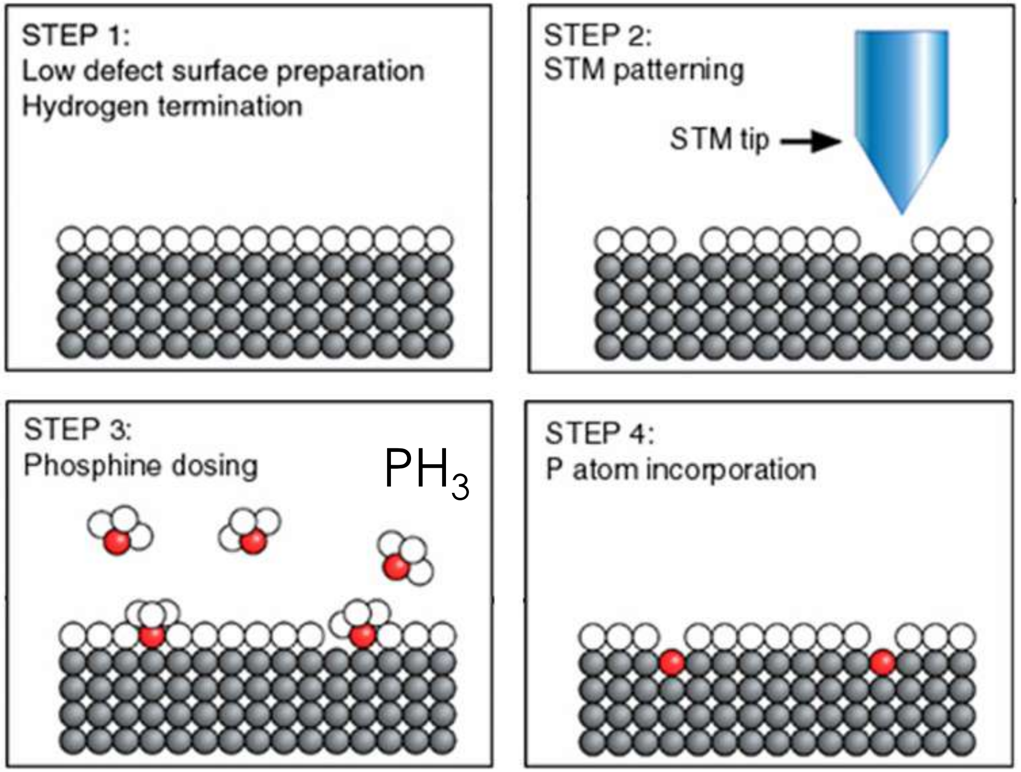
properties of individual dopants

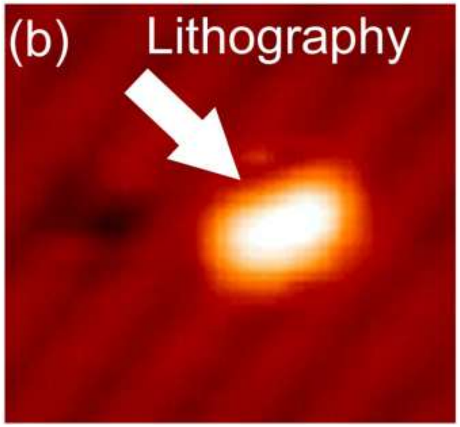
Example:

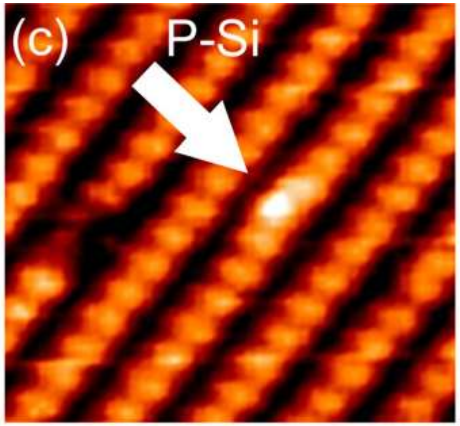


A single-atom transistor, Fuechsle et al.,
Nature Nanotechnology 7, 242 (2012).

Precise doposition of a single dopant on Si



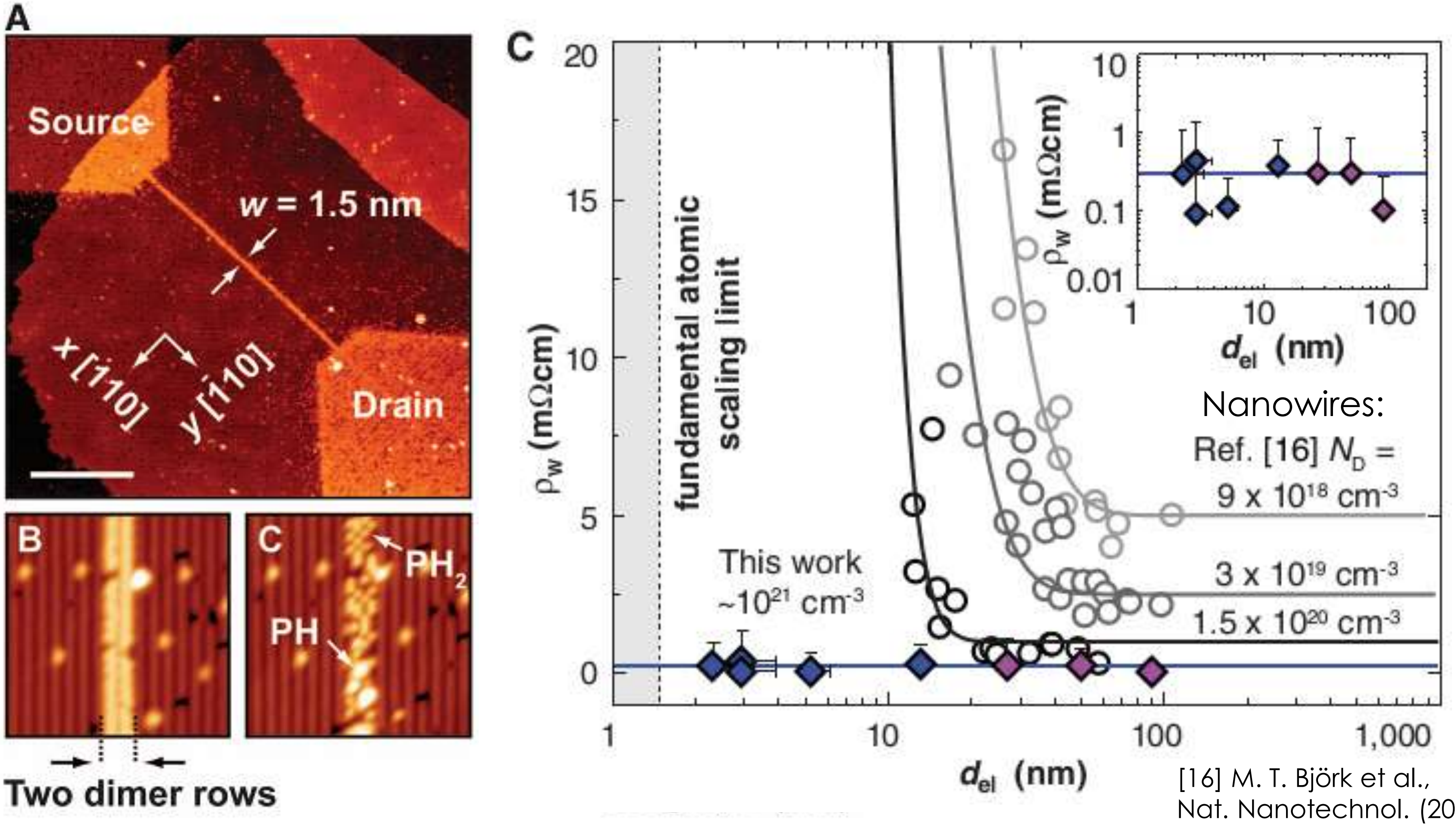




Schofield et al., J. Surf. Sci. Nanotech. 4, 609 (2006).

Wires with a thickness of a few atoms

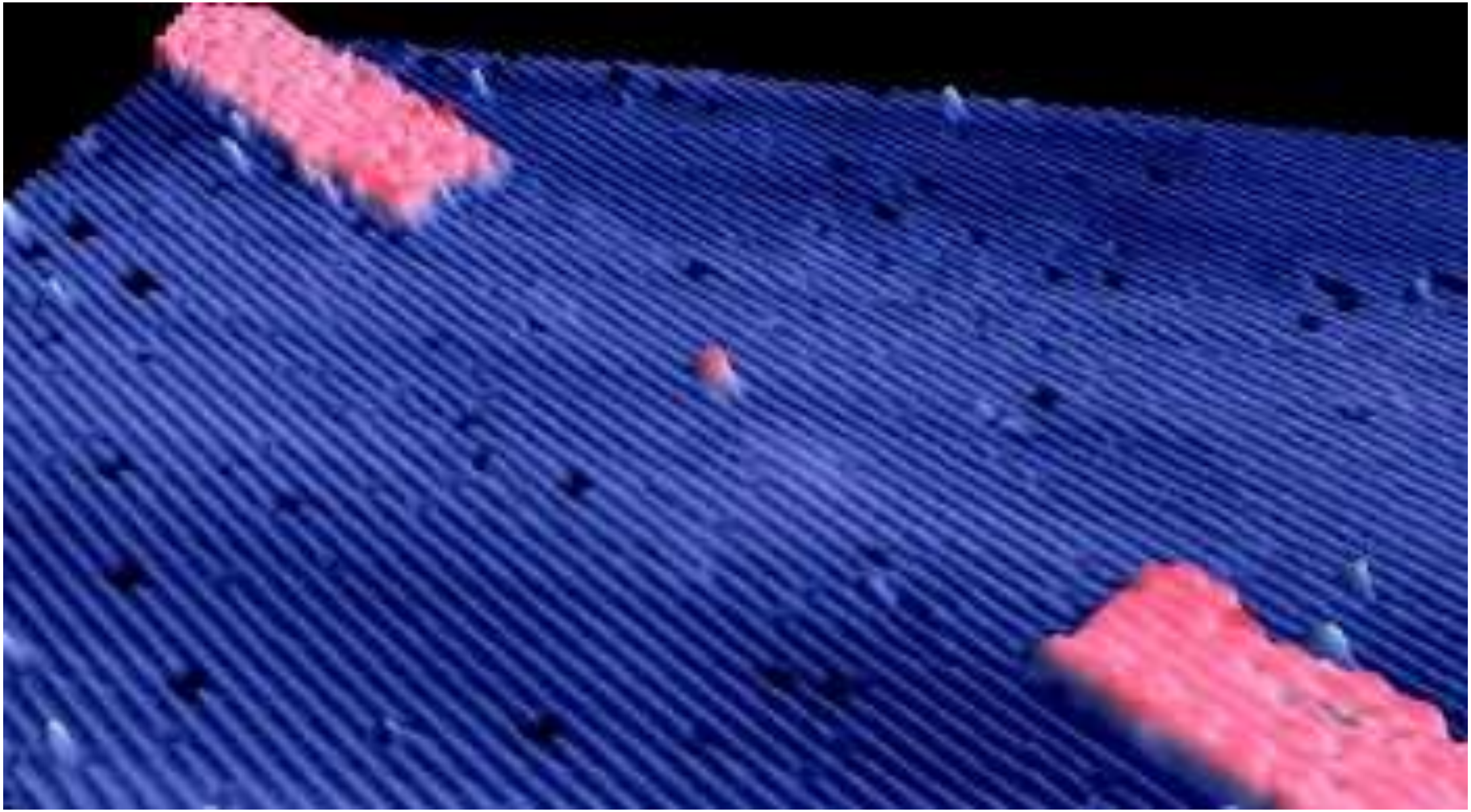
Ohm' s Law Survives to the Atomic Scale, B. Weber et al. Science 335, 64 (2012):



[16] M. T. Björk et al., Nat. Nanotechnol. (2009).

Diameter-independent resistivity down to 4 atoms of diamter!

Tunneling currents

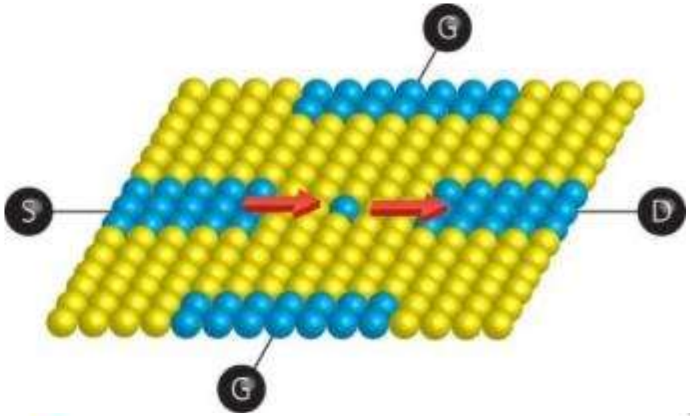


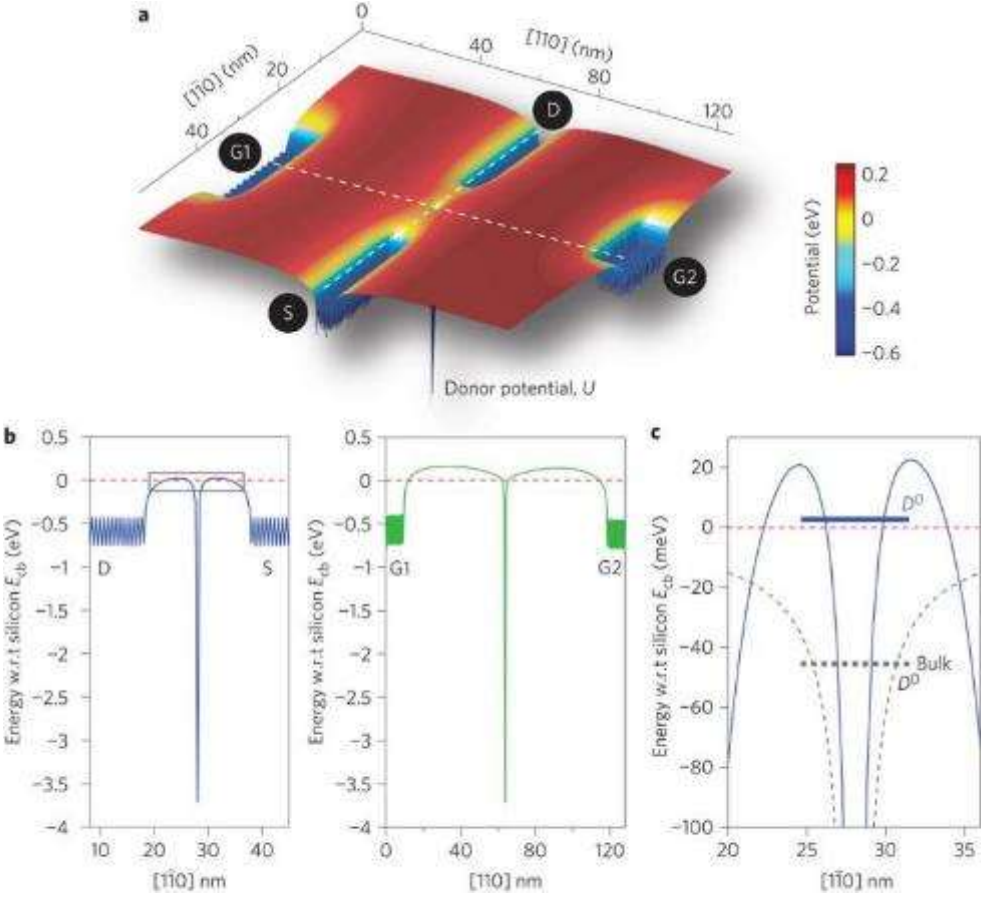
Fuechsle et al., Nature Nanotechnology 7, 242 (2012).

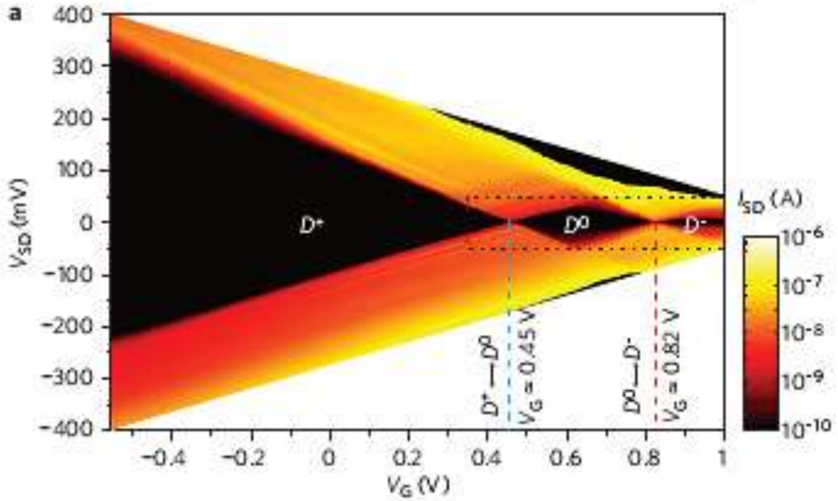
Single-atom transistor

A single-atom transistor, Fuechsle et al., Nature Nanotechnology 7, 242 (2012).

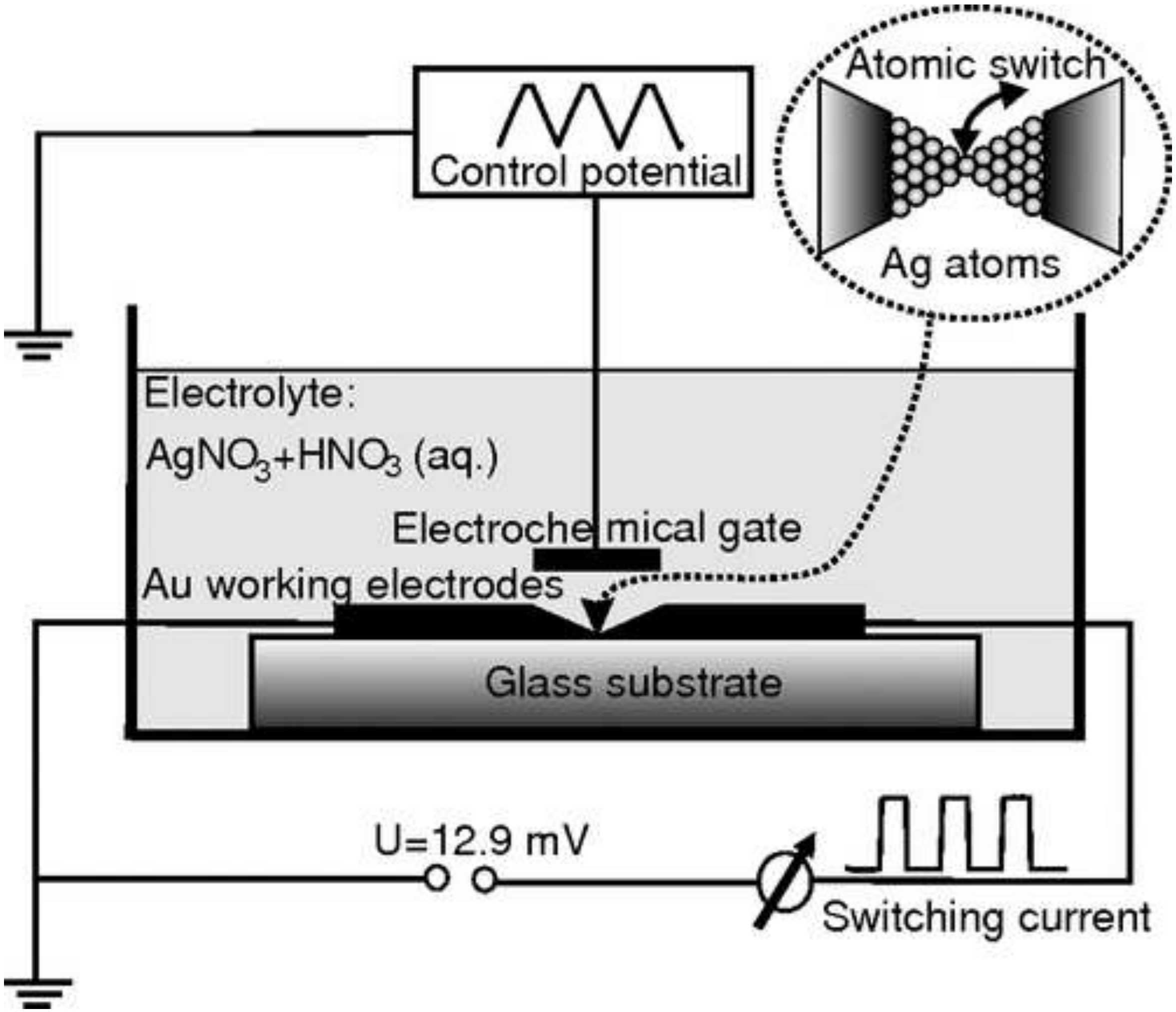
Nanoelectronics: Transistors arrive at the atomic limit,
G. P. Lansbergen, Nature Nanotechnology 7, 209 (2012).







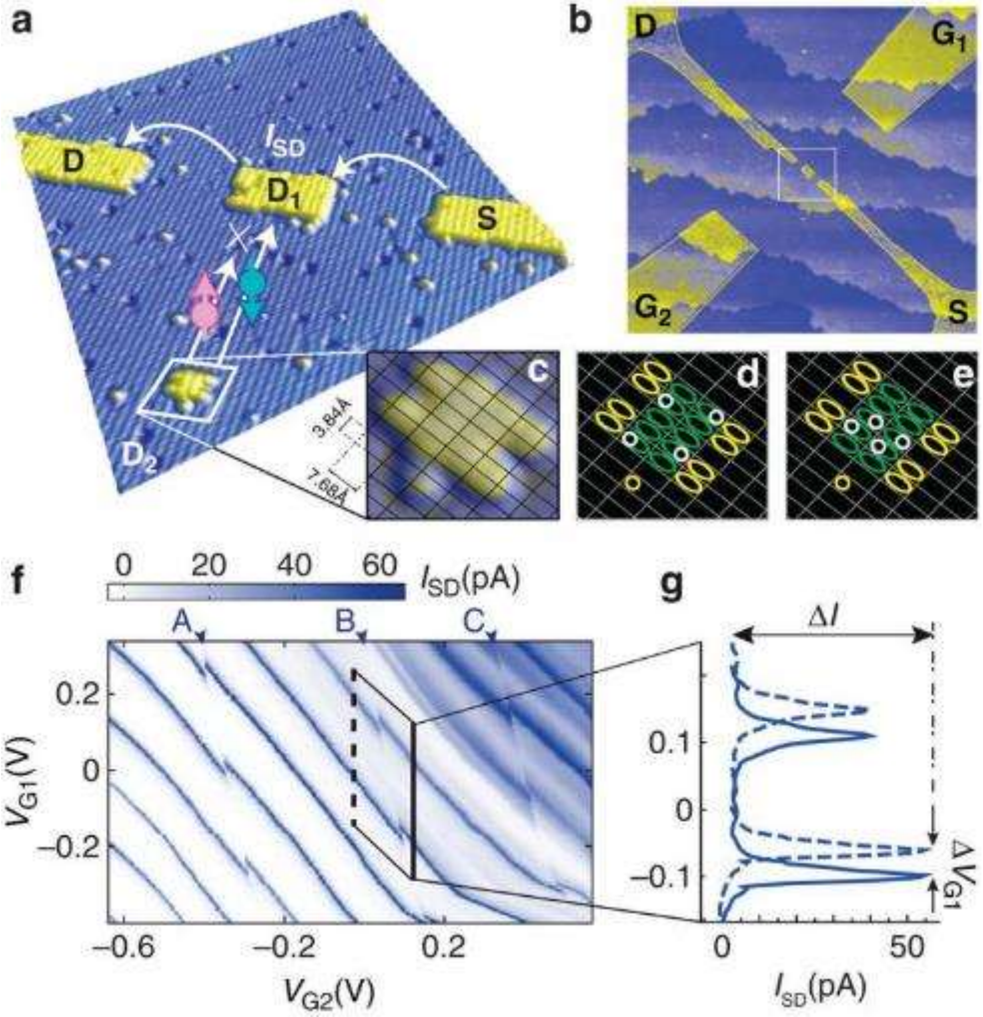
The first single-atom transistor



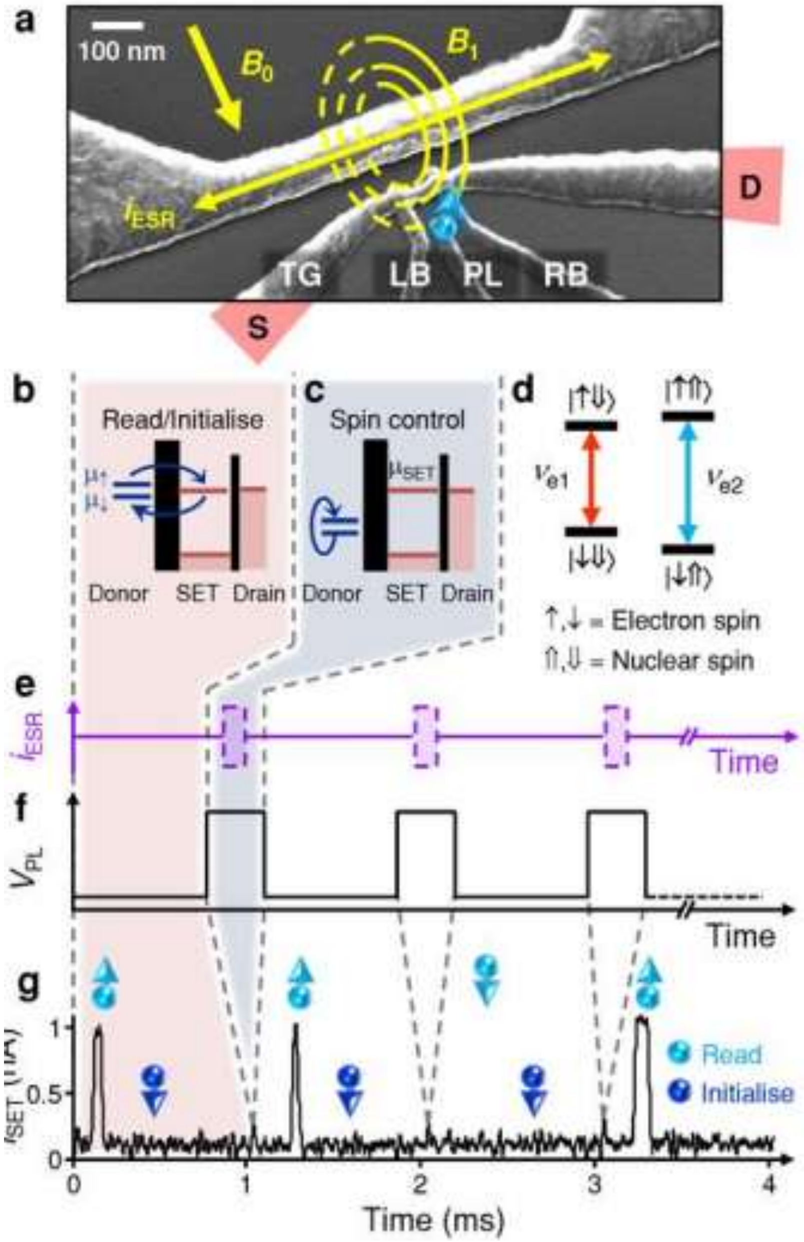
F.-Q. Xie, L. Nittler, Ch. Obermair, and Th. Schimmel
Phys. Rev. Lett. 93, 128303, Gate-Controlled Atomic Quantum Switch

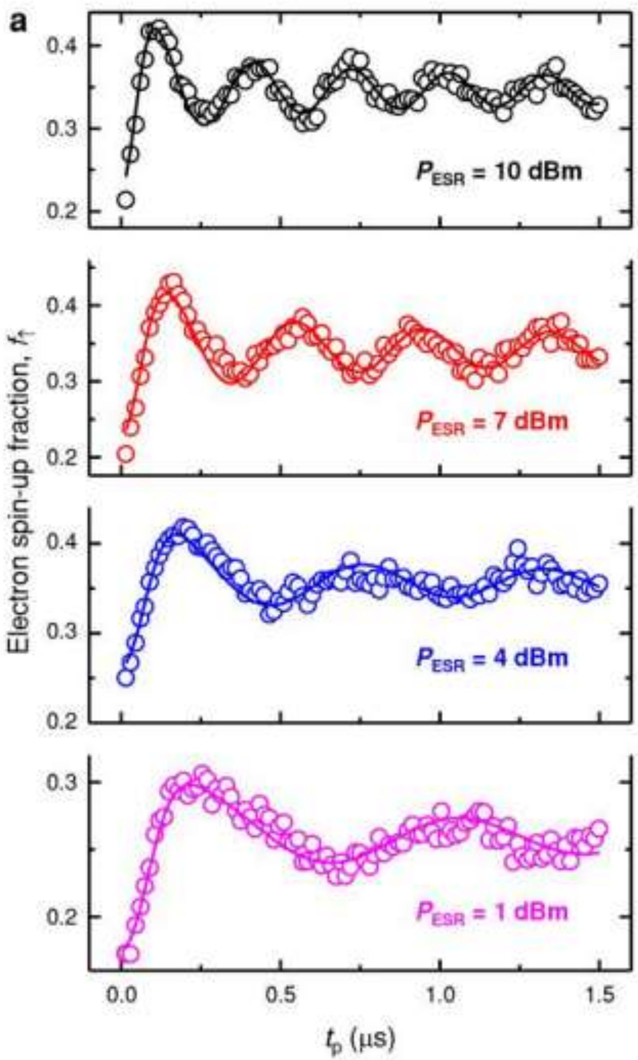
Single spin read-out

Spin readout and addressability of phosphorus-donor clusters in silicon, Büch et al., Nature Communications 4, 2017 (2013).



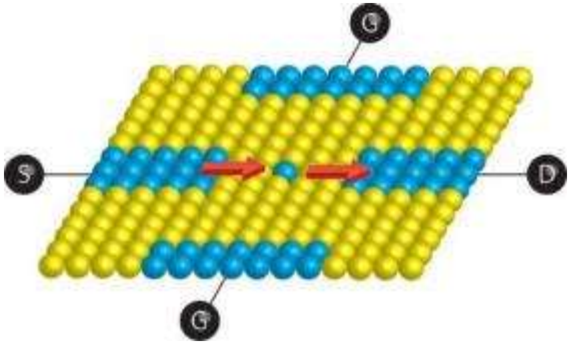
Single-atom qubit





Jarryd et al.., Nature 489, 541 (2012),
A single-atom electron spin qubit in silicon

Solotronics



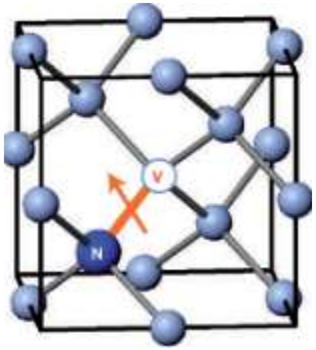
Single phosphorus atom on Si surface

- Ohmic wires
- Transistors
- Electron tunneling
- Qubits
- Integration with present electronics

Challenges:

- Very low temperatures (mK)
- Difficult optical access

e.g. Fuechsle et al., Nature Nanotechnology 7, 242 (2012).



N-V defect center in diamond

Advantages:

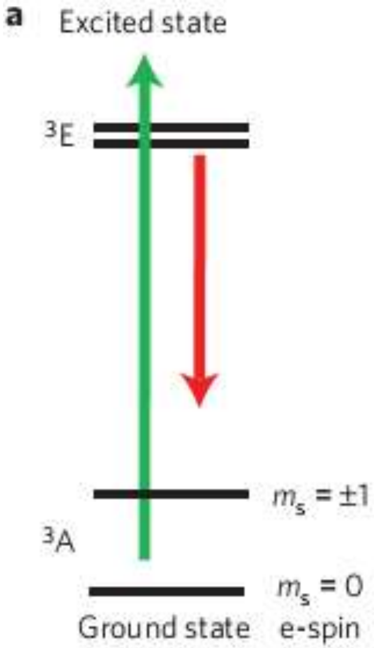
- Room temperature Qubit
- Good optical access

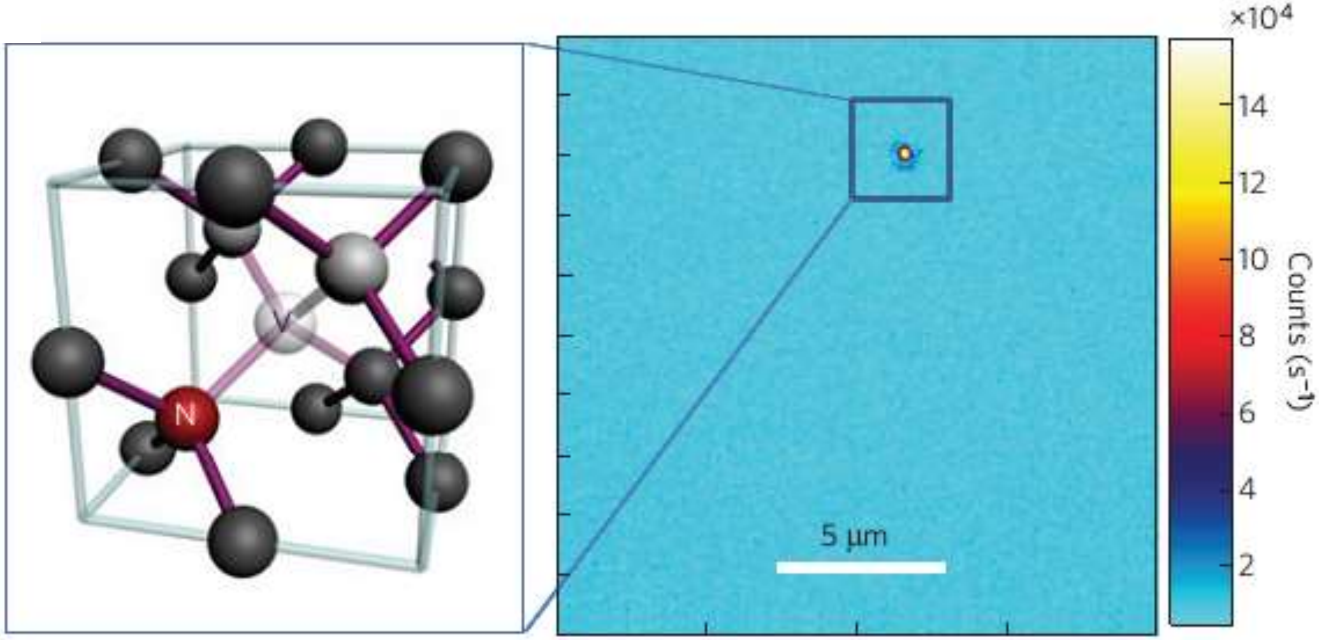
e.g. F. Dolde et al., Nature Physics 9, 139 (2013).
Balasubramanian et al. Nature Materials 8, 383 (2009).
R. Hanson et al., Science 320, 352 (2008).

N-V defect center in diamond

N – azot

V (vacancy) – missing carbon atom



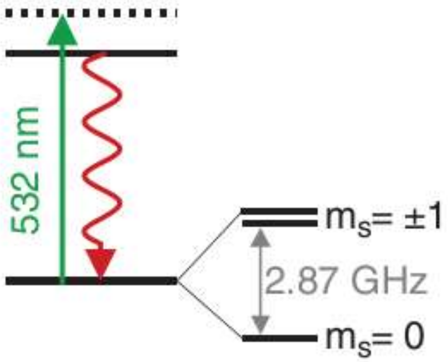


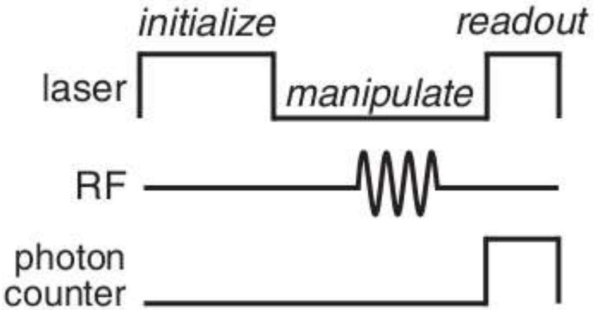
Balasubramanian et al. Nature Materials 8, 383 (2009).

