

Jacek.Szczytko@fuw.edu.pl (Yatzek Schtchitko)

Faculty of Physics, University of Warsaw





ELBYSIER

Electronics Beyond Silicon Era

Google: Jacek Szczytko



Faculty of Physics, University of Warsaw



Hoża 69: 1921-2014 r.





UNIA EUROPEJSKA EUROPEJSKI FUNDUSZ ROZWOJU REGIONALNEGO



The polariton laboratory



Dr Barbara Piętka

Mateusz Król

Rafał Mirek

The polariton laboratory



Laboratory of SQUID magnetometry



Andrzej Twardowski Andrzej Majhofer Anita Gardias Jarosław Rybusiński Maciej Marchwiany (Monte Carlo)







Magnetic nanoparticles



Article

pubs.acs.org/Biomac

Encapsulation

polymeric microvessel

nanoferrite

doxorubicin

Magnetic-Nanoparticle-Decorated Polypyrrole Microvessels: Toward Encapsulation of mRNA Cap Analogues

Krystyna Kijewska,[†] Anita Jarzębińska,[†] Joanna Kowalska,[‡] Jacek Jemielity,^{‡,§} Daria Kępińska,[†] Jacek Szczytko,^{||} Marcin Pisarek,[⊥] Katarzyna Wiktorska,[¶] Jarosław Stolarski,[#] Paweł Krysiński,[†] Andrzej Twardowski,^{||} and Maciej Mazur^{*,†}

THE JOURNAL OF PHYSICAL CHEMISTRY

Adsorption of Doxorubicin onto Citrate-Stabilized Magnetic Nanoparticles



aqueous layer

Magnetic Organic LC

Piotr Kaszyński (Univ. Vanderbilt USA, The Centre of Molecular and Macromolecular Studies, Lodz, Poland)

Ewa Górecka (Faculty of Chemistry, University of Warsaw) Damian Pociecha (Faculty of Chemistry, University of Warsaw)





Piotr .

CF₃





Magnetic Organic LC





Photoconductive Liquid-Crystalline Derivatives of 6-Oxoverdazyl

Aleksandra Jankowiak,[†] Damian Pociecha,[‡] Jacek Szczytko,[§] Hirosato Monobe,[∥] and Piotr Kaszyński^{*,†,⊥}

[†]Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, United States

[‡]Department of Chemistry, University of Warsaw, 02-089 Warsaw, Poland

[§]Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

^{II}Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, AIST Kansai Centre, Ikeda, Osaka 563-8577, Japan

¹Faculty of Chemistry, University of Łódź, Tamka 12, 91-403 Łódź, Poland



Communication pubs.acs.org/JACS



Tetragonal Phase of 6-Oxoverdazyl Bent-Core Derivatives with Photoinduced Ambipolar Charge Transport and Electrooptical Effects

Marcin Jasiński,[†] Damian Pociecha,[‡] Hirosato Monobe,[§] Jacek Szczytko,[∥] and Piotr Kaszyński^{*,†,⊥}

[†]Faculty of Chemistry, University of Łódź, Tamka 12, 91403 Łódź, Poland

[‡]Department of Chemistry, University of Warsaw, 02-089 Warsaw, Poland

[§]Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan

^{II}Institute of Experimental Physics, Faculty of Physics, University of Warsaw, Hoża 69, 00-681 Warsaw, Poland

¹Organic Materials Research Group, Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235, United States





- 1. Magnetic field and spin
- 2. Exchange interactions
- 3. Magnetism of matter
- 4. Spintronics
- 5. Organics spintronics
 - a. Magnetism
 - b. Transport
 - c. Light
 - d. Liquid crystals





Hamiltonian



Homogenous magnetic field

The Landau gauge solution

$$\left\{\frac{1}{2m}\left[\hat{p} - q\,\vec{A}(\vec{r},t)\right]^2 + q\phi(\vec{r},t) + U(\vec{r},t)\right\}\psi(\vec{r},t) = i\hbar\frac{d}{dt}\psi(\vec{r},t)$$

"free electron" (U(x, y, z) = U(z)) \Rightarrow Landau levels

Homogenous magnetic field

The Landau gauge solution

$$\left\{\frac{1}{2m}\left[\hat{p}-q\,\vec{A}(\vec{r},t)\right]^2+q\varphi(\vec{r},t)+U(\vec{r},t)\right\}\psi(\vec{r},t)=i\hbar\frac{d}{dt}\psi(\vec{r},t)$$

(unfortunately distinguishes **Landau gauge**: magnetic field $\vec{B} = (0,0,B_z) \Rightarrow B_z = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}$ direction) $\vec{A} = [0, B_z x, 0]$ czyli $A_v = B_z x \stackrel{\text{def}}{=} Bx$ q = -eWe assume that in a plane xy there is no other potential $\left\{\frac{1}{2m}\left[-\hbar^2\frac{\partial^2}{\partial x^2} + \left(-i\hbar\frac{\partial}{\partial y} + eBx\right)^2 - \hbar^2\frac{\partial^2}{\partial z^2}\right] + U(z)\right\}\psi(\vec{r}) = E\psi(\vec{r})$ Which gives: $\left| -\frac{\hbar^2}{2m} \nabla^2 - \frac{ie\hbar}{m} Bx \frac{\partial}{\partial y} + \frac{(eBx)^2}{2m} + U(z) \right| \psi(\vec{r}) = E\psi(\vec{r})$ The evidence of the Lorentz force Parabolic potential!

