

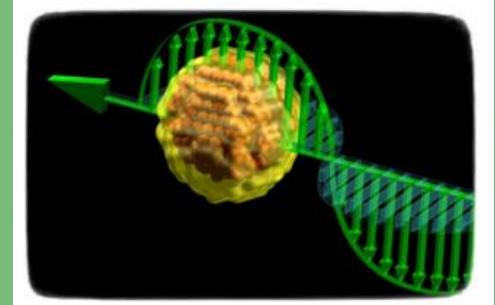
# Magneto-optics and Magneto-plasmonics

César de Julián Fernández



IMEM-CNR Parma

*Multifunctional Magnetic Materials*



Advanced magnetic materials and devices for biomedical applications

Italian School of Magnetism

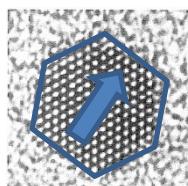
Turin , 21-25 May 2018

# Magneto-optics

# Magneto-plasmonics

## MAGNETISM

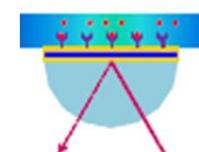
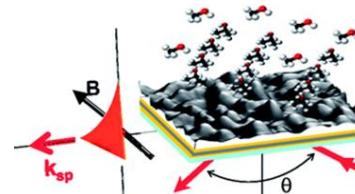
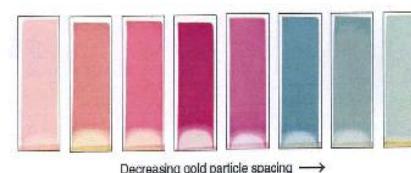
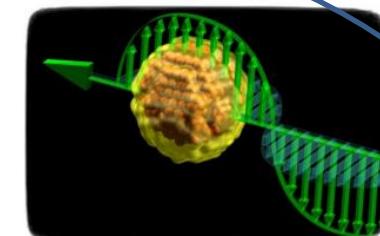
## PLASMONICS



## LIGHT



## HEALTH



## 1. Magneto-optics

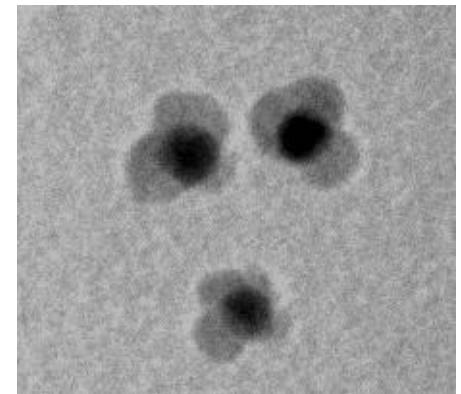
- a General phenomenology and materials
- b Applications of plasmonics in bio

## 2. Plasmonics

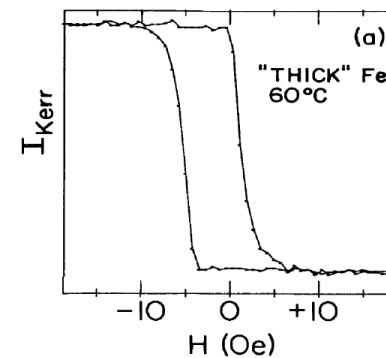
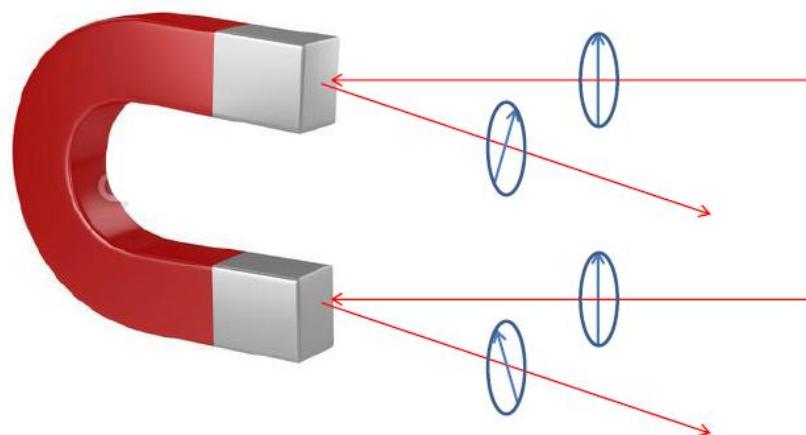
- a General phenomenology and materials
- b Applications of plasmonics in bio

## 3. Magnetoplasmonics

- a Plasmonics and magnetism?
- b Magnetoplasmonics materials and phenomena
- c Applications in bio



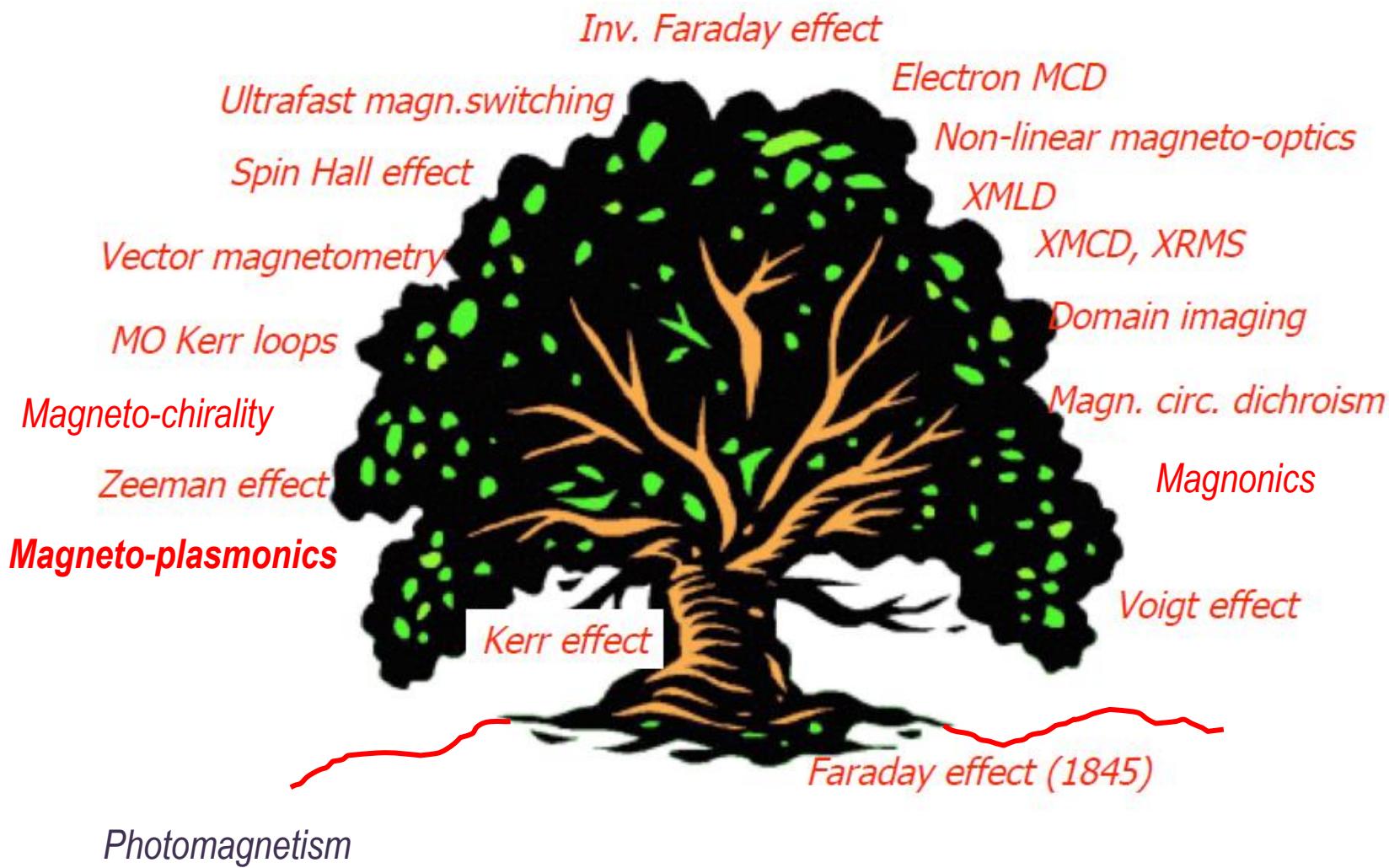
# A (brief) Introduction to Magneto-optics



