Nonlinear Optics on Ferroics & Multiferroics

Introduction
Part I – Symmetry
Part II – Nonlinear Optics
Part III – Experimental Techniques
Part IV – Multiferroic $R\text{MnO}_3$

Thomas Lottermoser

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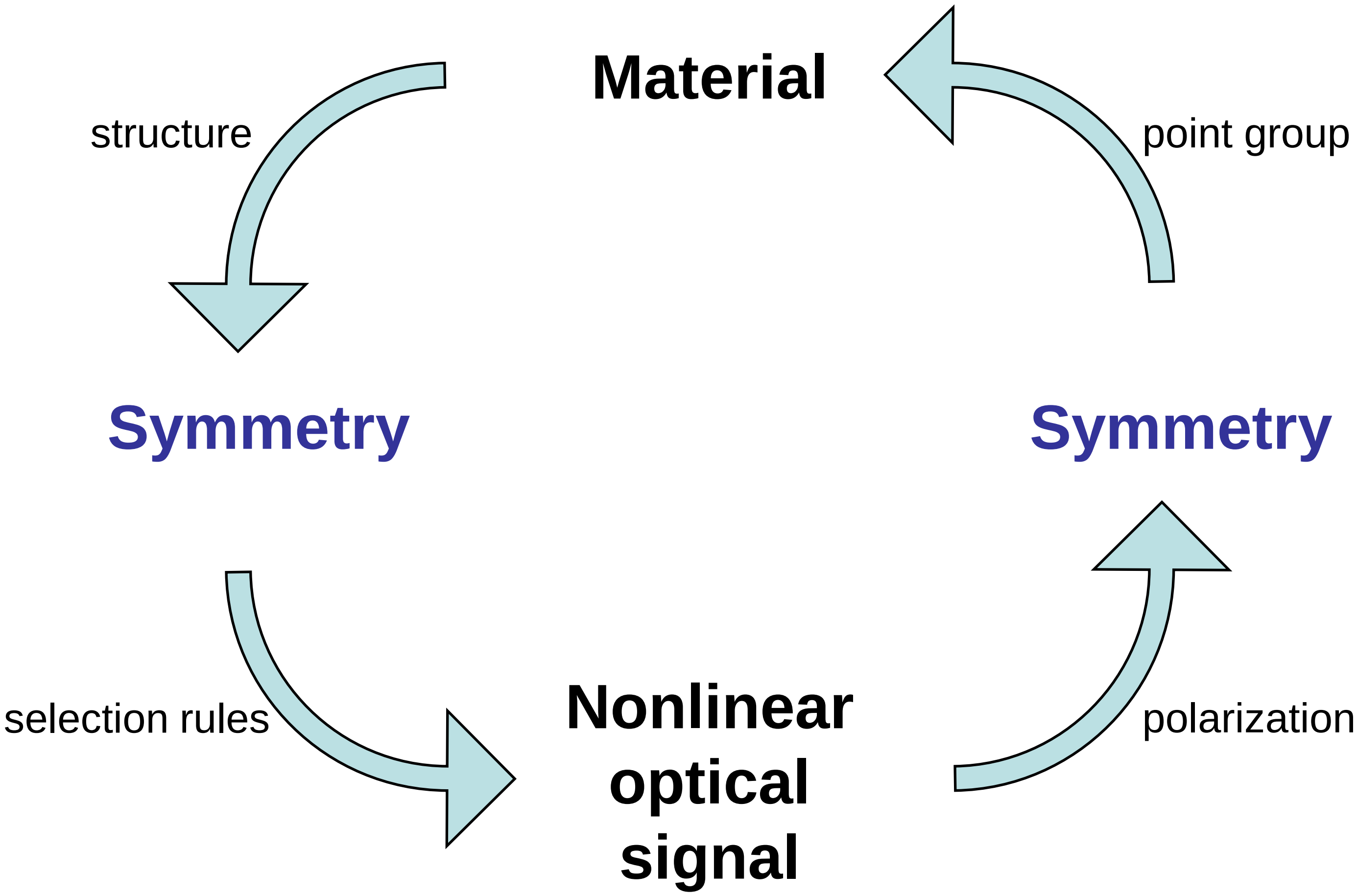
Principle of Nonlinear Optical Structure Analysis



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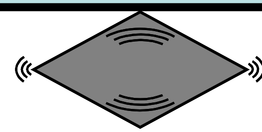
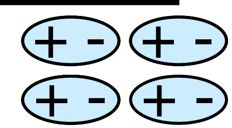
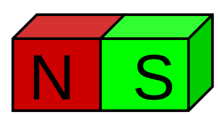
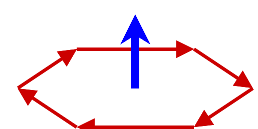
Symmetry and Multiferroics

Time \ Space	invariant	change
invariant	ferroelastic	ferroelectric
c		oidic

Time		ge
invariant		
change		

Ferroic properties determine space & time symmetry

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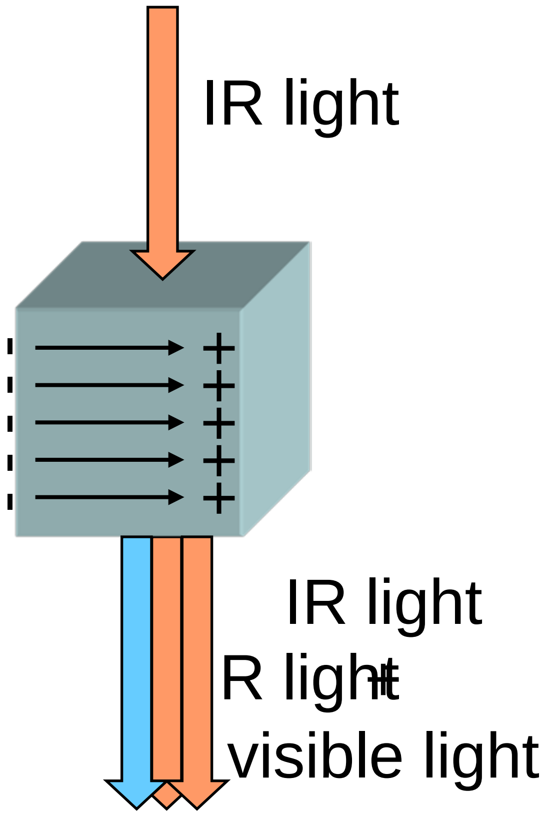
Symmetry and Nonlinear Optics

Case 1:

- Crystal in a paraelectric phase
- Inversion symmetry *not broken*

Case 2:

- Crystal in a ferroelectric phase
- Inversion symmetry *broken*



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Literature

- General introductions to nonlinear Optics:

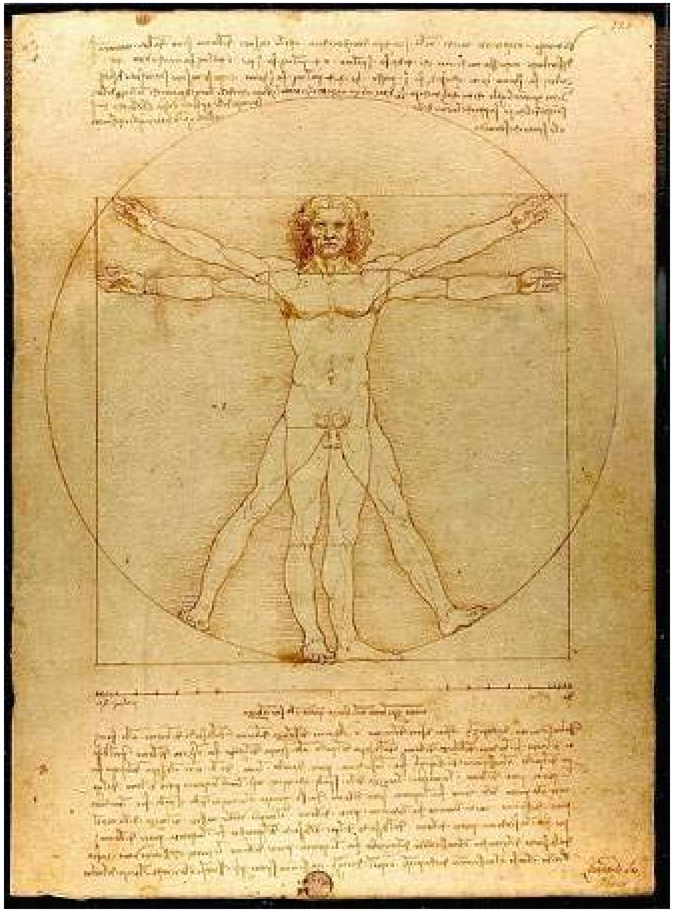
  Y.R. Shen, A. Yariv, or R.W. Boyd

- K.H. Bennemann: Nonlinear Optics in Metals

- R.R. Birss: Symmetry and Magnetism

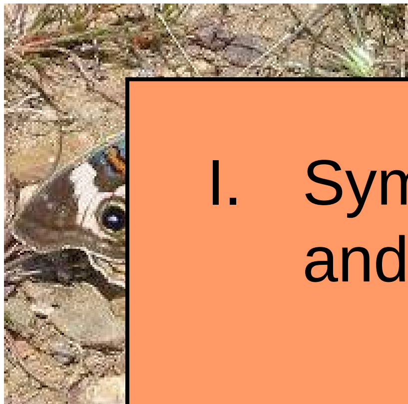
Part I - Symmetry

- Symmetry Operations
- Space & Time Inversion
- Tensors
- Point Groups



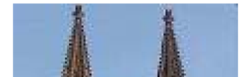
What's Symmetry?

Nature:



Art:

Architecture:

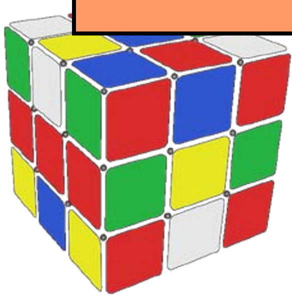


I. Symmetry is a property related to harmony and aesthetics

II. Symmetry describes the behaviour under certain transformations

Geo

:



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Pictures: en.wikipedia.org & commons.wikimedia.org

What's Symmetry?