", free electron" (U(x, y, z) = U(z)) \Rightarrow Landau levels

Homogenous magnetic field

The Landau gauge solution

$$\left\{\frac{1}{2m}\left[\hat{p}-q\,\vec{A}(\vec{r},t)\right]^2+q\varphi(\vec{r},t)+U(\vec{r},t)\right\}\psi(\vec{r},t)=i\hbar\frac{d}{dt}\psi(\vec{r},t)$$

(unfortunately distinguishes **Landau gauge**: magnetic field $\vec{B} = (0,0,B_z) \Rightarrow B_z = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}$ $\vec{A} = [0, B_z x, 0] \text{ czyli } A_y = B_z x \stackrel{\text{def}}{=} Bx \qquad q = -e$ $\begin{cases} \frac{1}{2m} \left[-\hbar^2 \frac{\partial^2}{\partial x^2} + \left(-i\hbar \frac{\partial}{\partial x} \right) (\text{usually}) \text{ we have no free electrons} \right] \\ \text{which give.} \quad \left[-\frac{\pi^2}{2m} \nabla^2 - \frac{ie\hbar}{m} Bx \frac{\partial}{\partial y} + \frac{(eBx)^2}{2m} + U(z) \right] \psi(\vec{r}) = E\psi(\vec{r}) \end{cases}$ direction) x that in a plane xymere is no other potential The evidence of the Lorentz force Parabolic potential!

", free electron" (U(x, y, z) = U(z)) \Rightarrow Landau levels

Hamiltonian

$$\left\{\frac{1}{2m}\hat{p}^2 + U(\vec{r},t)\right\}\psi(\vec{r},t) = i\hbar\frac{d}{dt}\psi(\vec{r},t)$$

Coulomb potential



Coulomb potential

 $E_n = -Ry \frac{1}{n^2} \qquad \Rightarrow |n, l, m_l\rangle$

FIRST:

Coulomb potential in 3D in the semiconductor of dielectric constant ε_r , effective mass m^* :

$$U(r) = -\frac{e^2}{4\pi\varepsilon_r\varepsilon_0}\frac{1}{r}$$

$$Ry = \left(\frac{e^2}{4\pi\varepsilon_0}\right)^2 \frac{m}{2\hbar^2} = \frac{\hbar^2}{2ma_B^2} = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0a_B} = 13.6 \text{ eV}$$

$$L^2 = -\hbar^2 \left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

$$l = 0, 1, 2 \dots$$



$$l = 0,1,2 \dots$$
$$E_n = -\left(\frac{m^*}{m_0}\right) \frac{1}{\varepsilon_r^2} Ry \frac{1}{n^2}$$
$$a_B^* = \frac{4\pi\varepsilon_r\varepsilon_0\hbar^2}{m_0e^2} \left(\frac{m_0}{m^*}\right) = a_B\varepsilon_r \left(\frac{m_0}{m^*}\right)$$

principal, angular, magnetic

 $H' = -\vec{m}\vec{B}$

Here \vec{m} is magnetic moment

Magnetic field:

clasically:

$$|\vec{m}| = |I\vec{S}| = \frac{e}{T}\pi r^2 = \frac{e}{2\pi r/v}\pi r^2 = \frac{e}{2}rv$$
 [Am²]

thus:
$$ec{m}=-rac{e}{2m_0}ec{L}=-rac{\mu_B}{\hbar}\widehat{L}$$

Bohr magneton $\mu_B = \frac{\hbar e}{2m_0}$ $\mu_B = 9,274009994(57) \times 10^{-24} \text{ J/T}$

$$H' = -\vec{m}\vec{B} = \frac{\mu_B}{\hbar}\hat{L}\vec{B}$$

circumference of a circle

2016-04-28

$$\mu_B = \frac{\hbar e}{2m_0}$$









• What is "mass"?

$$\overrightarrow{F} = m \overrightarrow{a}$$
$$F = G \frac{m_1 m_2}{r^2}$$



Mariusz Pudzianowski http://www.pudzian.pl/

• What is the "momentum"?

$$\overrightarrow{p} = m \overrightarrow{v}$$



• What is the "angular momentum"?

$$\overrightarrow{L} = \overrightarrow{r} \times \overrightarrow{p}$$



• What is the "charge"?

$$F = k \frac{q_1 q_2}{r^2}$$



• Spin?