The first MOKE measurement  
J. Kerr Philos. Mag 5 (1878) 161

# 1. Magneto-optics

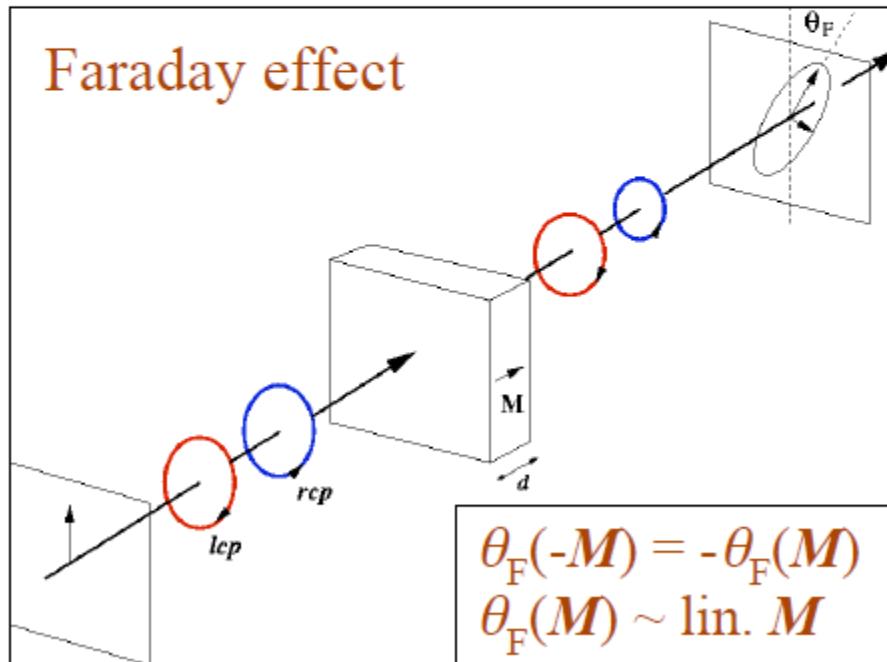
Modification of the light in interaction with a magnetized material



Modified from Oppeneer's lecture

## Magneto-optical Faraday effect (1845)

→ First observation of interaction light-magnetism  
enormous impact on development of science!



Michael Faraday  
(1791 – 1868)

Change of the polarization of the light after going through a magnetized material

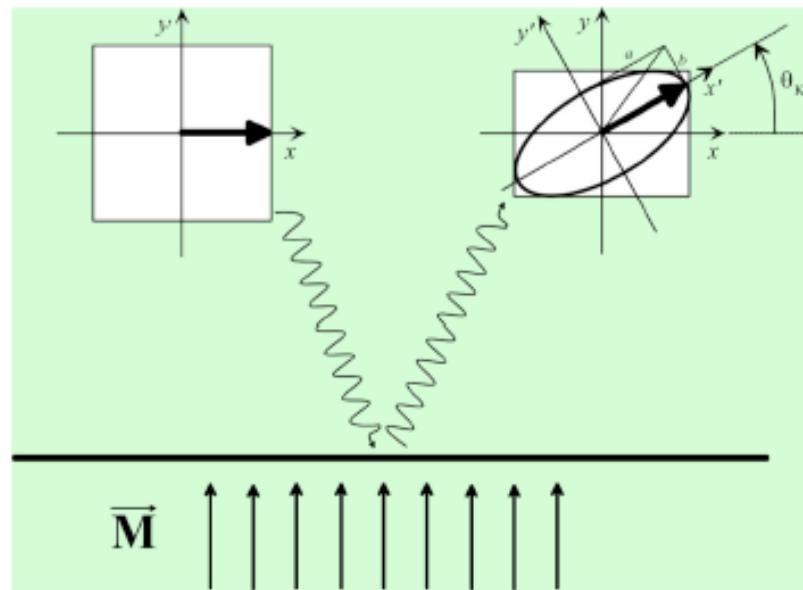
# Faraday Effect

- MO effect for optical transmission
  - Magnetic rotation  
(Faraday rotation)  $\theta_F$  (Faraday Ellipticity)  $\eta_F$
  - Absorption  
Magnetic Circular Dichroism MCD
- Comparison to Natural Optical Rotation
  - Faraday Effect is Nonreciprocal (Double rotation for round trip)
  - Natural rotation is Reciprocal (Zero for round trip)
- Verdet Constant
  - $\theta_F = VlH$  (For paramagnetic and diamagnetic materials)

# Kerr Effect

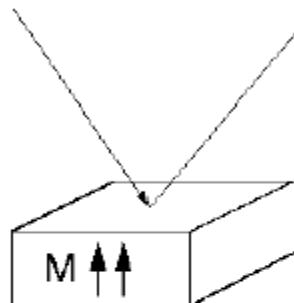


John Kerr  
(1824-1907)

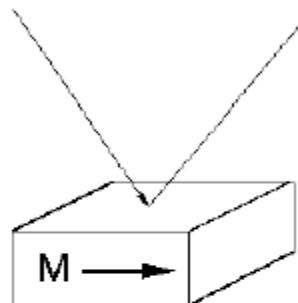


- Reflexion Configuration
- Ellipsometry

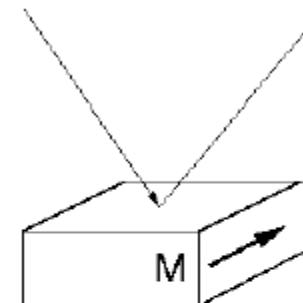
# Kerr Effect (MOKE)