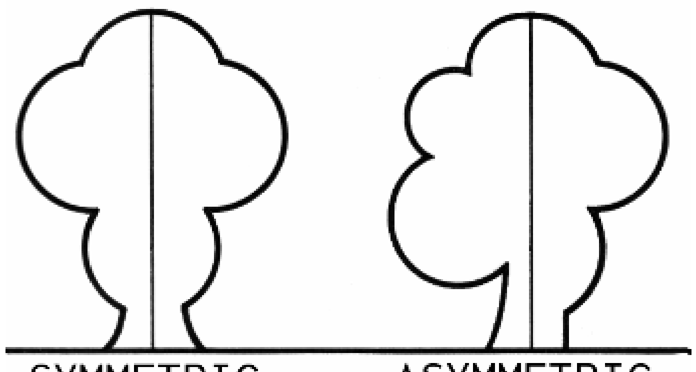
Symmetry:

Conservation of shape under applying a symmetry operation

Asymmetry:

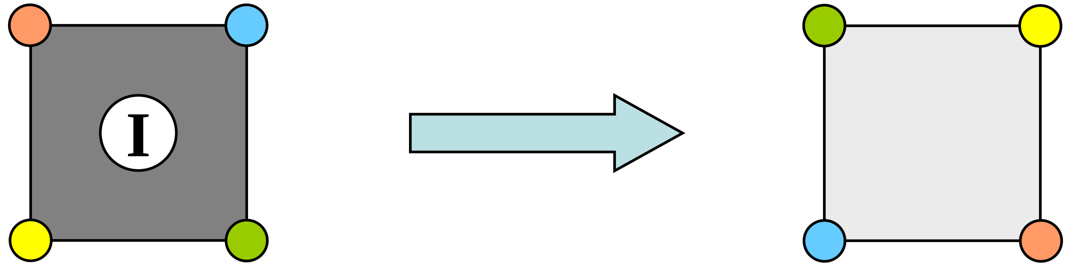
Change of shape under applying a symmetry operation

e.g. mirror symmetry

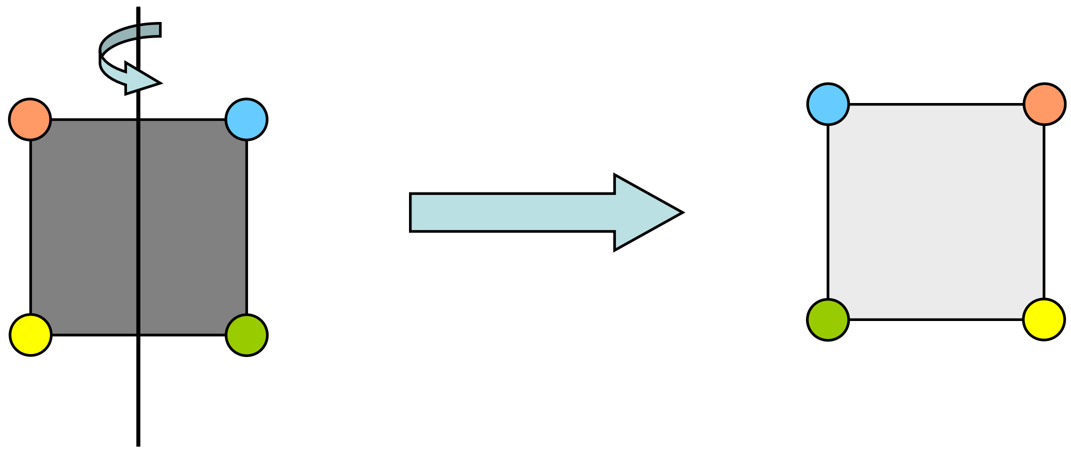


Symmetry Operations in Space

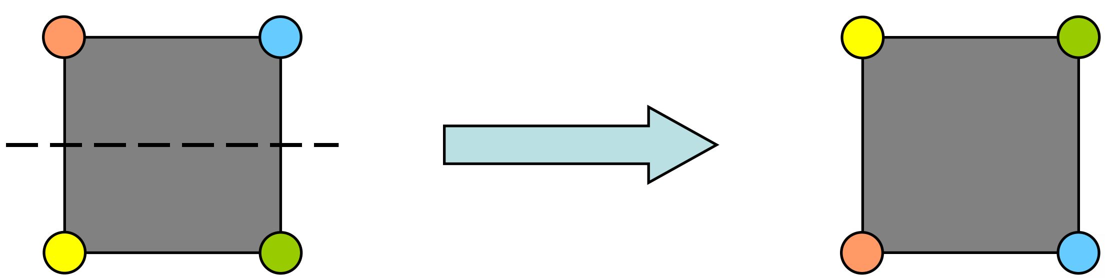
Inversion:



Rotation:

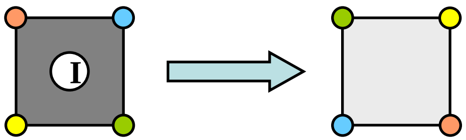


Mirroring:
(= I • R)



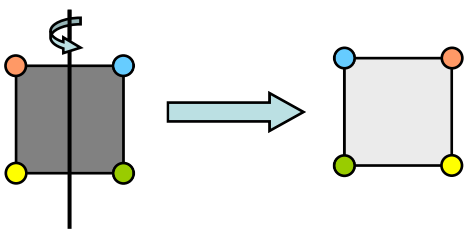
Mathematical Matrix Representation

Inversion:



$$I = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \equiv \left[\bar{1}\right]$$

Rotation:

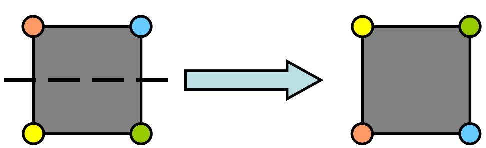


$$R(\varphi_y) = \begin{bmatrix} \cos(\varphi_y) & 0 & \sin(\varphi_y) \\ 0 & 1 & 0 \\ -\sin(\varphi_y) & 0 & \cos(\varphi_y) \end{bmatrix}$$

$$\Rightarrow R(180^\circ) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \equiv \left[2_y\right]$$

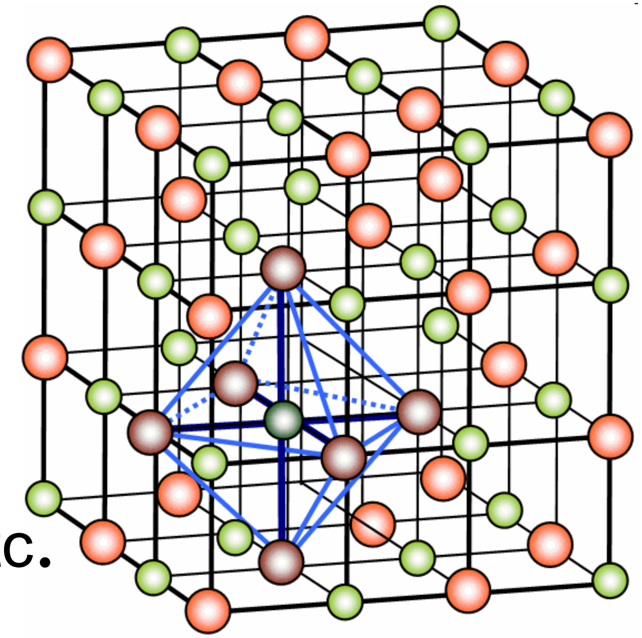
Mirroring:

(= I • R)



$$M_y = \left[\bar{1}\right] \cdot \left[2_y\right] = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \equiv \left[\bar{2}_y\right]$$

Point Symmetries in Crystals



Only discrete symmetries in crystals:

- Identity operation: $[1]$
- Inversion: $[\bar{1}]$
- Rotations: $[1_x],[2_x],[3_x],[4_x],[6_x]$, etc.
- Mirror planes: $[\bar{2}_x],[\bar{2}_y],[\bar{2}_z]$, etc.

$\Rightarrow$ System of **32 point groups** with different subsets of symmetry operations

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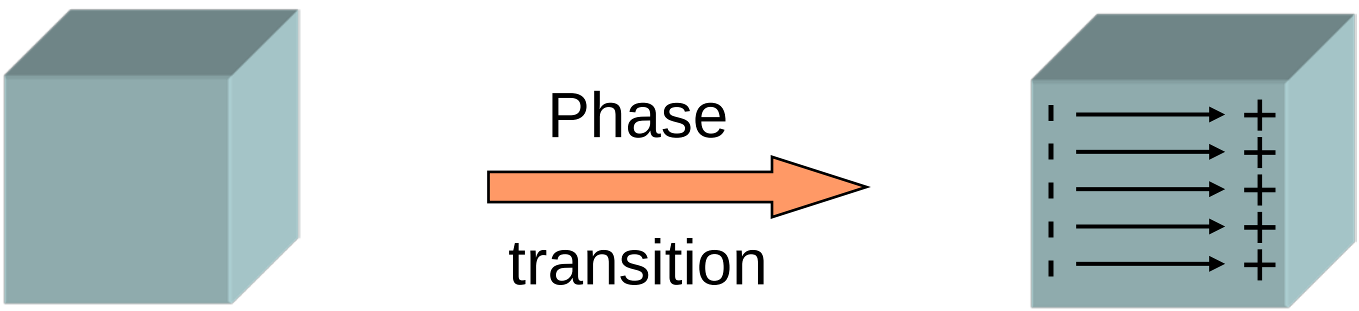
Symmetry and Physics

P. Curie, 1894: "C'est la dissymmétrie qui crée le phénomène"

e.g.: Ferroelectricity:

I. Paraelectric phase: II. Ferroelectric phase:



Cubic crystal with inversion symmetry

Polar tetragonal crystal without inversion symmetry

Curie’s Principle

The symmetry of a crystal exhibiting a certain effect is the intersection of the symmetries of the bare crystal and the effect itself

Crystal symmetry = G_c

Effect symmetry = G_E

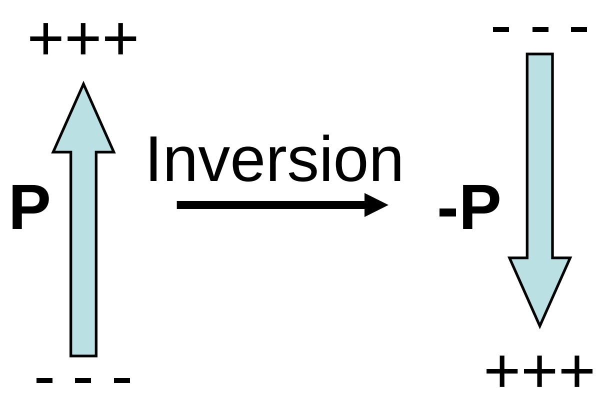
$$G_C \cap G_E \equiv G_{CE}$$

Symmetry of crystal + effect

Neumann's Principle

The physical properties of a crystal have at least the symmetry of the crystal

Example: Ferroelectricity



Electric polarization breaks inversion symmetry

$\Rightarrow$ *No* ferroelectricity in crystals possessing inversion symmetry!

Property & Field Tensors

Physical effects in crystals can be described by the equation:

E(ffect) = **P**(roperty) · **C**(ause)

E, **C**: Field tensors
P: Property tensor

} Anisotropic quantities

↳ Symmetry!