Sebastian Münster, Cosmographia in 1544

Disney

Spin, spin-orbit interaction

Spin operators $\hat{S}_{\chi}, \hat{S}_{y}, \hat{S}_{z}, \hat{S}^{2}$

$$\psi(\vec{r}, S_z) = \psi(\vec{r})\chi(S_z)$$

Spinor

$$\left[\hat{S}_x, \hat{S}_y\right] = i\hbar \hat{S}_z$$
, etc.

Pauli matrices: σ_x , σ_y , σ_z

$$\hat{S}_x = \frac{1}{2}\hbar\sigma_x = \frac{1}{2}\hbar\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$$
$$\hat{S}_y = \frac{1}{2}\hbar\sigma_y = \frac{1}{2}\hbar\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}$$
$$\hat{S}_x = \frac{1}{2}\hbar\sigma_z = \frac{1}{2}\hbar\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$$



only two orientations

projections of the spin on the axis z $\chi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\chi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Spin, spin-orbit interaction

Spin operators $\hat{S}_{\chi},\hat{S}_{y},\hat{S}_{z},\hat{S}^{2}$

$$H' = \frac{\mu_B}{\hbar} (\hat{L} + g\hat{S})\vec{B}$$
$$g \text{-factor for the agreement with}$$
$$[\hat{S}_x, \hat{S}_y] = i\hbar \hat{S}_z, \text{ etc.}$$

Pauli matrices:
$$\sigma_x$$
, σ_y , σ_z

$$\hat{S}_x = \frac{1}{2}\hbar\sigma_x = \frac{1}{2}\hbar\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$$
$$\hat{S}_y = \frac{1}{2}\hbar\sigma_y = \frac{1}{2}\hbar\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}$$
$$\hat{S}_x = \frac{1}{2}\hbar\sigma_z = \frac{1}{2}\hbar\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$$

projections of the spin on the axis z $\chi_{\uparrow} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}$, $\chi_{\downarrow} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$

Spin, spin-orbit interaction

Spin operators $\hat{S}_{\chi},\hat{S}_{y},\hat{S}_{z},\hat{S}^{2}$

$$H' = \frac{\mu_B}{\hbar} (\hat{L} + g\hat{S})\vec{B}$$
$$g \text{-factor for the agreement with}$$
$$[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z, \text{ etc.}$$

Pauli matrices: σ_x , σ_y , σ_z

$$\hat{S}_x = \frac{1}{2}\hbar\sigma_x = \frac{1}{2}\hbar\begin{bmatrix}0 & 1\\1 & 0\end{bmatrix}$$
$$\hat{S}_y = \frac{1}{2}\hbar\sigma_y = \frac{1}{2}\hbar\begin{bmatrix}0 & -i\\i & 0\end{bmatrix}$$
$$\hat{S}_x = \frac{1}{2}\hbar\sigma_z = \frac{1}{2}\hbar\begin{bmatrix}1 & 0\\0 & -1\end{bmatrix}$$

 $g = -2.00231930436182 \pm 0.0000000000052$

projections of the spin on the axis z $\chi_{\uparrow}=\begin{pmatrix}1\\0\end{pmatrix}$, $\chi_{\downarrow}=\begin{pmatrix}0\\1\end{pmatrix}$

QED – Quantum ElectroDynamics



There is the "spin"

The consequences?



Spin, spin-orbit interaction

Spin operators $\hat{S}_{\chi},\hat{S}_{y},\hat{S}_{z},\hat{S}^{2}$

$$H' = \frac{\mu_B}{\hbar} (\hat{L} + g\hat{S})\vec{B}$$
g-factor for the agreement with experiments

Total angular momentum operator $\hat{J} = \hat{L} + \hat{S}$, the base $|j, m_j\rangle$

Total magnetic moment
$$\widehat{M} = \widehat{M}_L + \widehat{M}_S = -g_L \frac{\mu_B}{\hbar} \widehat{L} - g_S \frac{\mu_B}{\hbar} \widehat{S}$$

 $\uparrow \qquad \uparrow$
 $=1 \qquad =2$

 $\widehat{M} \neq \widehat{J}$ - magnetic anomaly of spin

Spin-orbit interaction $\hat{H}_{SO} = \lambda \hat{L} \hat{S}$ with the base $|n, l, s, m_l, m_s\rangle$ For *s*-states $\hat{L} = 0 \Rightarrow \hat{L} \hat{S} = 0$

Total angular momentum operator $\hat{J} = \hat{L} + \hat{S}$, the base $|j, m_j\rangle$

$$\hat{H}_{SO} = \lambda \hat{L} \hat{S} = \lambda \frac{1}{2} \left(J^2 - L^2 - S^2 \right) = \lambda \left(L_z S_z + \frac{1}{2} (L_+ S_- + L_- S_+) \right)$$
fine-structure constant
$$\lambda = hc A = \frac{Z \alpha^2}{2} \left(\frac{1}{r^3} \right)$$

$$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137.037}$$

$$Ry = hc R_{\infty}$$

$$R_{\infty} = \frac{m_e e^4}{8\varepsilon_0^2 h^3 c}$$

$$R_{\infty} = 1,097 \times 10^7 \text{m}^{-1}$$

$$E_{SO} = \int \psi^* H_{SO} \psi \, dV = \frac{Z}{2(137)^2} \int \psi^* \frac{\hat{L}\hat{S}}{r^3} \, \psi \, dV$$

e.g. for ψ_{210} we get $\left\langle \frac{1}{r^3} \right\rangle = \frac{1}{24} \left(\frac{Z}{a_0} \right)^3$ and for general n (principal quantum number) $E_{SO} = \frac{Z^4}{2(137)^2 a_0^3 n^3} \left(\frac{j(j+1) - l(l+1) - s(s+1)}{2l(l+1/2)(l+1)} \right)$