(a) polar



(b) longitudinal



(c) transversal

Kerr (1876)

pol. analysis

Kerr (1878)

pol. analysis

Zeeman (1896)

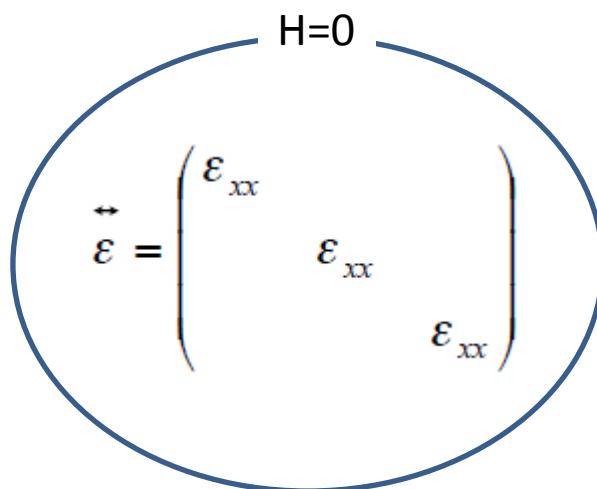
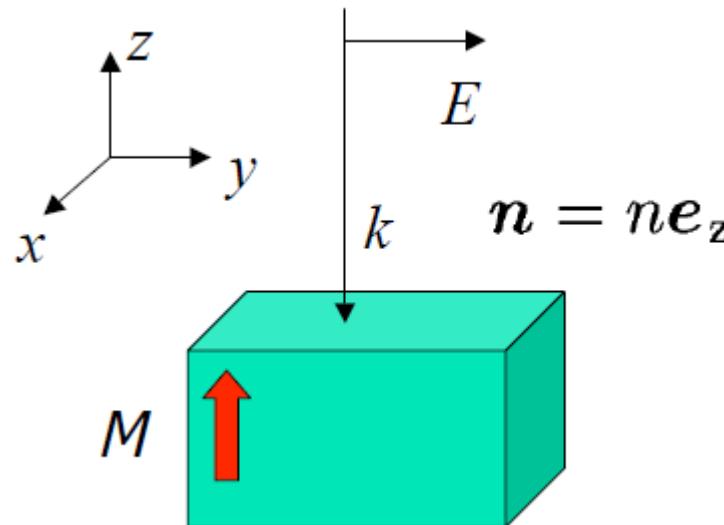
intensity measurement

Surface  
sensibilitySmall Effect  
 $10^{-4}$ Sub-nanometric  
sensibility

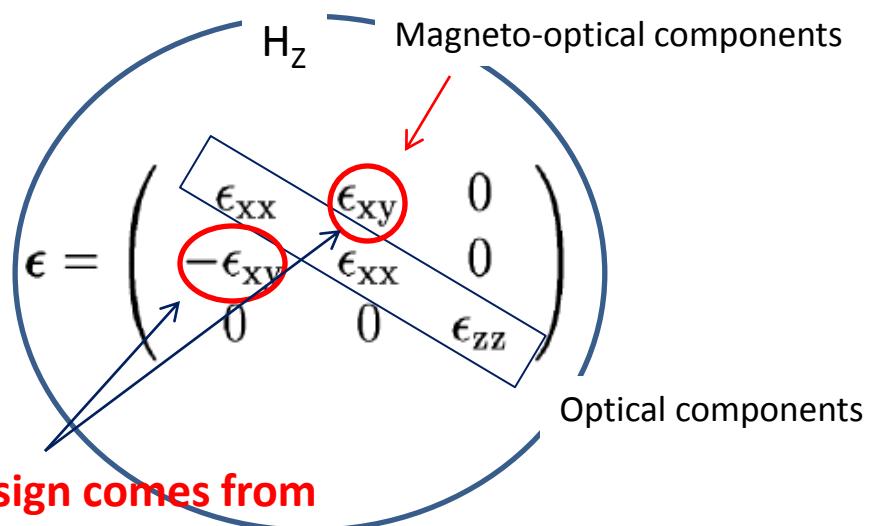
In metals ↗ Penetration length tens of nanometers  
Surface Magneto-optical Kerr effect: SMOKE

## Magneto-optical tensor

$$\mathbf{D} = \tilde{\epsilon} \epsilon_0 \mathbf{E}$$

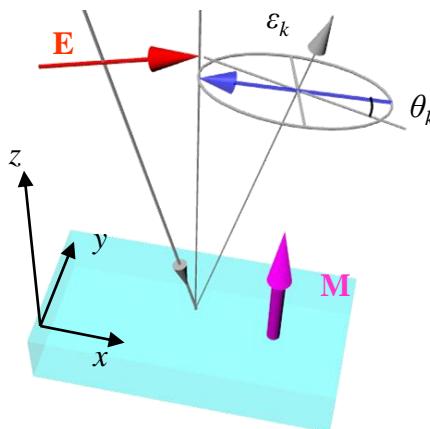


The change of sign comes from  
the Nonreciprocal nature of the  
MO effects

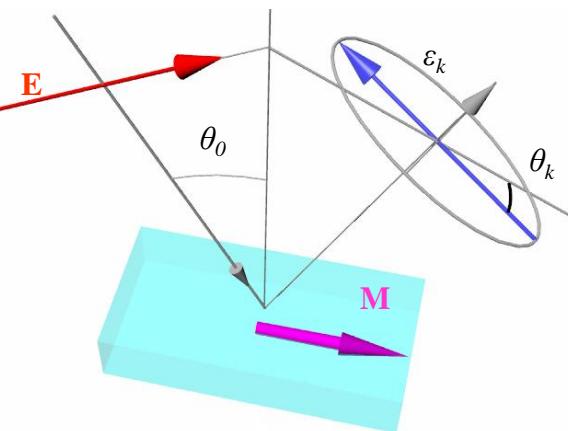


## 1. Magneto-optics

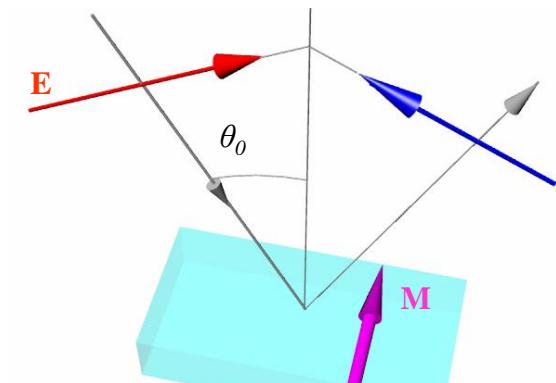
Kerr effect depends on relative orientation of  $M(B)$