<u>Examples:</u>

- Dielectric displacement **D** $\propto$ **ε** · **E**
- Magnetic induction **B** $\propto$ **μ** · **H**

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Neumann's Principle & Property Tensors

Property tensors must be invariant under all symmetry operations of the crystal

Example: Second harmonic generation (SHG)

$$\mathbf{P}(2\omega) \propto \chi^{(2)}\, \mathbf{E}(\omega)\, \mathbf{E}(\omega)$$

Inversion I $\Rightarrow$ $-\mathbf{P}(2\omega) \propto \chi'^{(2)}\, (-\mathbf{E}(\omega))(-\,\mathbf{E}(\omega))$

$\Rightarrow$ $\chi'^{(2)} = -\chi^{(2)}$ if inversion is symmetry operation

$\Rightarrow$ No SHG in crystals possessing inversion symmetry!

Classification of Tensors: Parity Operations

Symmetry operations with eigenvalues ±1

Spatial inversion I

Time inversion T

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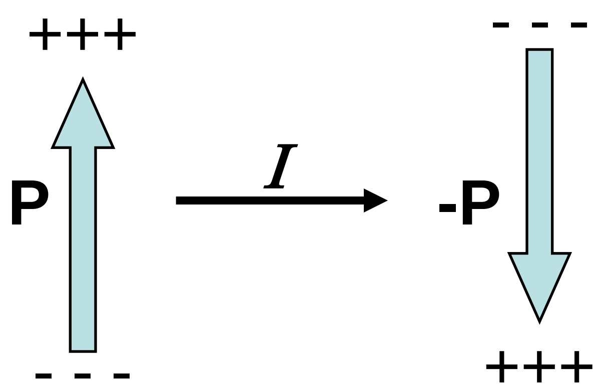
Parity Operations: Spatial Inversion

Polar tensors:

$$I\vec{P}(\vec{r},t) = -\vec{P}(-\vec{r},t)$$

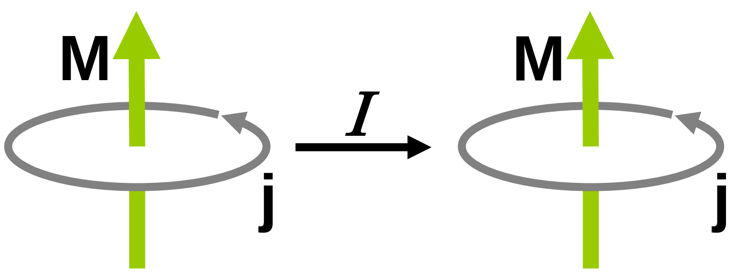
⇒ Polar tensors of *odd* rank are equal to zero in centrosymmetric crystals!



Axial tensors:

$$I\vec{M}(\vec{r},t) = \vec{M}(-\vec{r},t)$$

⇒ Axial tensors of *even* rank are equal to zero in centrosymmetric crystals!



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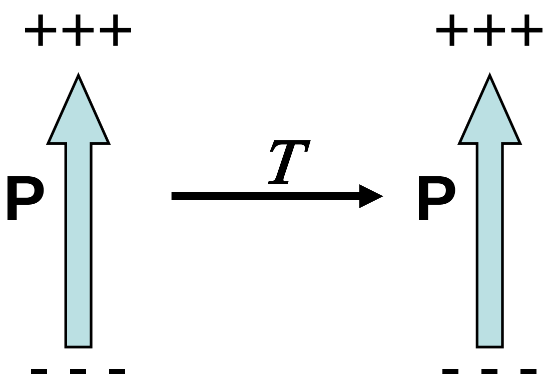
Parity Operations: Time Inversion

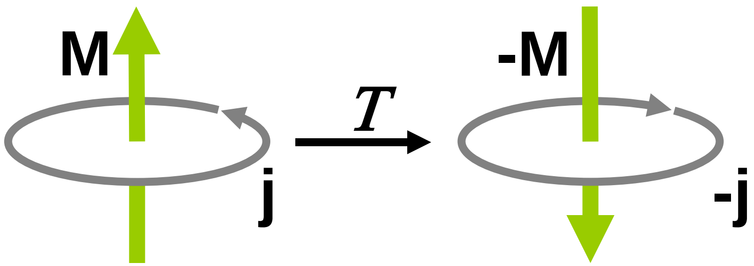
i-tensors:

$$T\vec{P}(\vec{r},t) = \vec{P}(\vec{r},-t)$$



c-tensors:

$$T\vec{M}(\vec{r},t) = -\vec{M}(\vec{r},-t)$$



⇒ c-tensors in non-magnetic crystals are equal to zero!

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Time Inversion = Going Back in Time?

Answer: NO!

Here: Only static effects $\leftrightarrow$ no increase of entropy!

e.g. electric current: $j_i = \sigma_{ij} E_j$

j_i: c-tensor

E_i: i-tensor

$\Rightarrow$ Neumann's principle:

σ_{ij} must also be a c-tensor!

Only current flow in magnetic crystals!

In this context:
Time reversal equivalent to spin reversal!

General Classification of Symmetry Operations

1-, 2-, 3-, 4-, and 6-fold rotations $\Rightarrow$ 11 Laue-groups

+ Spatial inversion I $\Rightarrow$ 32 crystallographic point groups

+ Time inversion T $\Rightarrow$ 122 magnetic point groups

+ Translation $\Rightarrow$ 230 crystallographic space groups & 1651 magnetic space groups

Optical regime: λ **>> a**

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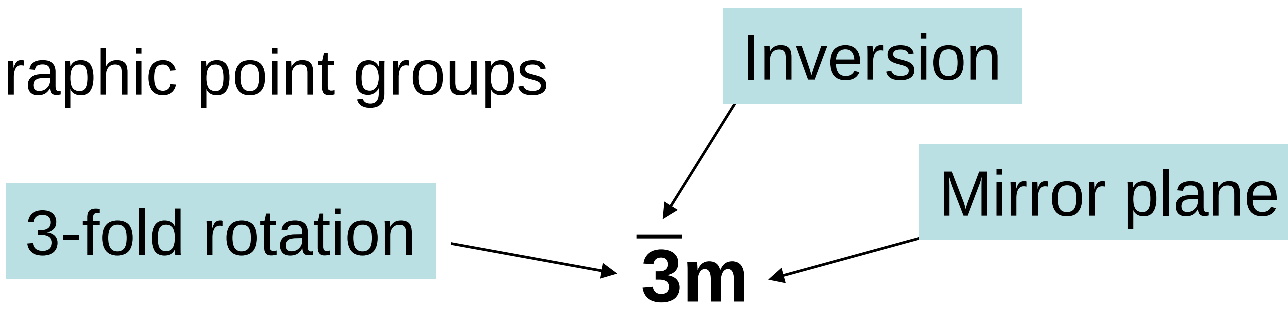
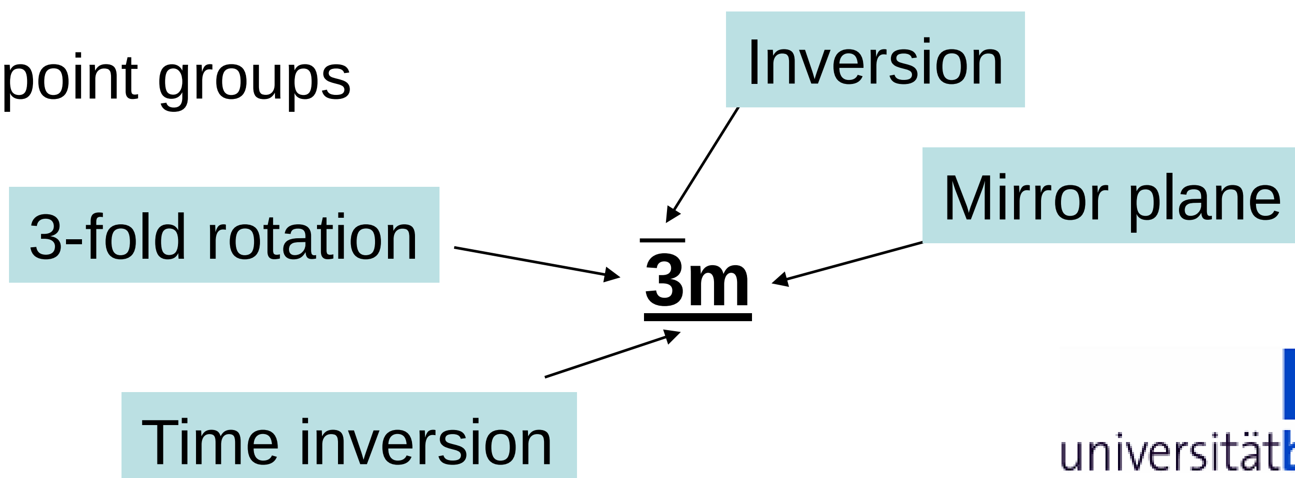
Nomenclature of Point Groups

<u>System after Hermann-Mauguin:</u>
Directly derived from the allowed symmetry operations, but only 'significant' subset is used.

I. Crystallographic point groups
e.g. $\bar{3}m$



II. Magnetic point groups
e.g. $\underline{\bar{3}m}$



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‘Forbidden’ Effects

What symmetry *can not* do:

- No definite prediction of a certain effect
- No microscopic/quantitative description of physical effects

What symmetry *can* do:

- A prediction which effects are possible
- A prediction which effects are definitely forbidden

e.g. no ferroelectricity in centrosymmetric crystals

The Magnetoelectric (ME) Effect

$$P_i = \varepsilon_0 \chi^{e}_{ij} E_j + \frac{1}{c} \alpha_{ij} H_j \qquad M_i = \chi^{m}_{ij} H_j + \frac{1}{\mu_0 c} \alpha_{ij} E_j$$

P_i, E_j = first rank polar i-tensors,
M_i, H_j = first rank axial c-tensors

$\Rightarrow \alpha_{ij}$ = second rank axial c-tensor

- second rank axial → Only allowed in non-centrosymmetric crystals
- c-tensor → Only allowed in magnetic crystals