Spin-orbit interaction $\hat{H}_{SO} = \lambda \hat{L} \hat{S}$ with the base $|n, l, s, m_l, m_s \rangle$

For *s*-states $\hat{L} = 0 \Rightarrow \hat{L}\hat{S} = 0$

Total angular momentum operator $\hat{J} = \hat{L} + \hat{S}$, the base $|j, m_j\rangle$

 $\bar{L}\bar{S} = \frac{1}{2}(\bar{J}^2 - \bar{L}^2 - \bar{S}^2) = L_z S_z + \frac{1}{2}(L_+ S_- + L_- S_+)$



the base: $|n, l, s, j, m_j\rangle$ shortly: $|j, m_j\rangle$

Multi-electron atom

Term symbol $2S+1 L_I$

an abbreviated description of the angular momentum quantum numbers in a multi-electron atom

Total wavefunction must be antisymmetric (under interchange of any pair of particle)



Multi-electron wavefunction:

$$\psi\left(\vec{r}_1,\ldots,\vec{r}_N,\vec{S}_1,\ldots,\vec{S}_N\right) = \psi\left(\vec{r}_1,\ldots,\vec{r}_N\right)\chi\left(\vec{S}_1,\ldots,\vec{S}_N\right)$$

Antisymmetric wavefunction + Pauli exclusion principle + Coulomb interaction =

Exchange interaction

Exchange interaction

Antisymmetric wavefunction + Pauli exclusion principle + Coulomb interaction = Exchange interaction

 $\Psi = \varphi_{orbital} \times \chi_{spin}$ <u>Antisymmetric!</u>

Example:



Two electrons localized on one centrum

$$\mathcal{H}(1,2) = H_0(1) + H_0(2) + \frac{e^2}{r_{12}}$$

Exchange interaction

201

Antisymmetric wavefunction + Pauli exclusion principle + Coulomb interaction = **Exchange interaction**

 $\Psi = \varphi_{orbital} \times \chi_{spin}$ <u>Antisymmetric!</u>

Hund's rules,
$$E_{\tau} < E_{s}$$

$$\frac{1}{\sqrt{2}} \begin{bmatrix} \varphi_{A}(1)\varphi_{B}(2) - \varphi_{A}(2)\varphi_{B}(1) \end{bmatrix} \times \begin{bmatrix} \chi_{\uparrow}(1)\chi_{\downarrow}(2) \\ \frac{1}{\sqrt{2}} [\chi_{\uparrow}(1)\chi_{\downarrow}(2) + \chi_{\downarrow}(1)\chi_{\uparrow}(2)] \\ \chi_{\downarrow}(1)\chi_{\downarrow}(2) \end{bmatrix}$$

$$\frac{1}{\sqrt{2}} \begin{bmatrix} \varphi_{A}(1)\varphi_{B}(2) + \varphi_{A}(2)\varphi_{B}(1) \end{bmatrix} \frac{1}{\sqrt{2}} [\chi_{\uparrow}(1)\chi_{\downarrow}(2) - \chi_{\downarrow}(1)\chi_{\uparrow}(2)]$$
Antisymmetric wavefunction + Pauli exclusion principle + Coulomb interaction = Exchange interaction

 $\Psi = \varphi_{orbital} \times \chi_{spin}$ <u>Antisymmetric!</u>



Antisymmetric wavefunction + Pauli exclusion principle + Coulomb interaction = Exchange interaction

 $\Psi = \varphi_{orbital} \times \chi_{spin}$

$$\frac{1}{\sqrt{2}} \left[\varphi_A(1)\varphi_B(2) - \varphi_A(2)\varphi_B(1) \right] \times \begin{bmatrix} \chi_{\uparrow}(1)\chi_{\downarrow}(2) \\ \frac{1}{\sqrt{2}} \left[\chi_{\uparrow}(1)\chi_{\downarrow}(2) + \chi_{\downarrow}(1)\chi_{\uparrow}(2) \right] \\ \chi_{\downarrow}(1)\chi_{\downarrow}(2) \end{bmatrix}$$

$$\frac{1}{\sqrt{2}} \left[\varphi_A(1)\varphi_B(2) + \varphi_A(2)\varphi_B(1) \right] \frac{1}{\sqrt{2}} \left[\chi_{\uparrow}(1)\chi_{\downarrow}(2) - \chi_{\downarrow}(1)\chi_{\uparrow}(2) \right]$$