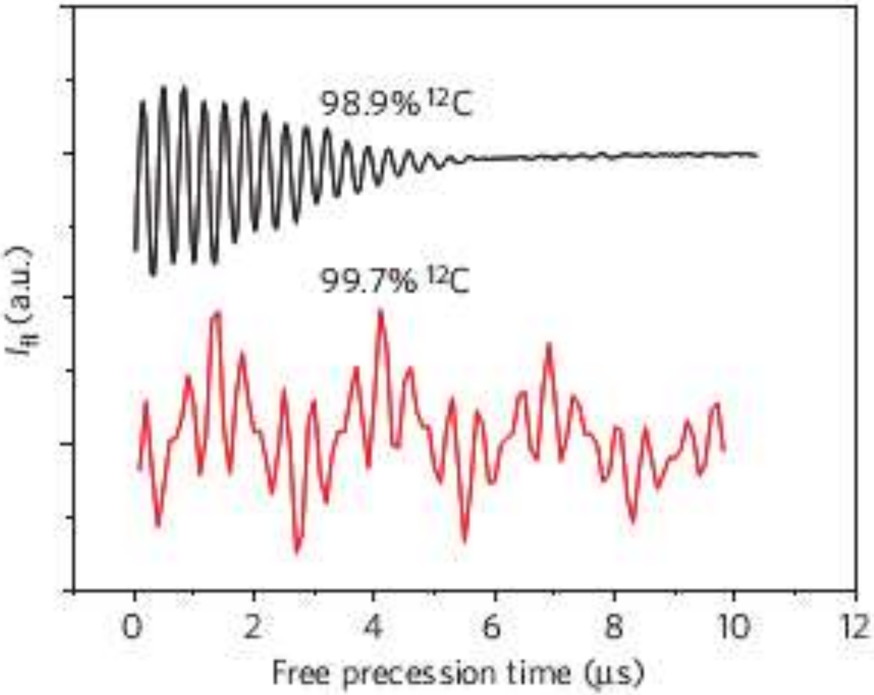
Manipulation of single N-V center

Ultralong spin coherence time in isotopically engineered diamond
Balasubramanian et al. Nature Materials 8, 383 (2009).

Coherent Dynamics of a Single Spin…, R. Hanson et al., Science 352, 320 (2008).

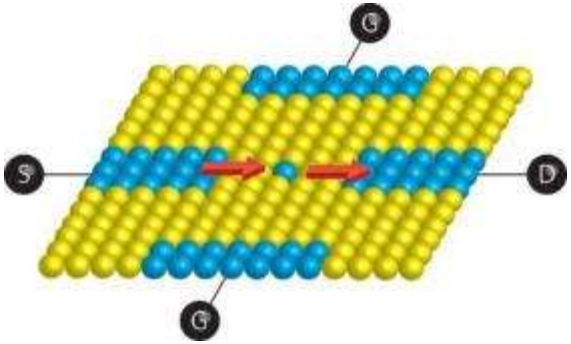


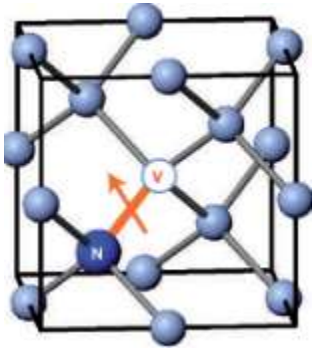




Lower nuber of nuclear spin is increasing coherence time

Solotronics





Single phosphorus atom on Si surface

- Ohmic wires
- Transistors
- Electron tunneling
- Qbits
- Integration with present electronics

Challenges:

- Very low temperatures (mK)
- Difficult optical access

e.g. Fuechsle et al., Nature Nanotechnology 7, 242 (2012).

N-V defect center in diamond

Advantages:

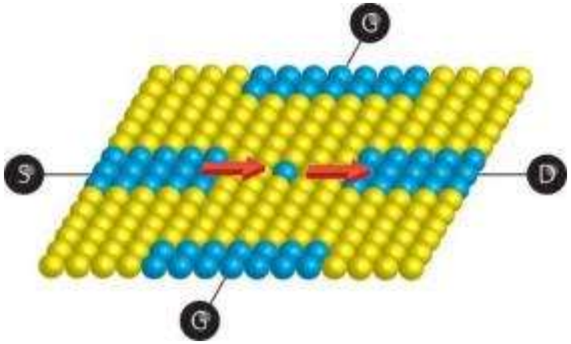
- Room temperature Qubit
- Good optical access
- Coupling to nuclear spin, N dopant or other N-V defect

Challenges :

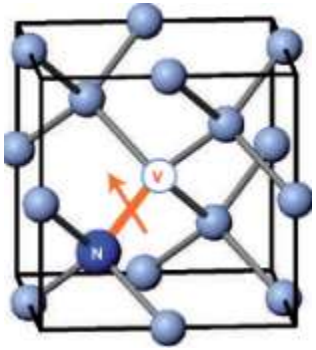
- Difficult integration with electronics

e.g. F. Dolde et al., Nature Physics 9, 139 (2013).
Balasubramanian et al. Nature Materials 8, 383 (2009).
R. Hanson et al., Science 320, 352 (2008).

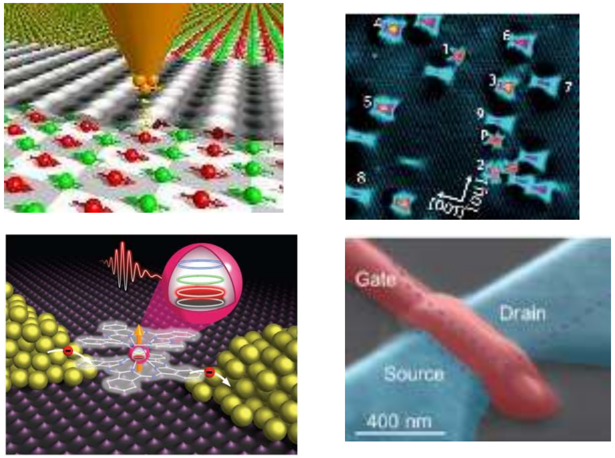
Solotronics



Single phosphorus atom on Si surface



N-V defect center in diamond



- On a surface
- In a transistor

Magnetic ion

Atomic-scale magnetic resolution

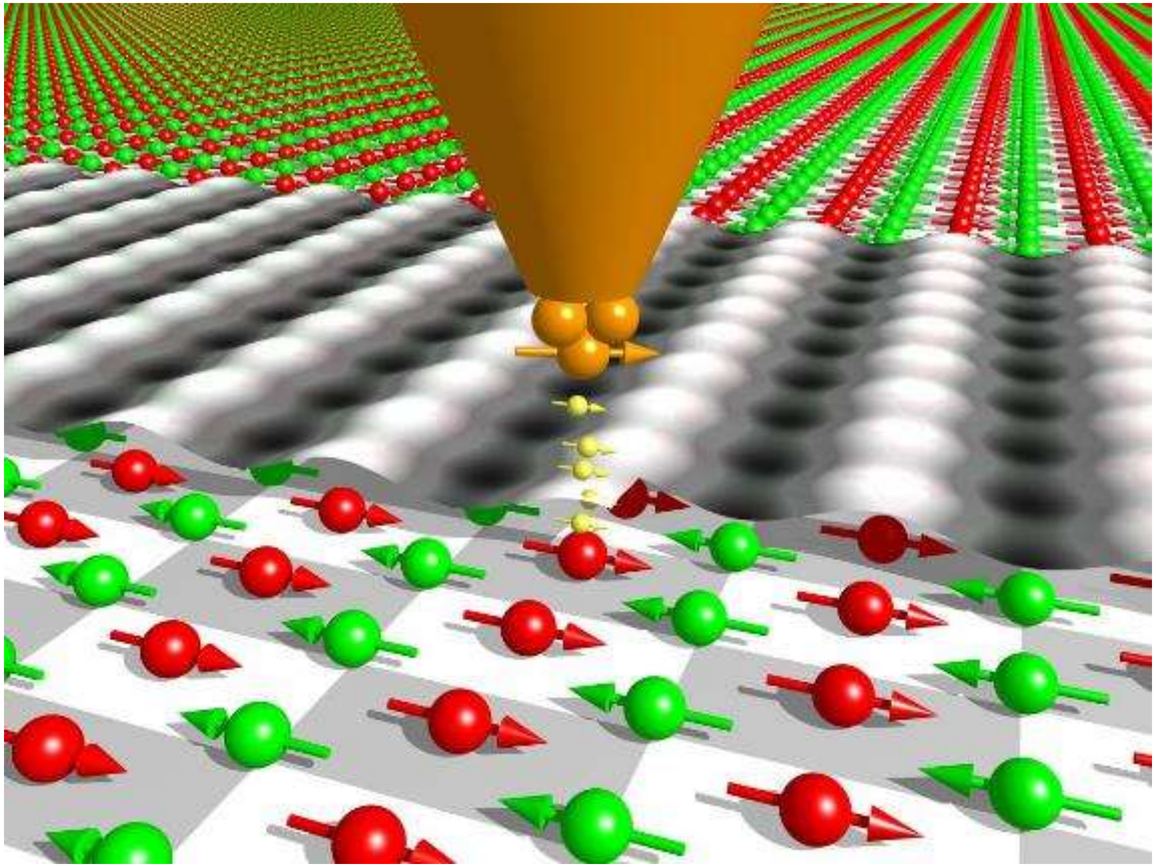
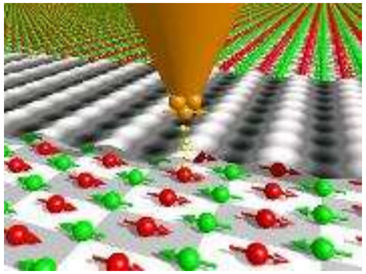
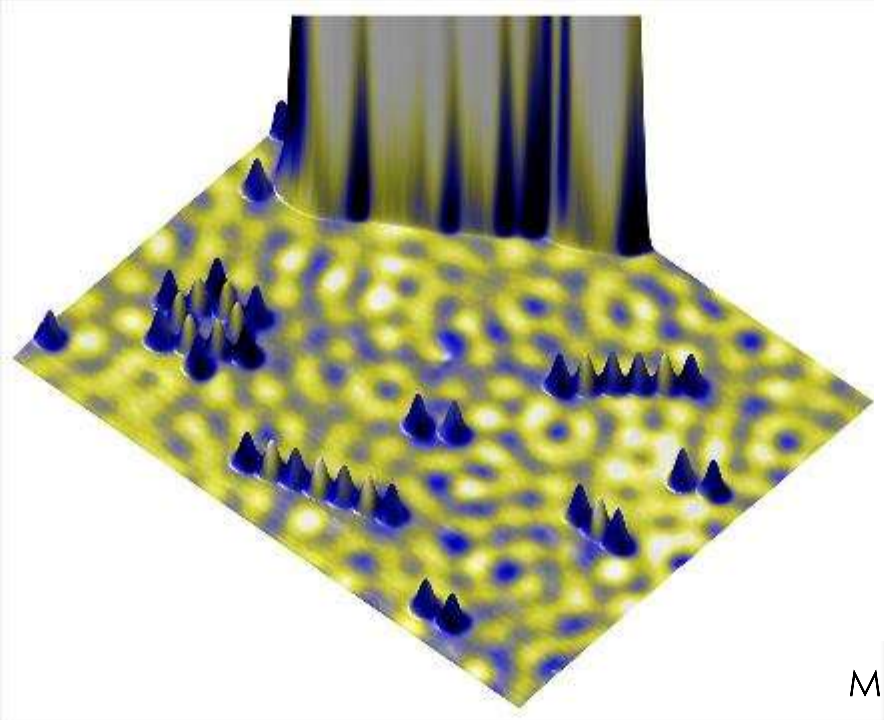


Illustration of atomic-scale magnetic resolution with a scanning tunneling microscope (STM) using a magnetic tip

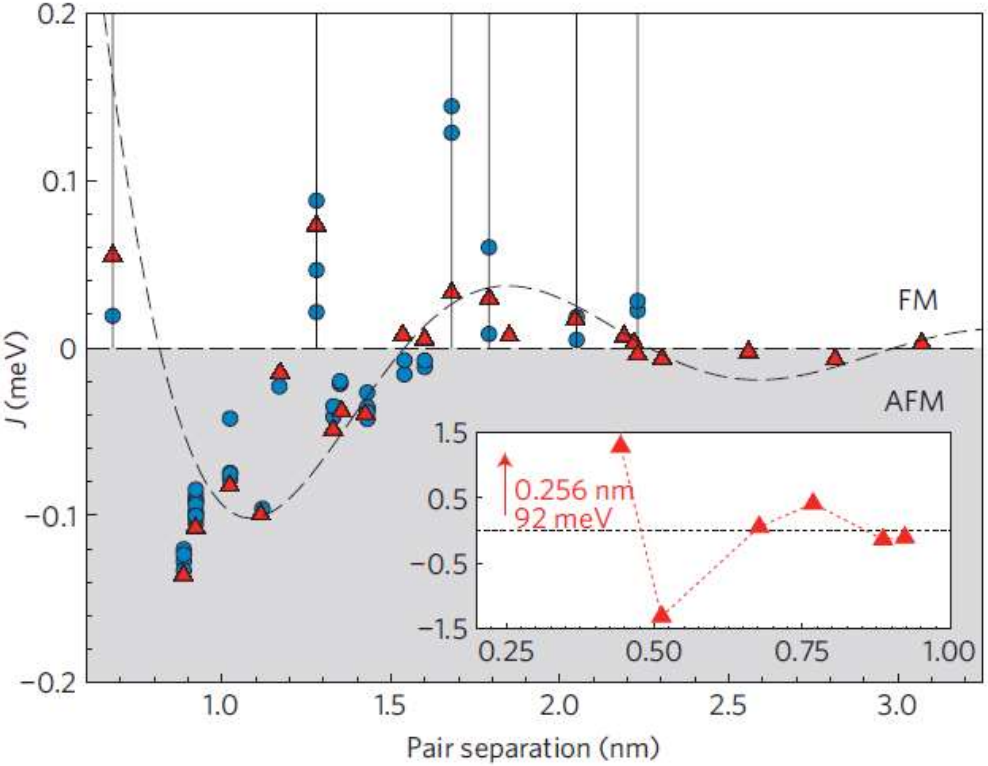
S. Heinze, R. Wiesendanger, University of Hamburg

Iron atoms on the (111) surface of copper.





Study of exchange interaction vs distance

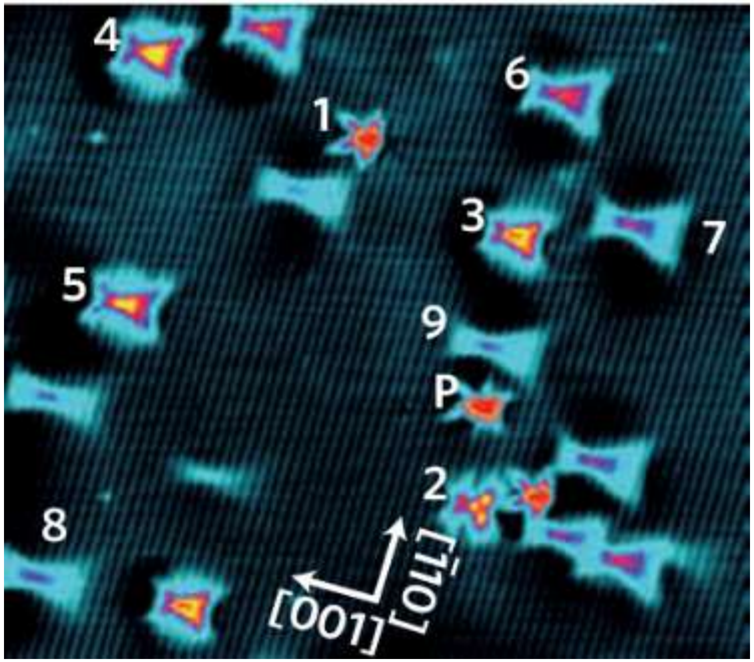


Measured (blue circles) and calculated (red triangles)

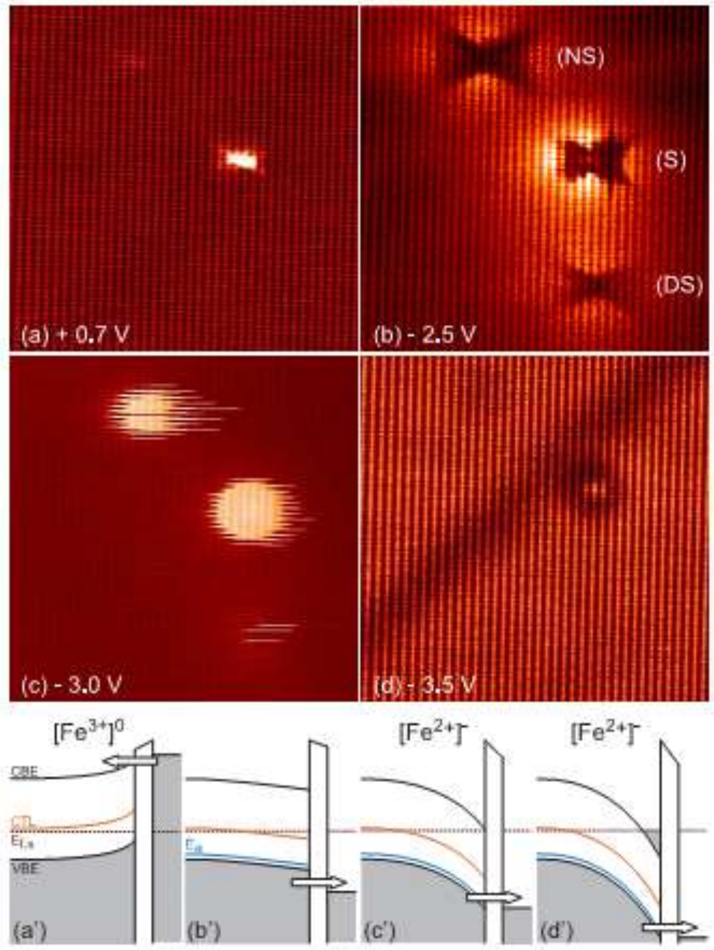
A. A. Khajetoorians, J. Wiebe, B. Chilian, S. Lounis, S. Blügel.
R. Wiesendanger, Nature Physics 8, 497 (2012).

Mn and Fe atoms close to GaAs surface

Mn in GaAs



Fe in GaAs

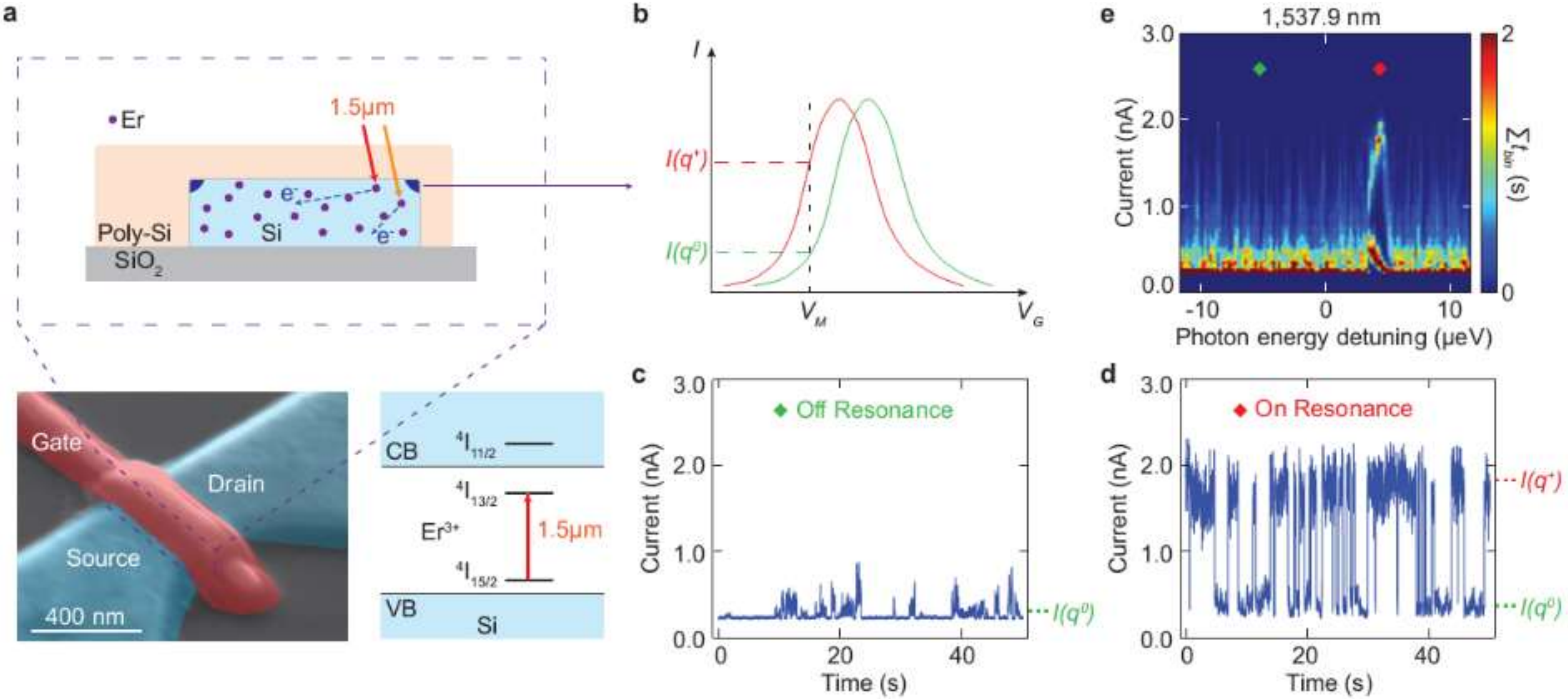


Images with scanning tunneling microscope (STM)

Celebi et al., Phys. Rev. Lett. 104, 086404 (2010).

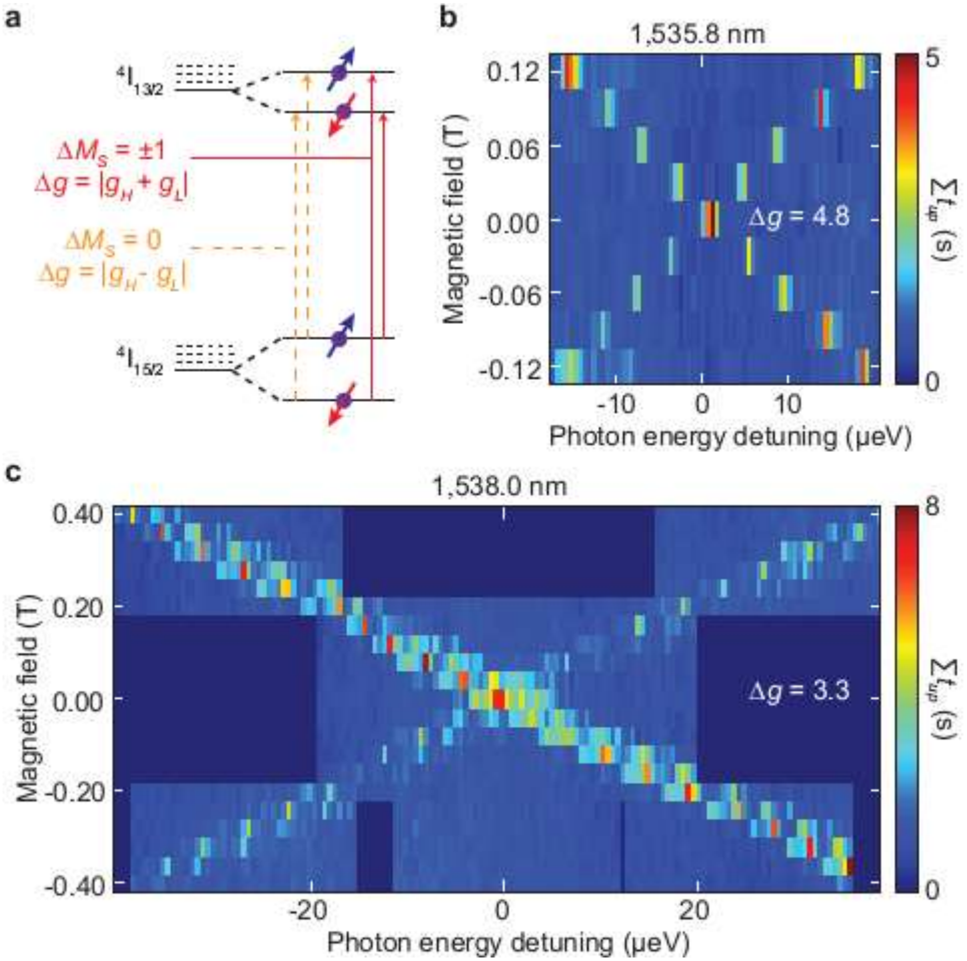
J. Bocquel et al.,Phys. Rev. B 87, 075421 (2013)

Single Er^{3+} in Si



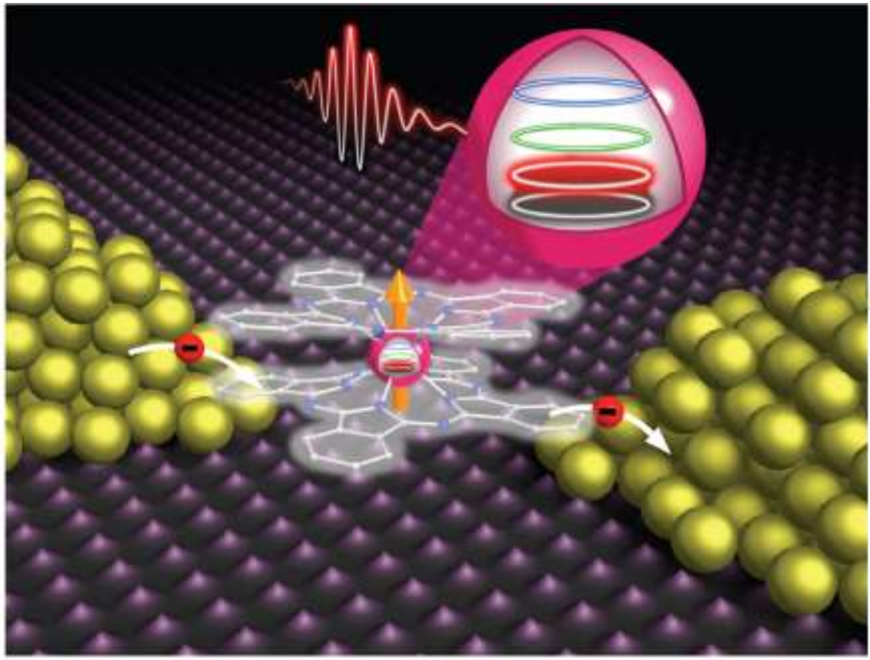
Optical addressing of an individual erbium ion in silicon,
Chunming Yin et al., Nature 497, 91 (2013).

Single Er^{3+} in Si

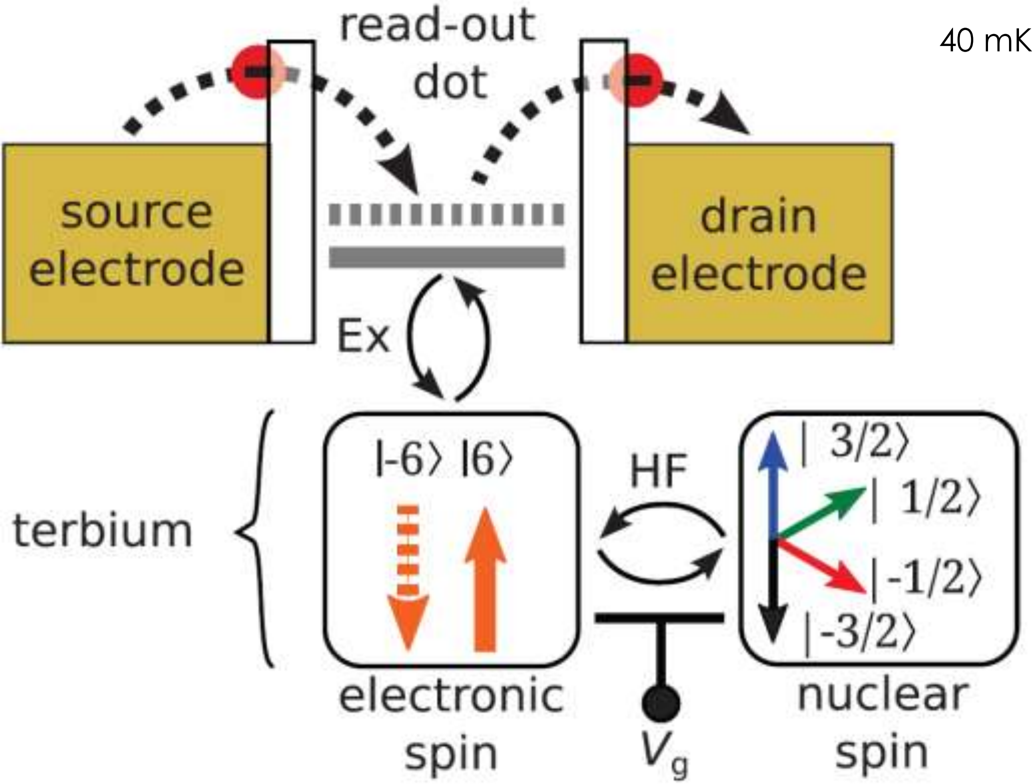


Optical addressing of an individual erbium ion in silicon, Chunming Yin et al., Nature 497, 91 (2013),

Single-molecule magnets

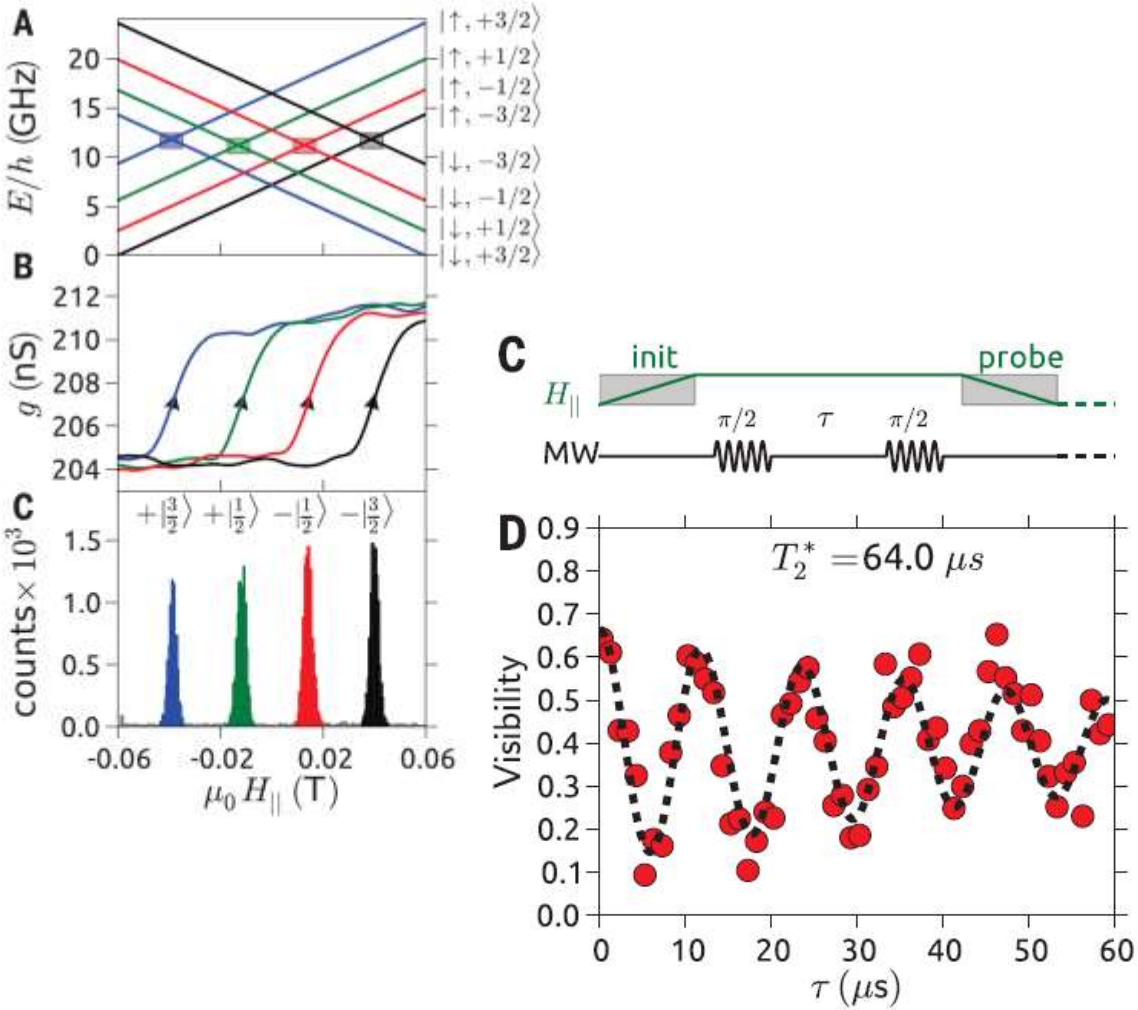


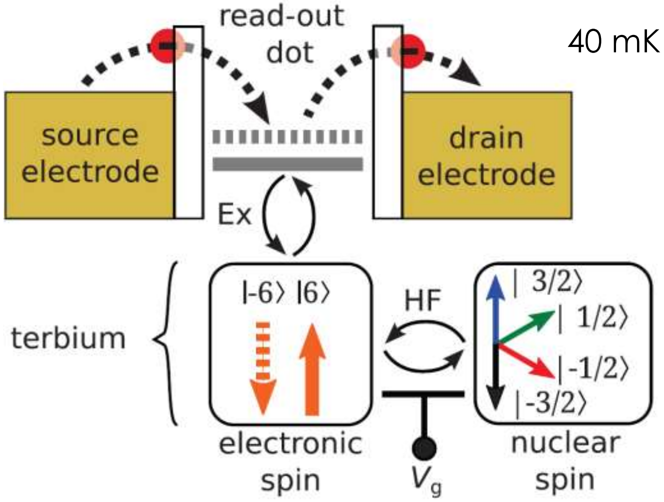
40 mK



S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, Science 344, 1135 (2014).

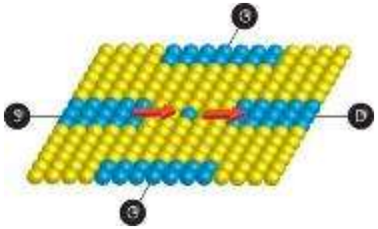
Single molecular magnet

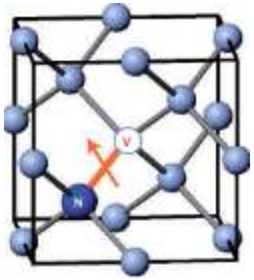




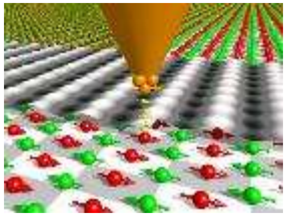
S. Thiele, F. Balestro, R. Ballou, S. Klyatskaya, M. Ruben, W. Wernsdorfer, Science 344, 1135 (2014).