Polar



Longitudinal



Transverse

$$\theta + i\varepsilon = f(M_z)$$

$$\begin{pmatrix} \varepsilon & aM_z & 0 \\ -aM_z & \varepsilon & 0 \\ 0 & 0 & \varepsilon \end{pmatrix}$$

$$\theta + i\varepsilon = f(M_x)$$

$$\begin{pmatrix} \varepsilon & 0 & 0 \\ 0 & \varepsilon & aM_x \\ 0 & -aM_x & \varepsilon \end{pmatrix}$$

$$R_{pp} = f(M_y)$$

$$\begin{pmatrix} \varepsilon & 0 & -aM_y \\ 0 & \varepsilon & 0 \\ aM_y & 0 & \varepsilon \end{pmatrix}$$

$$\varepsilon_{xy} \propto M_z(H)$$

$$\varepsilon_{xy} \propto M_x(H)$$

$$\varepsilon_{xz} \propto M_y(H)$$

Optical properties are controlled by an external magnetic field or with the magnetic state

# 1. Magneto-optics

## Magneto-optical tensor

In Faraday Configuration ( $\mathbf{k} \parallel \mathbf{M}$ )

$$\varepsilon(\omega, \mathbf{M}) = \begin{pmatrix} \varepsilon^0 + G_{12}M_z^2 & KM_z & 0 \\ -KM_z & \varepsilon^0 + G_{12}M_z^2 & 0 \\ 0 & 0 & \varepsilon^0 + G_{11}M_z^2 \end{pmatrix} \rightarrow \begin{aligned} \varepsilon_{ij}(\omega, -\mathbf{M}) &= \varepsilon_{ji}(\omega, \mathbf{M}) \\ \varepsilon_{ij}(\omega) &= \varepsilon'_{ij}(\omega) + \varepsilon''_{ij}(\omega) \end{aligned}$$

Faraday Configuration

$$n_{1,2}^2 \equiv n_{\pm}^2 = \varepsilon_{xx} \pm i\varepsilon_{xy}$$

MOKE Configuration

$$\theta_F = \frac{k_0}{2} \operatorname{Re} \left[ \frac{-2i\varepsilon_{xy}}{2\sqrt{\varepsilon_0}} \right] \approx \frac{k_0 \varepsilon''_{xy}}{2\bar{n}'} K'' M$$

$$\psi_F = \frac{1}{d} \tanh \left[ \frac{k_0}{2} (n''_- - n''_+) d \right] \approx \frac{k_0}{2\bar{n}'} K' M$$

$$\frac{E_{refl}}{E_{inc}} = \frac{n-1}{n+1} r$$

$$\theta_K = -\operatorname{Im} \left[ \frac{n_+ - n_-}{n_+ n_- - 1} \right] \approx \frac{-K'}{(\varepsilon^0 - 1)\sqrt{\varepsilon^0}} M$$

$$\psi_K = -\operatorname{Re} \left[ \frac{n_+ - n_-}{n_+ n_- - 1} \right] \approx \frac{K''}{(\varepsilon^0 - 1)\sqrt{\varepsilon^0}} M$$

Magnetometry

Spectroscopy

Magnetic properties

**MO**

Electronic properties

# Origin of the MO effects

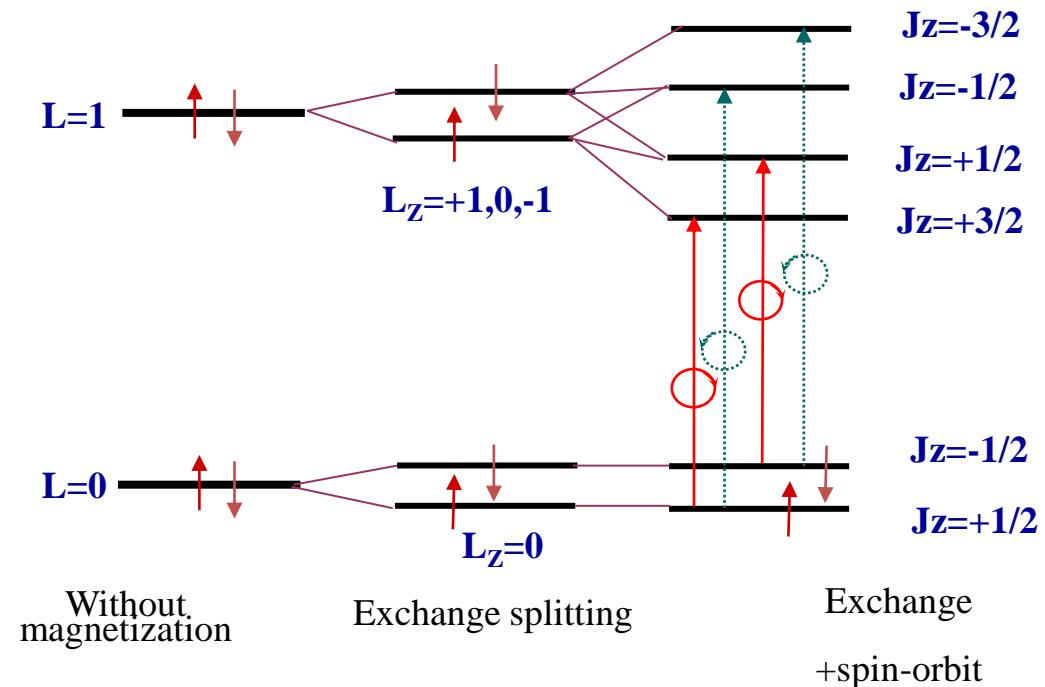
Fermi Golden Rules

$$P_{a \rightarrow j} = (\pi^2/h^2) \left| \left\langle j \left| \sum (q_k/m_k c) \mathbf{A}^{0*} \cdot \mathbf{P}_k \exp(i2\pi\nu z_k/c) \right| a \right\rangle \right|^2 \rho_{aj}(\nu)$$