Chemical bonds, $\mathbf{E}_{\mathsf{S}} < \mathbf{E}_{\mathsf{T}}$

Exchange interaction = Coulomb interaction + Pauli principle













$$E = 2E_A + U \gg E_A + E_B$$



$$E = 2E_A + U \gg E_A + E_B$$

$$E_n(\lambda) = E_n^{(0)} + \lambda \left\langle n^{(0)} \right| V \left| n^{(0)} \right\rangle + \lambda^2 \sum_{k \neq n} \frac{\left| \left\langle k^{(0)} \right| V \left| n^{(0)} \right\rangle \right|^2}{E_n^{(0)} - E_k^{(0)}} + O(\lambda^3)$$



Kinetic exchange

A specal case – superexchange



Kinetic exchange

A specal case – superexchange



No excited states for both spins

Kinetic exchange

A specal case – superexchange



There are an excited state for BOTH spins! J < 0 (antiferromagnetic exchange)

Kinetic exchange

A specal case – superexchange

The superexchange is antiferromagnetic, even over long distances.



 $|J_1| > |J_2| > |J_3| > \dots$

There are an excited state for BOTH spins! J < 0 (antiferromagnetic exchange)

Crystal field splitting (the presence of the ligants) \Rightarrow quenching of the orbital momentum





Mn³⁺ (d⁴)

Tetrahedral

ONCSSM 2003

d_{yz} Tetrahedral

Octahedral



Crystal field (CF) splitting

Double exchange (in mixed vallence compounds)





Ferromagnetism



Ferromagnetism



Spin density of states



Fig. 1. A schematic representation of the density of electronic states that are available to electrons in a normal metal and in a ferromagnetic metal whose majority spin states are completely filled. *E*, the electron energy; E_F , the Fermi level; N(E), density of states.



$$M(T,H) = -\frac{\partial E(T,H)}{\partial H}$$

$$\chi(T,H) = -\frac{\partial M(T,H)}{\partial H}$$

$$M = \frac{\sum_{n} - \left(\frac{\partial E_{n}}{\partial H}\right) \exp\left(-\frac{E_{n}}{k_{B}T}\right)}{\sum_{n} \exp\left(-\frac{E_{n}}{k_{B}T}\right)}$$

$$\chi = \frac{2N_A g^2 \mu_B}{k_B T \left(3 + \exp\left(-\frac{J}{k_B T}\right)\right)}$$

Example: 2 ions of spin $S = \frac{1}{2}, J < 0$







Example: 2 ions of spin $S = \frac{1}{2}$, J < 0



Experiment

Ewa Górecka , Adam Krówczyński, Jadwiga Szydłowska, Jacek Szczytko <u>students</u>: <u>Paweł Majewski</u> *Department of Chemistry, University of Warsaw Structural Research Laboratory*



Isomeric bimetallic copper(II) Cu²⁺ and nickel(II) Ni²⁺ complexes



coordinate bonds with lone pairs of electrons





		$Cu^{2+} - n - Cu^{2+}$
1294	1 × Cu ²⁺	
1344	2 × Cu ²⁺ biphenyl	n = 8
2955	2 × Cu ²⁺ pyrazine 〈	○ N = 4



	C	u ²⁺ – n – Cu ²
1294	1 × Cu ²⁺	
1344	2 × Cu ²⁺ biphenyl	n = 8
2955	2 × Cu²+ pyrazine 🤇) n = 4
2567	2 × Cu ²⁺ oxamide	n = 3











Isomeric bimetallic copper(II) Cu²⁺ and nickel(II) Ni²⁺ complexes



n = 8

n = 4

n = 3

n = 3

n = 3



Isomeric bimetallic copper(II) Cu²⁺ and nickel(II) Ni²⁺ complexes



Cu²⁺– n – Cu²⁺

-	1294	1 × Cu ²⁺			
	1344	2 × Cu ²⁺ bifenyl		n =	8
_	2955	2 × Cu ²⁺ pirazyna	\bigcirc	n =	4
_	2567	2 × Cu ²⁺ oksamid		n =	3
_	2356	2 × Cu ²⁺ oksamid		n =	3
-	2975	2 × Cu ²⁺ pirymidyna	\bigcirc	n =	3




Results



Hypothesis



Isomeric bimetallic copper(II) Cu²⁺ and nickel(II) Ni²⁺ complexes



Ni²⁺- n - Ni²⁺

1 × Ni²⁺







Isomeric bimetallic copper(II) Cu²⁺ and nickel(II) Ni²⁺ complexes



Ni²⁺- n - Ni²⁺

1421 1 × Ni²⁺

Szydłowska, Szczytko et al.CHEMPHYSCHEM 11,1735-1741 (2010)









		Ni ²⁺ – n – Ni ²⁺
2763	1 × Ni ²⁺	
1421	1 × Ni ²⁺	





























Giant Magnetoresistance



The Nobel Prize in Physics 2007 Albert Fert, Peter Grünberg

The Nobel Prize in Physics 2007



Photo: U. Montan Albert Fert



Peter Grünberg



The Nobel Prize in Physics 2007 was awarded jointly to Albert Fert and Peter Grünberg "for the discovery of Giant Magnetoresistance"

Photos: Copyright @ The Nobel Foundation

Ferromagnetism



(in)organic spintronics

Magnetoelectronics

Gary A. Prinz



Fig. 1. A schematic representation of the density of electronic states that are available to electrons in a normal metal and in a ferromagnetic metal whose majority spin states are completely filled. E, the electron energy; E_F , the Fermi level; N(E), density of states.