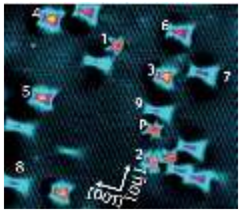
How to access and manipulate single dopant?

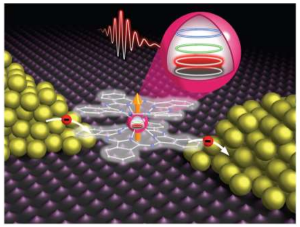


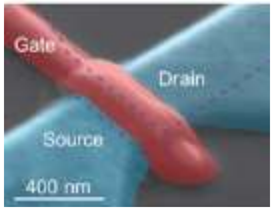


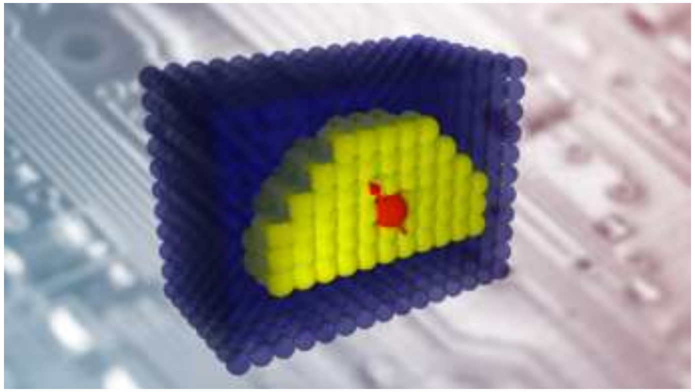
- Current affected by a dopant
- Intra-center optical transitions
- STM tip







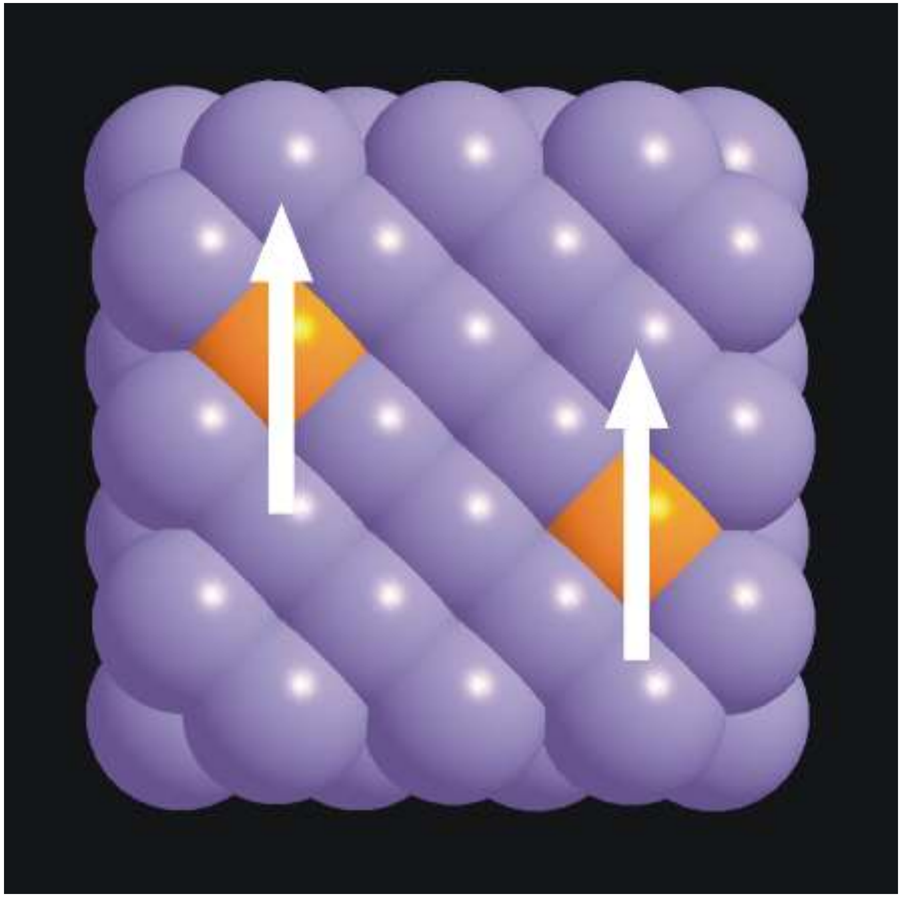




Magnetic ion in a semiconductor QD

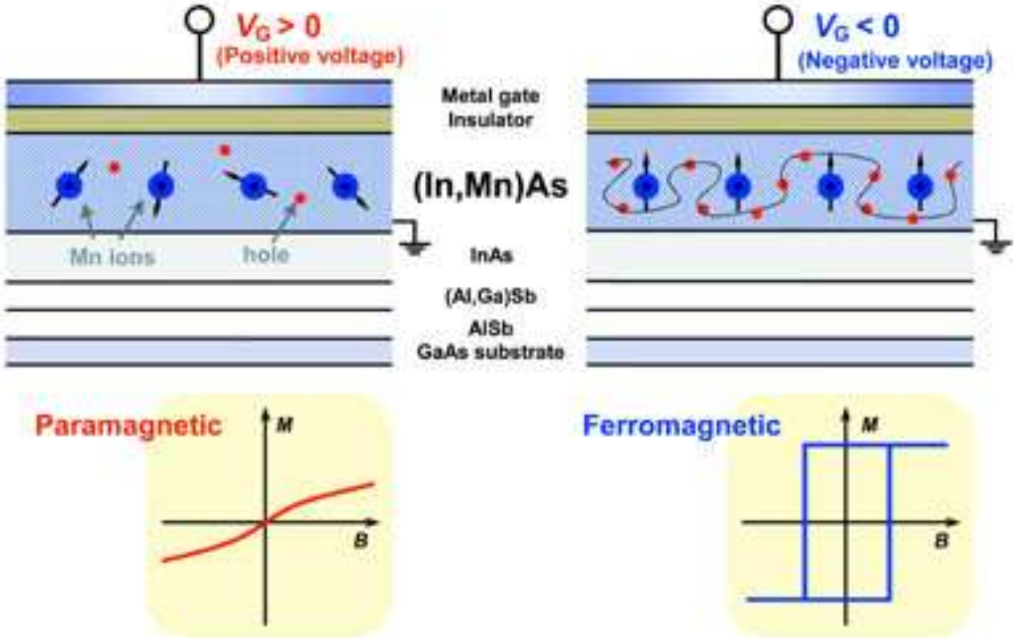
- Excitonic transitions
- Polarized carriers

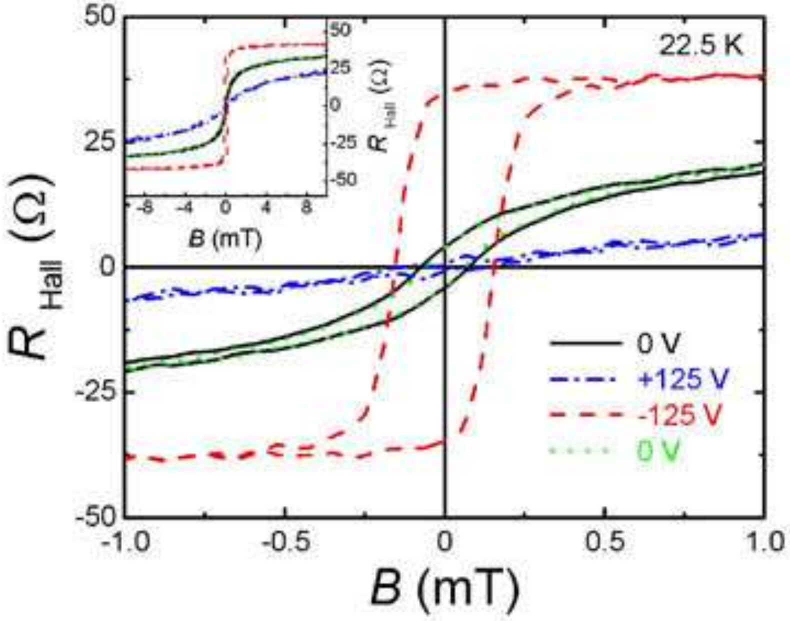
Magnetic ions in a semiconductor



Graphics: http://www.physics.rutgers.edu

Ferromagnetism in $Ga_{1-x}Mn_xAs$



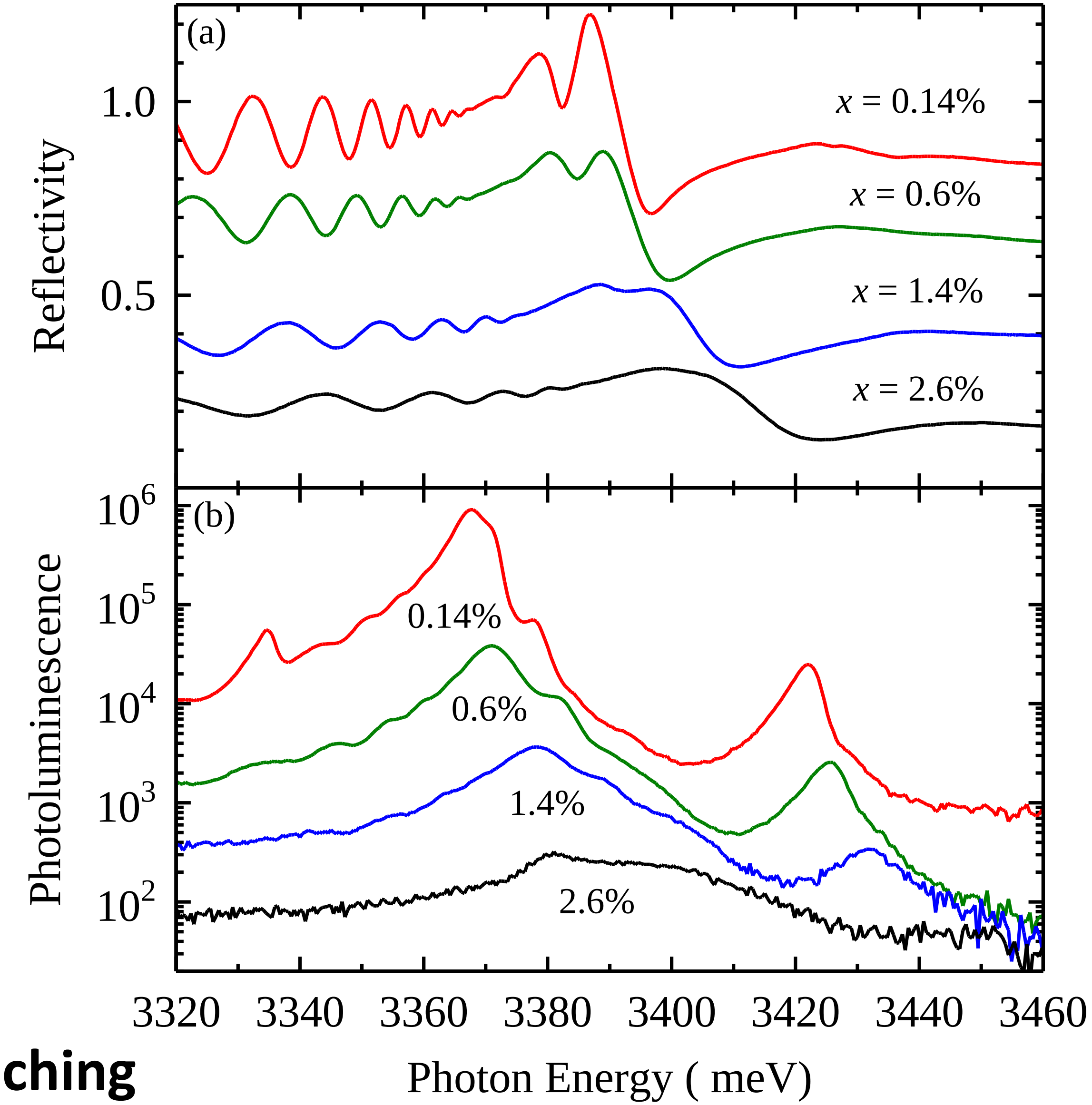


H. Ohno et al., Nature 408, 944 (2000).
H. Ohno, Science 281, 951 (1998).

Influence of magnetic ions on a semiconductor

recent Example: $Zn_{1-x}Mn_xO$

B = 0



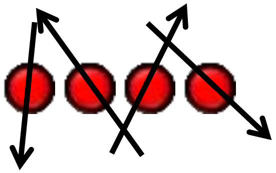
Increase of energy gap

Broadening of lines

Photoluminescence quenching

W. Pacuski et al., PRB 2011

Magnetic ions in a semiconductor

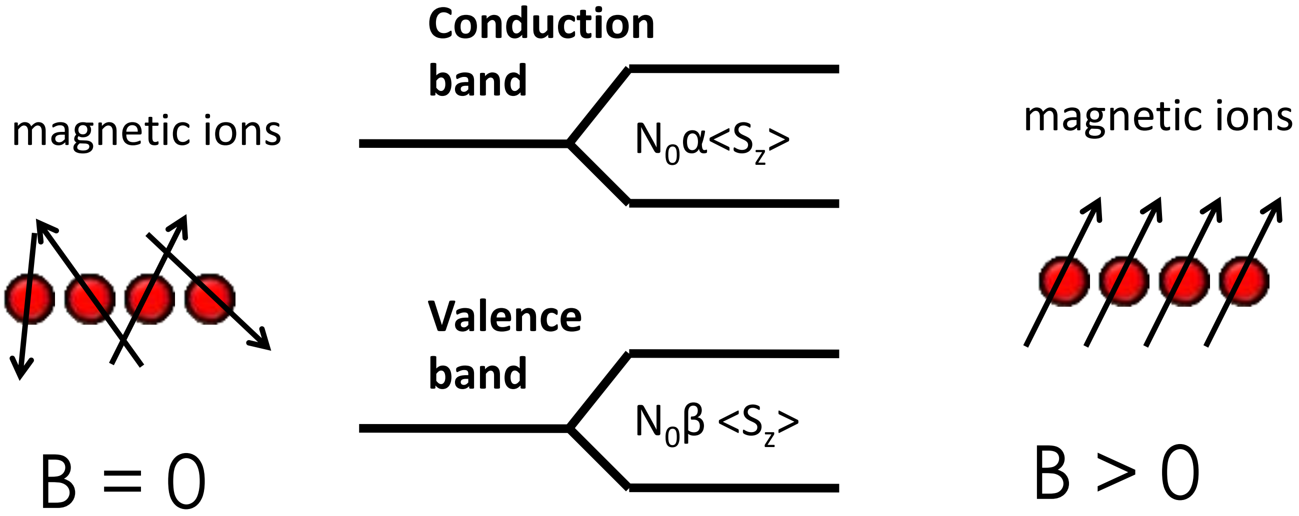

magnetic ions

B = 0

Increase of energy gap
Broadening of lines
Photoluminescence quenching

Magnetic ions in a semiconductor

Diluted magnetic semiconductor



magnetic ions

Conduction band

$N_0\alpha\langle S_z\rangle$

Valence band

$N_0\beta\ \langle S_z\rangle$

magnetic ions

$B = 0$

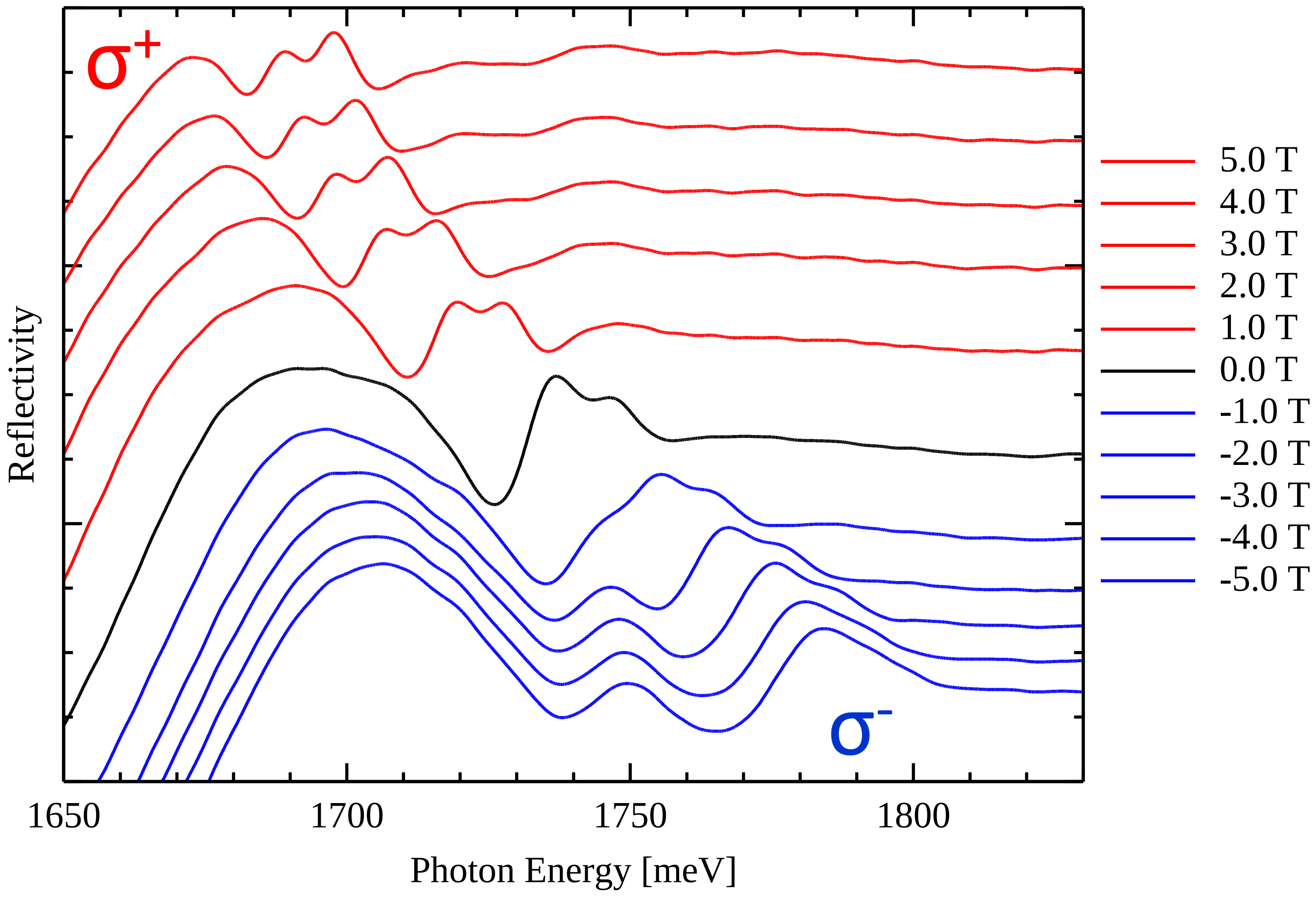
$B > 0$

Increase of energy gap
Broadening of lines
Photoluminescence quenching

Giant Zeeman splitting

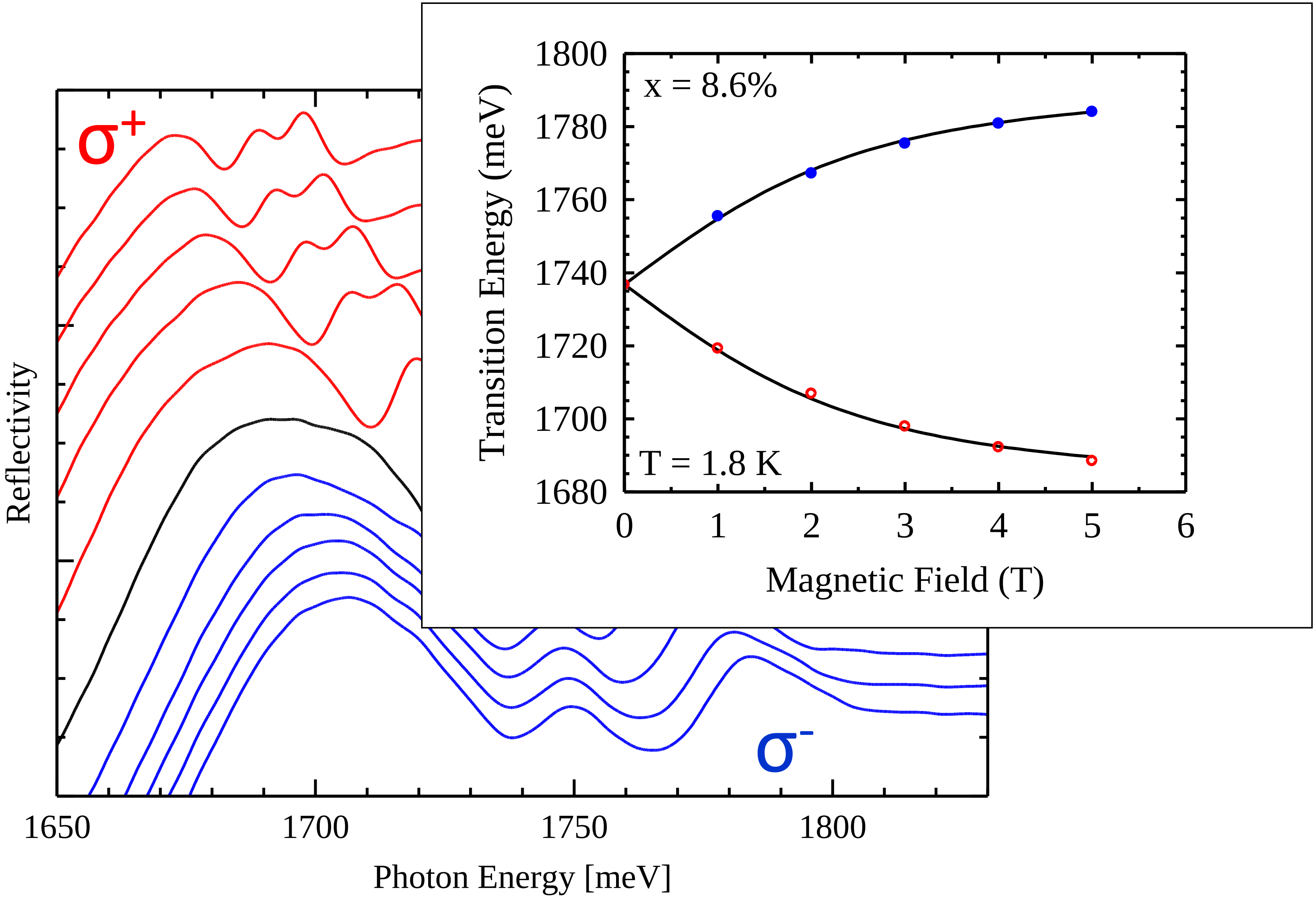
AV Komarov et al., JETP 73, 608 (1977).
J. A. Gaj, R. R. Gałązka, M. Nawrocki, SSC (1978).
J.A. Gaj, R. Planel, G. Fishman, SSC(1979).

Giant Zeeman effect in $Cd_{1-x}Mn_xTe$



K. Gietka et al., Acta Phys. Pol. A (2012)

Giant Zeeman effect in $Cd_{1-x}Mn_xTe$

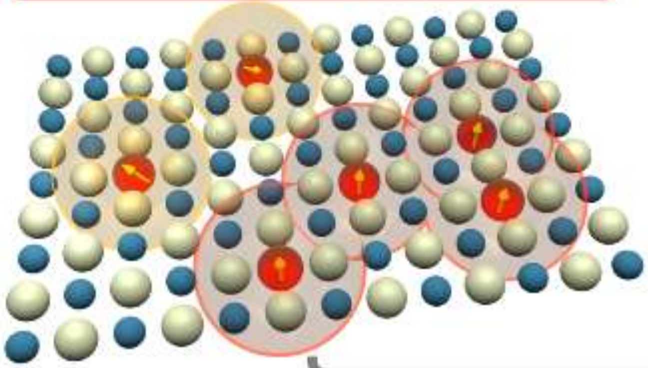


K. Gietka et al., Acta Phys. Pol. A (2012)

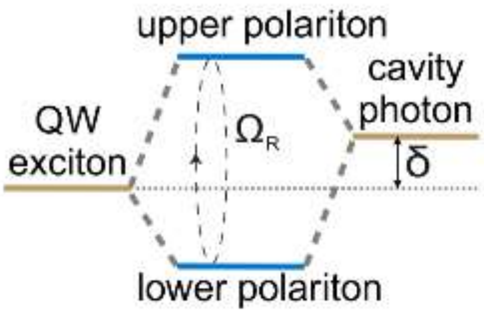
Motivation: enhancement of magneto-optical effects

Semimagnetic Excitons

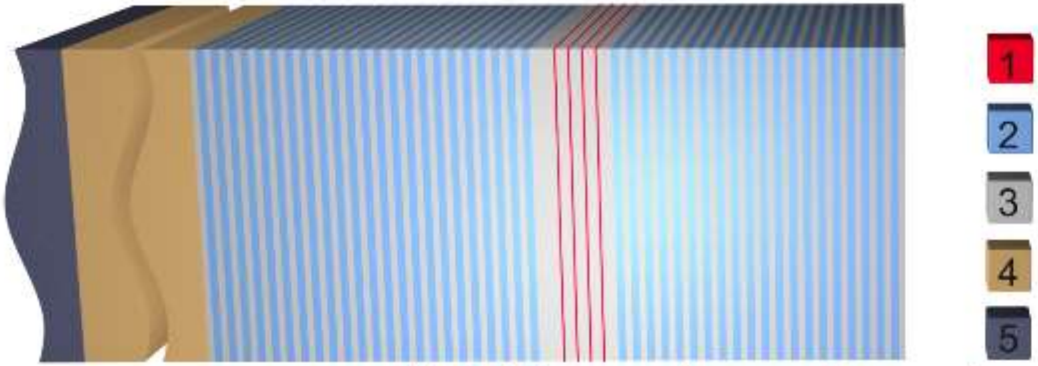
sp-d exchange interaction between charge carriers and magnetic ions
Giant Zeeman effect



Cavity Polaritons



Semimagnetic Cavity Polaritons

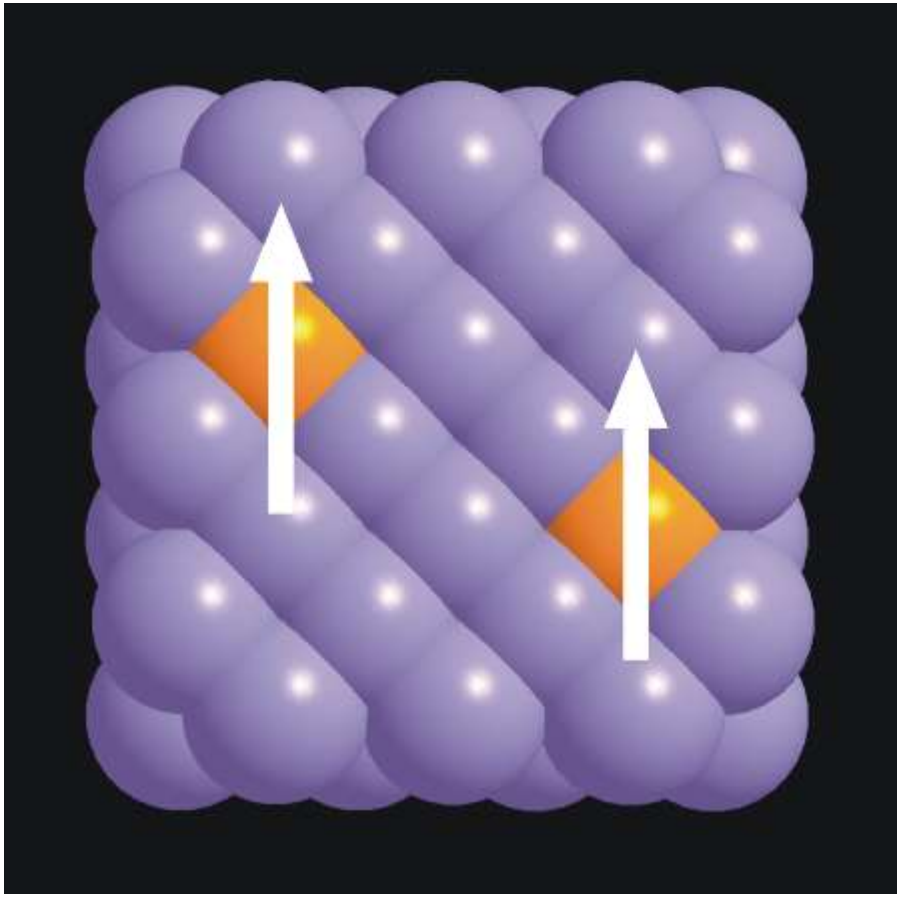


CdMnTe

non-magnetic DBR + semimagnetic quantum well

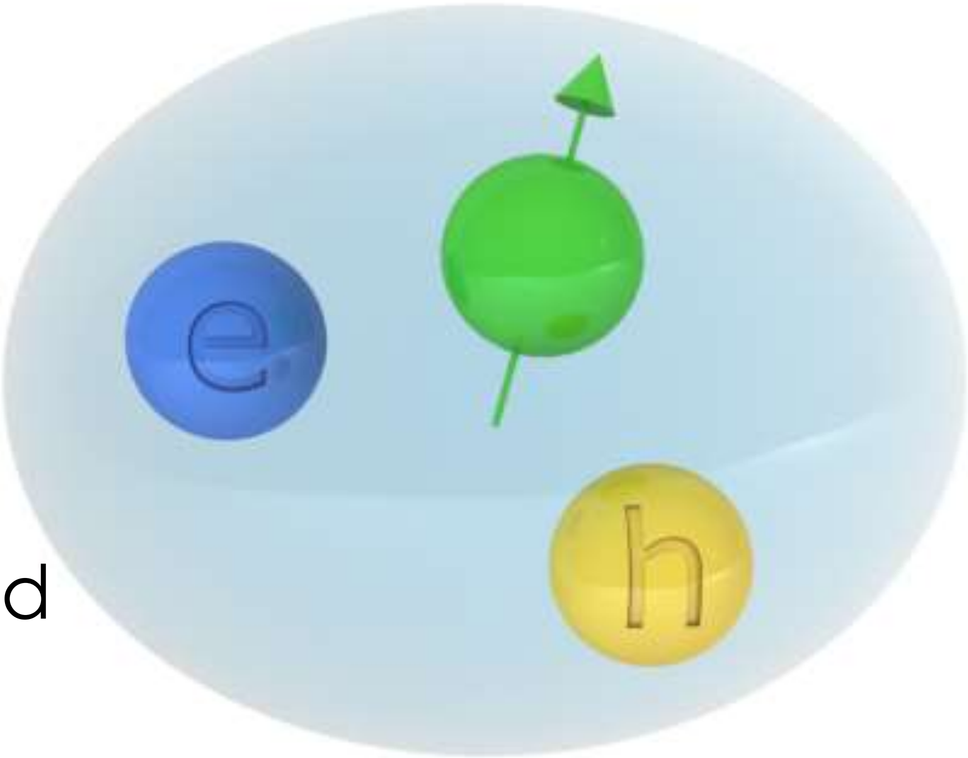
R. Mirek et al., arXiv:1609.00405v2 (2017), Phys. Rev. B (2017).