$\Delta L = \pm 1$

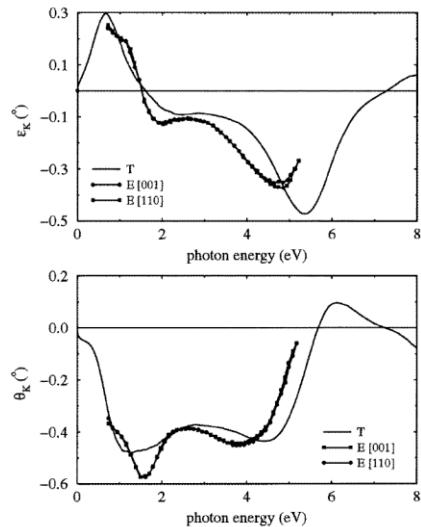
Selectivity to some transitions

Correlated with the Spin-orbit coupling

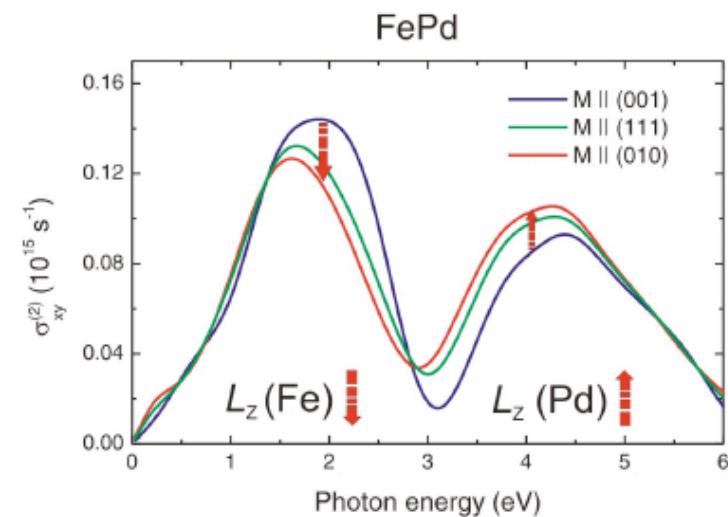


# Magneto-optics

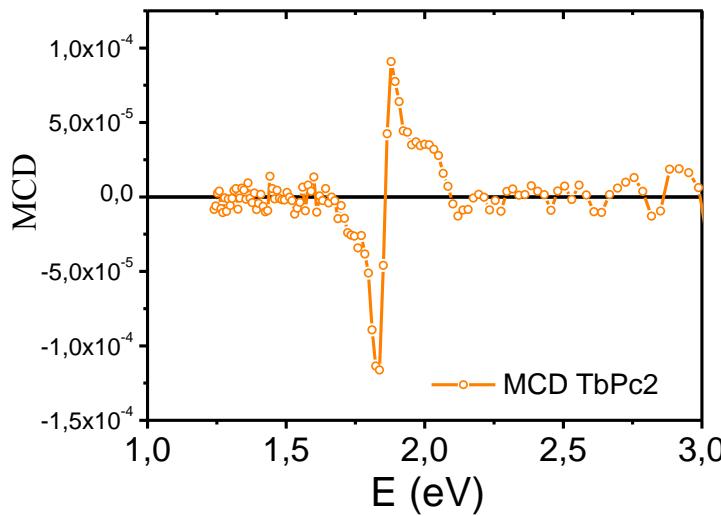
## Metals (Cobalt fcc)



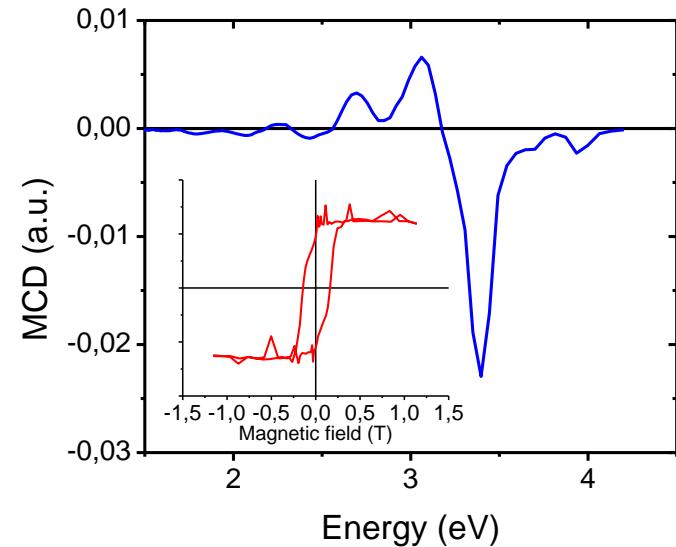
## Alloys



## Molecules (2nm TbPc2)



## Sc-Ba hexaferrites NanoPlatelets



# 1. Magneto-optics

## Magnetite

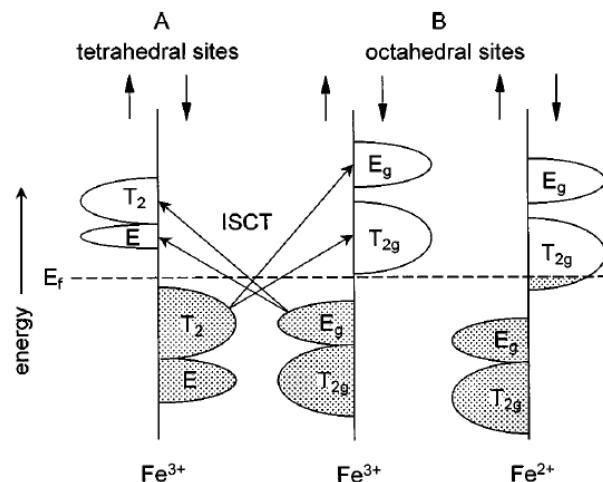


FIG. 1. Schematic representation of the electron energy levels of the Fe ions in  $\text{Fe}_3\text{O}_4$ , including the relevant ISCT transitions.

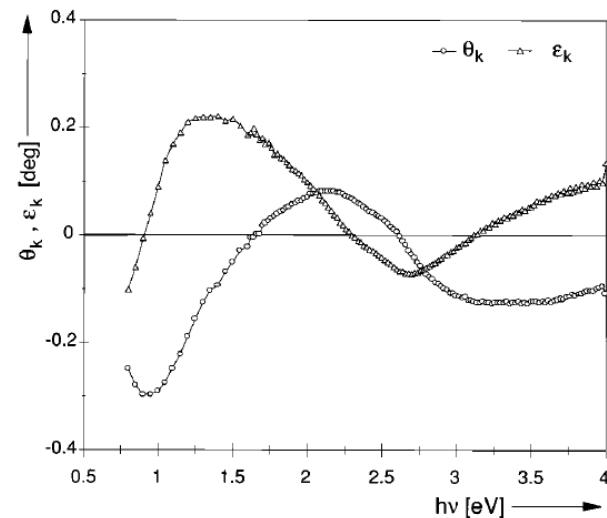


FIG. 4. The Kerr rotation  $\theta_k$  and Kerr ellipticity  $\epsilon_k$  of  $\text{Fe}_3\text{O}_4$ .