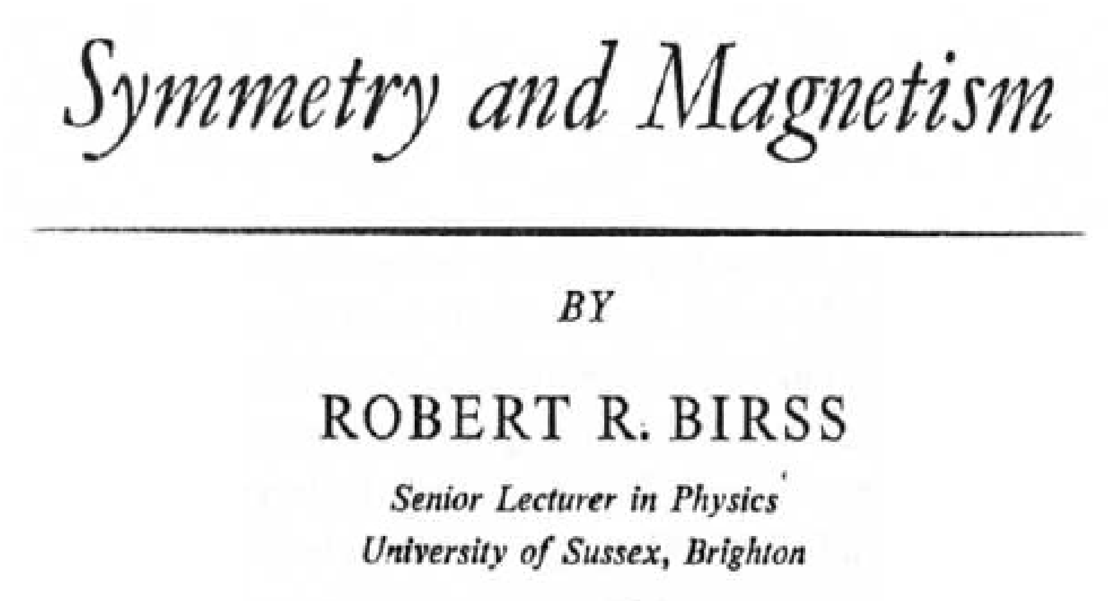
ME forbidden in at least 53 of the 122 magnetic point groups!

How to Derive Tensor Components?

1. Be smart and solve for each allowed symmetry operation 3^n equations of the type:

$$d_{ijk\ldots n} = \sigma_{ip}\sigma_{jq}\sigma_{kr}\ldots\sigma_{nu}\,d_{pqr\ldots u}$$

2. Be even smarter and look them up in the book of Birss:


Symmetry and Magnetism

BY

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Magnetoelectric Effect in Cr_2O_3

1. Symmetry and symmetry operations for Cr_2O_3

Tri-gonal	$\bar{3}m$	$\bar{6}\cdot m$	—	—	$1, \bar{1}, 3(2_\perp), 3(\bar{2}_\perp), \pm 3_z, \pm \bar{3}_z$	$\sigma^{(1)}, \sigma^{(2)}, \sigma^{(6)}$	—
	$\bar{3}\underline{m}$	$\bar{6}\cdot\underline{m}$	$\bar{3}$	$\bar{6}$	$1, \bar{1}, +3_z, +\bar{3}_z, 3(\underline{2}_\perp), 3(\underline{\bar{2}}_\perp)$	$\sigma^{(1)}, \sigma^{(6)}$	$\underline{\sigma}^{(2)}$
	$\underline{\bar{3}}\underline{m}$	$\underline{\bar{6}}\cdot\underline{m}$	32	3:2	$1, 3(2_\perp), \pm 3_z, \underline{\bar{1}}, 3(\underline{\bar{2}}_\perp), \pm\underline{\bar{3}}_z$	$\sigma^{(2)}, \sigma^{(6)}$	$\underline{\sigma}^{(1)}$

2. The mag

System	Magnetic point group $\mathscr{M}'$
Fe_2O_3	$\bar{3}m$
	$\bar{3}\underline{m}$
Cr_2O_3	$\underline{\bar{3}}\underline{m}$

The magnetoelectric tensor in Cr_2O_3:

$$\alpha = \begin{pmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{xx} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}$$

3. The components of α

$m = 2$	xx	yy	zz	xy	yx	$xz(2)$	$yz(2)$
K_2	xx	xx	zz	xy	$-xy$	0	0
L_2	xx	xx	zz	0	0	0	0
M_2	0	0	0	xy	$-xy$	0	0

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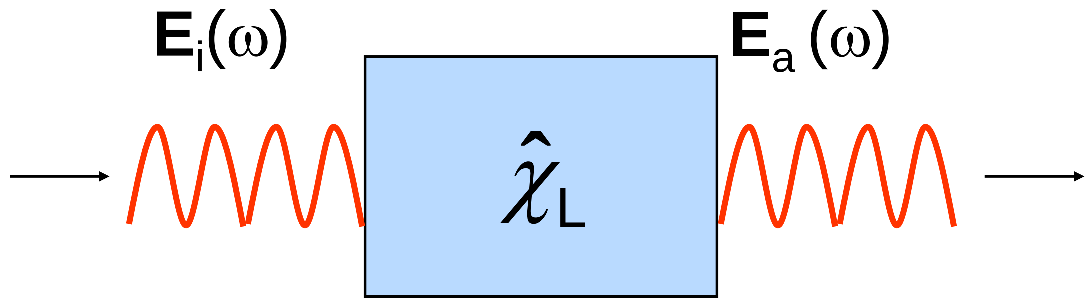
Part II – Nonlinear Optics

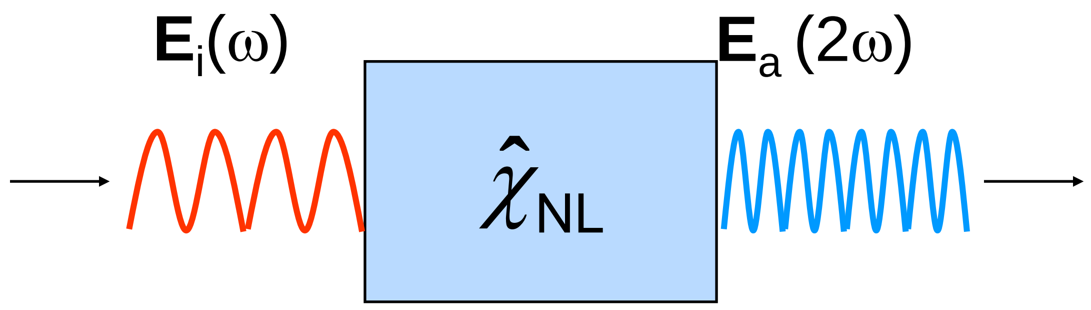
- Introduction & overview
- Second harmonic generation (SHG)
- Determination of tensor components
- SHG & (multi-)ferroic order

Nonlinear Optics

Linear optics:



Nonlinear optics:



Nonlinear Optics

$$P_i(\omega) \propto \underbrace{\chi_{ij}^{(1)} E_j(\omega_1)}_{P^L} + \underbrace{\chi_{ijk}^{(2)} E_j(\omega_1) E_k(\omega_2) + \chi_{ijkl}^{(3)} E_j(\omega_1) E_k(\omega_2) E_l(\omega_3) + \ldots}_{P^{NL}}$$

<u>Quadratic effects:</u> Frequency doubling $\omega = 2\omega_1$

Pockels effect $P_i(\omega) \propto \chi_{ijk}^{(2)} E_j(\omega) E_k(0)$

<u>Cubic effects:</u> Sum frequency generation $\omega = \omega_1 + \omega_2 + \omega_3$

Difference frequency $\omega = 2\omega_1 - \omega_2$

But: $\chi^{(1)} \approx 1$, $\chi^{(2)} \approx 10^{-10}$ cm / V, $\chi^{(3)} \approx 10^{-17}$ cm^2 / V^2

Conventional light sources E ≈ 1 V/cm

$\Rightarrow$ Laser

First Observation of Optical Harmonic Generation

P. A. Franken, A. E. Hill, C. W. Peters, and G. Weinreich

Generation of Optical Harmonics
Phys. Rev. Lett. 7, 118 (1961)

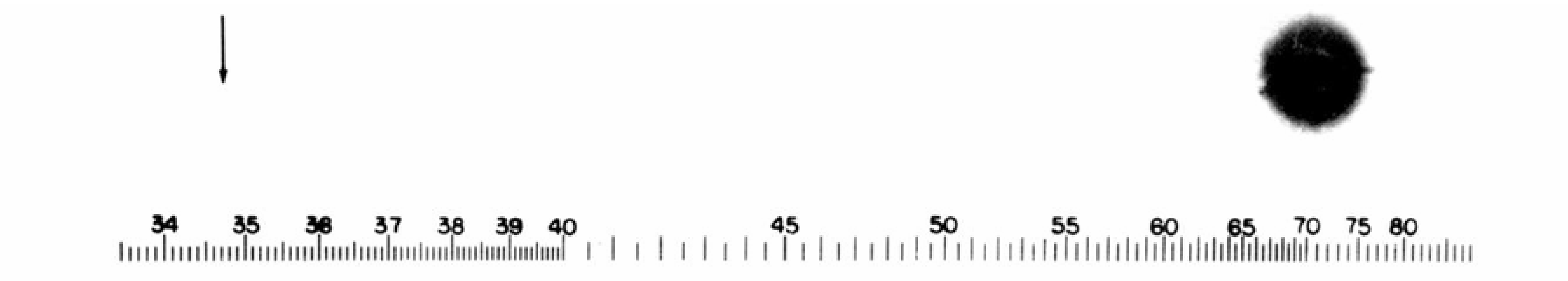


FIG. 1. A direct reproduction of the first plate in which there was an indication of second harmonic. The wavelength scale is in units of 100 A. The arrow at 3472 A indicates the small but dense image produced by the second harmonic. The image of the primary beam at 6943 A is very large due to halation.

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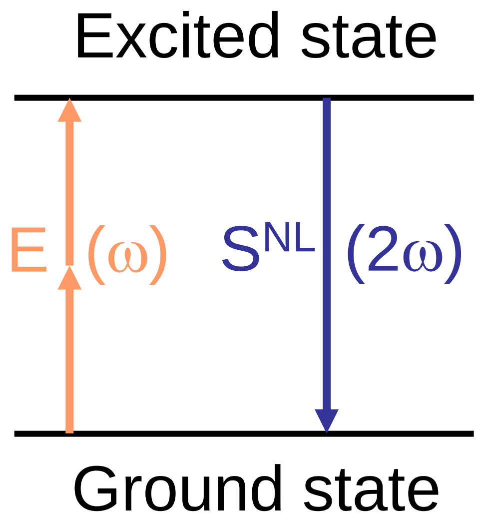
Optical Second Harmonic Generation (SHG)



SH-source term:

$$S^{NL}(2\omega) \propto P^{NL}(2\omega) \propto \chi(2\omega)E(\omega)E(\omega)$$

SH intensity:

$$I_{SH} \propto |S^{NL}|^2 \propto |\chi\ EE|^2 = |\chi|^2\ I_0^2$$

$P^{NL}(2\omega)$, $E(\omega)$: polar tensors of first rank

$\Rightarrow \chi(2\omega)$ polar tensor of third rank

⇒ No SHG in centrosymmetric crystals!