Magnetic ions in a semiconductor



Enhancment of magnetic and,
in particular, magneto-optical properties

Studying single magnetic ions in QDs



confined electron and hole

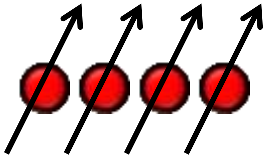
Quantum dots offer

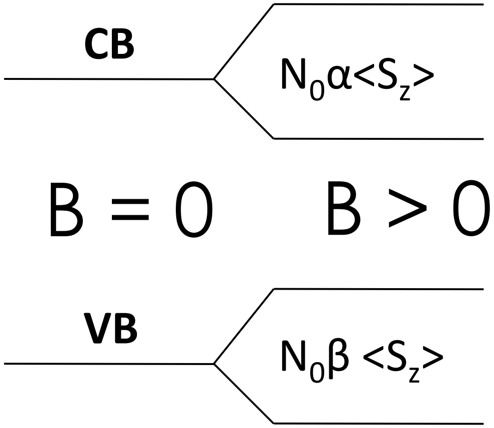
- s,p-d exchange interaction between magnetic ion and confined carriers
- optical readout and manipulation of a single magnetic ion spin

Studying single magnetic ions in QDs

bulk

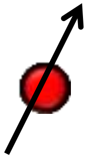
magnetic ions

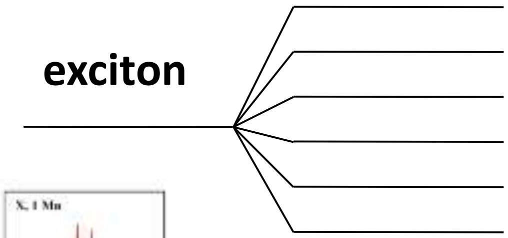


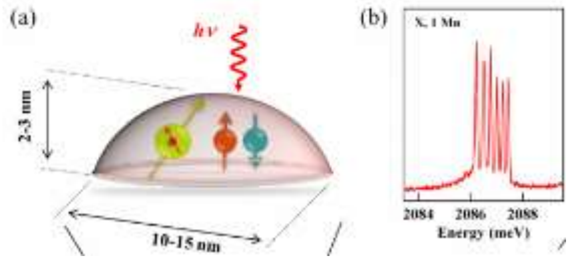


quantum dot

magnetic ion

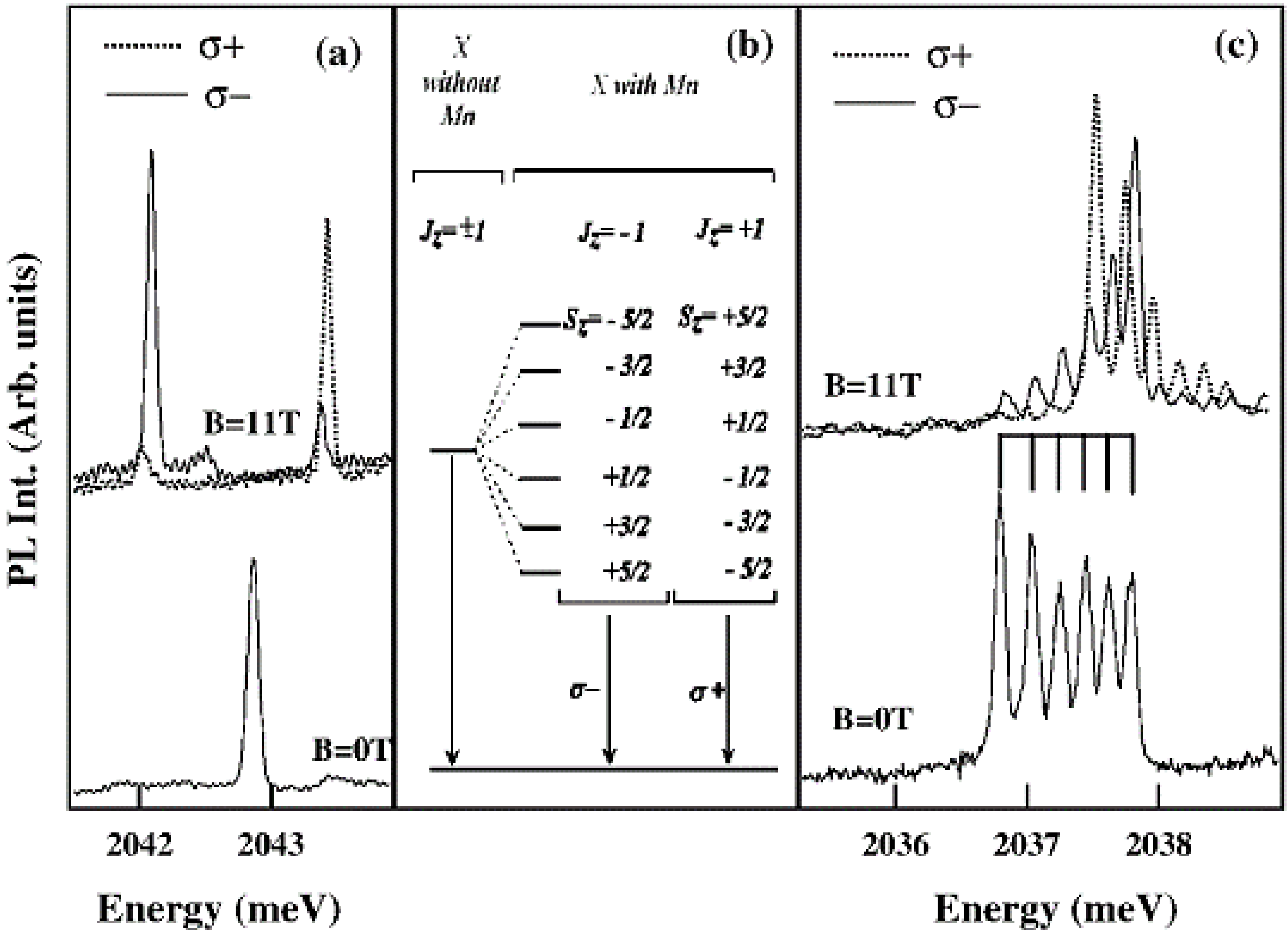






L. Besombes et al., PRL (2004).

Studying single magnetic ions in QDs



CdTe/ZnTe
QD with a
single Mn ion

L. Besombes et al., Phys. Rev. Lett. 93, 207403 (2004)

Selenides vs tellurides

➕

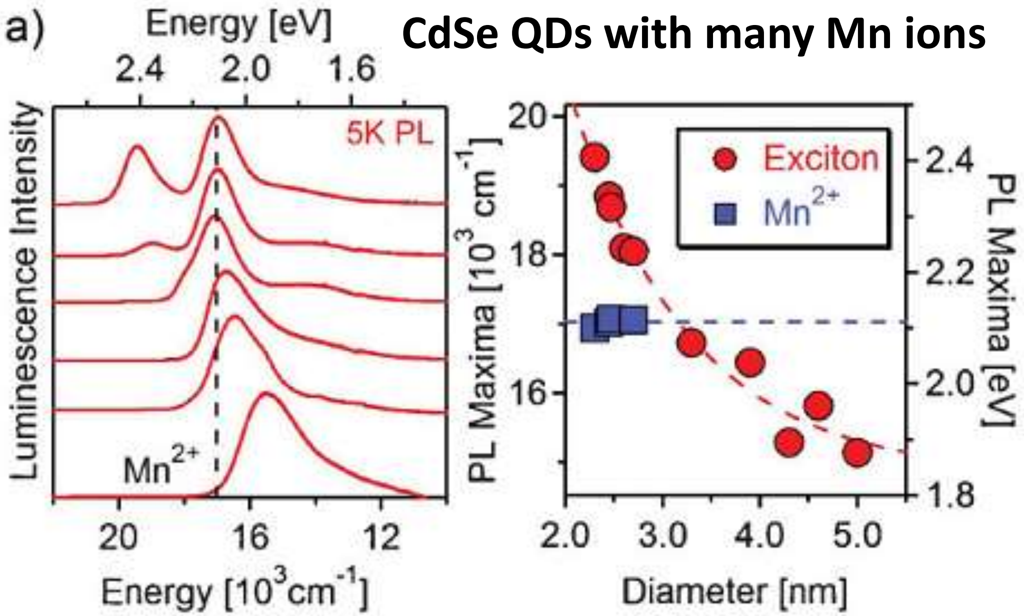
- Stronger *p-d* exchange interaction
- Weaker spin-orbit interaction
- Slower spin relaxation

➖

- Wider energy gap -> a danger of PL quenching

Energy transfer excitons - magnetic ions

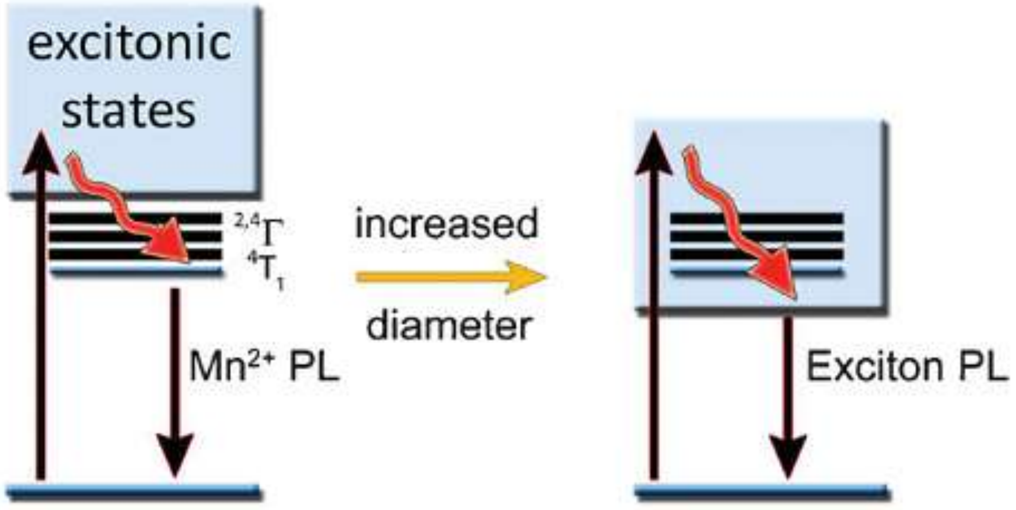
CdSe QDs with many Mn ions



← **CdSe/ZnSe QDs**

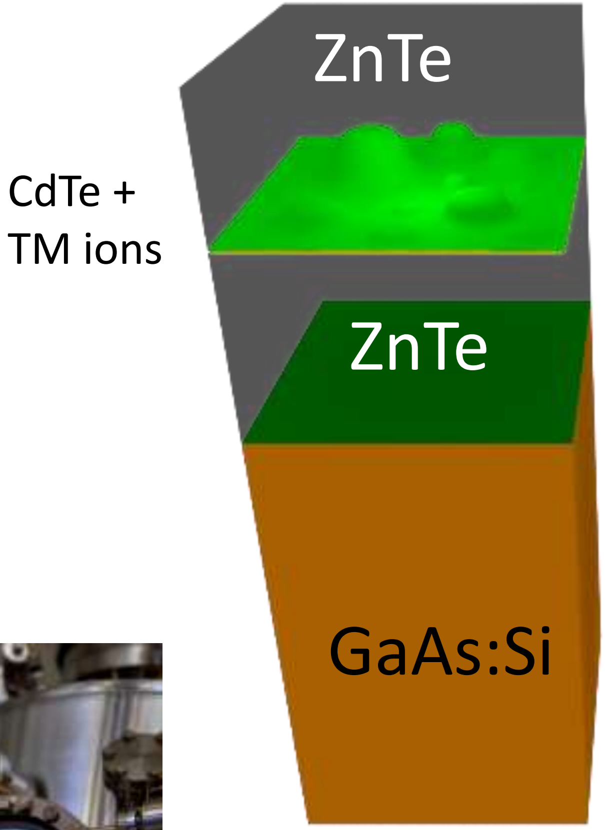
← **Mn^{2+} transitions**

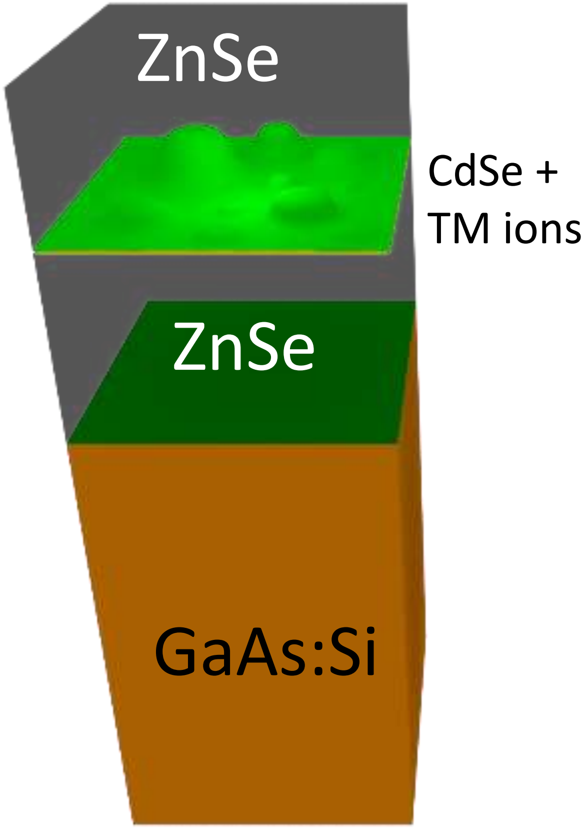
← **CdTe/ZnTe QDs**

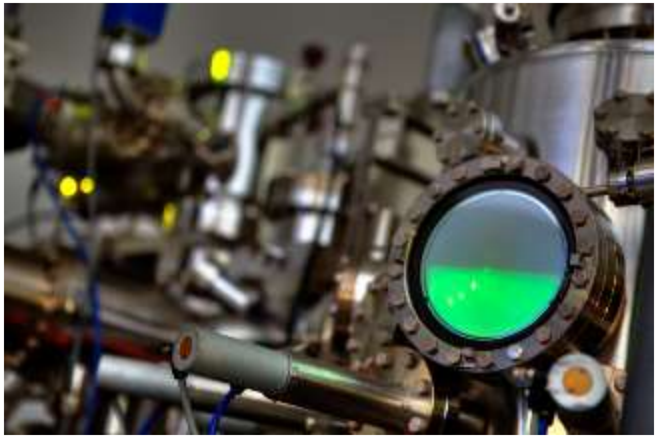


R. Beaulac, P. I. Archer,
S. T. Ochsenbein,
D. R. Gamelin, Ad. Fun.
Mat. (2008)

Samples

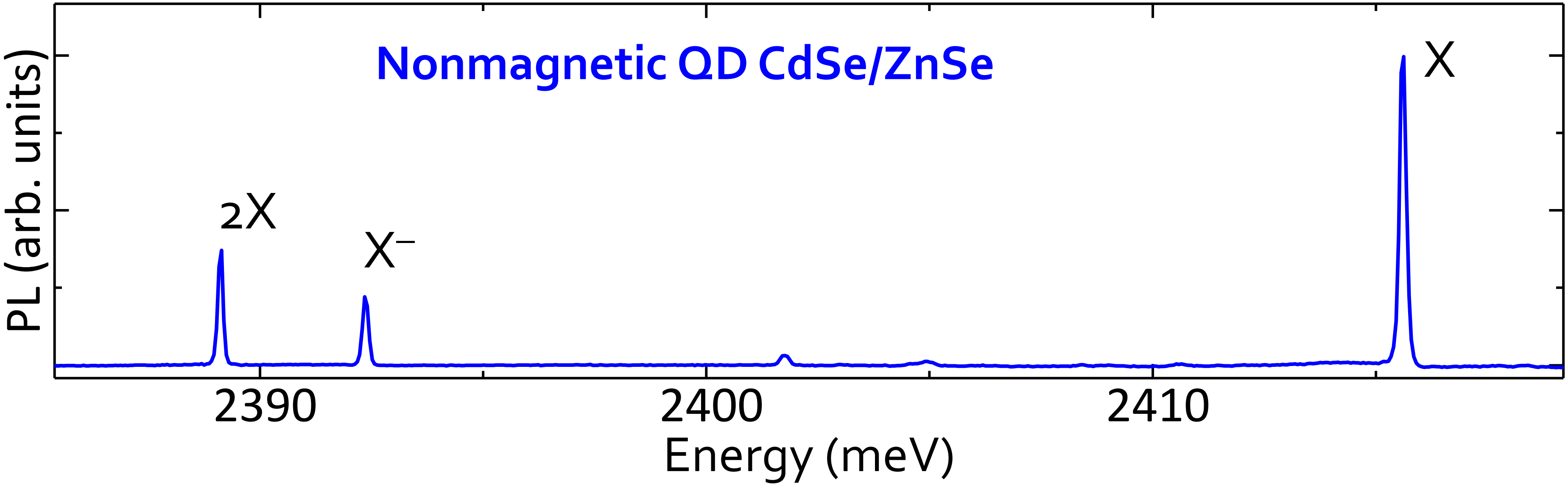


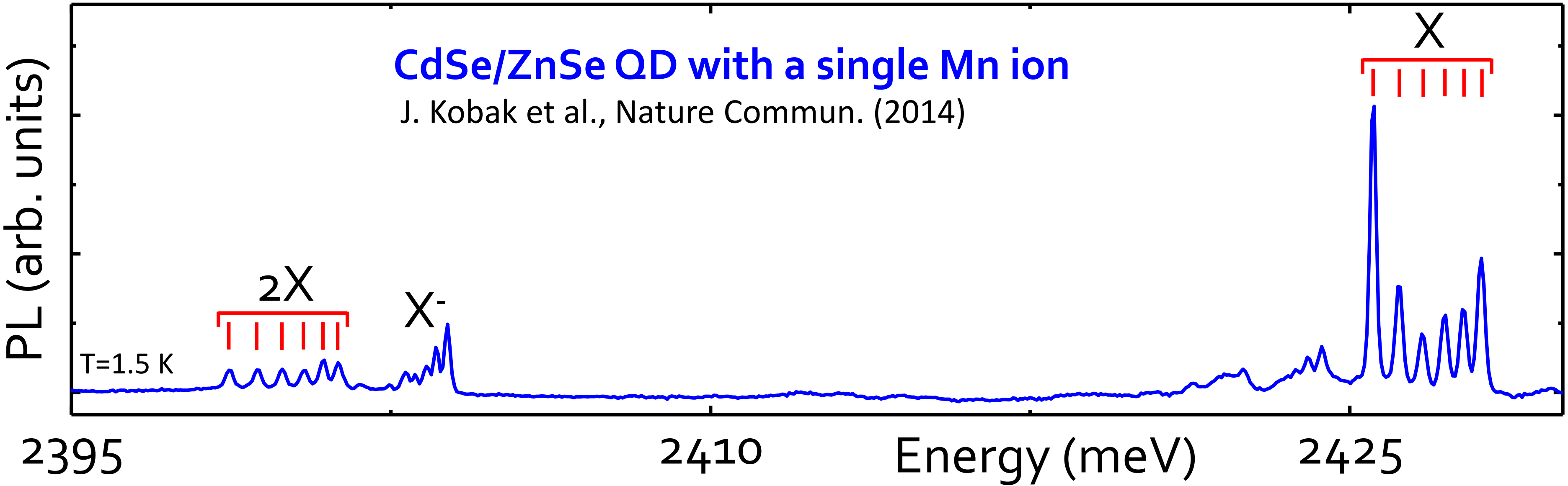




MBE lab
Univeristy of
Warsaw

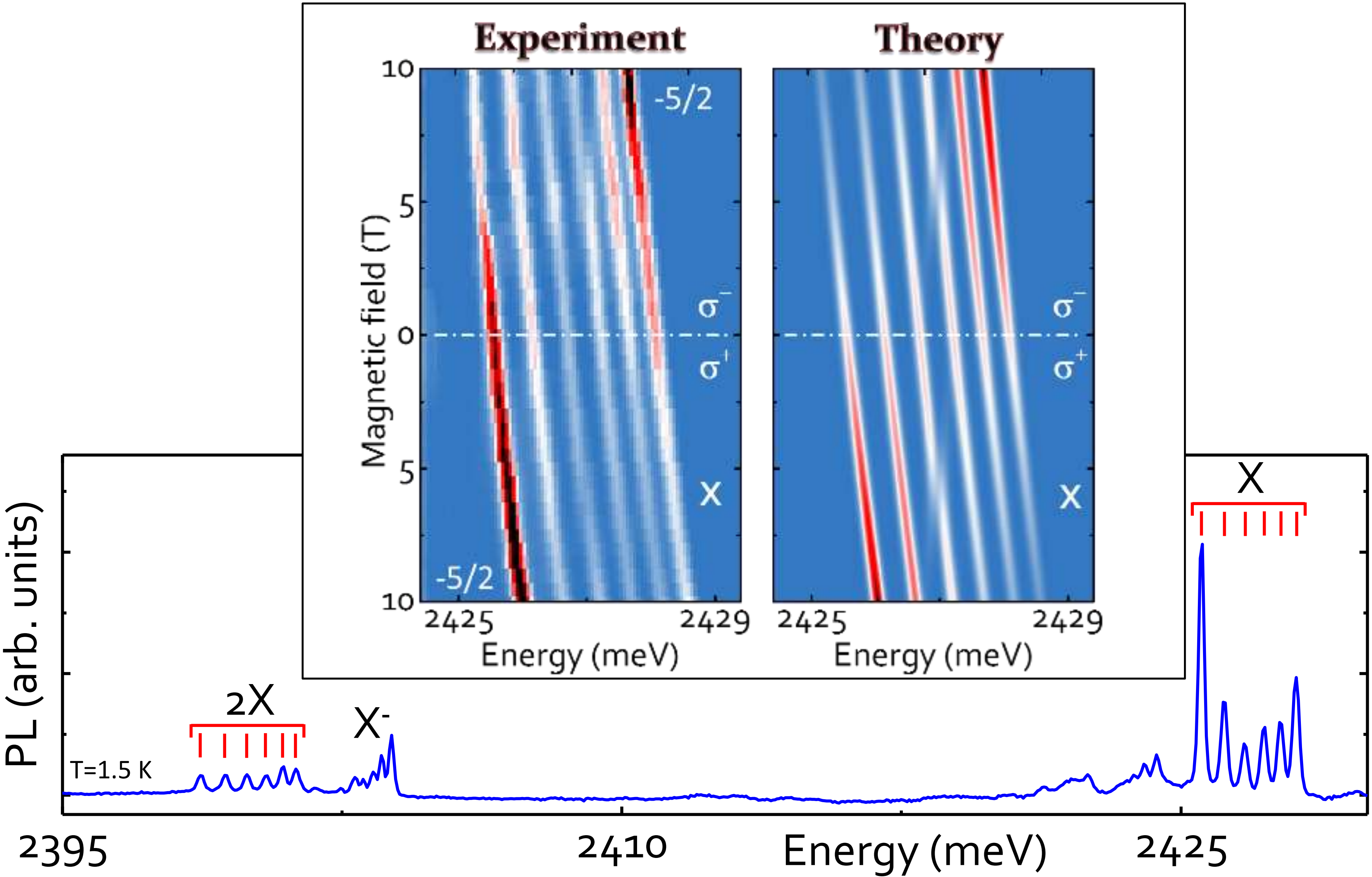
CdSe/ZnSe QD with a single Mn ion



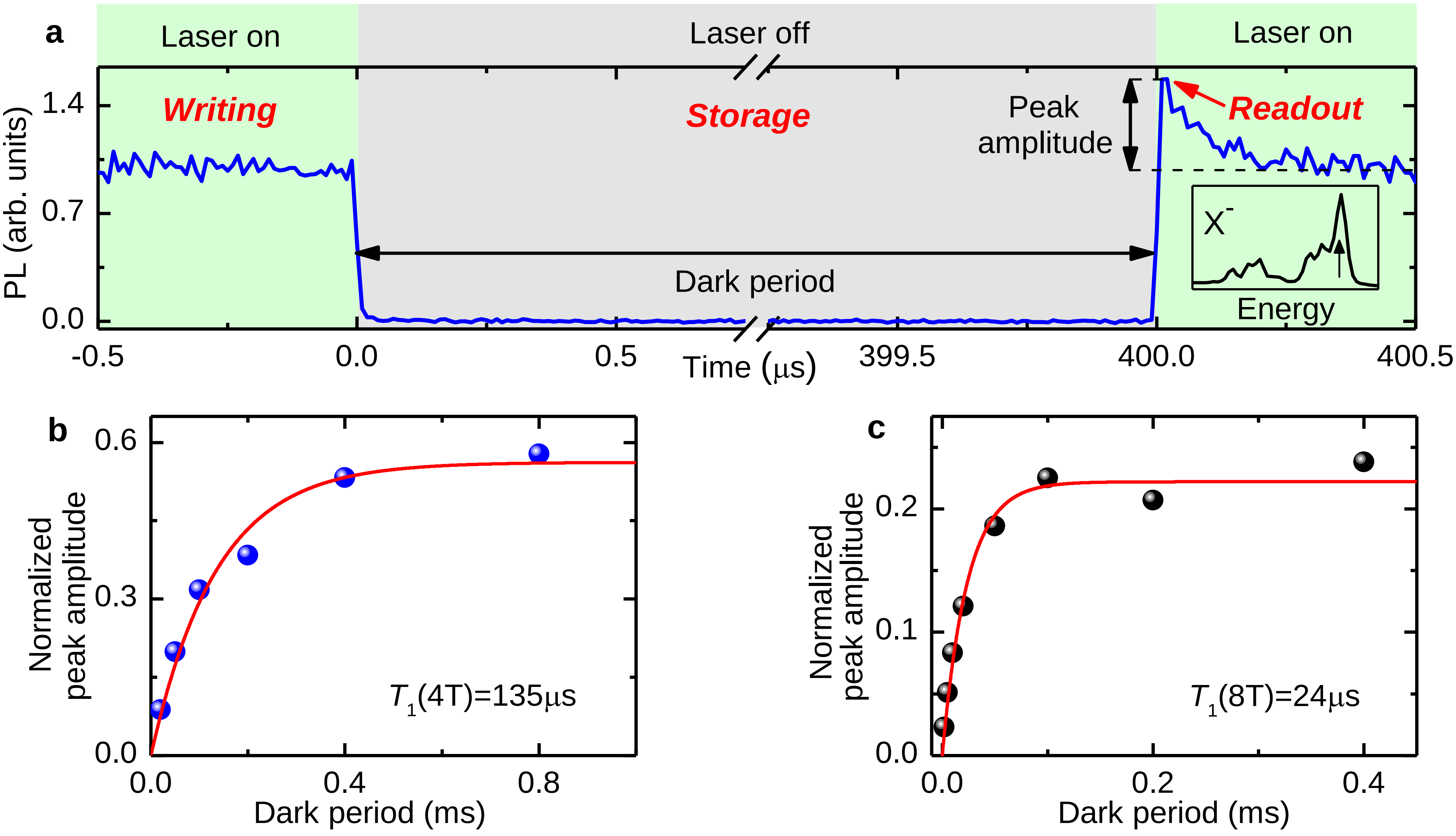


J. Kobak et al., Nature Commun. (2014)

CdSe/ZnSe QD with a single Mn ion

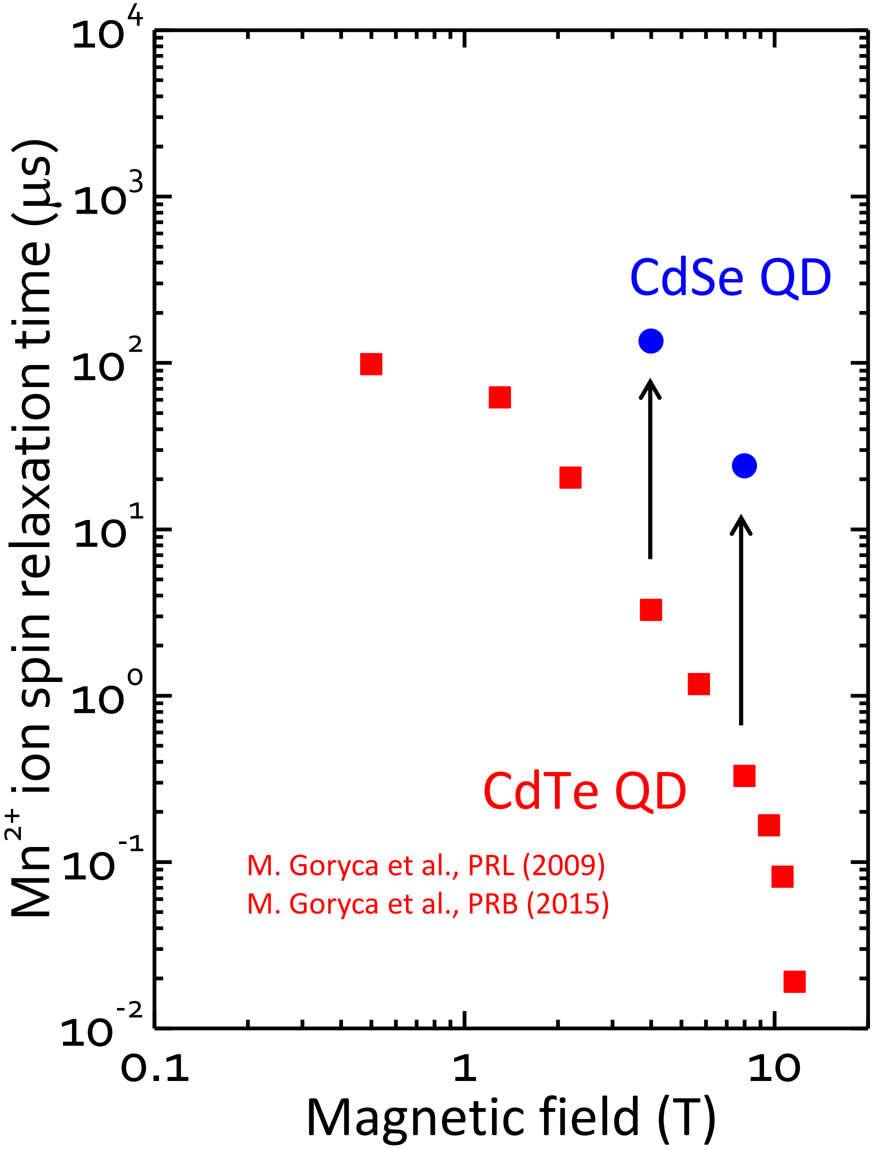


Relaxation of a single Mn^{2+} in a CdSe QD



J. Kobak et al., Nature Communications (2014)

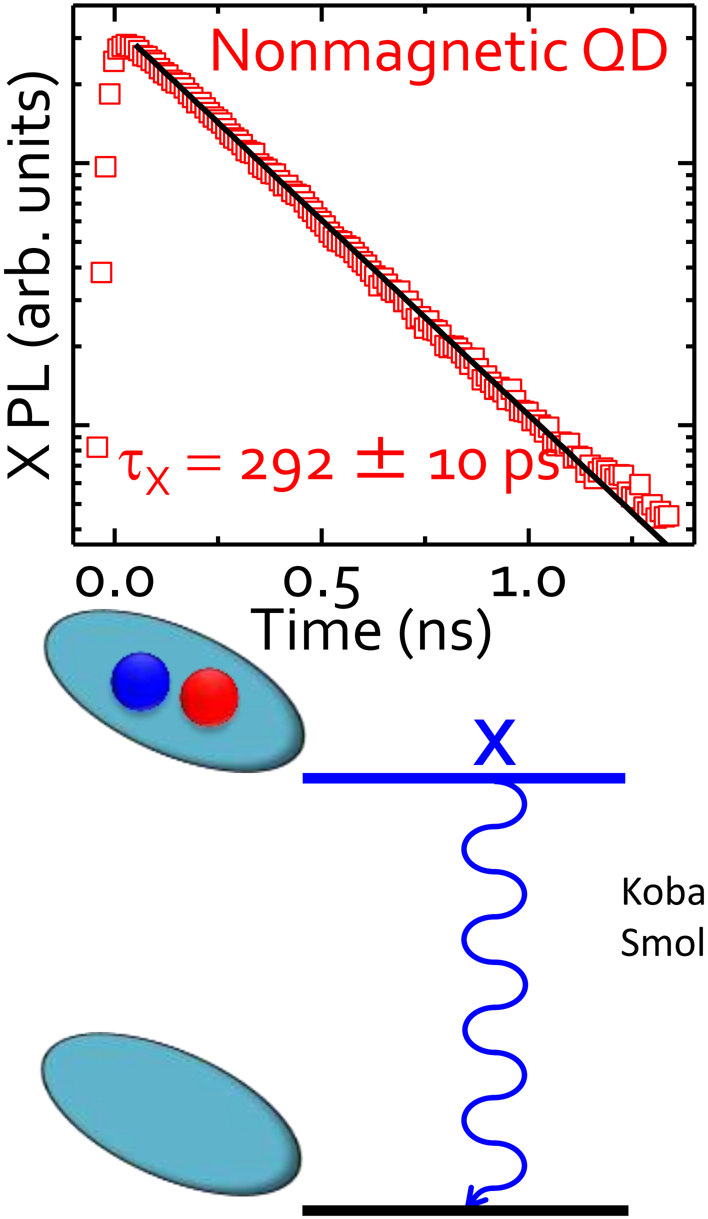
Mn^{2+} spin relaxation time: CdSe vs. CdTe QD



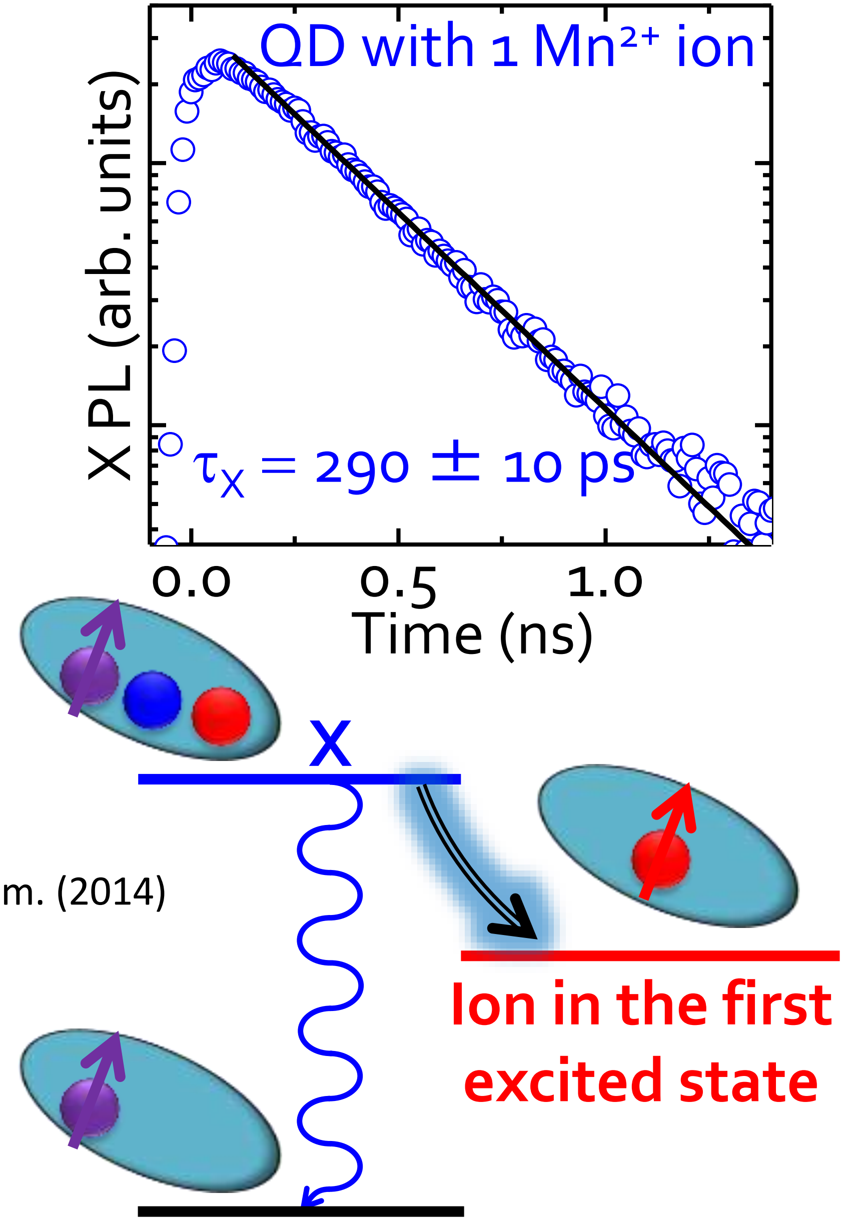
Slow relaxation
for Mn in CdSe QDs:

J. Kobak et al., Nature Communications (2014)

Negligible quenching of excitonic PL

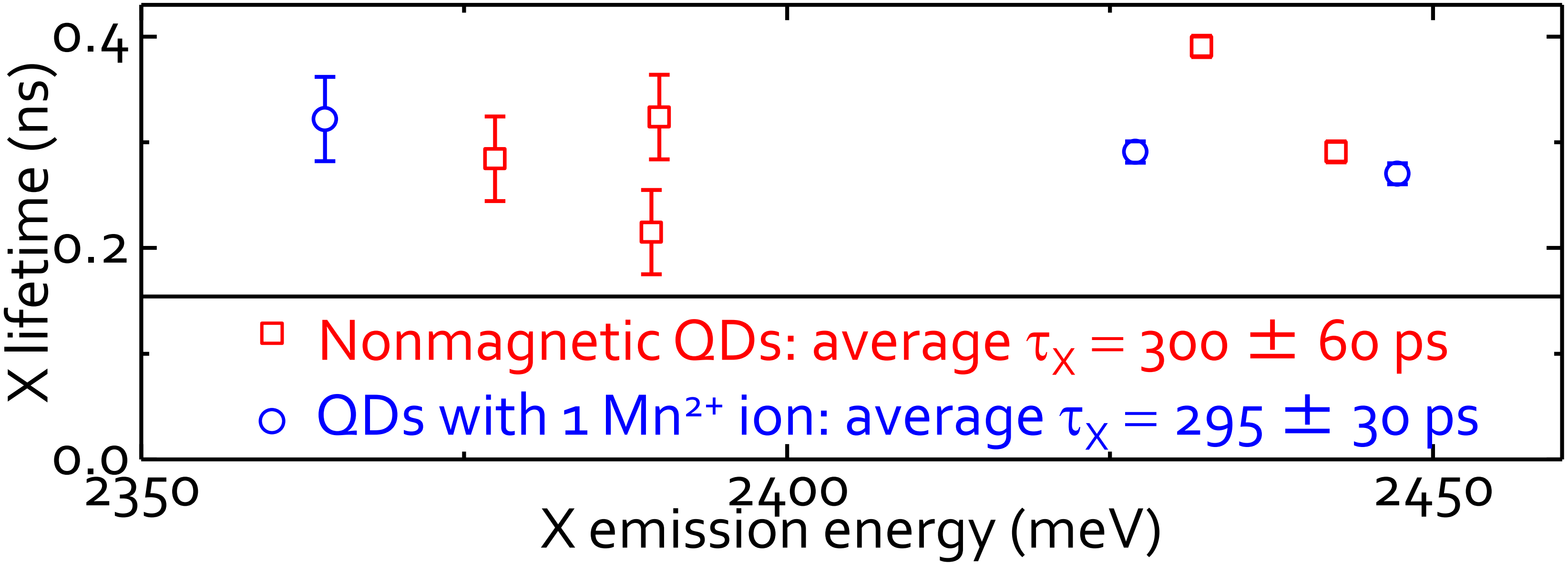


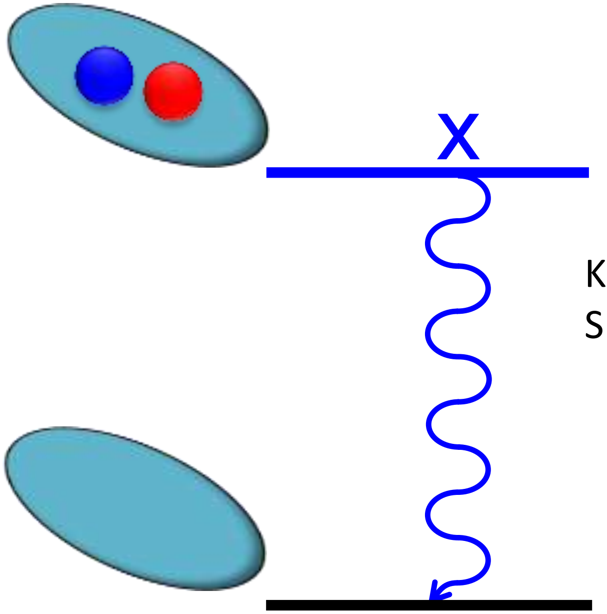
Kobak et al., Nat. Comm. (2014)
Smoleński, JAP (2015)