## Ferrites

(Dipole moment orientation and square crystallographic orientation)

Sample	Assignment	IVCT	IVCT	IVCT	IVCT	ISCT	ISCT	ISCT
		$[\text{Fe}^{2+}]_{t_{2g}} \rightarrow [\text{Fe}^{2+}]_{t_{2g}}$	$[\text{Fe}^{2+}]_{t_{2g}} \rightarrow [\text{Fe}^{2+}]_{e_g}$	$[\text{Fe}^{2+}]_{t_{2g}} \rightarrow (\text{Fe}^{2+})_e$	$[\text{Fe}^{2+}]_{t_{2g}} \rightarrow (\text{Fe}^{2+})_{t_2}$	$(\text{Fe}^{3+})_{t_2} \rightarrow [\text{Fe}^{2+}]_{t_{2g}}$	$(\text{Fe}^{3+})_{t_2} \rightarrow [\text{Fe}^{2+}]_{t_2}$	$(\text{Fe}^{3+})_{e_g} \rightarrow [\text{Fe}^{2+}]_{t_2}$
$\text{Fe}_3\text{O}_4$	$\omega$	0.56	1.94	3.11	3.93	2.61	3.46	3.94
	$\Gamma$	0.21	0.45	0.61	0.37	0.20	0.42	0.51
	$(\epsilon_{xy})_{\max}$	-0.085	0.044	0.031	-0.039	-0.004	0.014	0.065
	shape	para	para	dia	dia	dia	dia	dia
$\text{MgFe}_2\text{O}_4$	$\omega$					2.64	3.47	3.95
	$\Gamma$					0.30	0.31	0.56
	$(\epsilon_{xy})_{\max}$					-0.009	0.022	0.032
	shape					dia	dia	dia
$\text{Li}_{0.5}\text{Fe}_{2.5}\text{O}_4$	$\omega$					2.63	3.46	4.09
	$\Gamma$					0.23	0.39	0.64
	$(\epsilon_{xy})_{\max}$					-0.026	0.036	0.050
	shape					dia	dia	dia

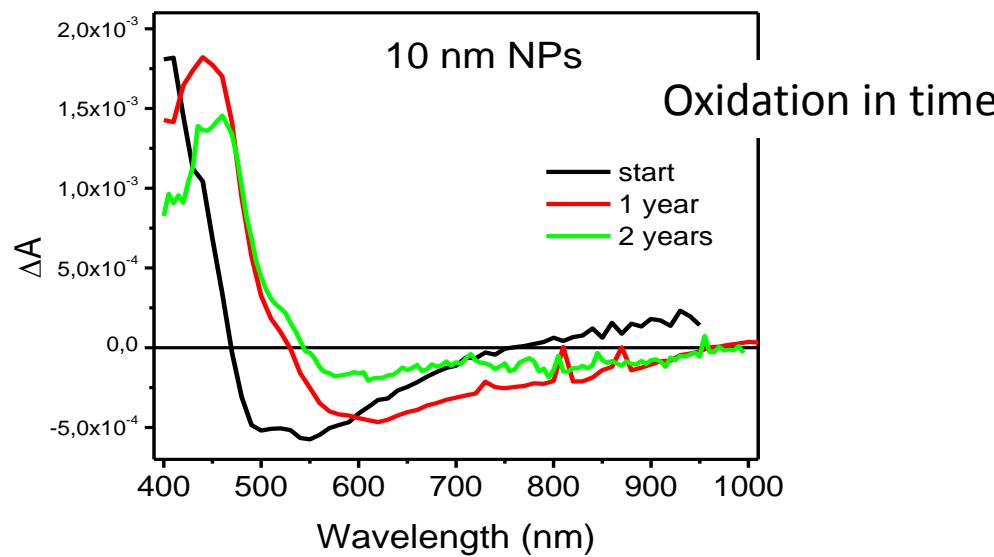
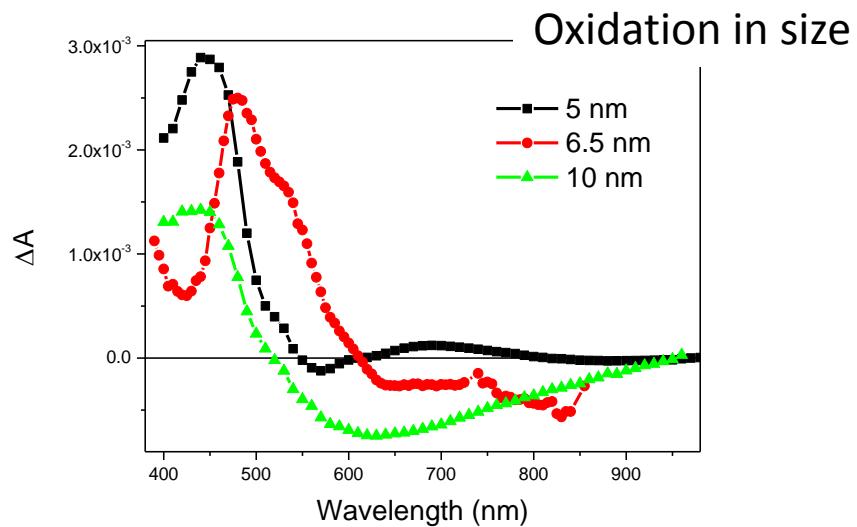
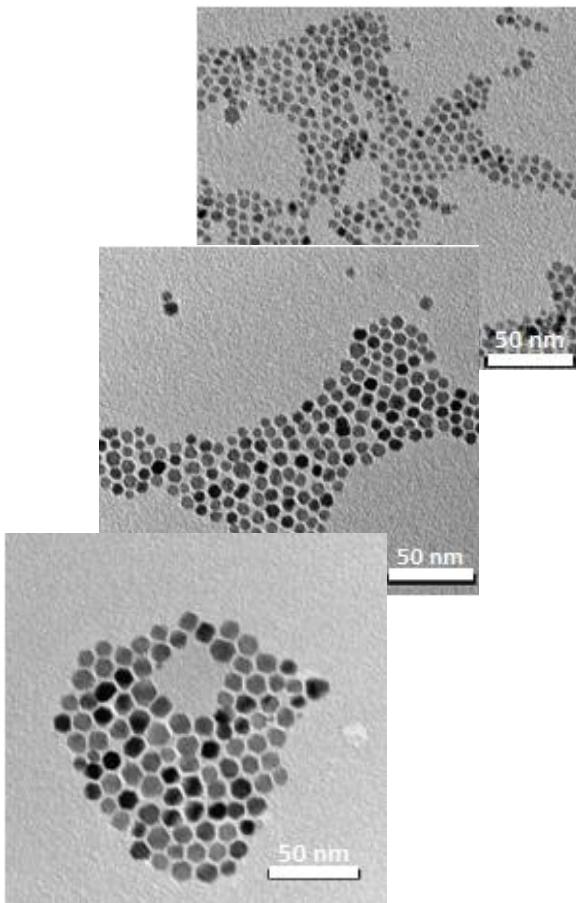
ISCT: Intersublattice Charge transitions A  $\rightarrow$  B