Fig. 2. Schematic representations of spin-polarized transport from a ferromagnetic metal, through a normal metal, and into a second ferromagnetic metal for aligned and antialigned magnetic moments. Ø, disallowed channel.





Low resistance

Fig. 3. Schematic representations of transport that is parallel to the plane of a layered magnetic metal sandwich structure for aligned (low resistance) and antialigned (high resistance) orientations.

(in)organic spintronics

Magnetoelectronics

Gary A. Prinz



High resistance



Low resistance

Fig. 3. Schematic representations of transport that is parallel to the plane of a layered magnetic metal sandwich structure for aligned (low resistance) and antialigned (high resistance) orientations.



Fig. 4. A schematic representation of a GMR read head (green) that passes over recording media containing magnetized regions. The magnetization direction of the soft layer in the head responds to the fields that emanate from the media by rotating either up or down. The resulting change in the resistance is sensed by the current *i* passing through the GMR element.

(in)organic spintronics

Magnetoelectronics

Gary A. Prinz



Fig. 6. A magnetic tunnel junction formed by a thin insulating barrier separating two ferromagnetic metal films. Current passing through the junction encounters higher resistance when the magnetic moments are antialigned and lower resistance when they are aligned.



Fig. 5. A schematic representation of RAM that is constructed of GMR elements connected in series. The elements are manipulated for writing or reading by applying magnetic fields that are generated by currents passing through lines above and below the elements.

(in)organic spintronics – spin valve





Figure 1. Schematic diagram of the cross-section of a spin-valve transistor showing the emitter, base and collector. The emitter is forward biased and the collector is reverse biased. I_E is the emitter current and I_C is the collector current. The base layer contains a spin valve (NiFe/Au/Co) in addition to a Si–Pt emitter diode and a Si–Au collector diode.

J. Phys. D: Appl. Phys. 33 (2000) 2911–2920

Diluted Magnetic Semiconductors

NATURE | VOL 408 | 21/28 DECEMBER 2000 | www.nature.com

Electric-field control of ferromagnetism

H. Ohno, D. Chiba, F. Matsukura, T. Omiya, E. Abe, T. Dietl*, Y. Ohno & K. Ohtani



(in)organics spintronics – spin valve





Figure 3. Magnetization as a function of the magnetic field of the spin valve (NiFe (3 nm)/Au (3.5 nm)/Co (3 nm)) grown on Si/Pt (2 nm). The curve shows well defined switching of the Co and permalloy layers at the respective coercive fields.



Figure 4. The magnetoresistance against the magnetic field of the spin valve (NiFe (3 nm)/Au (3.5 nm/Co (3 nm)/Au (2 nm)) grown on Si/Pt (2 nm) showing a magnetoresistance of about 1%.

Spintronics

Magnetic tunnel junction (MTJ)

Ferr
Insula
Ferr

Ferromag. (soft)

Insulator (barrier)

Ferromag. (hard)

Ferromag. Co, Py, FeCo, etc. Barrier Al2O3, MgO, etc.

 $TMR(\%) = (R_{AP} - R_{P})/R_{P} * 100$



Giant Magnetoresistance





Spin-dependent tunneling conductance of Fe|MgO|Fe sandwiches W. H. Butler, X.-G. Zhang, T. C. Schulthess, and J. M. MacLaren Phys. Rev. B 63, 054416 (2001)

Organic Spintronics – spin valve



letters to nature

Giant magnetoresistance in organic spin-valves

Z. H. Xiong, Di Wu, Z. Valy Vardeny & Jing Shi

Department of Physics, University of Utah, Salt Lake City, Utah 84112, USA


S. Sanvito, Nature Physics 6, 562 (2010)

science terface C

suggests that the metal/organic interface is key, paving the way for a new field in which interfaces are specifically govern the injection of spins into organic molecules. A new study designed for spin applications. This is this field of 'spinterface' science. ittle is known about the mechanisms that

Stefano Sanvito



Figure 1 Schematic of the spin-filtering mechanism at an organic/inorganic hybrid interface. **a**, When the magnetic metal (left) and the molecule (right) are well separated, the overall DOS is simply the superposition of the individual DOS of the two spin components (blue represents the spin-up DOS and red the spin-down DOS) — that is, a broad spin-polarized DOS for the metal and a series of discrete energy levels for the molecule (here only the HOMO is represented). In this case, the DOS of the metal alone determines the spin-polarization of the tunnelling current. **b**,**c**, When the molecule is brought into contact with the metal the DOS gets modified into two ways: the energy levels broaden (**b**) (the broadening is exaggerated in the figure) and their position shifts in energy (**c**). In both cases new peaks in the DOS might appear at the *E*_F of the electrodes, arising from new hybrid interfacial states. It is this new DOS that determines the spin-polarization of the injected current, which can be dramatically different, and even reversed, compared with the polarization of the electrodes (as in **b**).