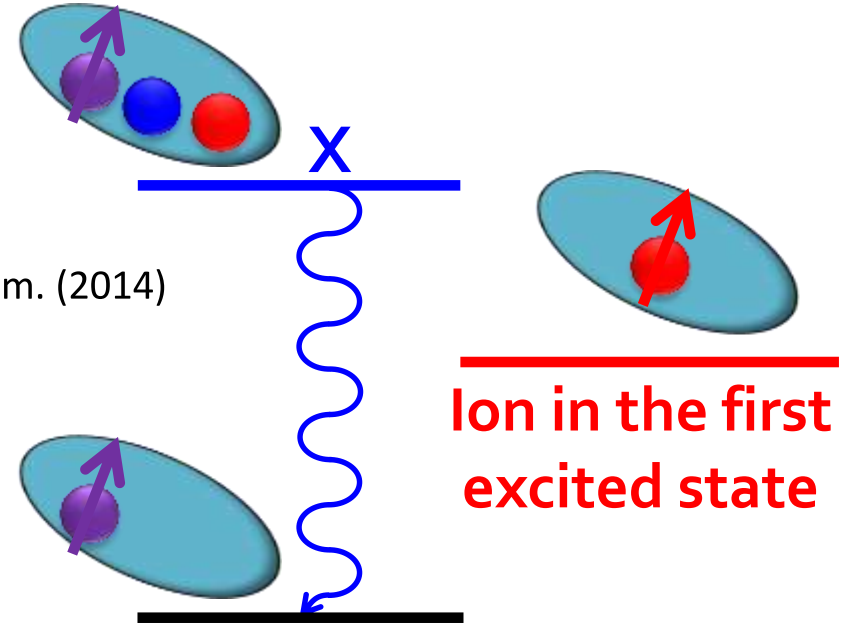
Ion in the first excited state

Negligible quenching of excitonic PL

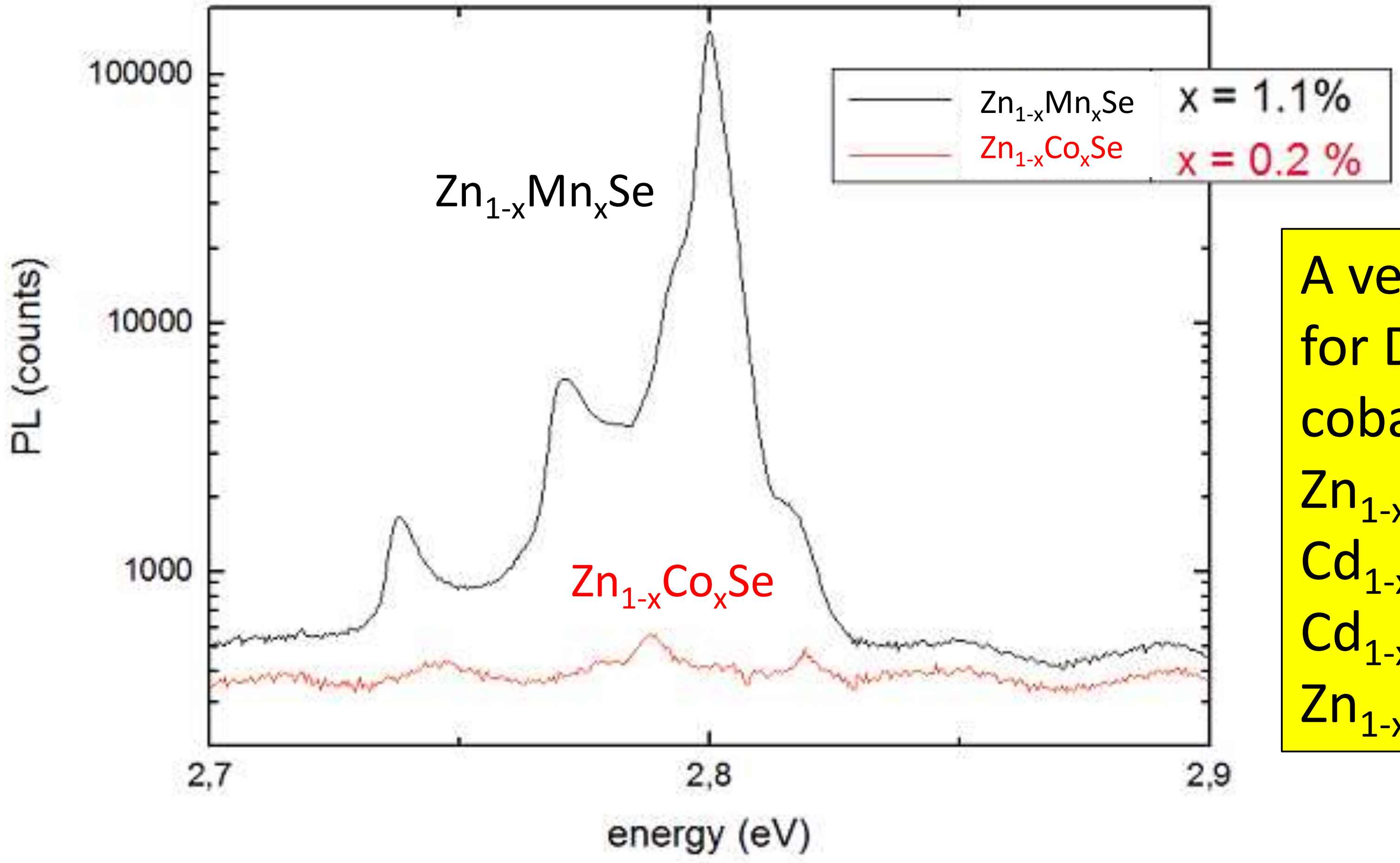




Kobak et al., Nat. Comm. (2014)
Smoleński, JAP (2015)



PL quenching in bulk DMS with cobalt



A very weak PL for DMSs with cobalt:

$Zn_{1-x}Co_xSe$

$Cd_{1-x}Co_xSe$

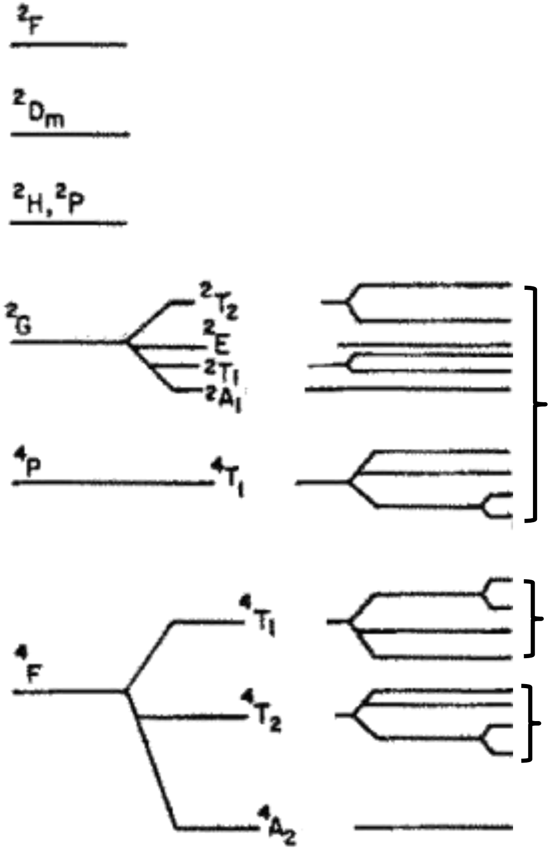
$Cd_{1-x}Co_xTe$

$Zn_{1-x}Co_xO$

M.J. Grzybowski, A. Golnik, M. Sawicki, W. Pacuski, Solid State Commun. (2015).
M. Papaj, J. Kobak, J.G. Rousset, E. Janik, M. Nawrocki, P. Kossacki, A. Golnik, W. Pacuski, J. Cryst. Growth (2014).
W. Pacuski, D. Ferrand, J. Cibert, C. Deparis, J. A. Gaj, P. Kossacki, and C. Morhain, PRB (2006)

Intraionic levels of Co^{2+} (d^7)

Co^{2+} (d^7)



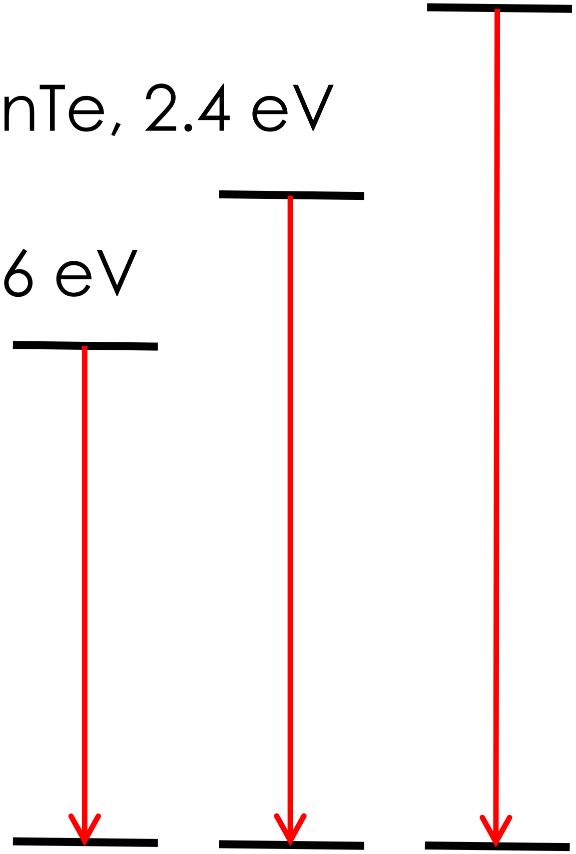
≈ 1.3 - 1.6 eV

≈ 0.6 - 0.8 eV

≈ 0.36 - 0.40 eV

0

H.A. Weakliem et al.,
J. Chem. Phys. 36, 2117 (1962)



Energy gap

ZnO, 3.4 eV

ZnTe, 2.4 eV

CdTe, 1.6 eV

Cobalt vs Manganese

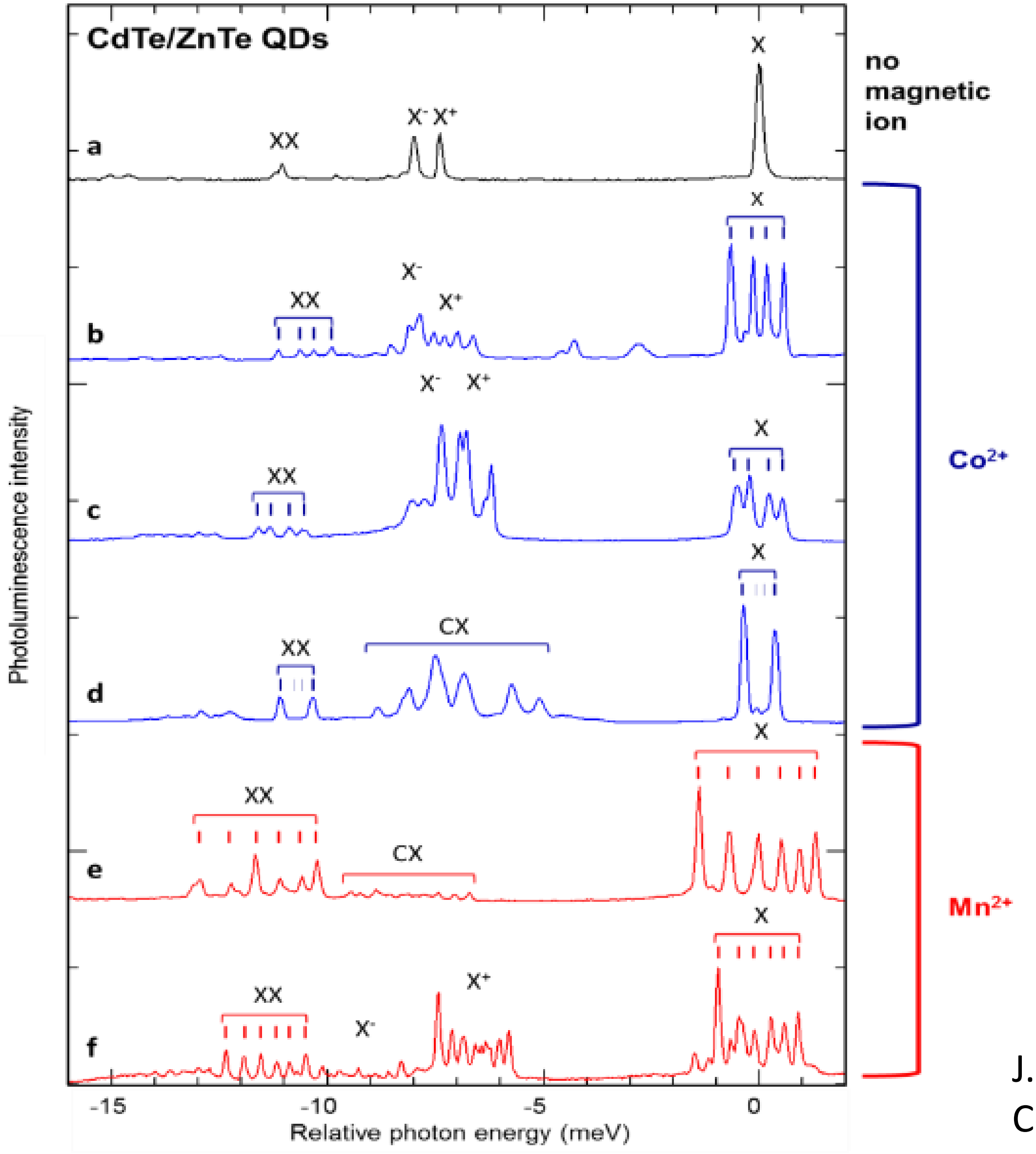
+

- Stronger *p-d* exchange interaction
- Sensitivity on strain (due to orbital m.)
- Magnetic anisotropy

−

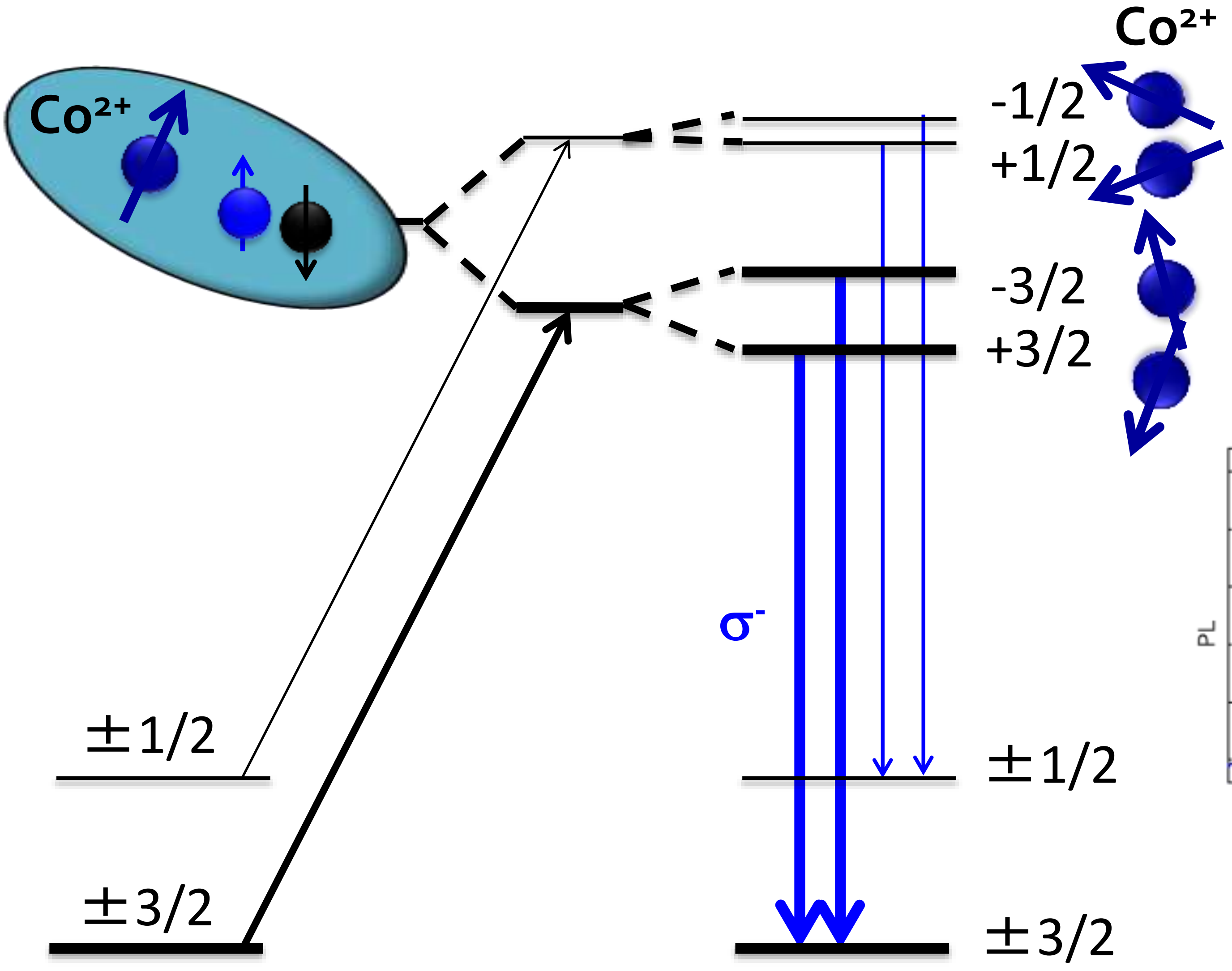
- Known excitonic emission killer in DMS -> danger of PL quenching

PL spectra of CdTe/ZnTe QD with magnetic ions

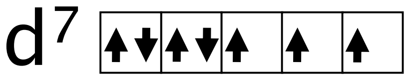


J. Kobak et al., Nature Communications (2014)

Spin read-out of Co^{2+} in a CdTe QD

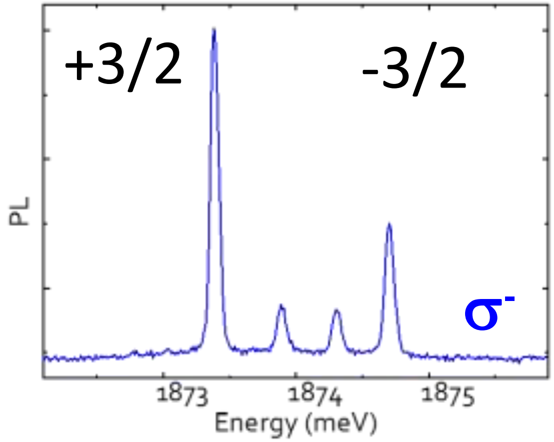


Co^{2+} without carriers



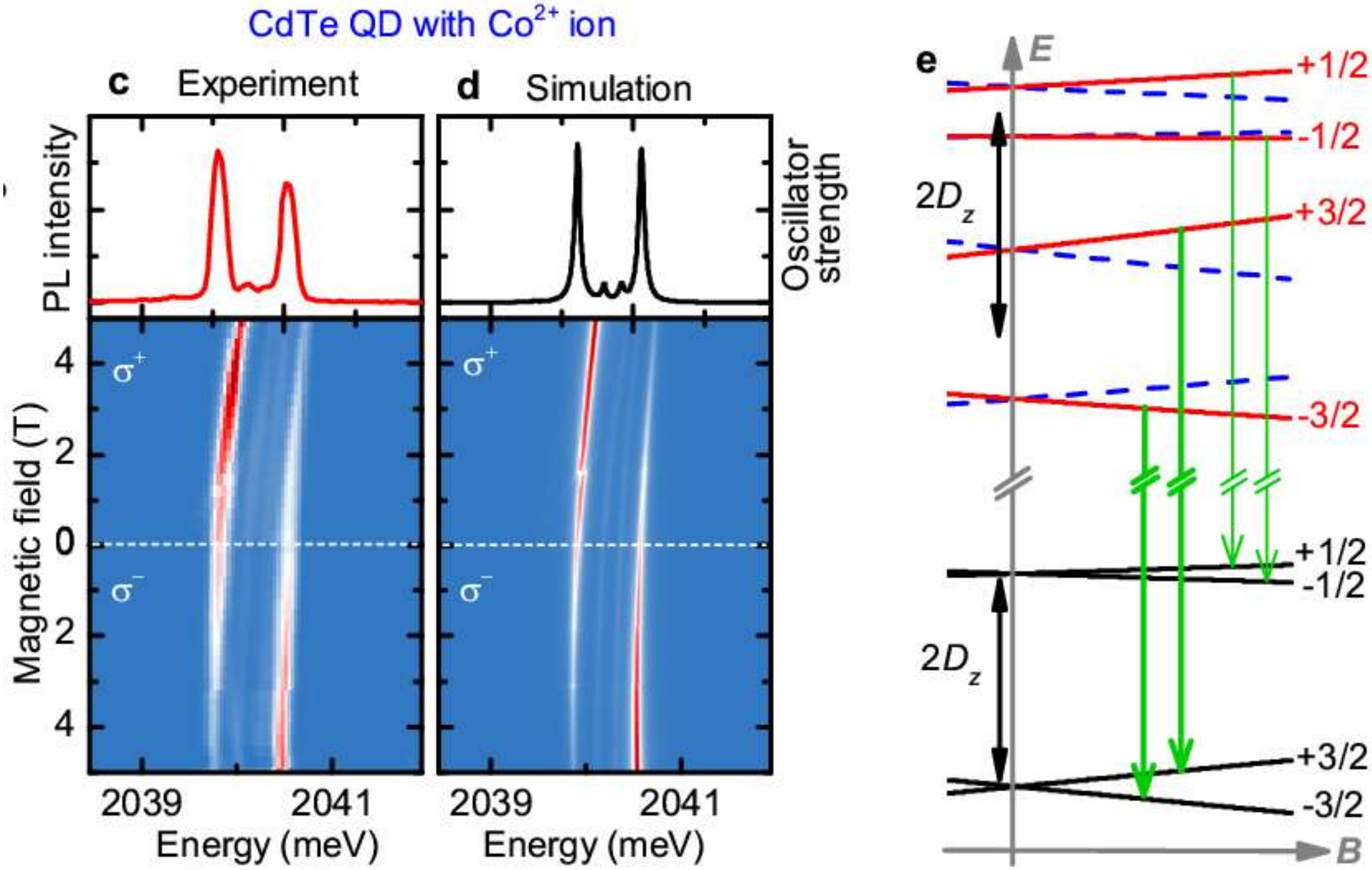
S = (5-2)*1/2 = 3/2

Neutral exciton in CdTe/ZnTe QD with a single Co^{2+}



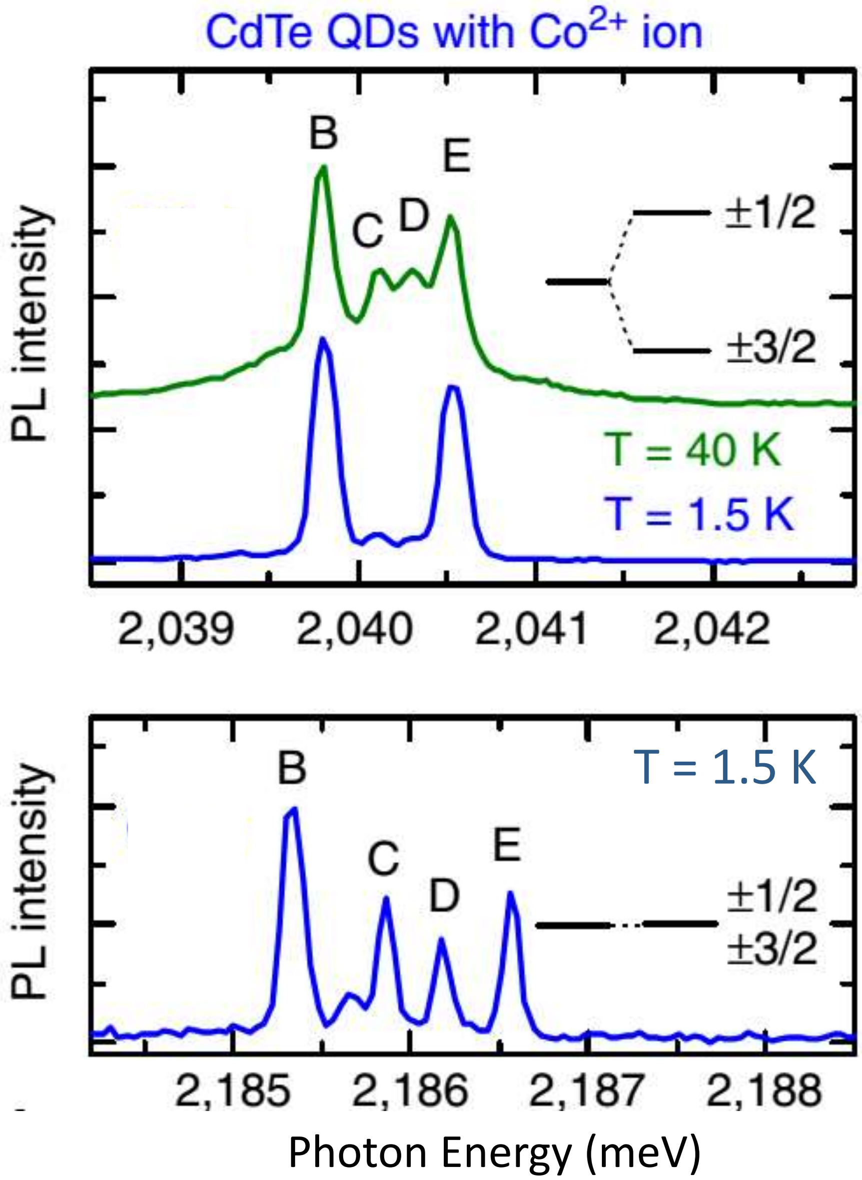
J. Kobak et al., Nature Communications (2014)

QD with a strained Co^{2+}



J. Kobak et al., Nature Communications (2014)

Effect of strain on Co^{2+} spin states



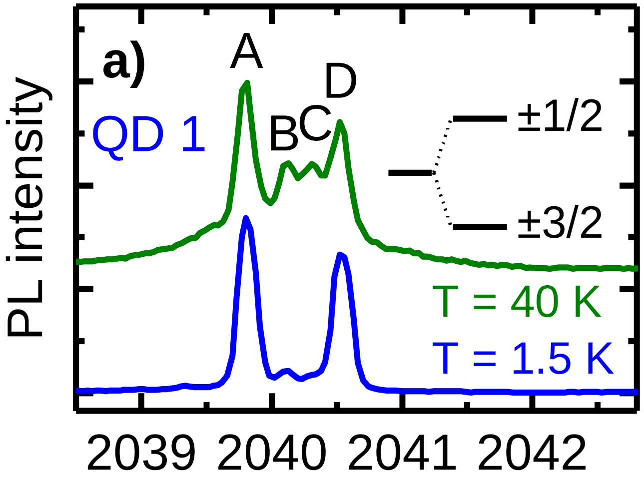
High compressive strain
(typical case)

Low strain

J. Kobak et al., Nature Communications (2014)

How to determine splitting of Co^{2+} spin states?

1. Measurement of the ratio of Co^{2+} states occupancy as a function of temperature

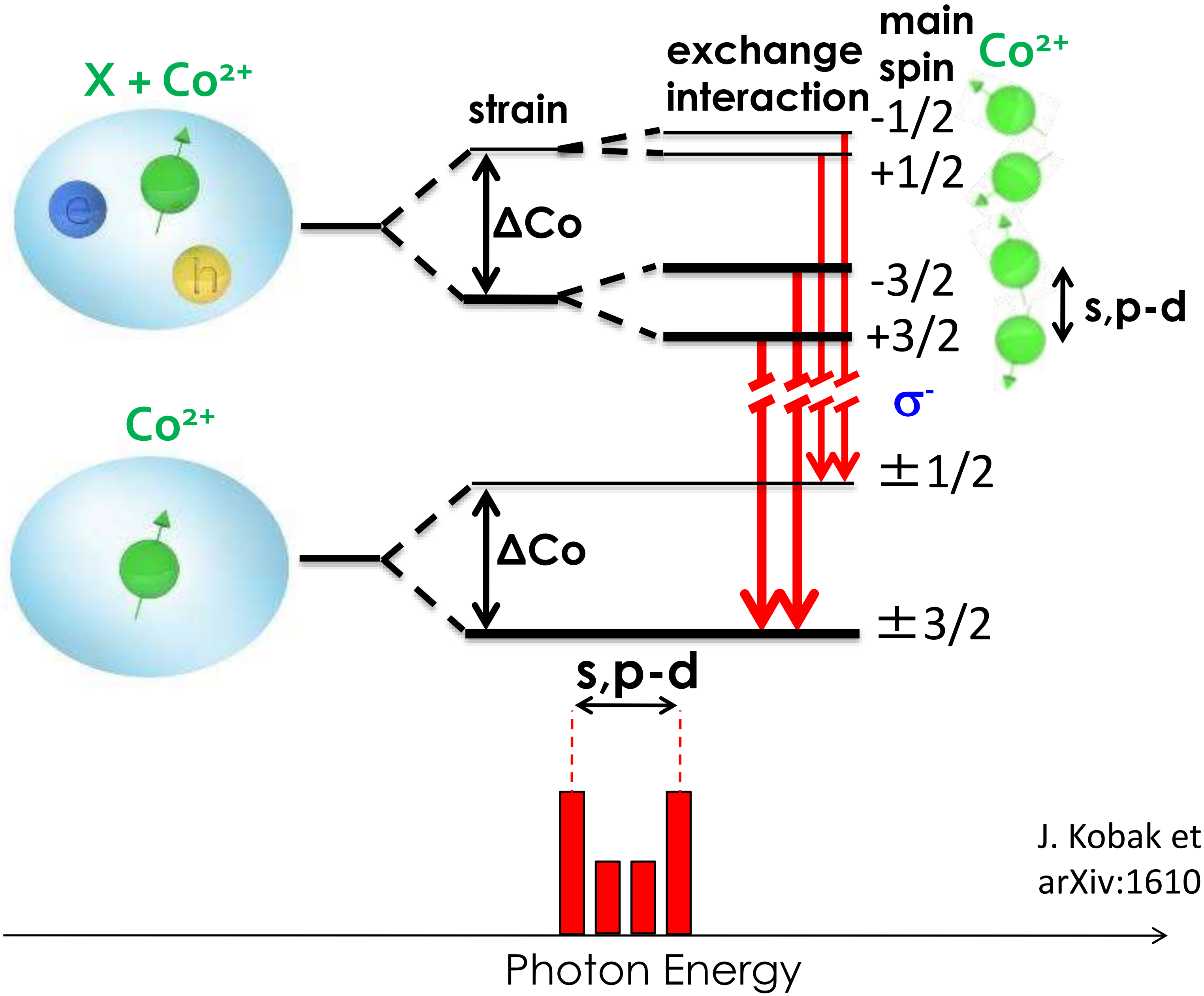


Ad. 1. Non-equilibrium state of the exciton - cobalt indescribable by Boltzmann distribution

2. Measurement of "forbidden" transitions with the change of Co^{2+} spin ✓

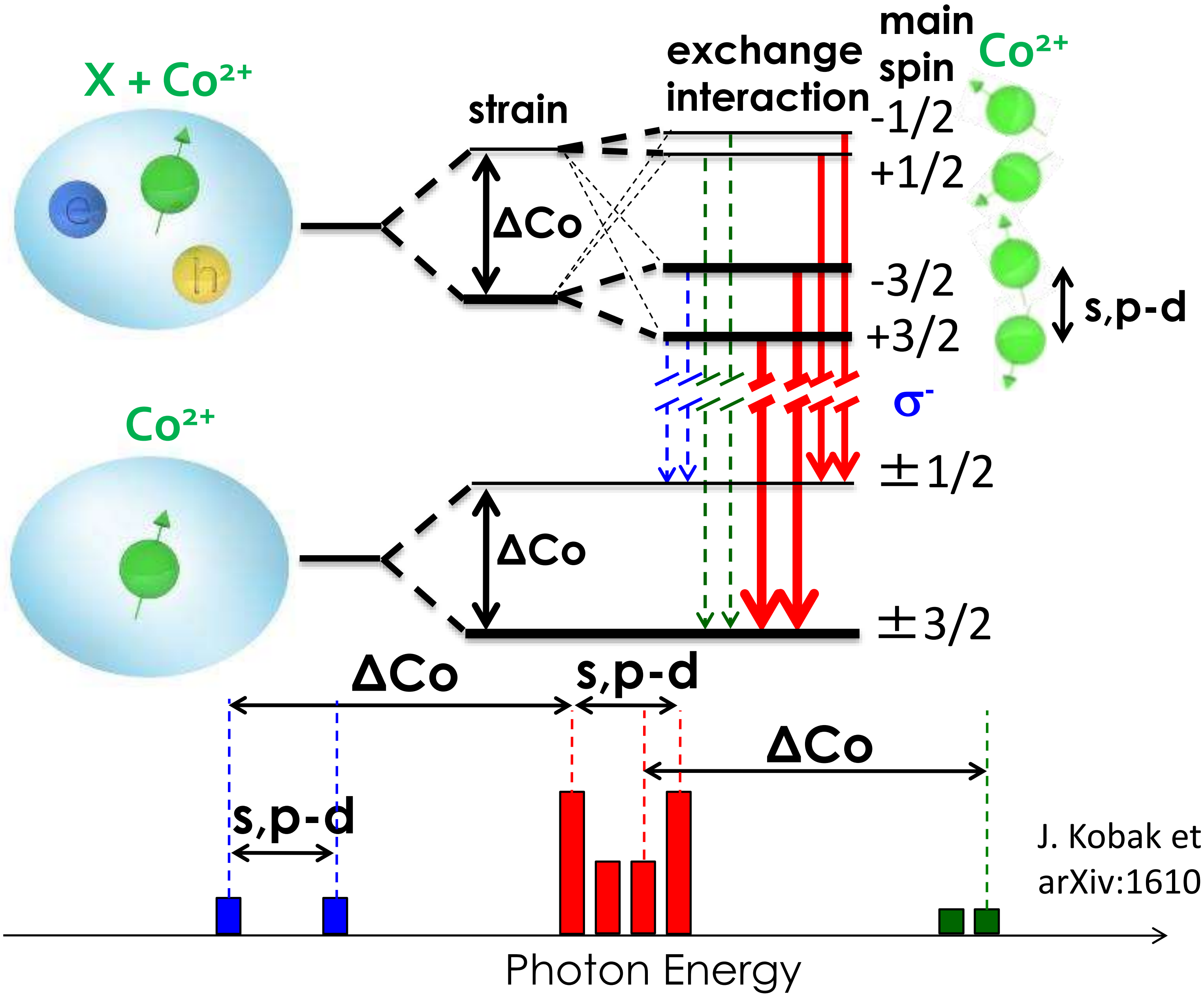
J. Kobak et al., arXiv:1610.05732 (2016)

How to determine splitting of Co^{2+} spin states?