IVCT: Intervalence charge transitions A  $\rightarrow$  A , B  $\rightarrow$  B

Others: Crystal field transitions

# 1. Magneto-optics

## Magnetite Nanoparticles



## Applications

### Magneto-optical recording



### Magneto-Optical isolator

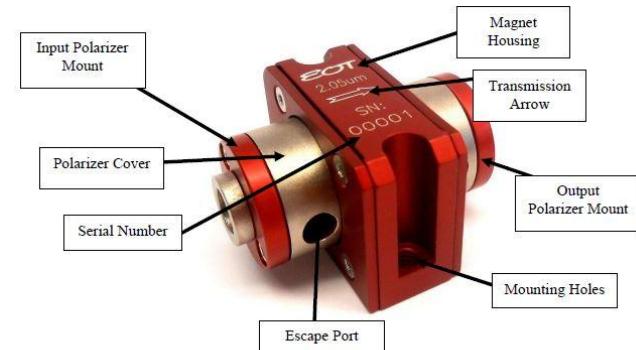


Figure 1: *Makros Series Optical Isolator*

**EOT**<sup>®</sup>  
Electro-Optics Technology, Inc.

### Biomedical applications

*Sensing and Diagnostic tests*

Immunoassays

Malaria detection



*Magnetometry*

Biomagnetic fields

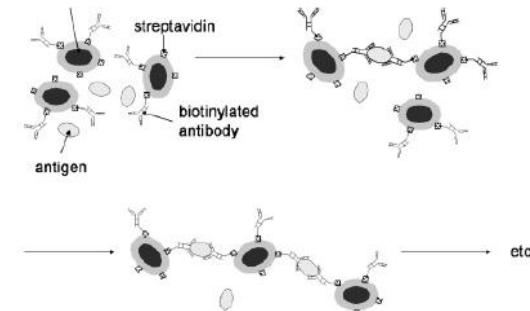
Budker Nat. Phys. 3 (2007) 227

# 1. Magneto-optics

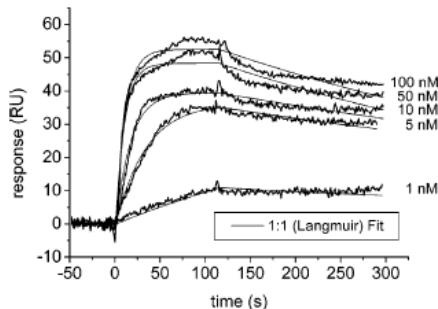
## Applications: Sensing

### Immunassays

- Detection of the MO response of magnetic Nanoparticles
- Measurement of the binding dynamics



### Test with streptavidin

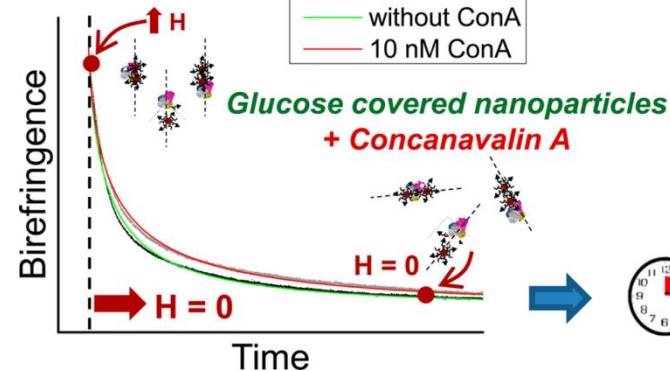


**Figure 8.** Sensorgrams of immobilized anti-hEotaxin binding hEotaxin. Sensorgrams are plotted as the mass of protein binding (in RU) to immobilized anti-hEotaxin as a function of time. Experimentally derived curves (black lines) from two repeated injections of hEotaxin at various concentrations are shown overlaid. Curves were globally fitted with BIAevaluation 4.1 software using a 1:1 (Langmuir) model (thin lines) to determine the kinetic parameters.

Aurich Anal. Chem. 2007, 79, 580-586

Sensibility comparable to SPR

### Interaction proteins with glucose



Kober Anal. Chem. 86 (2014) 12159

Sensibility comparable to ELISA

# 1. Magneto-optics

## Applications: MOT for Malaria detection



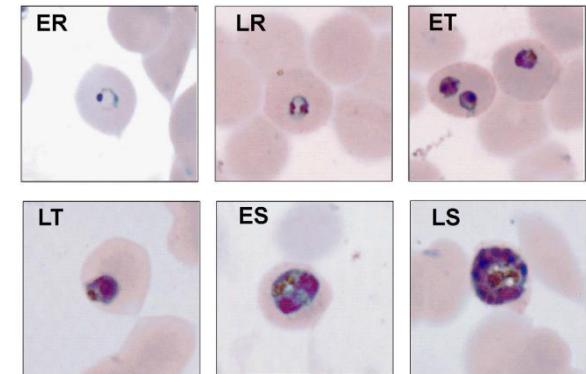
Courtesy of: [http://www.cbc.ca/gfx/pix/malaria\\_mosquito020717.jpg](http://www.cbc.ca/gfx/pix/malaria_mosquito020717.jpg)

Plasmodium parasite  
(protozoans)



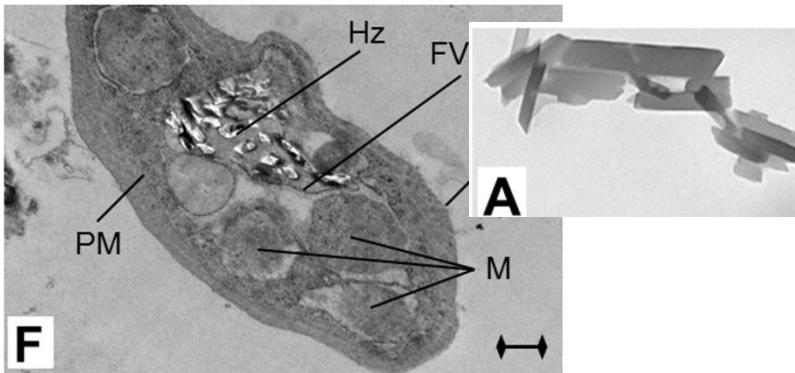
From wikipedia

Distribution of parasite life cycle stages in the two Plasmodium falciparum cultures

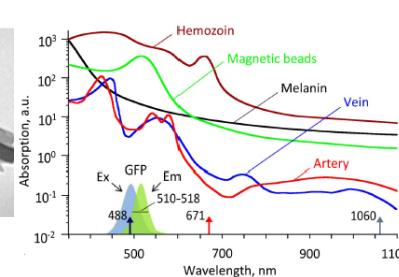


Orban Plus ONe 9 (2014) e96981

### MO detection of Hemozoin pigments generated by the plasmodium



Mens Malaria Journal 9 (2010) 207



Absorption spectra of hemozoin [17,18], melanin [4], magnetic beads [3], arterial tissue (~96%) and venous (oxygenation ~70%) blood [18]. Similarity in absorption of hemozoin and magnetic beads indicate a potential to use magnetic beads as a phantom for calibration of PAFC. Excitation (Ex) and emission (Em) spectra of oresent protein (GFP) expressed by parasites [18]. Arrows indicate laser wavelengths 8 nm (for continuous wave fluorescence excitation), and 671 nm and 1060 nm (for