MOLECULAR SPINTRONICS



Figure 1. A general scheme illustrating the energy level alignment due to the interaction between an organic molecule and a metallic surface. (a) Physisorption creates a weak molecule-metal interaction causing renormalization of the highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap in the molecule due to polarization effects.^{18,19} (b) Chemisorption creates a strong molecule-metal interaction where the atomic-type orbitals that initially form the molecular orbitals hybridize with the metallic bands, leading to bonding and anti-bonding hybrid bands with mixed molecular-metallic character. Note: $E_{\rm F}$, Fermi energy level.



FIG. 3 (color online). Overview SP-STM image of a multidomain (blue/yellow) 2 ML Fe stripe on W(110) with intact and few metalized H₂Pc present in three distinct orientations. Experimental (22 Å × 22 Å) SP-STM images for H₂Pc adsorbed on 2 ML Fe/W(110) at U = +0.05 V for both spin channels [i.e., up (†) and down (↓)] and local spin polarization. H₂Pc molecules show a high, locally varying spin polarization ranging from attenuation to inversion with respect to the ferromagnetic Fe film.

Nicolae Atodiresei et al. Phys. Rev. Lett. 105, 066601 (2010)

APPLIED PHYSICS LETTERS 106, 082408 (2015)



Is spin transport through molecules really occurring in organic spin valves? A combined magnetoresistance and inelastic electron tunnelling spectroscopy study

Marta Galbiati,¹ Sergio Tatay,¹ Sophie Delprat,¹ Hung Le Khanh,¹ Bernard Servet,² Cyrile Deranlot,¹ Sophie Collin,¹ Pierre Seneor,^{1,a)} Richard Mattana,^{1,b)} and Frédéric Petroff¹ ¹Unité Mixte de Physique CNRS/Thales, 1 Av. A. Fresnel, 91767 Palaiseau, France and Université Paris-Sud,

91405 Orsav. France

²Thales Research & Technology, 1 Av. A. Fresnel, 91767 Palaiseau, France















ADVANCED _____ MATERIALS

DOI: 10.1002/adma.200700559

Bistable Spin-Crossover Nanoparticles Showing Magnetic Thermal Hysteresis near Room Temperature**

By Eugenio Coronado,* José Ramón Galán-Mascarós,* María Monrabal-Capilla, Javier García-Martínez, and Pablo Pardo-Ibáñez

 $Fe(II)(LS) \implies Fe(II)(HS)$

Low Spin

High Spin





Scheme 1. Polymeric structure of the $[Fe(trz)_3]X_2^{[15]}$ family.

N--N

N—N

Ēе



·Fe

S = 0 Fe-N = 1.8 Å



Fe

Crystal field splitting (the presence of the ligants) \Rightarrow quenching of the orbital momentum





Fe²⁺ (d⁶)

Tetrahedral

ONCSSM 2003

d_{yz} Tetrahedral

Octahedral



Crystal field (CF) splitting

DOI: 10.1002/adma.200700559

Bistable Spin-Crossover Nanoparticles Showing Magnetic Thermal Hysteresis near Room Temperature**

By Eugenio Coronado,* José Ramón Galán-Mascarós,* María Monrabal-Capilla, Javier García-Martínez, and Pablo Pardo-Ibáñez



Figure 3. Magnetic thermal hysteresis for as-prepared $[Fe(Htrz)_2(trz)](BF_4)$ nanoparticles (magnetic moment represented per mole of Fe).



Scheme 1. Polymeric structure of the $[Fe(trz)_3]X_2^{[15]}$ family.



Figure 2. TEM image of as-prepared [Fe(Htrz)₂(trz)](BF₄) nanoparticles.

DOI: 10.1002/adma.200700559

Bistable Spin-Crossover Nanoparticles Showing Magnetic Thermal Hysteresis near Room Temperature**

By Eugenio Coronado,* José Ramón Galán-Mascarós,* María Monrabal-Capilla, Javier García-Martínez, and Pablo Pardo-Ibáñez



Figure 1. Bistability of a suspension of the title nanoparticles in octane: in the low-spin state (left) and in the high-spin state (right).



Scheme 1. Polymeric structure of the $[Fe(trz)_3]X_2^{[15]}$ family.



Figure 2. TEM image of as-prepared [Fe(Htrz)2(trz)](BF4) nanoparticles.





Long spin relaxation time due to the small spin-orbit couplin and small hyperfine interaaction \Rightarrow **spin qbits**





M. Shiddiq, D. Komijani, Y. Duan, A. Gaita-Arino, E. Coronado, S. Hill "Enhancing coherence in molecular spin qubits via atomic clock transitions" Nature 531, 348 (2016).