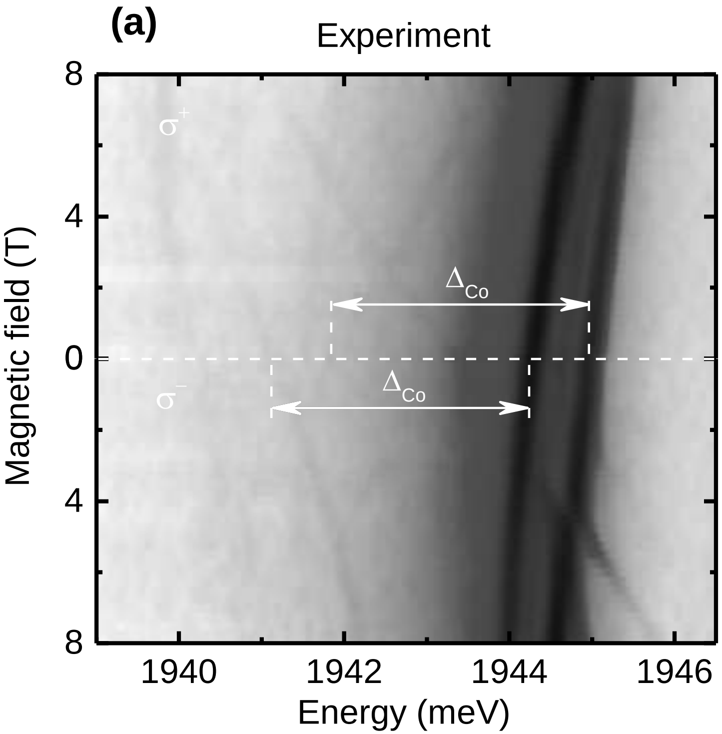
J. Kobak et al., arXiv:1610.05732 (2016)

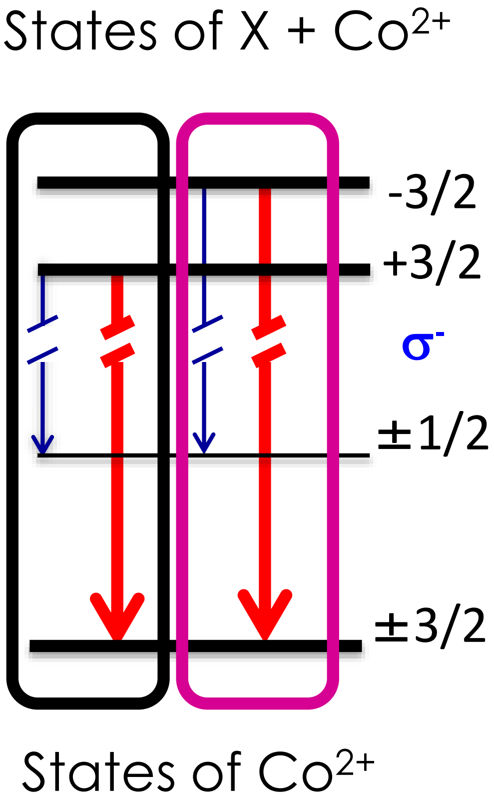
How to determine splitting of Co^{2+} spin states?



J. Kobak et al.,
arXiv:1610.05732 (2016)

How to determine splitting of Co^{2+} spin states?

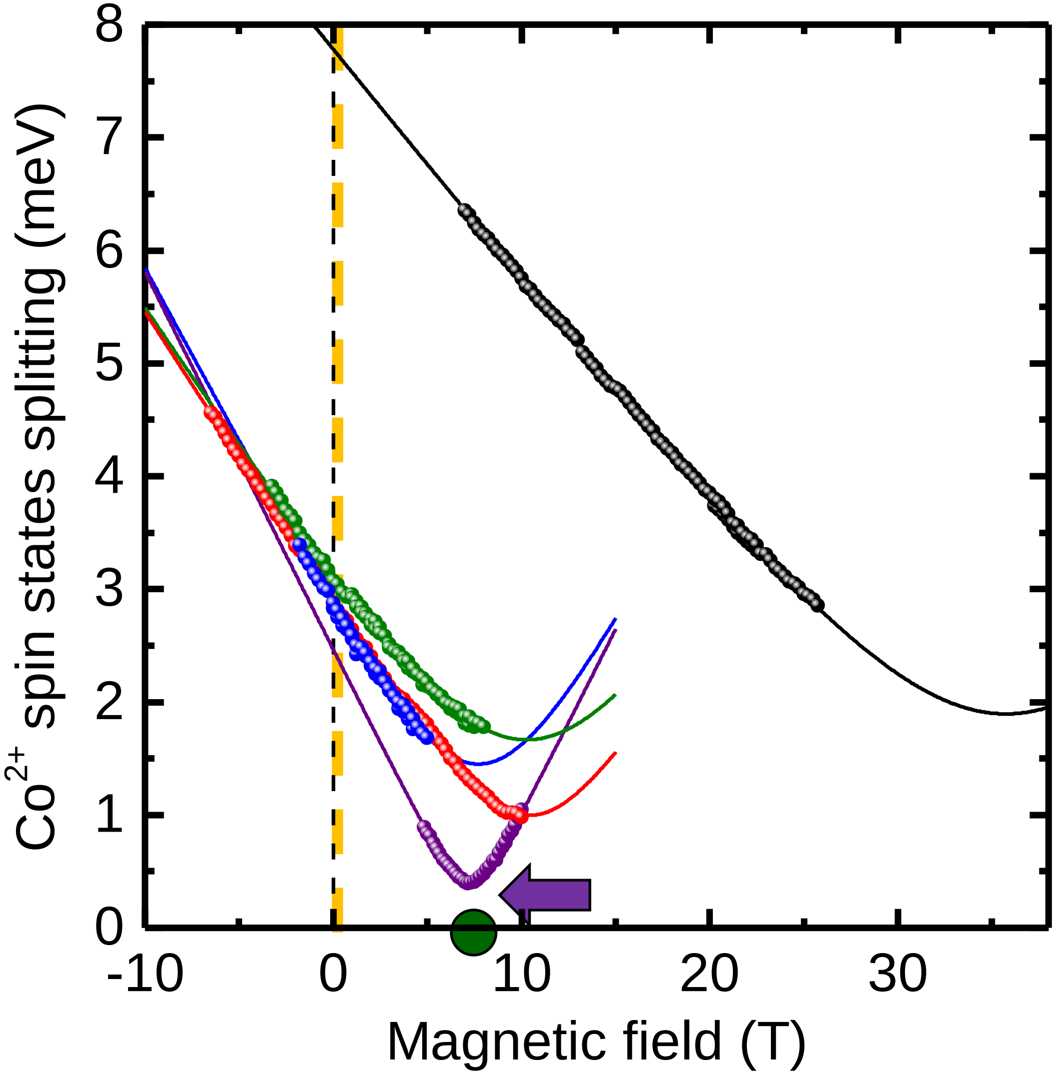



States of X + Co^{2+}

States of Co^{2+}

J. Kobak et al.,
arXiv:1610.05732 (2016)

How to determine splitting of Co^{2+} spin states?



Zeeman effect

Magnetic ion anisotropy

$$\mathcal{H}_M = \mu_B B g_M J_z + \boldsymbol{D} J_z^2 + \boldsymbol{E}(J_y^2 - J_x^2)$$

$$\Delta_{Co}(B) = 2\sqrt{3E^2 + (g\mu_B B - D)^2}$$

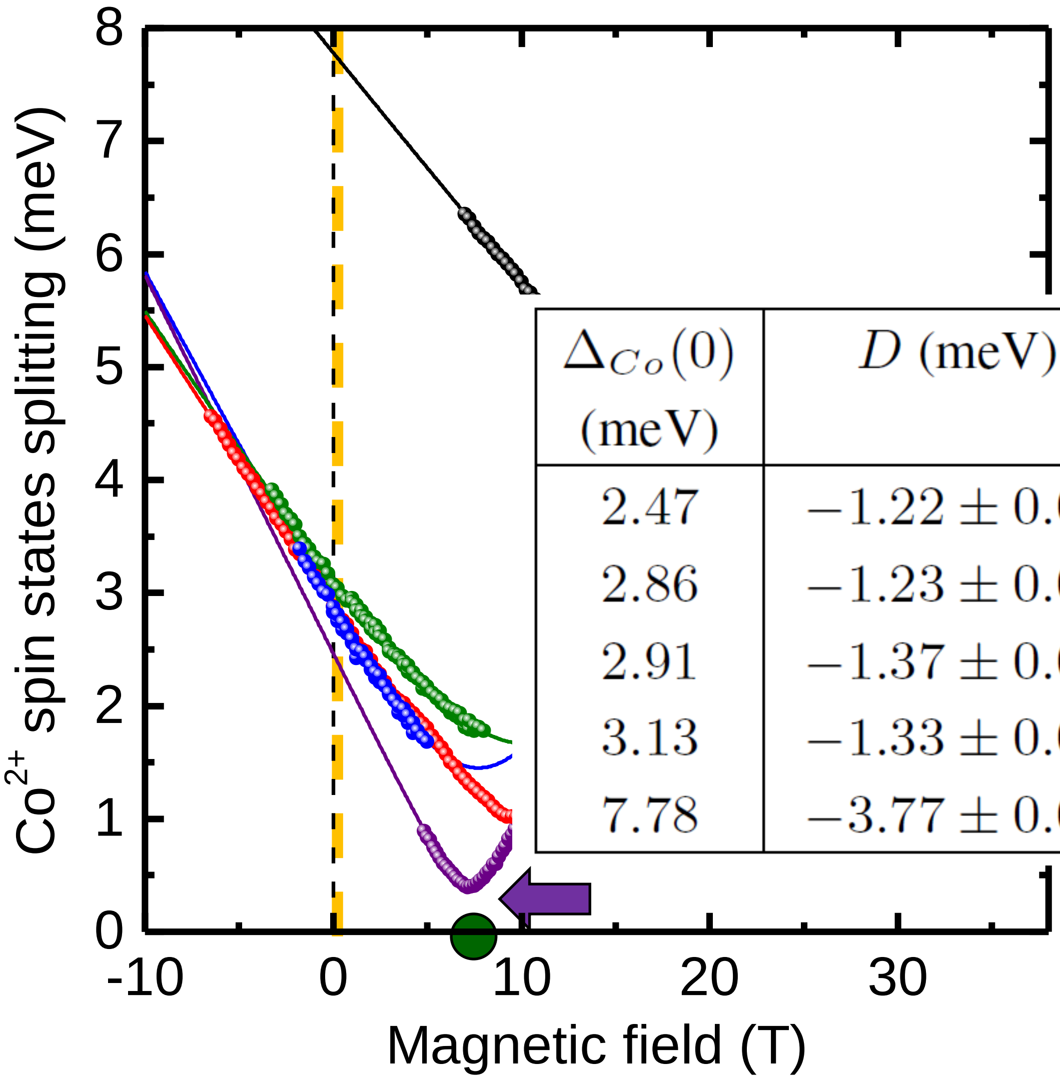
$$\boldsymbol{\Delta_{Co}(B_{min\Delta}) = 2\sqrt{3}E}$$

$$\boldsymbol{\Delta_{Co}(0) = 2\sqrt{3E^2 + D^2}}$$

$$\boldsymbol{B_{Min} = D/g_M \mu_B}$$

J. Kobak et al.,
arXiv:1610.05732 (2016)

How to determine splitting of Co^{2+} spin states?



$\Delta_{Co}(0)$ (meV)	D (meV)	E (meV)	g_{Co}
2.47	-1.22 ± 0.01	0.12 ± 0.01	2.91 ± 0.02
2.86	-1.23 ± 0.02	0.42 ± 0.02	2.76 ± 0.09
2.91	-1.37 ± 0.01	0.29 ± 0.01	2.27 ± 0.01
3.13	-1.33 ± 0.01	0.48 ± 0.01	2.23 ± 0.03
7.78	-3.77 ± 0.01	0.55 ± 0.02	1.82 ± 0.02

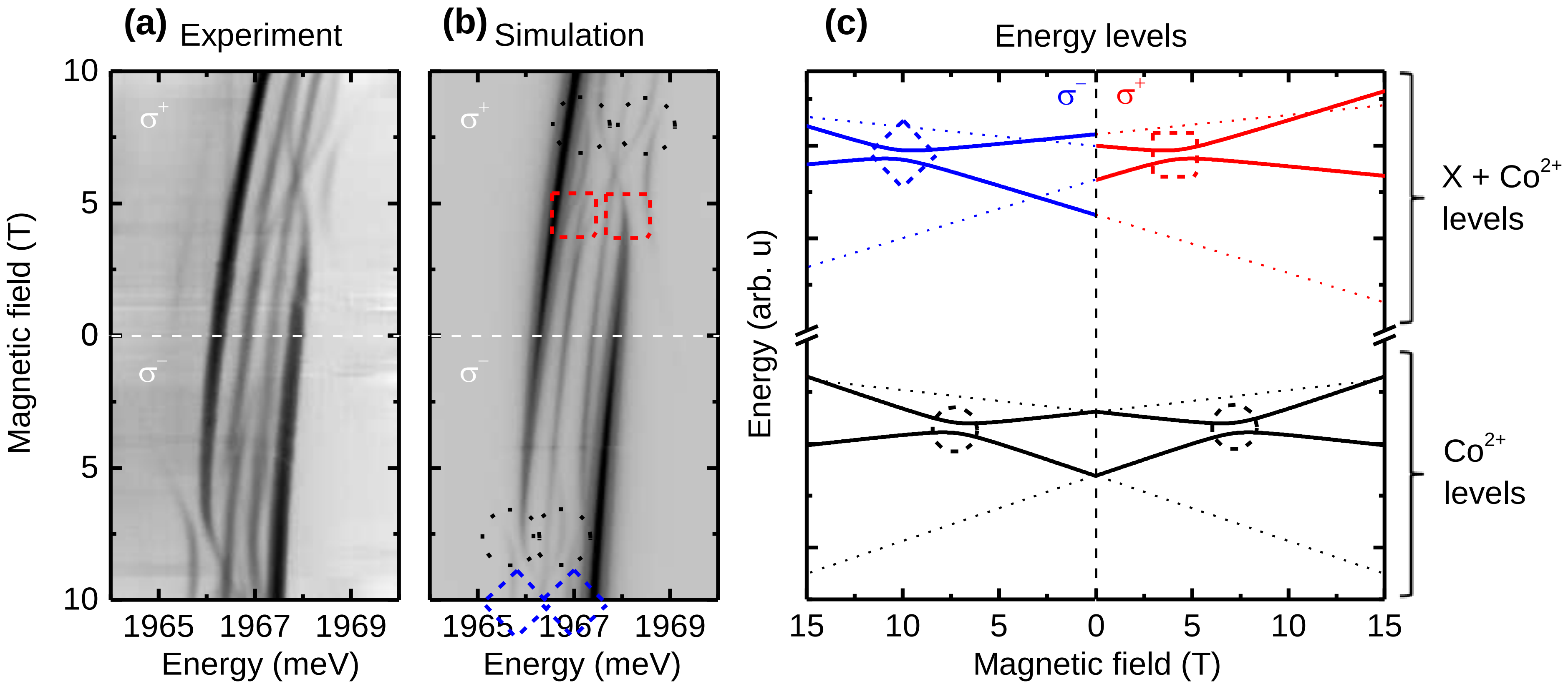
Zeeman effect

Magnetic ion anisotropy

$$\mathcal{H}_M = \mu_B B g_M J_z + \boldsymbol{D} J_z^2 + \boldsymbol{E}(J_y^2 - J_x^2)$$

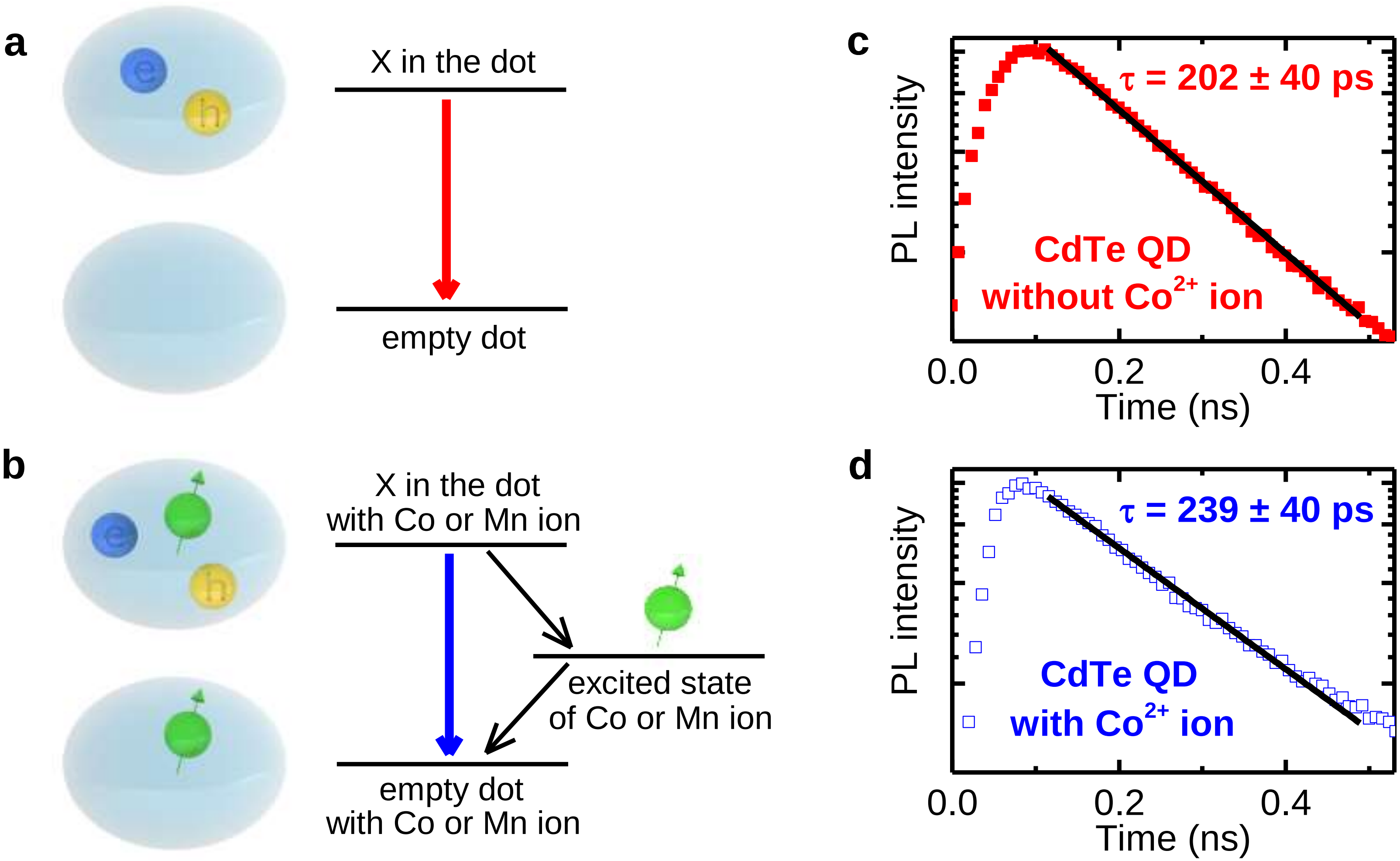
J. Kobak et al., arXiv:1610.05732 (2016)

Anticrossing of Co^{2+} states



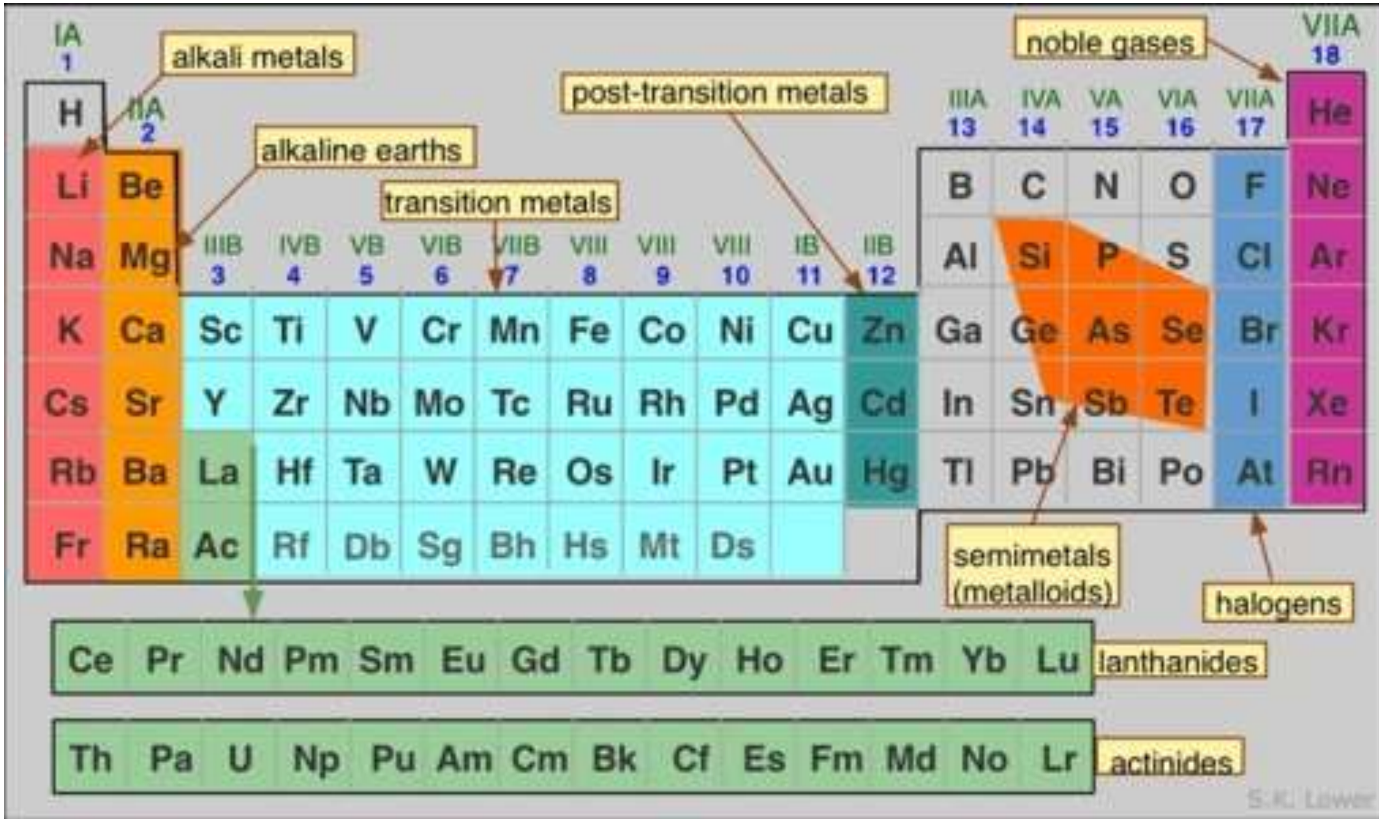
J. Kobak, A Bogucki, et al.,
arXiv:1610.05732 (2016)

Negligible quenching of excitonic PL in QDs

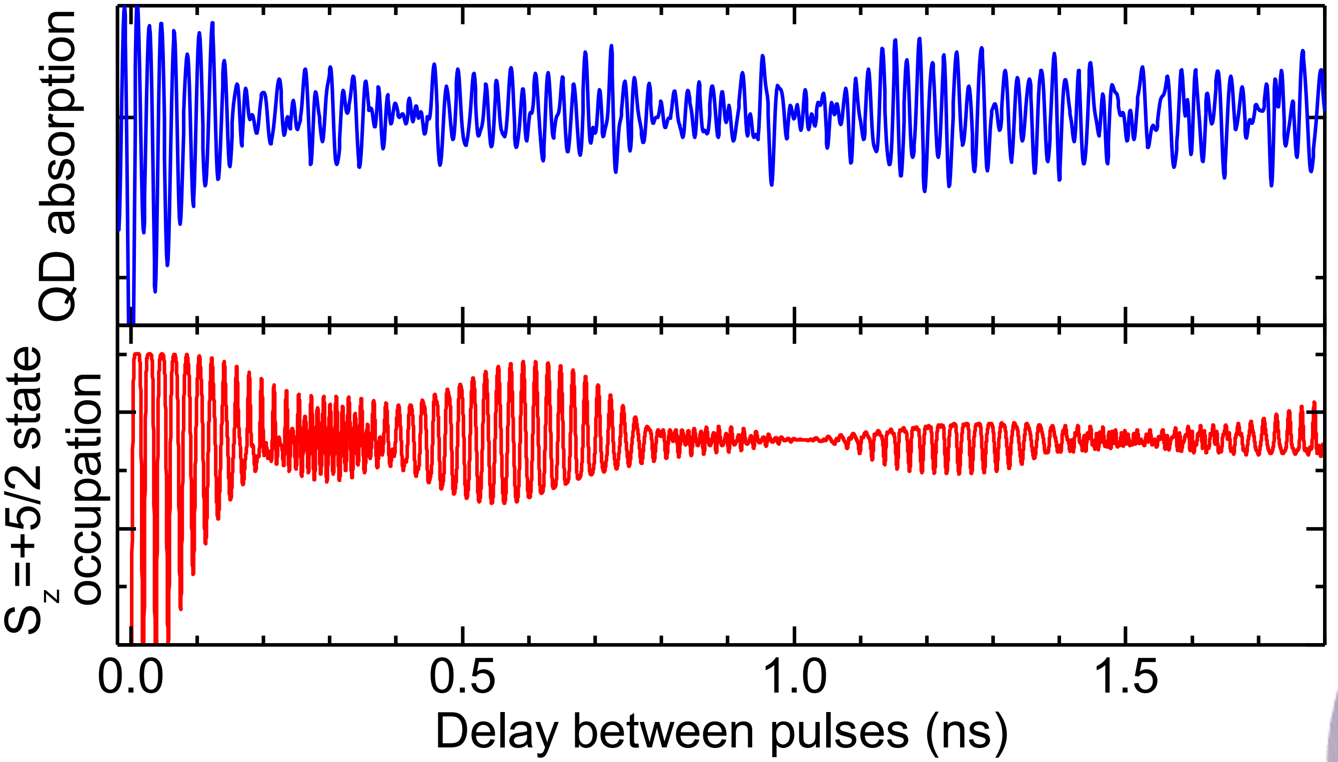


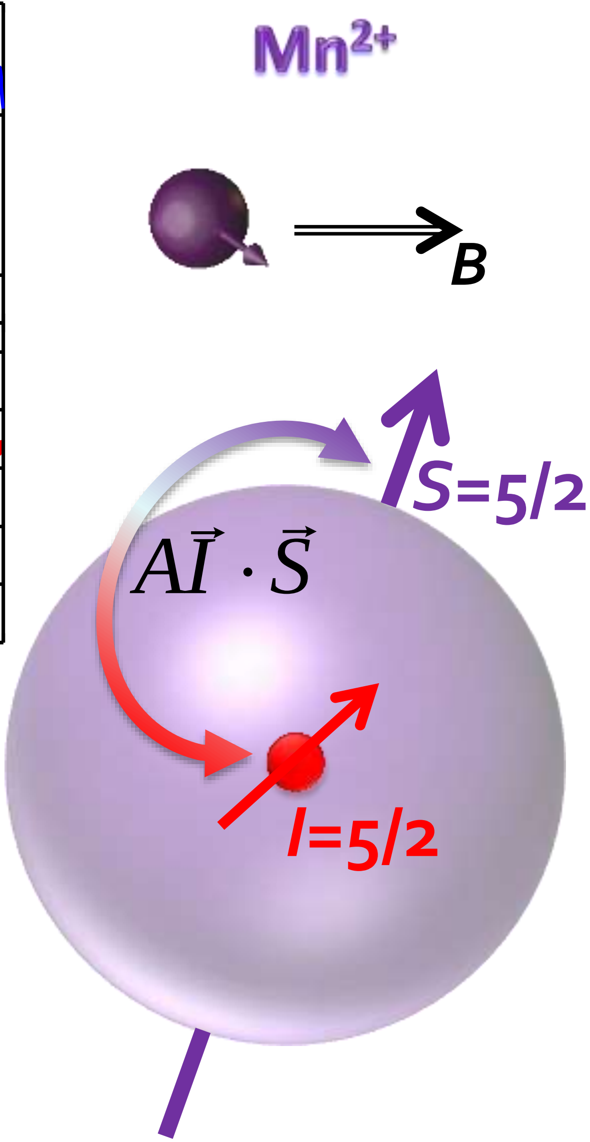
J. Kobak et al., Nature Communications (2014)

Choice of transition metals



Coherent oscillations of Mn^{2+} with nuclear spin





Coherent evolution of Mn in empty dot:

M. Goryca *et al.*, Phys. Rev. Lett 2014 (Univ. Of Warsaw and IFPAN)

Coherent evolution of Mn – X complex:

A. Lafuente-Sampietro, H. Boukari, L. Besombes, Phys. Rev. B 2015 (CNRS and Univ. Grenoble Alpes)

Toward nuclear-spin-free systems
Cr, Fe, Ni
instead Mn and Co

J. Kobak et al., Nature Communications (2014)

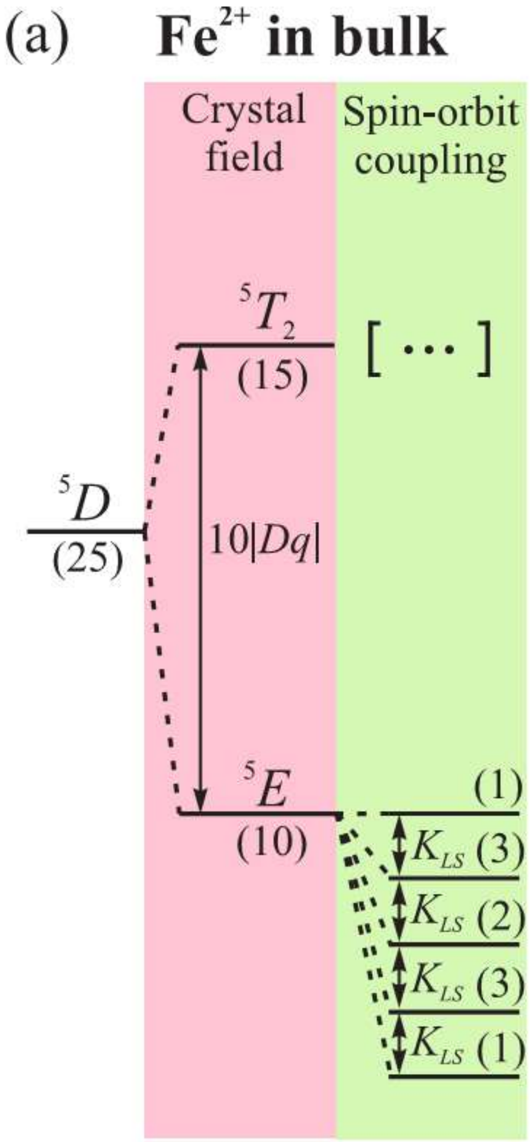
Iron vs Manganese or Cobalt

- No nuclear spin (natural abundance 98%)
- Two configurations: Fe^{2+} and Fe^{3+}
- Long coherence time for Fe^{3+} in bulk*
- Nonmagnetic ground state of Fe^{2+} in bulk**

* J. Tribollet, J. Behrends, K .Lips, Europhysics Letters (2008) .

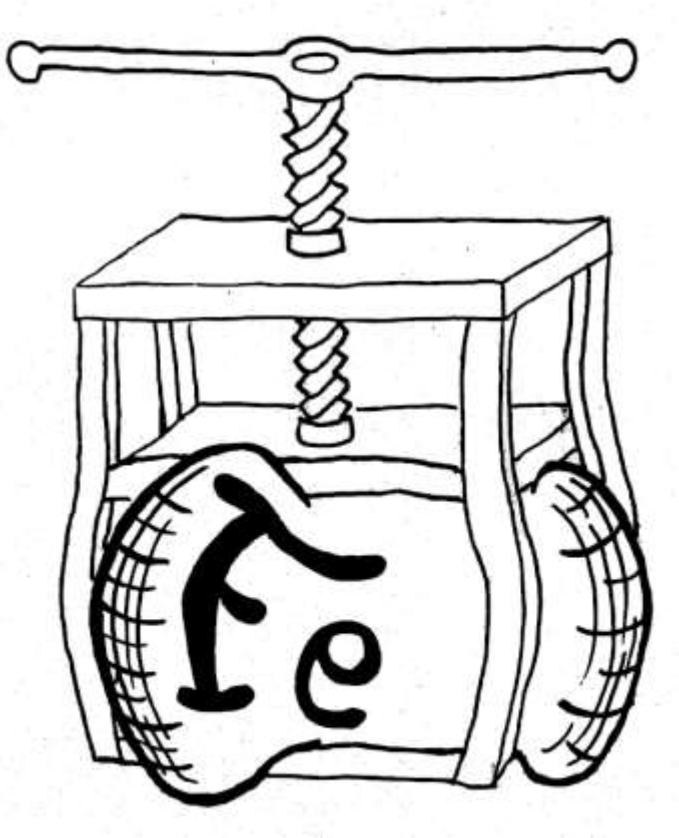
** G. A. Slack, S. Roberts, J. T. Vallin, Phys. Rev. 187, 511 (1969).