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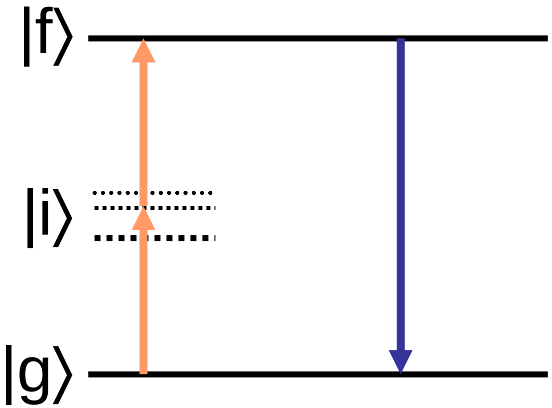
The Nonlinear Susceptibility χ



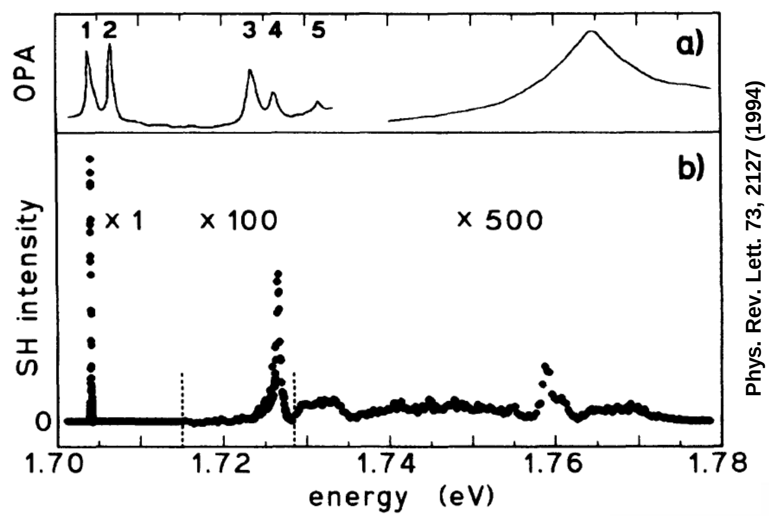
For SHG follows from perturbation theory:

$$\hat{\chi}(2\omega) \propto \sum_{i,f} \frac{\left\langle g \,|\, \hat{H}(2\hbar\omega) \,|\, f \right\rangle \left\langle f \,|\, \hat{H}(\hbar\omega) \,|\, i \right\rangle \left\langle i \,|\, \hat{H}(\hbar\omega) \,|\, g \right\rangle}{\left(E_f - E_g - 2\hbar\omega\right)\left(E_i - E_g - \hbar\omega\right)}$$

States ⟨ i | are real states that are excited with large energy mismatch: $\Delta E \cdot \Delta t \sim \hbar$

SHG is a coherent, resonant process!

e.g. SHG spectra of antiferromagnetic Cr_2O_3



Nonlinear Multipole Contributions

Light-matter interaction Hamiltonian:

$$\hat{H} \propto \vec{p} \cdot \vec{A} \quad \text{with} \quad \vec{A} = \sum_{\vec{k}} \vec{A}_{\vec{k}} e^{i\vec{k}\vec{r}} + \text{c.c.}$$

$\vec{p}$: Electron impulse operator, $\vec{A}$: Light field vector potential

In crystals usually $\lambda \propto \left|\vec{k}\right|^{-1} >> a$ (= lattice constant)

$$\Rightarrow \quad \exp(i\vec{k}\vec{r}) \cong 1 + i\vec{k}\vec{r} + \ldots \quad \Rightarrow \quad \hat{H} = \underbrace{\hat{H}_{ED}}_{\text{Zero order}} + \underbrace{\hat{H}_{MD} + \hat{H}_{EQ}}_{\text{First order}}$$

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Nonlinear Multipole Contributions

Three nonlinear contributions:

Electric dipole (ED): $\vec{P}^{NL}(2\omega) \propto \chi^{ED}(2\omega)E(\omega)E(\omega)$

Magnetic dipole (MD): $\vec{M}^{NL}(2\omega) \propto \chi^{MD}(2\omega)E(\omega)E(\omega)$

Electric quadrupole (EQ): $\hat{Q}^{NL}(2\omega) \propto \chi^{EQ}(2\omega)E(\omega)E(\omega)$

$\Rightarrow$ Multipole expansion of source term $\vec{S}$ for SHG:

$$\vec{S} = \underbrace{\mu_0 \frac{\partial^2 \vec{P}^{NL}}{\partial t^2}}_{} + \mu_0 \left(\vec{\nabla} \times \frac{\partial \vec{M}^{NL}}{\partial t} \right) - \mu_0 \left(\vec{\nabla} \frac{\partial^2 \hat{Q}^{NL}}{\partial t^2} \right)$$

Leading contribution of the order α larger,
but maybe symmetry forbidden!

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SHG in (Multi-)ferroics

Sa et al. Eur. Phys. J. B **14** (2000):

$$\chi^{SHG}(T < T_O) = \chi(T > T_O)\circlearrowleft$$

→ Order parameter

→ Susceptibility in the para phase

→ Susceptibility in the ferroic phase

- χ^{SHG} is a function of the order parameter $\circlearrowleft$
- Non-zero components of χ^{SHG} obtained from symmetry of the order parameter and the crystal in the para phase
  $\rightarrow$ ***Curie's principle***

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Order Parameter $\mathcal{O}$

Properties:

- Zero for $T>T_O$, non-zero for $T<T_O$
- Invariant under symmetries of the group of the ordered phase
- Non-invariant under the symmetries lost at the phase transition
- Each orientation of $\mathcal{O}$ represents one ferroic domain state

Here:

$\mathcal{O}$ is the lowest rank tensor that fulfils all of the properties above

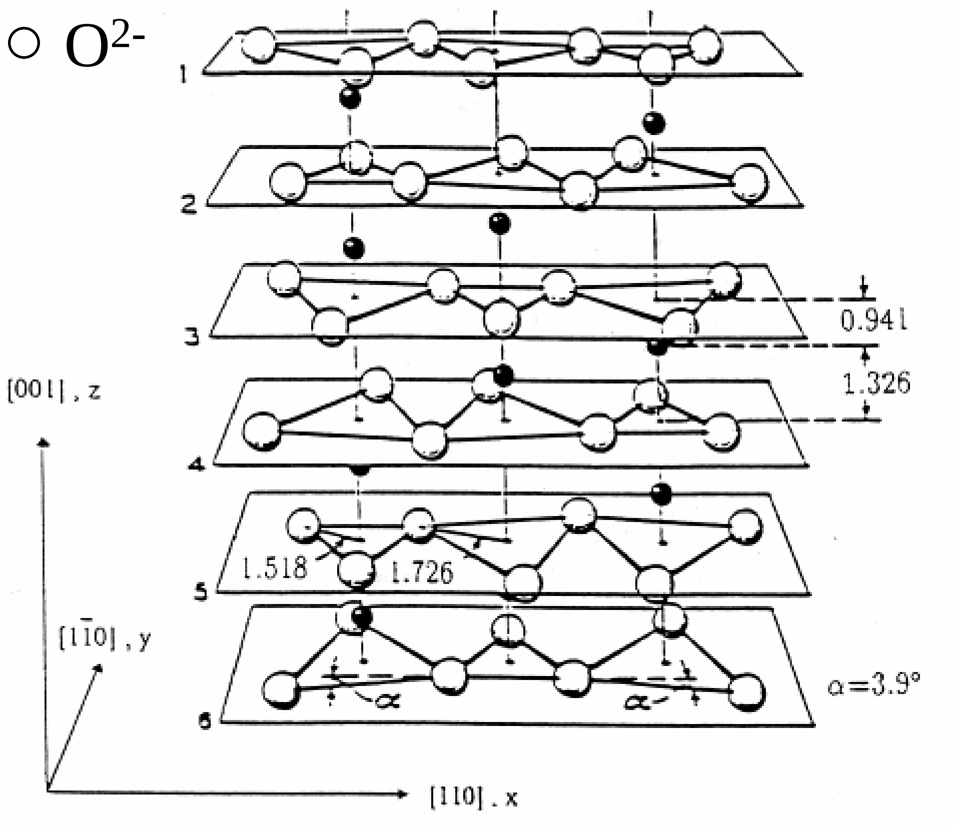
e.g. the polarization **P** in a ferroelectric or
magnetization **M** in ferromagnetic crystal

Antiferromagnetic Cr_2O_3

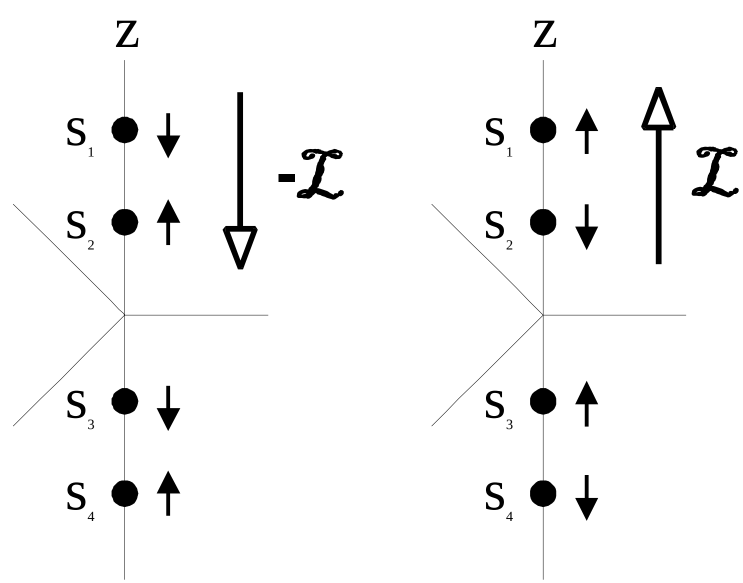
Crystallographic point group $\bar{3}m$

- Cr^{3+}

○ O^{2-}



Magnetic point group $\underline{\bar{3}m}$



Order parameter:

$$\mathcal{L}_z = \mathbf{S}_{1,z} - \mathbf{S}_{2,z} + \mathbf{S}_{3,z} - \mathbf{S}_{4,z}$$

Antiferromagnetic Cr_2O_3

Properties of orderparameter $\mathcal{L}_z$:

- Symmetry $\underline{\bar{3}m}$
- c-axial scalar

$$\Rightarrow \chi_{ijk}^{SHG}(T < T_N) = \chi_{ijk}(T > T_N)\mathcal{L}_z$$

i-axial, third rank: $\chi_{yyy} = -\chi_{yxx} = -\chi_{xyx} = -\chi_{xxy}$

c-axial, third rank: $\chi_{yyy} = -\chi_{yxx} = -\chi_{xyx} = -\chi_{xxy}$

Antiferromagnetic Cr_2O_3

Tensor components: $\chi_{yyy} = -\chi_{yxx} = -\chi_{xyx} = -\chi_{xxy}$

$$\Rightarrow \quad P(2\omega) \propto \begin{pmatrix} 2\chi_{yyy}(2\omega)E_x(\omega)E_y(\omega) \\ \chi_{yyy}(2\omega)\left(E_x^2(\omega) - E_y^2(\omega)\right) \\ 0 \end{pmatrix}$$

k-direction & polarization selection rules:

1. k||x: Only signal for E||y & P||y

2. k||y: No signal

3. k||z: All components allowed

Set of yes or no type rules to determine symmetry and structure

Generalized Description

Higher order contributions of $\mathcal{O}$:

$$\chi(T < T_O) = \chi_0(T > T_O) + \chi_1(T > T_O)\mathcal{O} + \chi_2(T > T_O)\mathcal{O}\mathcal{O} + \ldots$$

Multiple order parameters $\mathcal{O}_1$, $\mathcal{O}_2$,… (T_{O1}<T_{O2}<…):

$$\begin{aligned}\chi(T < T_{O1}) &= \chi_0(T > T_{O1}) + \chi_1(T > T_{O1})\mathcal{O}_1 + \ldots \\ &= \chi_{00}(T > T_{O2}) + \chi_{01}(T > T_{O2})\mathcal{O}_2 + \ldots \\ &+ \chi_{10}(T > T_{O2})\mathcal{O}_1 + \chi_{11}(T > T_{O2})\mathcal{O}_2\mathcal{O}_1 + \ldots \\ &\vdots\end{aligned}$$

Analogue contributions for ED, MD and EQ:

Up to 12 χ-tensors for two order parameter compounds!

SHG in a Multiferroic Compound

ED contribution for magnetic ferroelectrics:

$$\vec{P}^{NL}(2\omega) = \varepsilon_0 \left[\hat{\chi}(0) + \hat{\chi}(\wp) + \hat{\chi}(\ell) + \hat{\chi}(\wp\,\ell) + \ldots \right] \vec{E}(\omega)\vec{E}(\omega)$$

$\chi(0)$:	Paraelectric paramagnetic contribution	always allowed
$\chi(\mathcal{P})$:	(Anti)ferroelectric contribution	allowed below the respective ordering temperature
$\chi(\ell)$:	(Anti)ferromagnetic contribution	
$\chi(\mathcal{P}\ell)$:	Magnetoelectric contribution	

- SHG allows simultaneous investigation of magnetic and electric structures
- Selective access to electric and magnetic sublattices
- Ferroelectromagnetic contribution reveals the magneto-electric interaction between the sublattices

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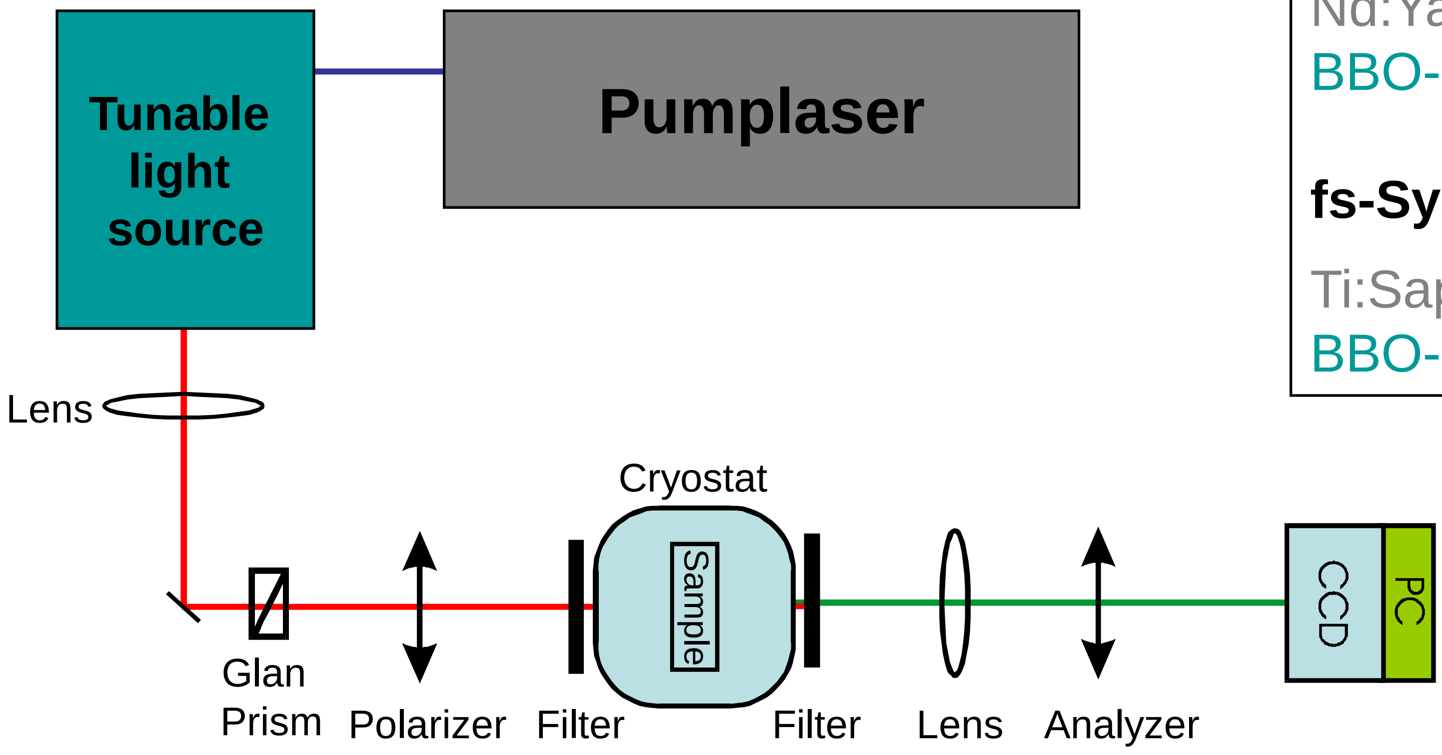
Part III - Experimental Techniques

- Spectral sensitivity
- Freedom of k-direction and light polarizations
- Temperature variation
- External magnetic and electric fields
- Optical phase sensitivity
- Spatial resolution
- Transmission & Reflection measurements
- Surface & interface sensitivity
- Time resolution

Basic Experimental Setup



ns-System:

Nd:Yag-Laser
BBO-OPO

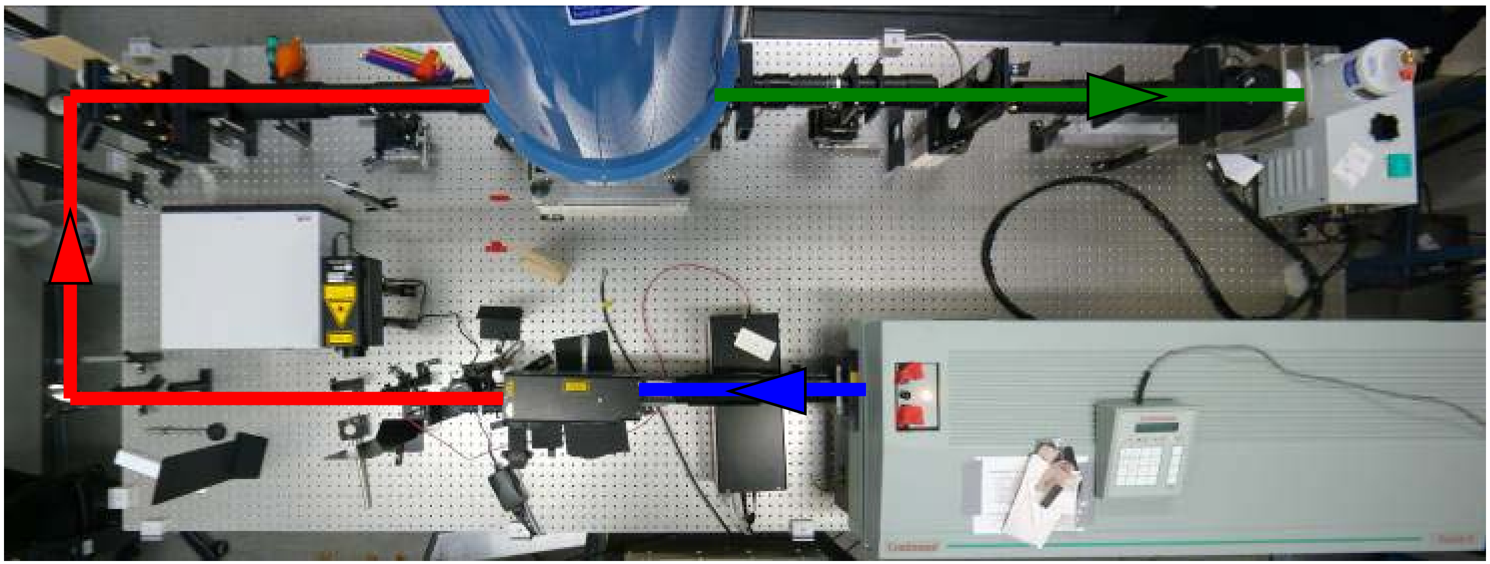
fs-System:

Ti:Saphire-Laser
BBO-OPA

Spectroscopy & Imaging Setup

Magnet
cryostat

CCD camera



BBO-OPO

Nd:YAG laser

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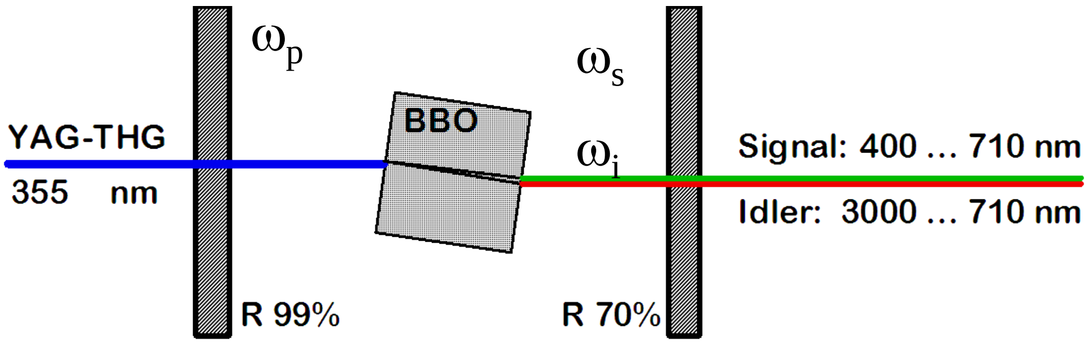
Optical Parametric Oscillator