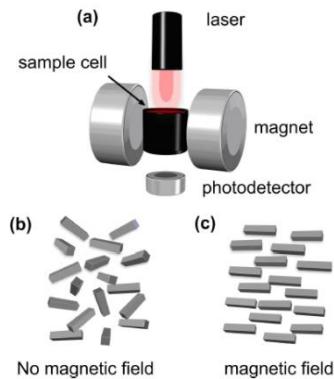
Meniev Biomedical Expr Optics 7 (2016) 260295

# 1. Magneto-optics

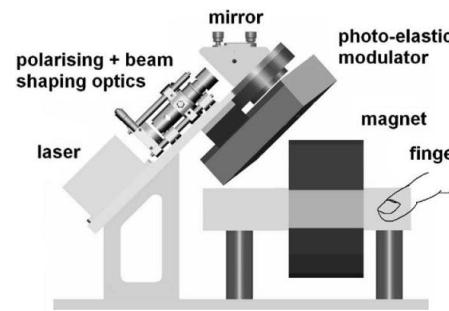
## EU-F6 Project MOT-TEST “Novel Magneto-optical Biosensors for Malaria Diagnostics”

### Cotton –Moutton detection

Induced optical dichroism



### Original design



Newman IEEE J Sel Top Quan Electr 16 (2010) 573

Mens Malaria Journal 9 (2010) 207

### Light transmission

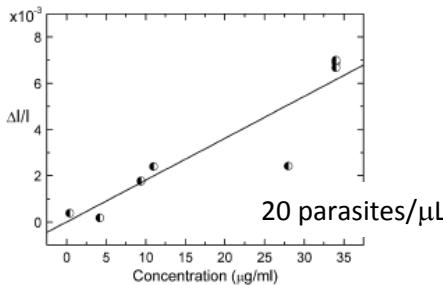
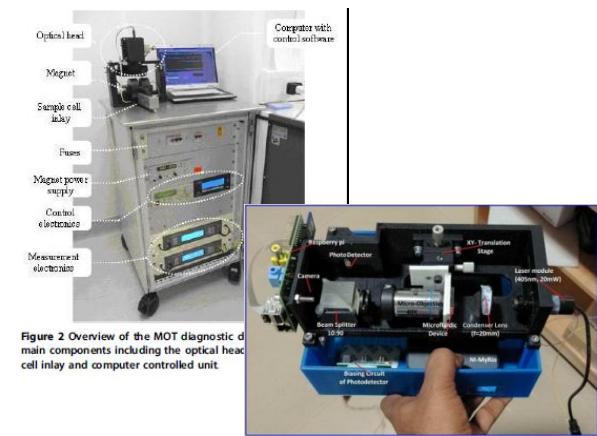


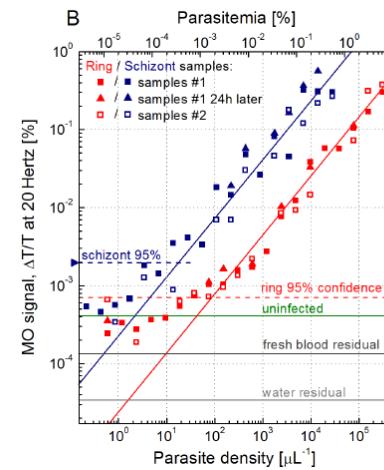
FIGURE 3 Fractional change in transmittance  $\Delta I/I$  associated with magnetically induced dichroism arising from rotation of hemozoin crystals within the cell vacuoles of live parasitized cells grown and sampled from nonsynchronous culture.

### Device



Banoth Appl Optics 55 (2016) 8637

### MO signal



## Results

TABLE 1 Results of evaluating a small set of clinical samples of individuals with fever or no fever but from a disease-endemic country with health complaints

Patient characteristics	Result rapid diagnostic test for malaria	Final clinical diagnosis based on extensive diagnostic procedures	MOT diagnosis	MOT fractional change $\Delta I/I$
Nigerian child with fever	Positive	<i>P. falciparum</i> infection	Positive	8.2E-5
Nigerian child with fever	Positive	<i>P. falciparum</i> infection	Positive	4.7E-5
Nigerian child with fever	Positive	<i>P. falciparum</i> infection	Positive	7.8E-5
Nigerian child with fever	Positive	<i>P. falciparum</i> infection	Positive	9.3E-5
Nigerian child with fever	Positive	<i>P. falciparum</i> infection	Positive	5.3E-5
Dutch returned traveler	Positive	<i>P. ovale</i> infection	Positive	4.4E-5
Dutch returned traveler	Positive	<i>P. falciparum</i> infection	Positive	5.9E-3
Tanzanian adult asymptomatic for malaria	Negative	Sickle cell anemia	Negative	—
Tanzanian adult asymptomatic for malaria	Negative	$\beta$ -thalassemia	Negative	—
Tanzanian adult asymptomatic for malaria	Negative	Rheumatic-associated disease	Negative	—
Dutch returned traveler with fever	Negative	Undifferentiated fever	Negative	—
Dutch returned traveler with fever	Inconclusive	Undifferentiated fever	Negative	—
Dutch returned traveler with fever	Negative	Visceral leishmaniasis	Negative	—

# 1. Magneto-optics

## Limits:

- Small MO signal
- Weak selectivity
- Unexplored multifactor dependence
  - Size , concentration, shape, composition
  - Scattering- transmission
  - Chemical instability of magnetic nanoparticles
- Toxicity of the materials with largest MO signal
- Few studies *in vitro* and *in vivo*

MO detection of Ferritin and mimetics

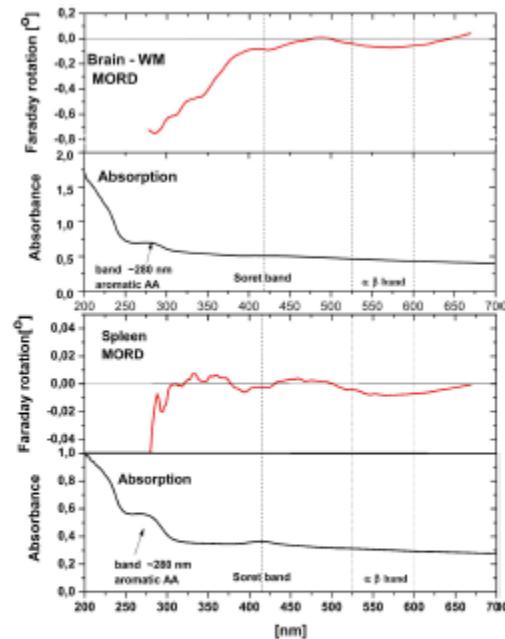


Fig. 3. Wavelength dependence of the Faraday rotation and absorption spectra for human brain and spleen tissues – upper and lower panel respectively,  $H = 2350$  Oe. Bands position related to heme-iron and aromatic amino acids are shown by dotted vertical line and arrow respectively.