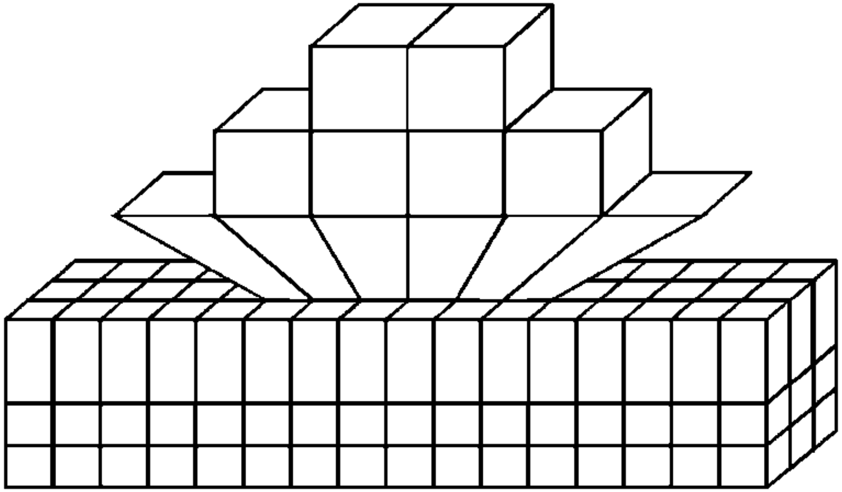
Ground state of Fe^{2+}



G. A. Slack, S. Roberts, and J. T. Vallin, Phys. Rev. 187, 511 (1969).

Effect of strain on Fe^{2+} dopant

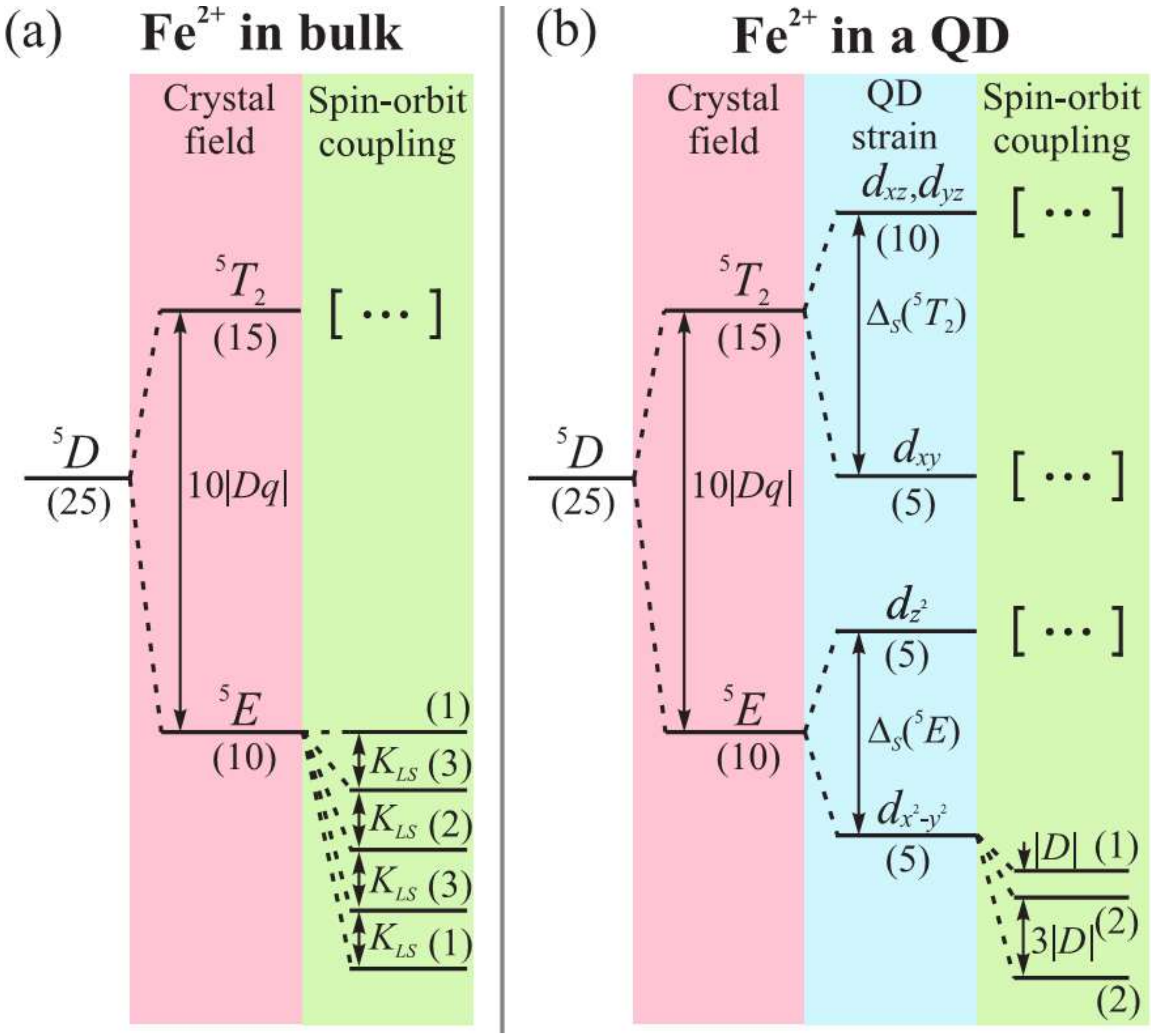




Strain due to lattice mismatch

Fig. A. Bogucki

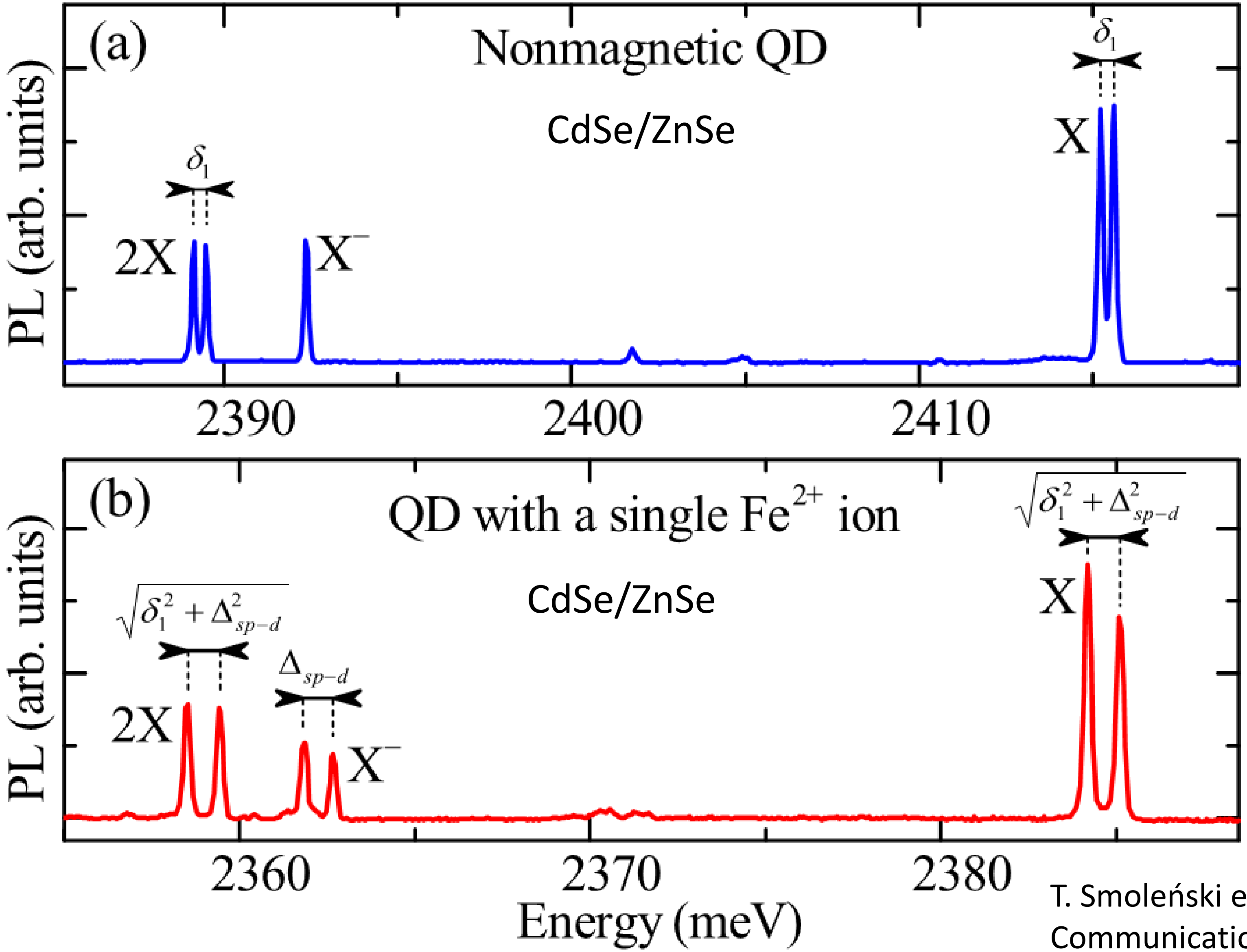
Ground state of Fe^{2+}



G. A. Slack, S. Roberts, and J. T. Vallin, Phys. Rev. 187, 511 (1969).

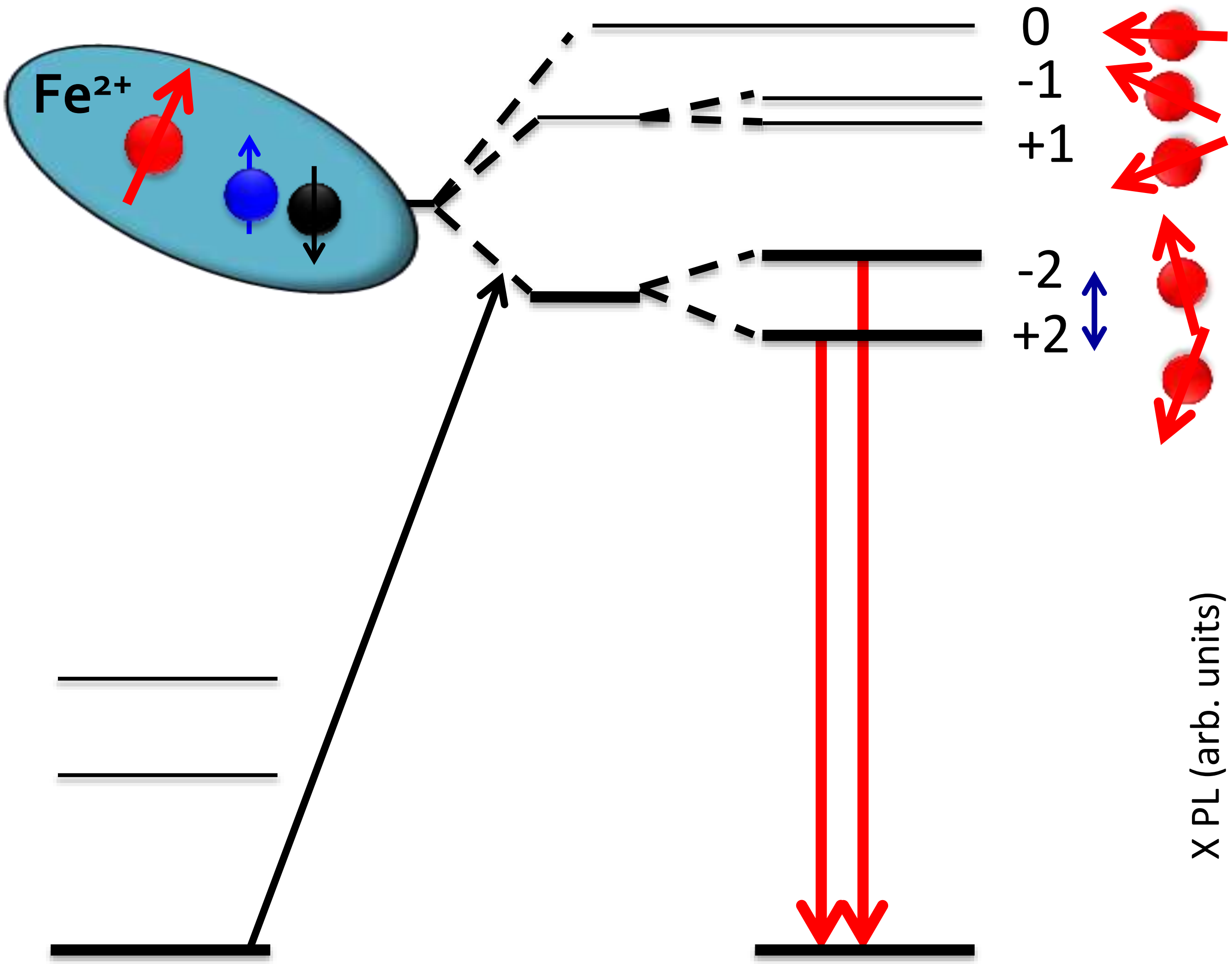
T. Smoleński et al., Nature Communications (2016)

PL of a QD with a single Fe^{2+}



T. Smoleński et al., Nature Communications (2016)

Spin read-out of Fe^{2+} in a CdSe QD

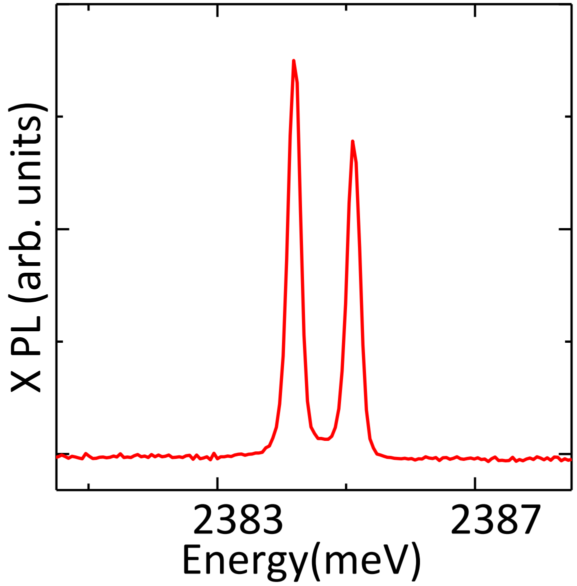


Fe^{2+} d^6

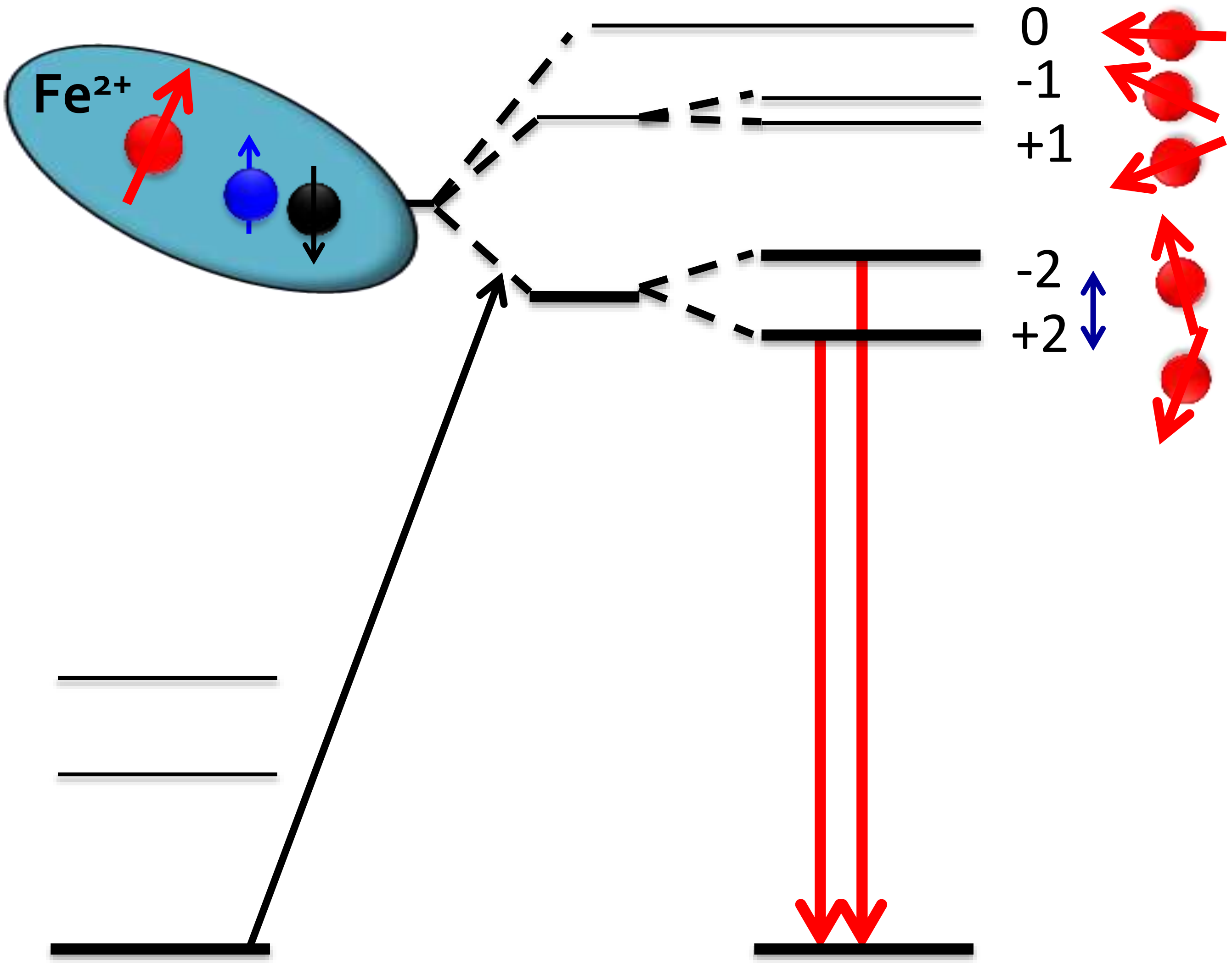
S = (5-1)*1/2 = 2

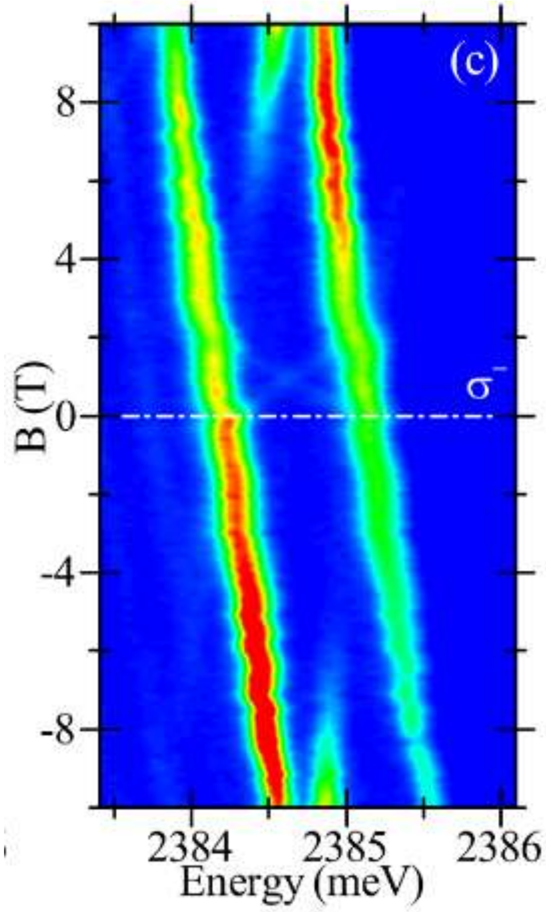
s,p-d

+2 ⟷ -2



Spin read-out of Fe^{2+} in a CdSe QD

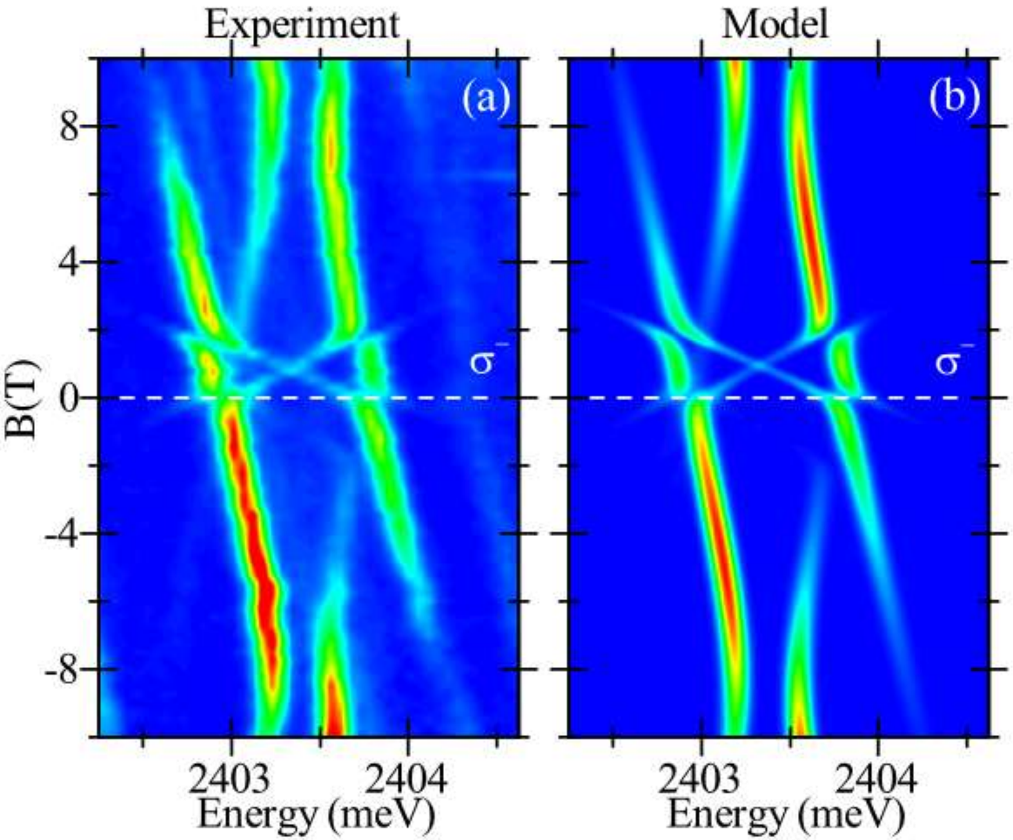




Magnetic ground state of Fe^{2+} in a strained QD confirmed

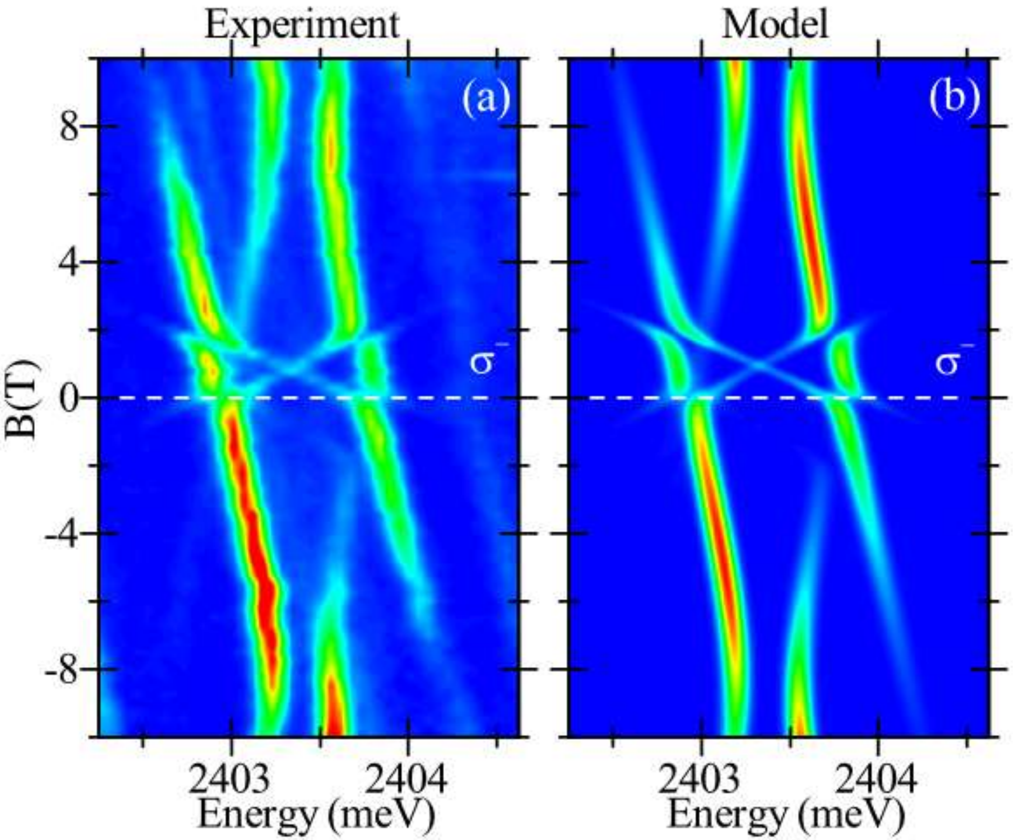
T. Smoleński et al.,
Nature Communications
(2016)

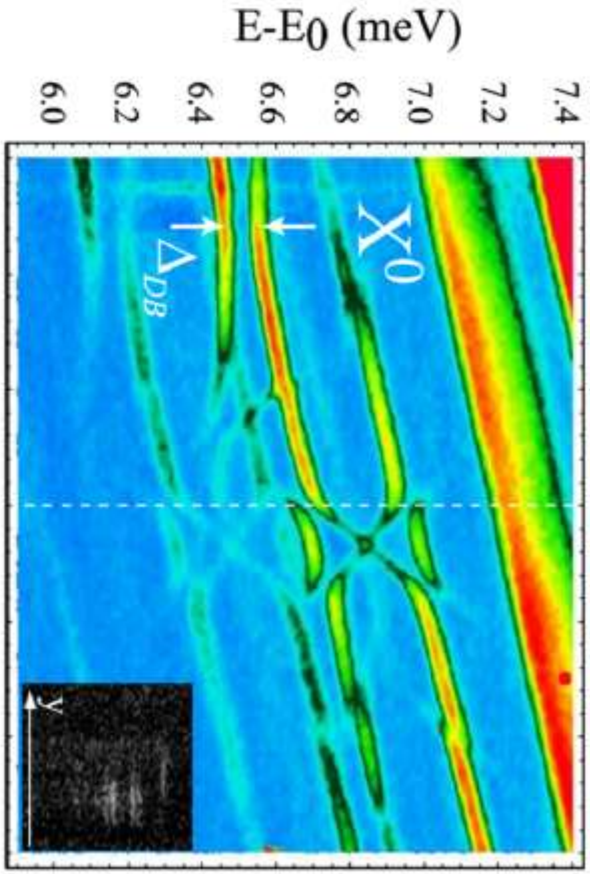
PL of a QD with a single Fe^{2+}



T. Smoleński et al., Nature Communications (2016).

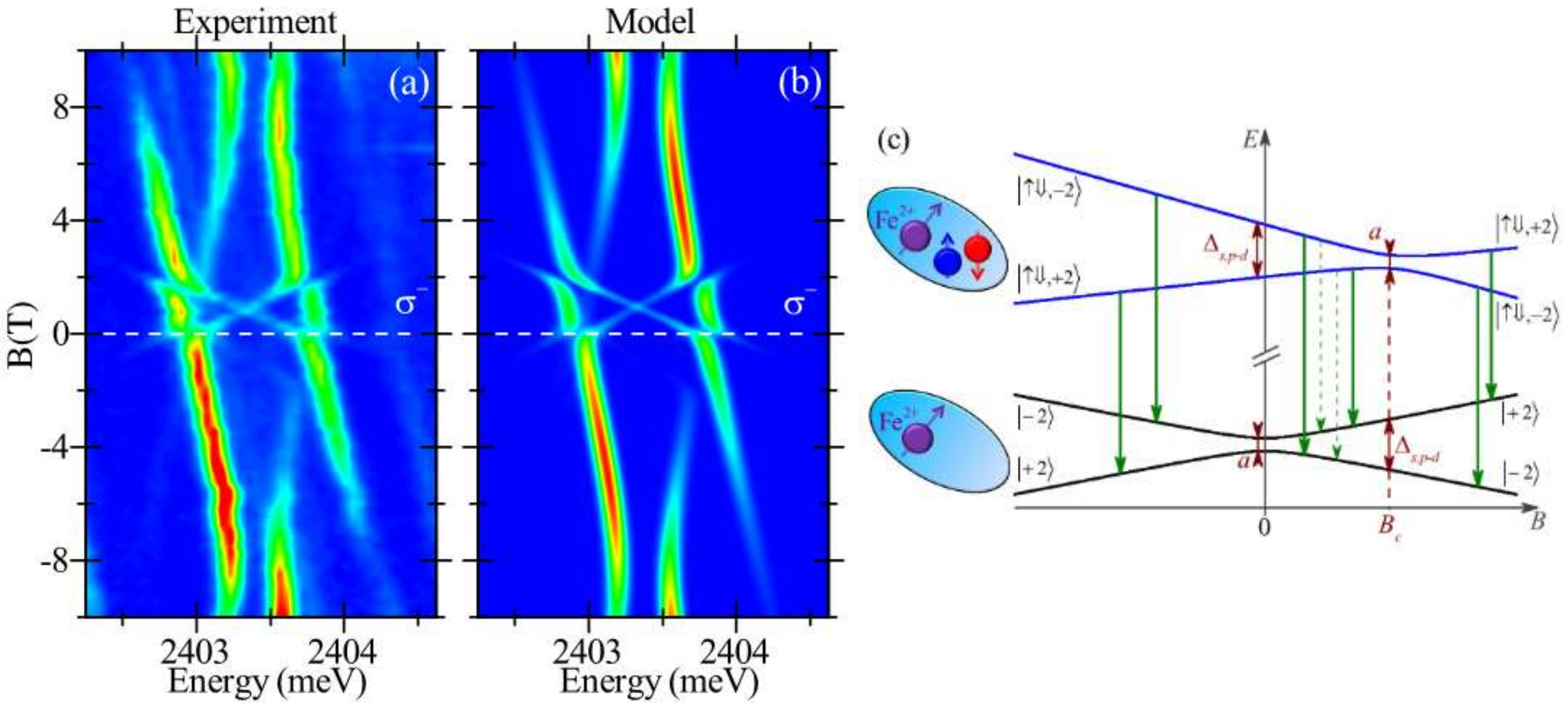
PL of a QD with a single Fe^{2+}





T. Smoleński et al., Nature Communications (2016).
Spectra similar to Mn^{2+} + hole in InAs/GaAs, A. Kudelski et al. PRL (2007).

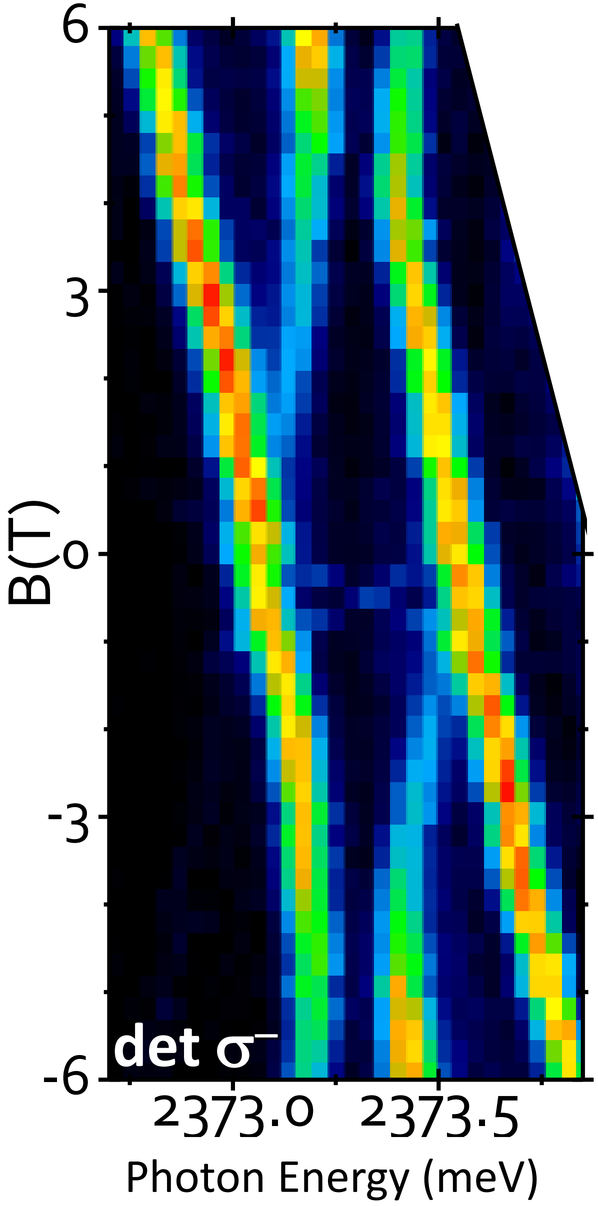
PL of a QD with a single Fe^{2+}



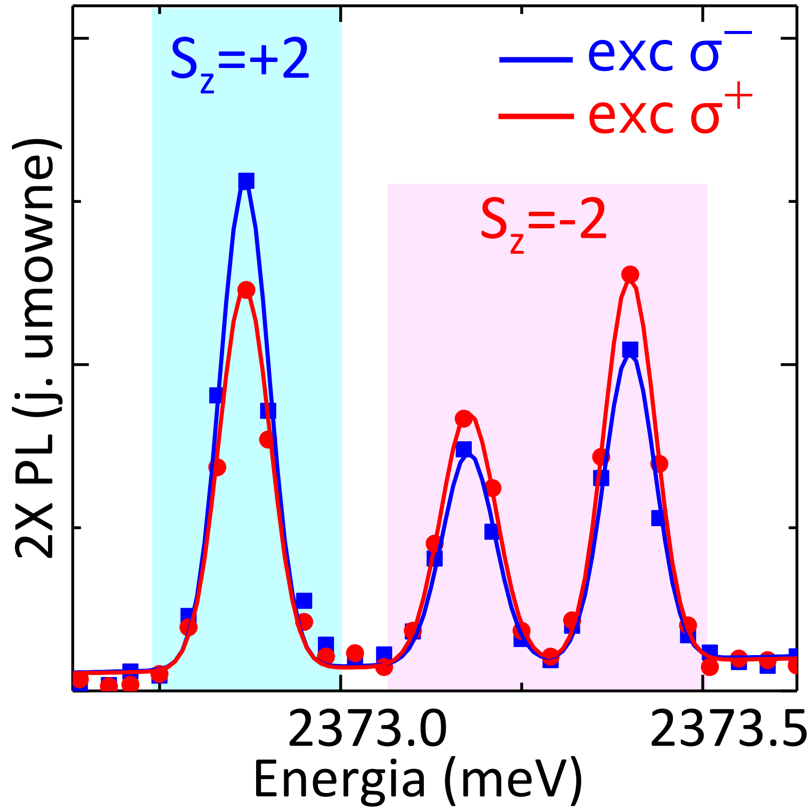
T. Smoleński et al., Nature Communications (2016).