Light



"Standard" spintronics

• There is a need for new materials (spin filters, spin transistors – Diluted Magnetic Semiconductors, Ferromagnetic Semiconductors, etc.)



NATURE | VOL 402 | 16 DECEMBER 1999 | www.nature.com

Magnetic Semiconductors

NATURE VOL 402 16 DECEMBER 1999 www.nature.com

Electrical spin injection in a ferromagnetic semiconductor heterostructure

Y. Ohno*, D. K. Young†, B. Beschoten†, F. Matsukura*, H. Ohno* & D. D. Awschalom†



Electroluminescence control using Magnetic field (Magneto-Electro Luminescence (MEL) effect)



Electroluminescence control using Magnetic field (Magneto-Electro Luminescence (MEL) effect)





Electroluminescence control using Magnetic field (Magneto-Electro Luminescence (MEL) effect)

Injection of chargé (e-, h+) in the EL device leads to the formation of two types of excitons





Vniver§itat dÿValència

E. Coronado

Electroluminescence control using Magnetic field (Magneto-Electro Luminescence (MEL) effect)

Injection of chargé (e-, h+) in the EL device leads to the formation of two types of excitons



In a spin valve the current is spin polarized \Rightarrow by applying an external magnetic field the ratio single-triplet (and thus electroluminescence EL) should be controlled!

E. Coronado

E. Coronado et al. Nature Chemistry 2, 1031–1036 (2010) doi:10.1038/nchem.898



a, View of the [TaS₂]^{-0.33} superconducting layer (Ta, blue spheres; S, yellow spheres). **b**, View of the [Ni_{0.66}Al_{0.33}(OH)₂]^{+0.33} magnetic layer (Ni, grey spheres; Al, white spheres; O, red spheres). **c**, Representation of the restacked mat...

Figure 1: Schematic representation of the layered components and the restacked material.

X

Organic Liquid Crystals Spintronics





n = 8, $R = C_8 H_{17}$ $n = 10, R = C_{10}H_{21}$ $n = 12, R = C_{12}H_{25}$





^aReagents and conditions: (i) H₂ (3 atm), Pd/C, THF-EtOH; (ii) RCOCl (5[n]-7[n]), DMAP, CH₂Cl₂, rt, 10 min.

Piotr Kaszyński, Jacek Szczytko et al. JACS 134 (5), 2465-2468 (2012) CHEM. COMMUN. 48, 7064-7066 (2012) JACS 136 (42), pp 14658-14661 (2014) LIQUID CRYSTALS 41, 1653-1660 (2014) LIQUID CRYSTALS 41, 385-392 (2014) J. OF MATERIALS CHEMISTRY C 2 319-324 (2014)





 Piotr Kaszyński, Jacek Szczytko et al.

 JACS 134 (5), 2465-2468 (2012)

 CHEM. COMMUN. 48, 7064-7066 (2012)

 JACS 136 (42), pp 14658-14661 (2014)

 LIQUID CRYSTALS 41, 1653-1660 (2014)

 LIQUID CRYSTALS 41, 385-392 (2014)

 J. OF MATERIALS CHEMISTRY C 2 319-324 (2014)

Figure 3. Optical textures of 1[8] obtained upon (a) slow cooling, (b) fast cooling, and (c) after 2 h at 30 °C [8× longer exposure than in (b)].



n = 6, R = C_6H_{13} n = 8, R = C_8H_{17} n = 10, R = $C_{10}H_{21}$



n = 10, R = $C_{10}H_{21}$ Fig. 9 B3LYP/6-31G(2d,p) optimized geometry for 7 with the imposed n = 12, R = $C_{12}H_{25}$ C₂ symmetry.



B3LYP/6-31G(d,p) derived total spin density in 1[1]c.



Figure 2. Optical textures of (a) N and (b) Sm phases in 1[8] and (c) Tet phase in 1[16].







supercooled liquid

Spintronics

Semiconductor Devices Transistors

IC, LSI, porcessors

Diodes (LED, Lasers)

Memory (RAM, EPROM, FLASH)



Magnetic Devices Non-volatile memory Storage (HDD, floppy, streamer) Magneto-optical devices

Optical isolators (Faraday rotation)



light

High-speed high-density nonvolatile memory Reconfigurable logic devices Integrated magneto-optical devices Quantum information processing with spin

Optical Devices

Telecomunication (fibres, amplifiers)

Diodes (LED, Lasers)

Photo detectors



Organic Semiconductor Devices

Transistors

IC, LSI, porcessors

Diodes (LED, Lasers)

Memory (RAM, EPROM, FLASH)



Organic Magnetic Devices



Scheme 1. Polymeric structure of the $[Fe(trz)_3]X_2^{[15]}$ family.



SPINTRONICS



light

Optical Devices

Telecomunication (fibres, amplifiers)

Diodes (LED, Lasers)

Photo detectors