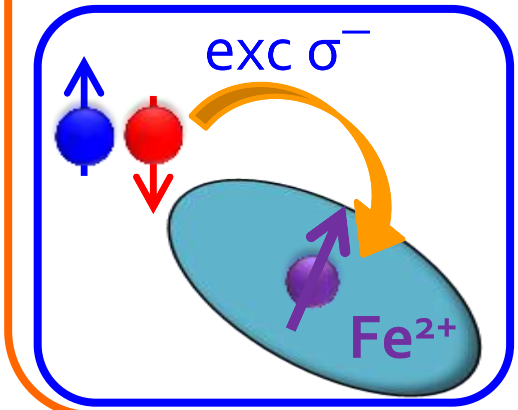
Two level system with nuclear-spin-free magnetic ion

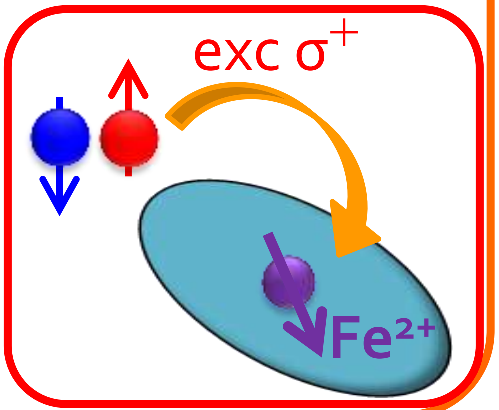
Optical orientation of single iron ion spin



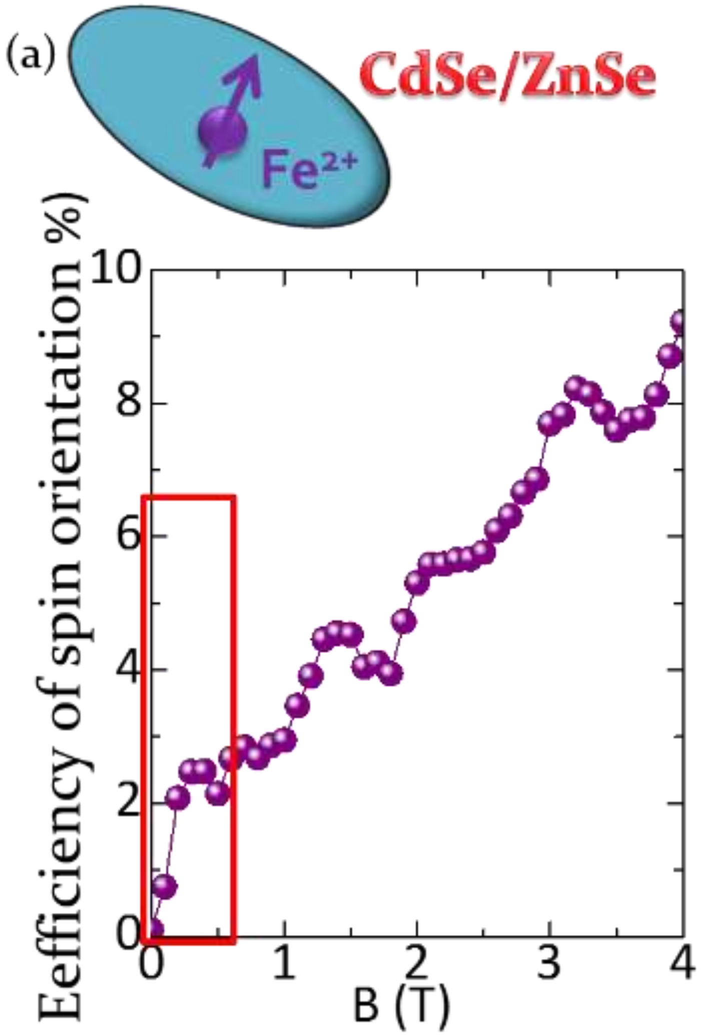
B = 4 T



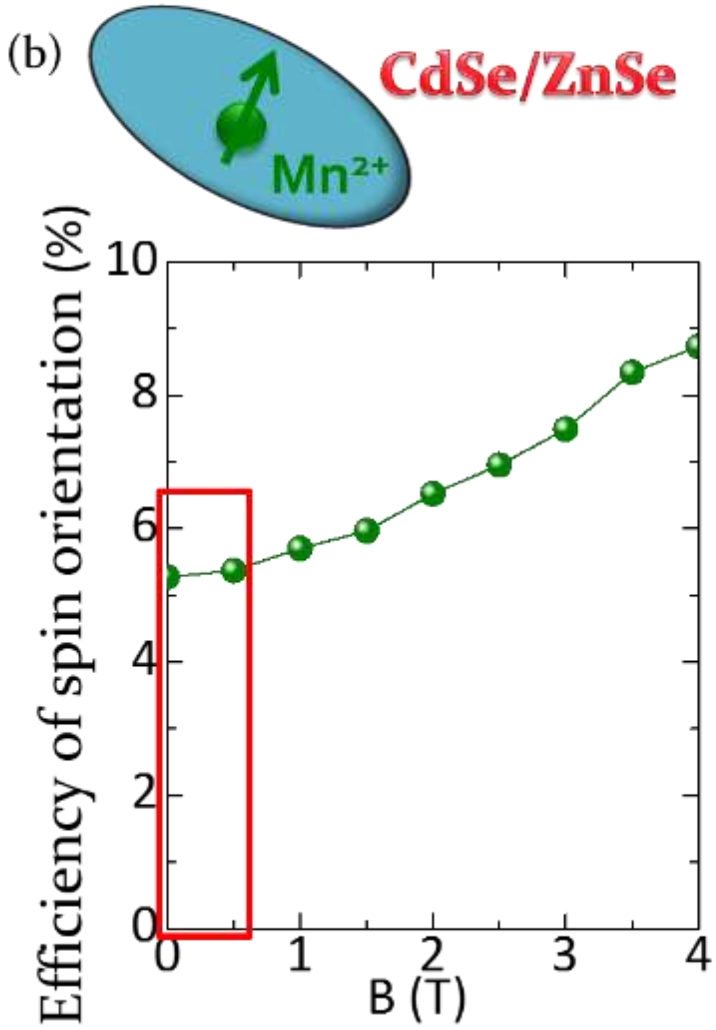




Optical orientation of single Fe and Mn spin



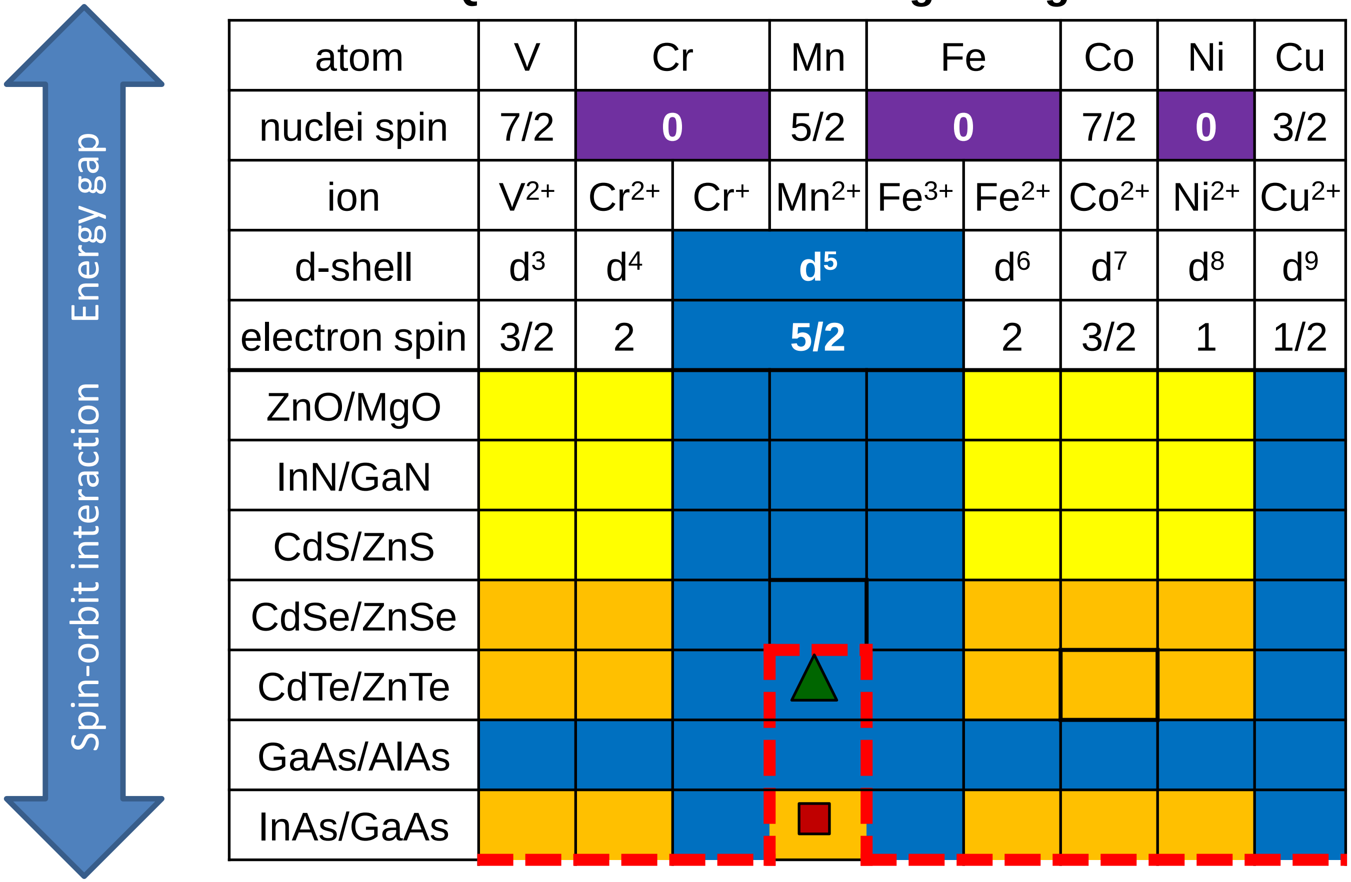
T. Smoleński et al., Nature Commun. (2016).



T. Smoleński et al., PRB(2015).

Quantum dots for solotronics 2013

Quantum dots with single magnetic ions



atom	V	Cr		Mn	Fe		Co	Ni	Cu
nuclei spin	7/2	**0**		5/2	**0**		7/2	**0**	3/2
ion	V^{2+}	Cr^{2+}	Cr^{+}	Mn^{2+}	Fe^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
d-shell	d^3	d^4	**d^5**			d^6	d^7	d^8	d^9
electron spin	3/2	2	**5/2**			2	3/2	1	1/2
ZnO/MgO	🟨	🟨	🟦	🟦	🟦	🟨	🟨	🟨	🟦
InN/GaN	🟨	🟨	🟦	🟦	🟦	🟨	🟨	🟨	🟦
CdS/ZnS	🟨	🟨	🟦	🟦	🟦	🟨	🟨	🟨	🟦
CdSe/ZnSe	🟧	🟧	🟦	🟦	🟦	🟧	🟧	🟧	🟦
CdTe/ZnTe	🟧	🟧	🟦	🟦 ▲	🟦	🟧	🟧	🟧	🟦
GaAs/AlAs	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
InAs/GaAs	🟧	🟧	🟦	🟧 ■	🟦	🟧	🟧	🟧	🟦

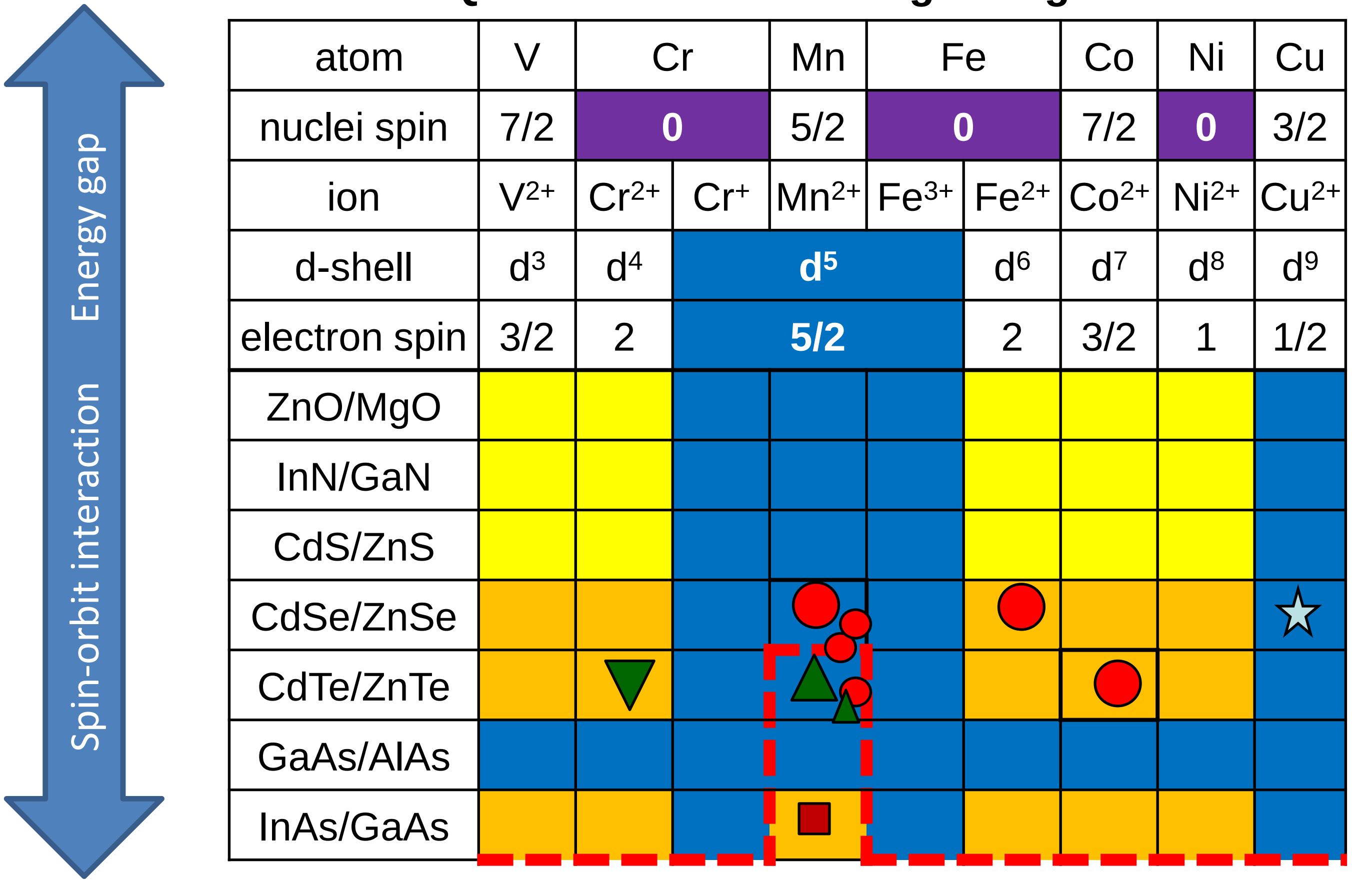
- - Intra-ionic transitions

	Anisotropy of magnetic ion:
🟦	weak (no orbital momentum, or spin 1/2, or strain free QD)
🟨	determined by wurtzite structure
🟧	affected by strain

▲ Grenoble
■ Marcoussis

Quantum dots for solotronics today

Quantum dots with single magnetic ions



atom	V	Cr		Mn	Fe		Co	Ni	Cu
nuclei spin	7/2	**0**		5/2	**0**		7/2	**0**	3/2
ion	V^{2+}	Cr^{2+}	Cr^{+}	Mn^{2+}	Fe^{3+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
d-shell	d^3	d^4	**d^5**			d^6	d^7	d^8	d^9
electron spin	3/2	2	**5/2**			2	3/2	1	1/2
ZnO/MgO	🟨	🟨	🟦	🟦	🟦	🟨	🟨	🟨	🟦
InN/GaN	🟨	🟨	🟦	🟦	🟦	🟨	🟨	🟨	🟦
CdS/ZnS	🟨	🟨	🟦	🟦	🟦	🟨	🟨	🟨	🟦
CdSe/ZnSe	🟧	🟧	🟦	🟦 ● ● ●	🟦	🟧 ●	🟧	🟧	🟦 ☆
CdTe/ZnTe	🟧	🟧 ▼	🟦	🟦 ▲ ● ▲	🟦	🟧	🟧 ●	🟧	🟦
GaAs/AlAs	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦	🟦
InAs/GaAs	🟧	🟧	🟦	🟧 ■	🟦	🟧	🟧	🟧	🟦

– – Intra-ionic transitions

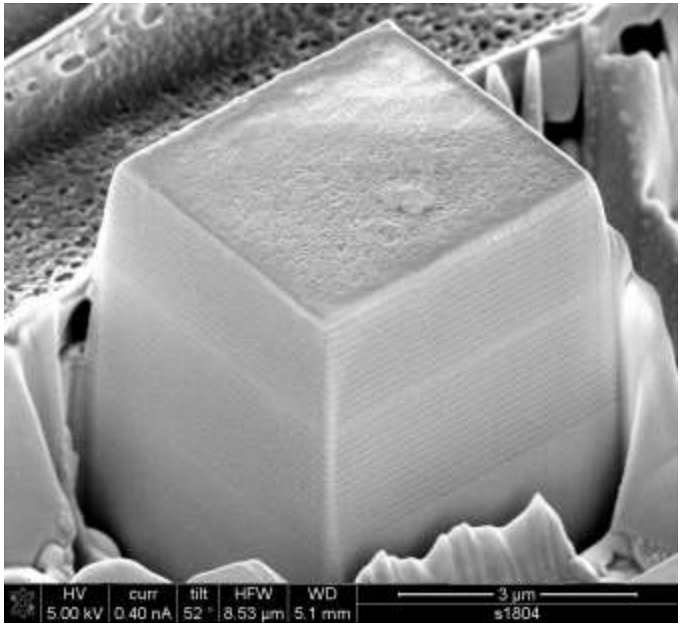
	Anisotropy of magnetic ion:
🟦	weak (no orbital momentum, or spin 1/2, or strain free QD)
🟨	determined by wurtzite structure
🟧	affected by strain

Modified barrier:
of CdSe QDs:
● (Zn,Cd)Se,

Modified barriers:
of CdTe QDs:
● ZnSe,
● (Cd,Zn,Mg)Te
▲ (Cd,Mg)Te

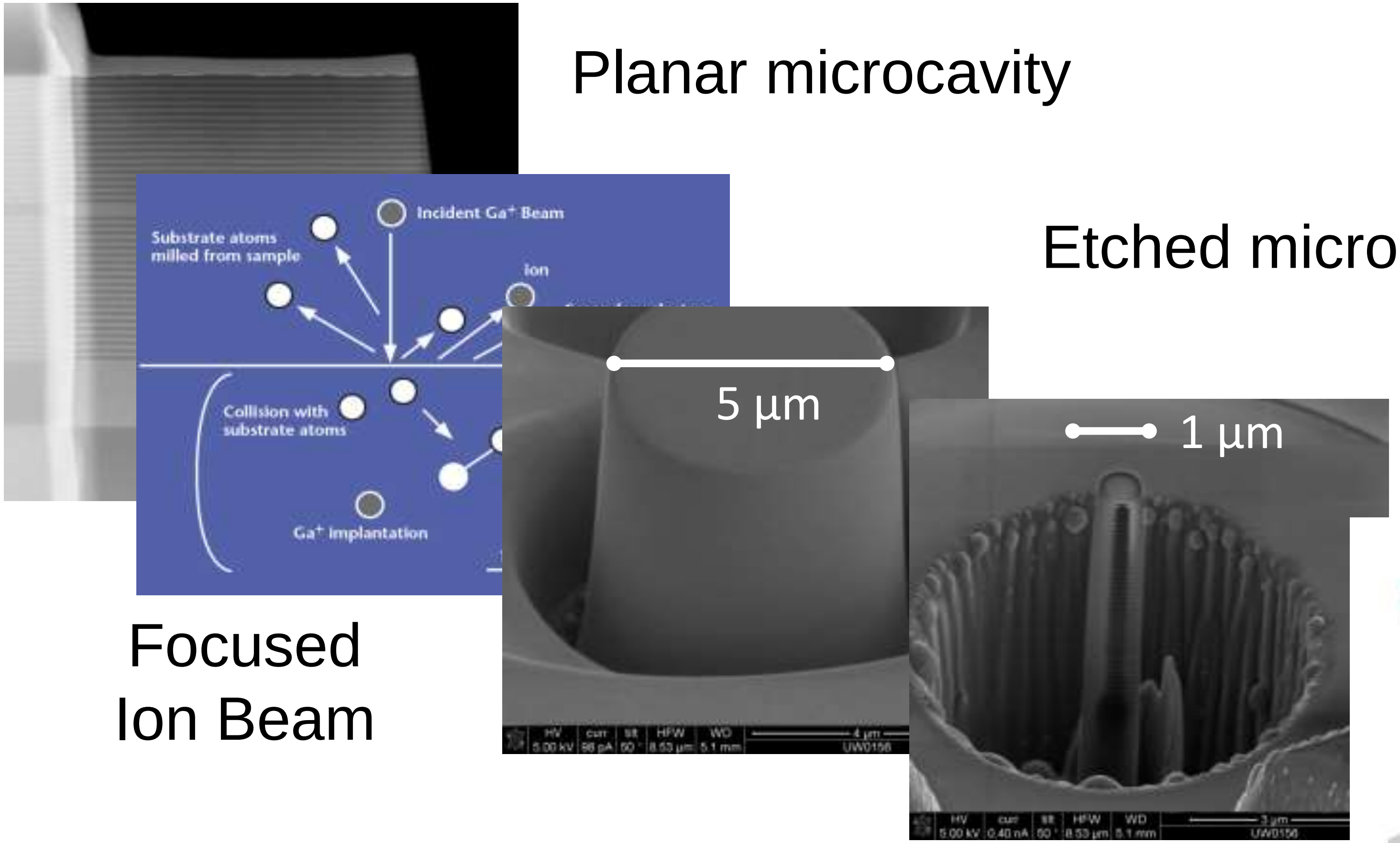
▲ Grenoble
■ Marcoussis
● University of Warsaw
▼ Tsukuba/Grenoble
☆ IFPAN Warsaw

Photonic micro-structures



Improving photon extraction efficiency

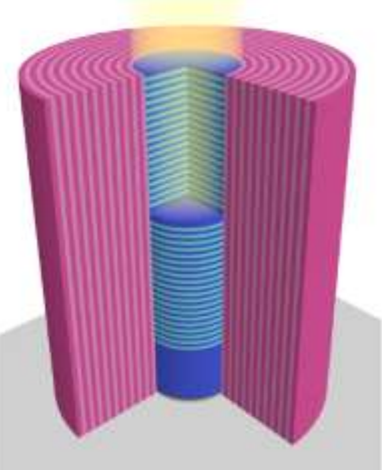
Microstructures for solotronics



Planar microcavity

Etched micropillars

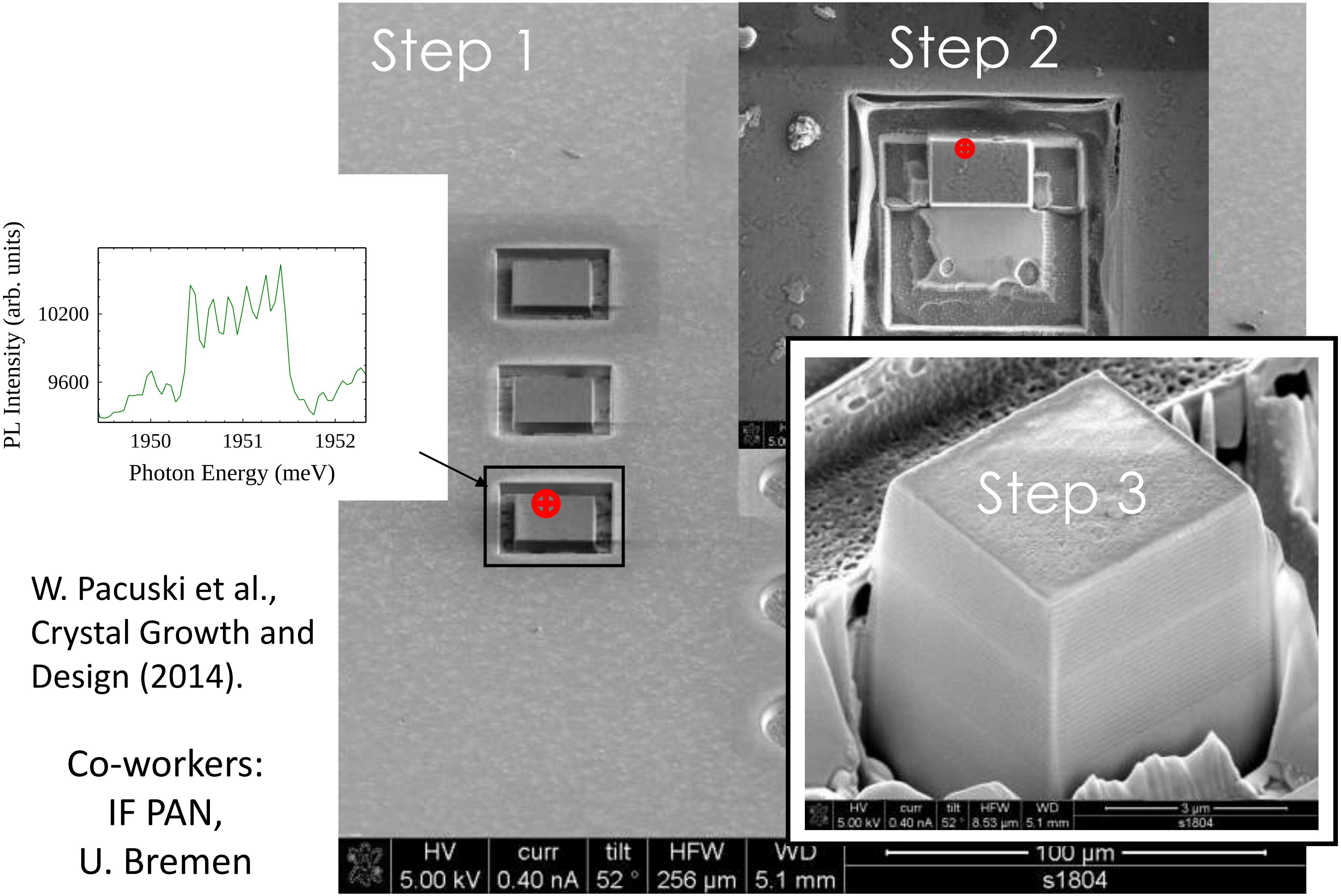
Focused Ion Beam



Technology of ZnTe-based photonic structures

- **Bragg Reflectors:** W. Pacuski et al., APL (2009).
- **Micropillars:** C. Kruse et al., Nanotechnology (2011).
- **Purcell effect:** T. Jakubczyket al., APL (2012), ACS Nano 2014.
- **Single Mn:** W. Pacuski et al., Crystal Growth and Design (2014).

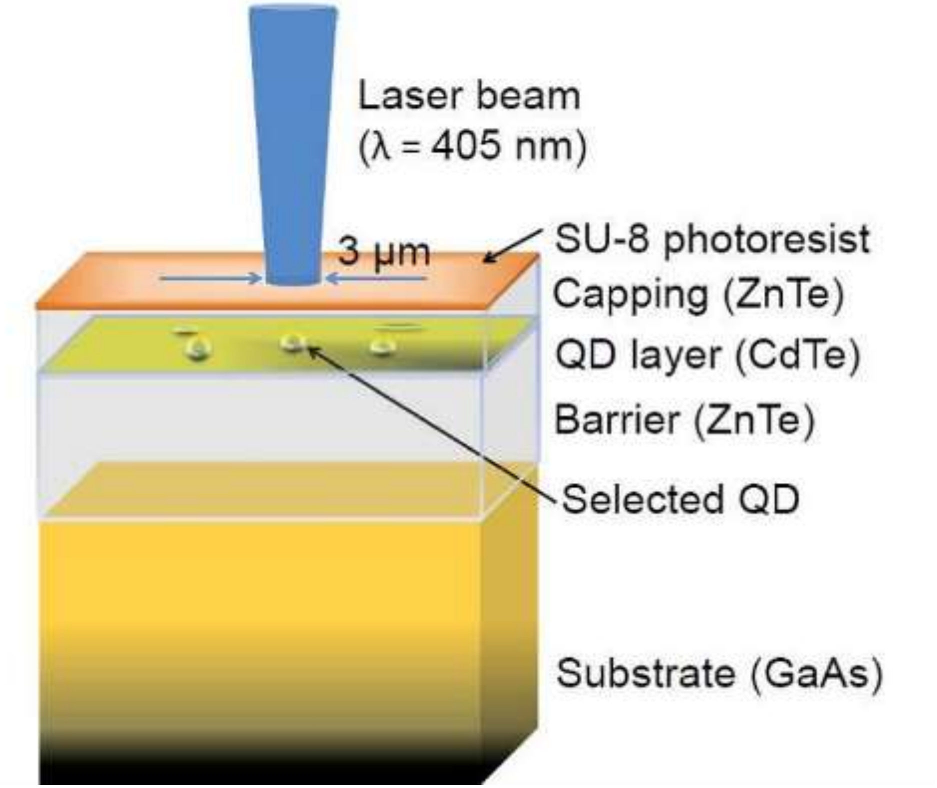
Microstructure containing a QD with a single Mn

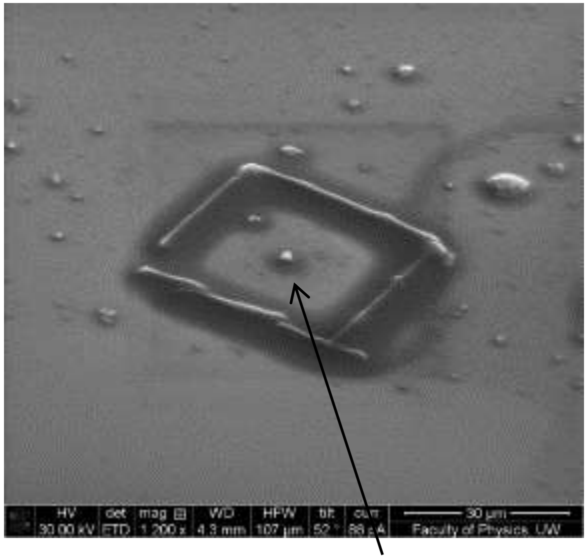


W. Pacuski et al.,
Crystal Growth and
Design (2014).

Co-workers:
IF PAN,
U. Bremen

Photolitography nanopositioning of a QD

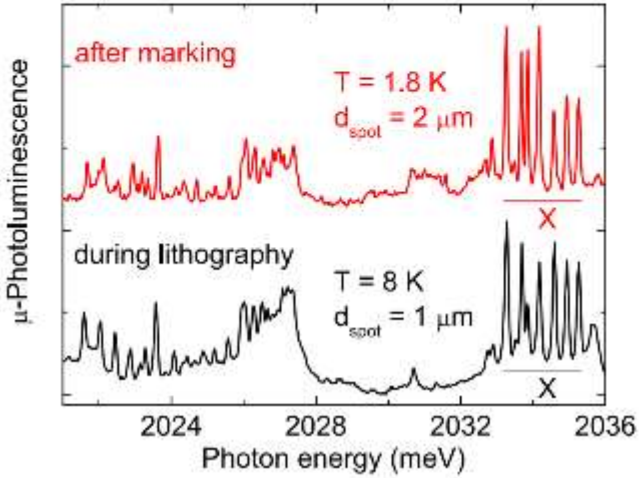




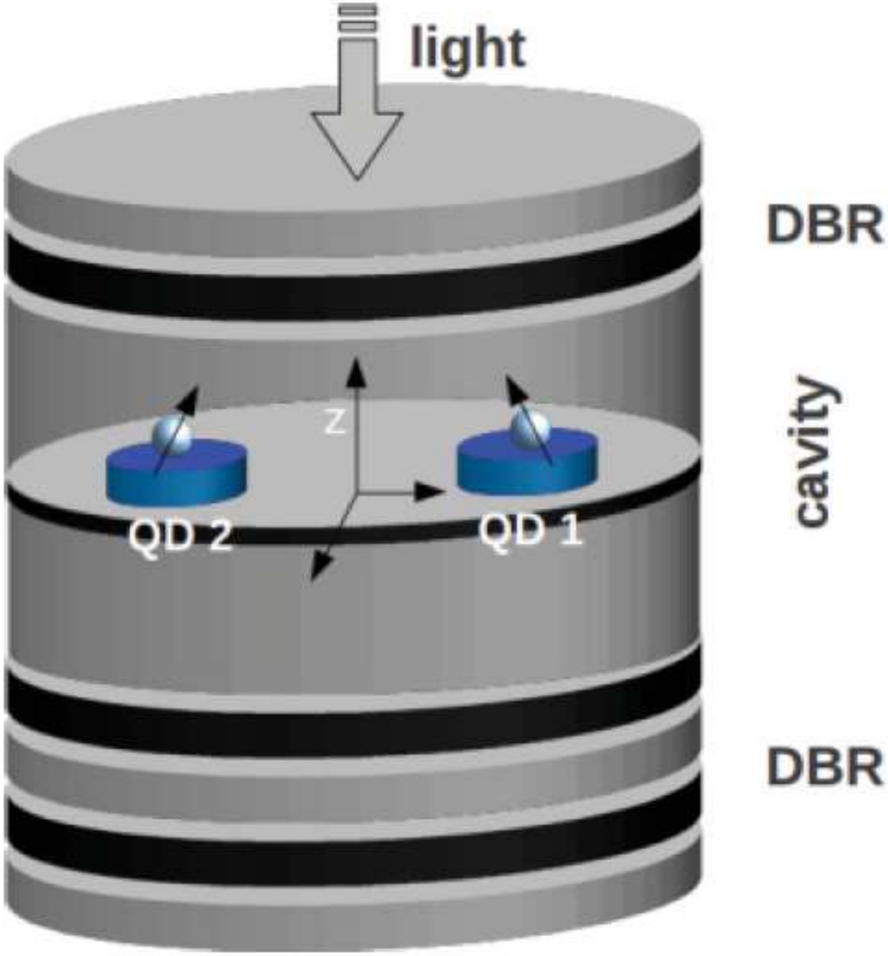
A QD with a single Mn ion under this spot

K. Sawicki et al. , Appl. Phys. Lett. (2015).
One color litography, designed for VIS

see also A. Dousse et al. PRL (2008)
Two color litography, designed for NIR

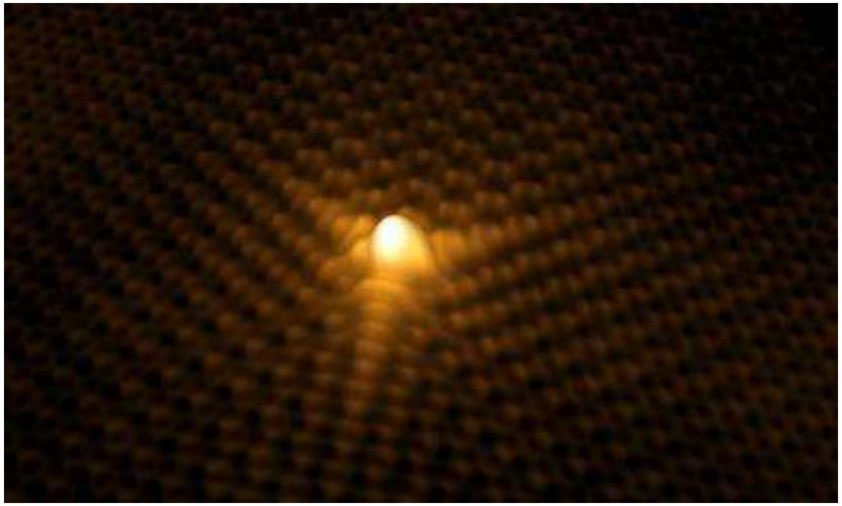


Outlook: coupling magnetic ions by cavity mode



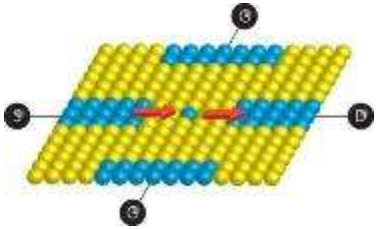
Theoretical proposal
J. A. Andrade et al., PRB (2012).

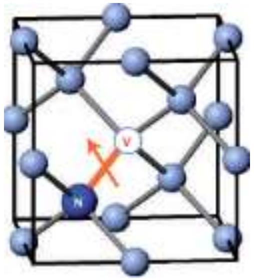
How to access and manipulate single dopant **in TMD?**

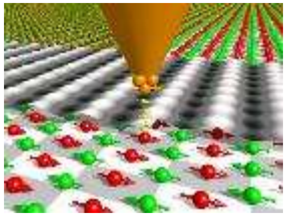


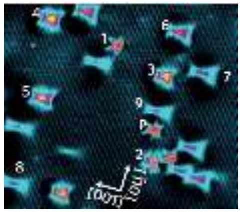
H. Gonzalez-Herrero et al., Science (2016).

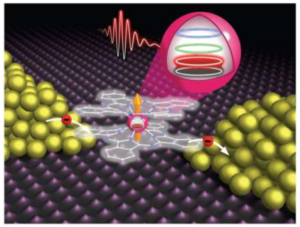
- **STM tip**
- Current affected by a dopant
- Intra-center optical transitions
- Excitonic transitions
- Polarized carriers
- Photonic structures

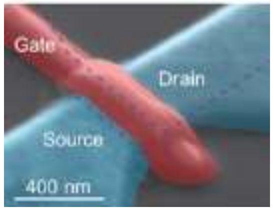


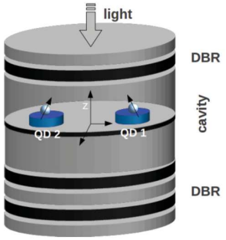












Our contribution to solotronics

3 new QD systems :

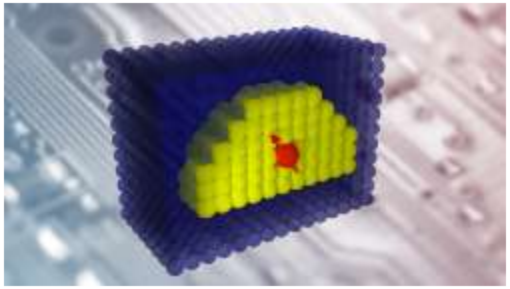
- Single Mn^{2+} in CdSe/ZnSe QD (long relaxation time T_1)
- Single Co^{2+} in CdTe/ZnTe QD (strain related anisotropy determined)
- Single Fe^{2+} (zero nuclear spin, magnetic ground state due to strain)

Single magnetic ion does not induce exciton PL quenching.

Manipulation of single magnetic ion spin

Coherent Larmor precession of single magnetic ion spin 5/2

Deterministic microstructures with single magnetic ions



J. Kobak et al., Nature Commun. (2014).
T. Smoleński et al., Nature Commun.(2016).
T. Smoleński et al., Phys. Rev. B (2015).
W. Pacuski et al. , Crystal Growth & Design (2014).
M. Goryca et al., Phys. Rev. Lett. (2014).
M. Goryca et al., Phys. Rev. Lett. (2009).