Passive tuneable laser light source in the range 400nm - 3000nm



Parametric oscillation of transparent nonlinear crystal with high $\chi^{(2)}$-coefficients (here: beta-barium-borate β-BaB_2O_4)

Conservation of energy: $\hbar\omega_p = \hbar\omega_s + \hbar\omega_i \rightarrow \omega_p = \omega_s + \omega_i$

Conservation of momentum: $\hbar k_p = \hbar k_s + \hbar k_i \rightarrow n_p\omega_p = n_s\omega_s + n_i\omega_i$

n – refractive index $\rightarrow$ frequency tuning by rotation of crystal

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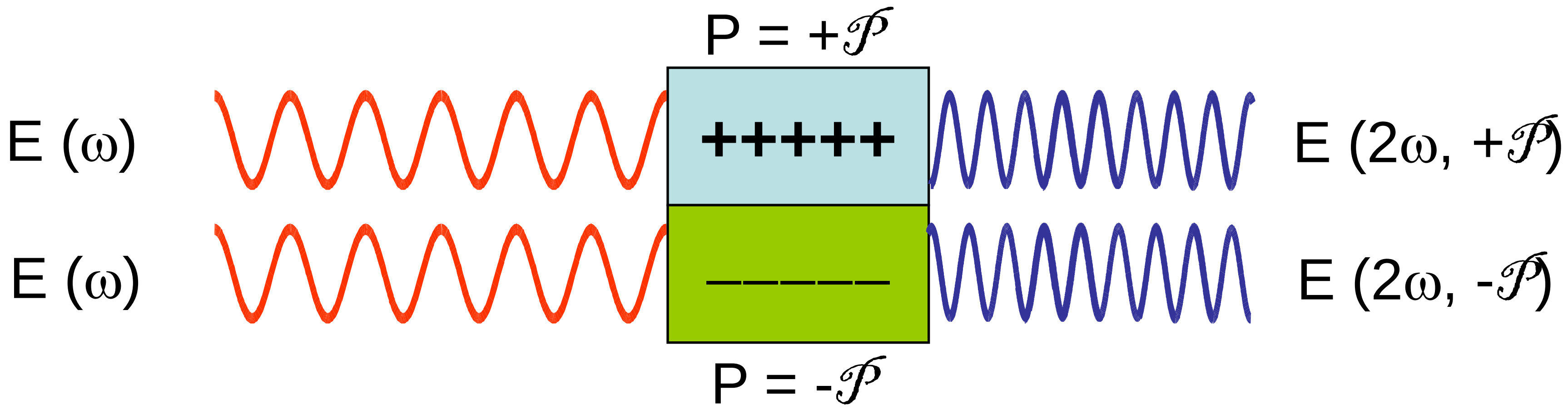
Part III - Experimental Techniques

Nonlinear optical phase measurements

Domain Imaging

Example: Ferroelectric 180° domains:



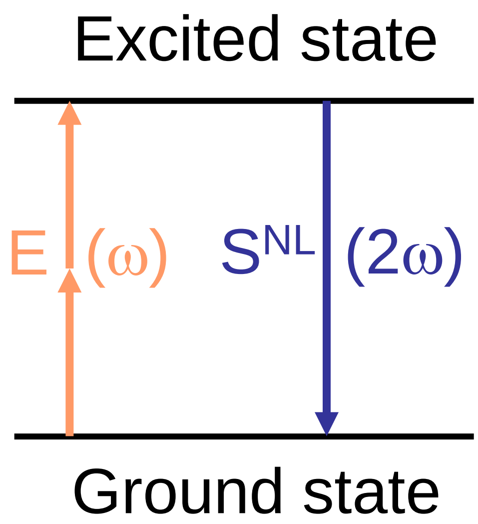
$$E(2\omega, +\mathcal{P}) \propto \chi(+\mathcal{P})\, E(\omega)E(\omega) = +\chi(|\mathcal{P}|)E(\omega)E(\omega)$$

$$E(2\omega, -\mathcal{P}) \propto \chi(-\mathcal{P})\, E(\omega)E(\omega) = -\chi(|\mathcal{P}|)\, E(\omega)E(\omega)$$

180° Phase difference!

→ Domains distinguishable by the phase of the nonlinear signal.

Phase Sensitive Measurements



<u>SH-source term:</u>

$$S^{NL}(2\omega) \propto \chi(2\omega)E(\omega)E(\omega)$$

<u>SH intensity:</u>

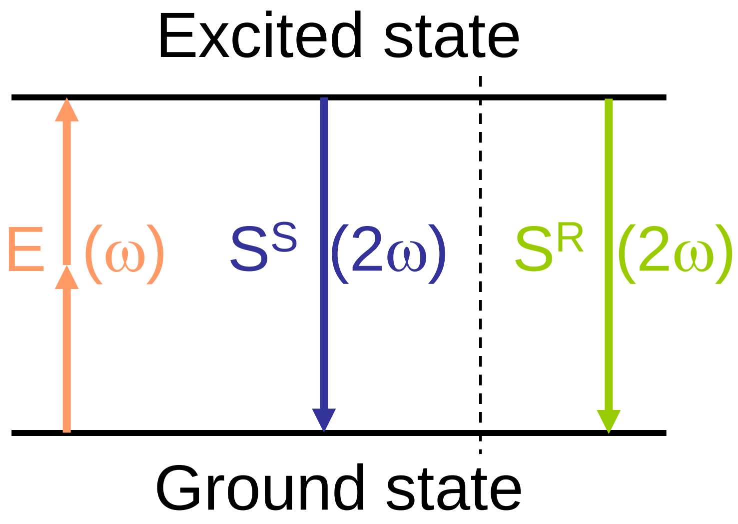
$$I_{SH} \propto |S^{NL}|^2 \propto |\chi\, EE|^2 = |\chi|^2\, I_0^{\,2}$$

Problem: Only direct measurement of intensity

$\Rightarrow$ No direct access to the phase!

Solution: Interference measurements

Phase Sensitive Measurements



Sample source term:

$$S^S(2\omega) \propto \chi^S(2\omega)\, E(\omega)E(\omega)$$

Reference source term:

$$S^R(2\omega) \propto \chi^R(2\omega)\, E(\omega)E(\omega)$$

Total intensity: $I_{SH} \propto |S^S + S^R|^2 \propto |\chi^S + Ae^{i\psi}\chi^R|^2\, I_0^{\,2}$

$$= (|\chi^S|^2 + |A\chi^R|^2 + 2\chi^S\chi^R \cos\psi)\, I_0^{\,2}(\omega)$$

always > 0 interference term

Experimental access to amplitude A and phase ψ!

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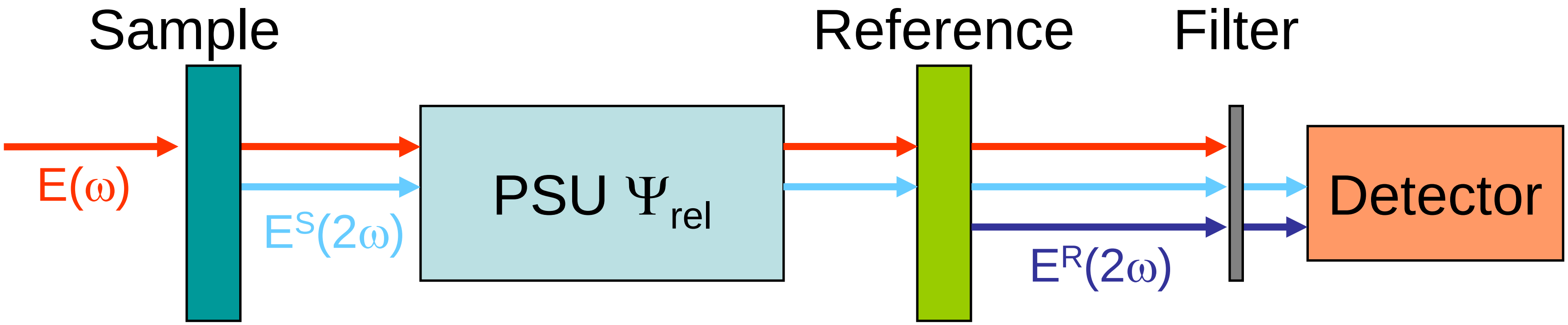
Experimental Realisation



PSU = Phase Shifting Unit:

Induces phase shift Ψ_{rel} between $E(\omega)$ and $E^S(2\omega)$ and therefore between $E^S(2\omega)$ and $E^R(2\omega)$

Experimental realisation:

- Gas pressure cell
- Rotated glass plates or shifted glass wedges
- Distance variation

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Experimental Realisation

<u>Measuring SH-intensity I as function of Ψ_{rel}:</u>

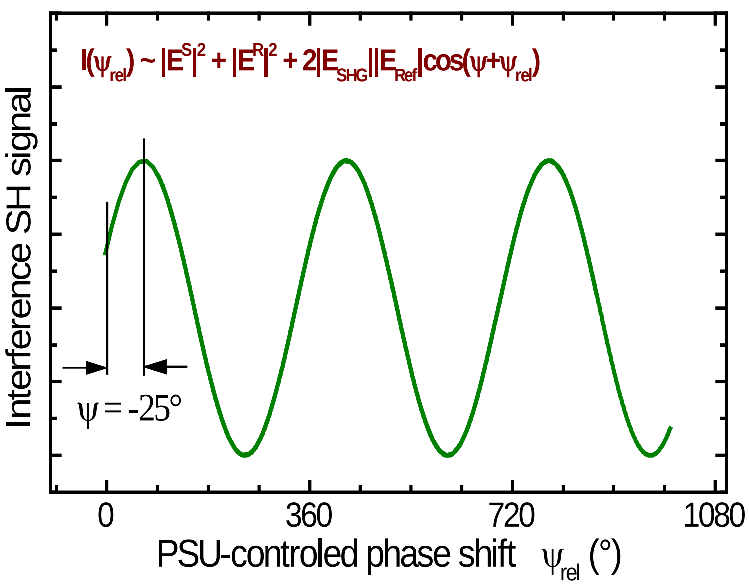
$$I(\Psi_{rel}) \propto |E^S + E^R|^2 = |E^S|^2 + |E^R|^2 + 2\,|E^S||E^R|\cos(\Psi + \Psi_{rel})$$

with $\Psi = \Psi^S + \Psi^R + \Psi_0$

(Ψ_0 by PSU and distance sample ↔ reference)

For $\Psi_0 \rightarrow 0$ and if Ψ^R known:

Absolute measurement of Ψ^S



Spatially resolved:

e.g. AFM domain in $YMnO_3$

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Disadvantages of the Standard Methods

- Only measurements with external reference (multiferroics)
- Distance sample ↔ reference reduces image quality
- Loss of coherence due to large sample ↔ reference distance ⇒ week interference signal
- Mechanical/optical instabilities due to moving parts

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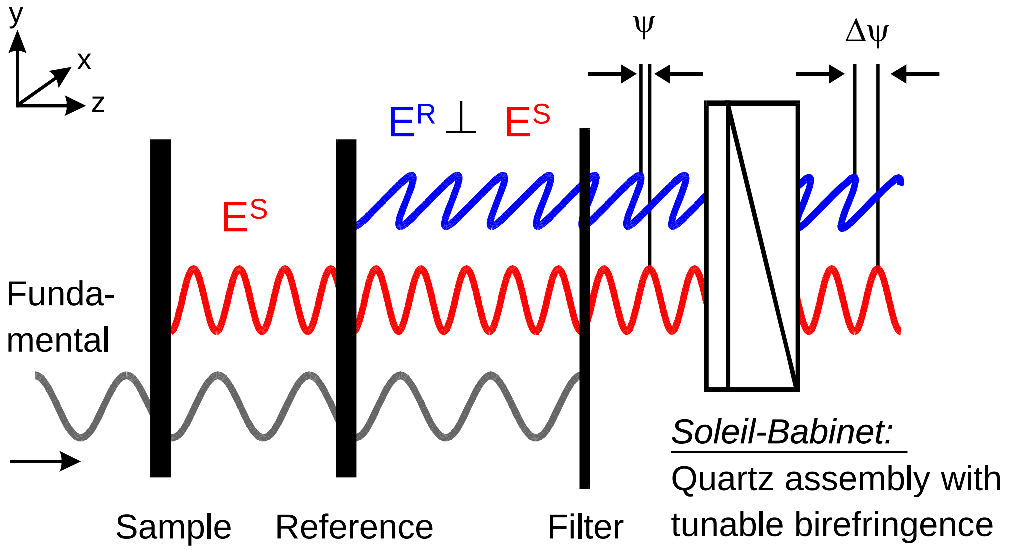
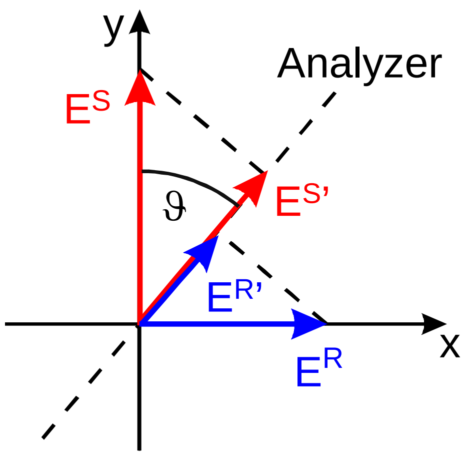
Phase Resolved SH Imaging





Soleil-Babinet compensator as PSU behind sample & reference:

⇒ Sample ↔ reference distance can be reduced to zero

⇒ Measurements with external or *internal* reference

E^S and E^R are projected on common direction via an analyzer:

⇒ Optimization of signal contrast

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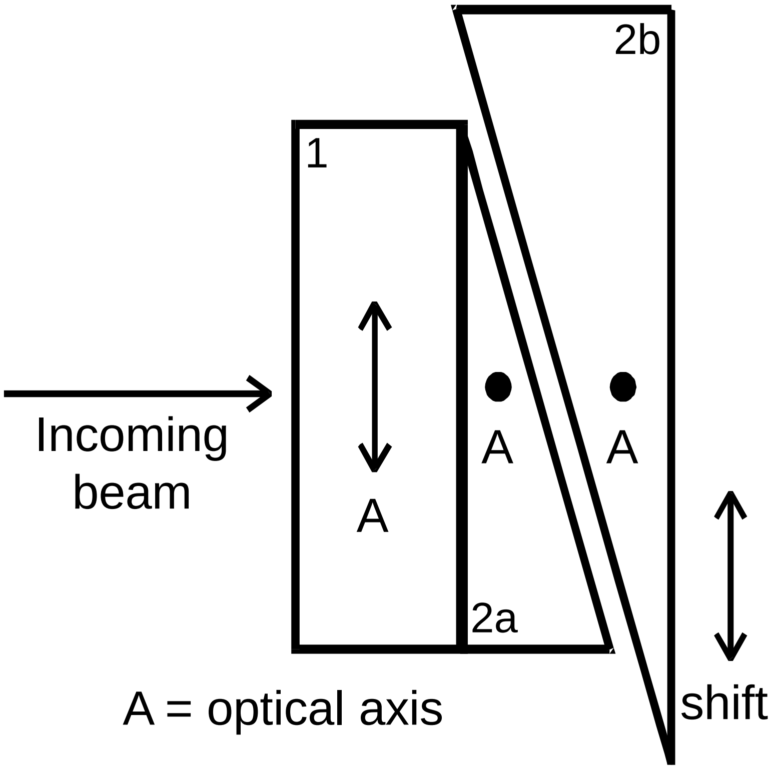
Soleil-Babinet Compensator

Quartz assembly made of
two wedged crystals (2a, 2b)
+ a compensation crystal

Phase shift Ψ:

$$\Psi = \frac{2\pi}{\lambda}(d_2 - d_1)\Delta n$$

d_1 : Thickness compensation crystal
d_2 : Total thickness of the wedges
λ : Wavelength
$\Delta n = n_e - n_o$: Refrective index missmatch



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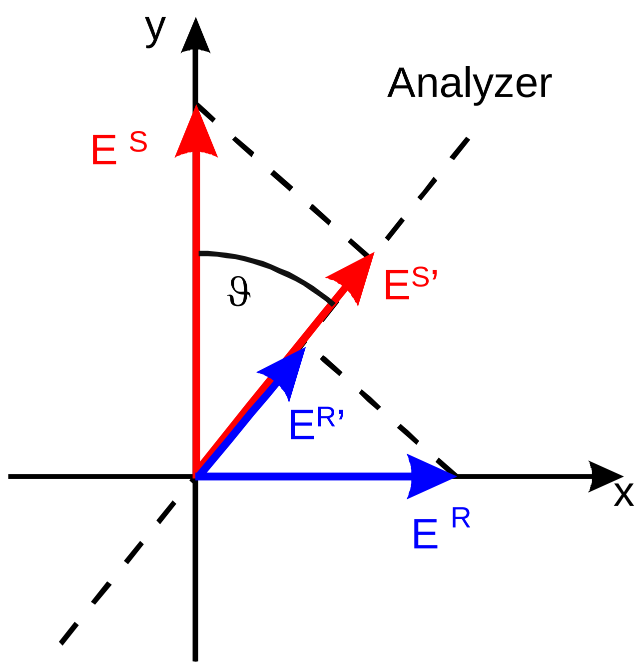
Signal Optimization

$$\left.\begin{aligned}\vec{E}^R &= E_0^R e^{i\Psi^R}\vec{e}_x \\ \vec{E}^S &= E_0^S e^{i\Psi^S}\vec{e}_y\end{aligned}\right\} \Rightarrow \left\{\begin{aligned}E^{R'}(\vartheta) &= E_0^R e^{i\Psi^R}\sin\vartheta \\ E^{S'}(\vartheta) &= E_0^S e^{i\Psi^S}\cos\vartheta\end{aligned}\right.$$



Interference:

$$I(\vartheta) = \left|E^{R'}(\vartheta) + E^{S'}(\vartheta)\right|^2 =$$

$$= \left|E_0^{R'}\sin\vartheta\right|^2 + \left|E_0^{S'}\cos\vartheta\right|^2 + 2\left|E_0^{R'}\right|\left|E_0^{S'}\right|\sin\vartheta\cos\vartheta\cos\left(\Psi^R - \Psi^S\right)$$

Contrast: $C = \frac{I_{max}}{I_{min}} = 1\ldots\infty$

Visibility: $V = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = 0\ldots1$

Maximum for $E^{R'}(\vartheta_0) = E^{S'}(\vartheta_0)$

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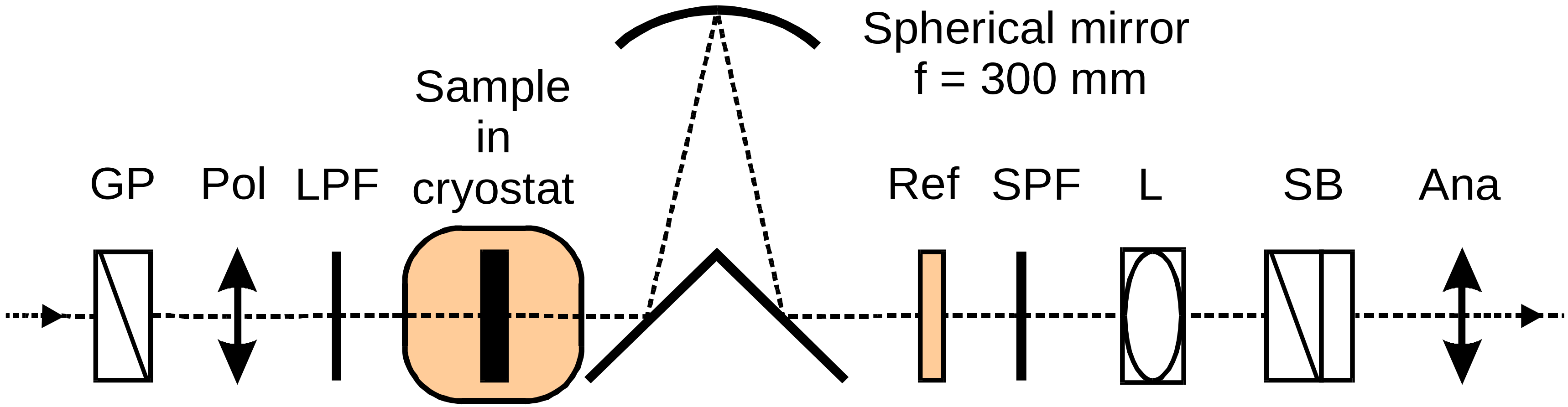
Phase Resolved SH Imaging (Setup)



- Measurements with external or internal reference
- Reference outside cryostat
  ⇒ high degree of experimental freedom
- Achromatic beam imaging for improved image quality and compensation of loss of (spatial) coherence

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Coherence Effects

Interference including
the effect of coherence:

$$I(\Psi) = I_1 + I_2 + 2\sqrt{I_1 I_2}|\gamma|\cos(\Psi_0 + \Psi)$$

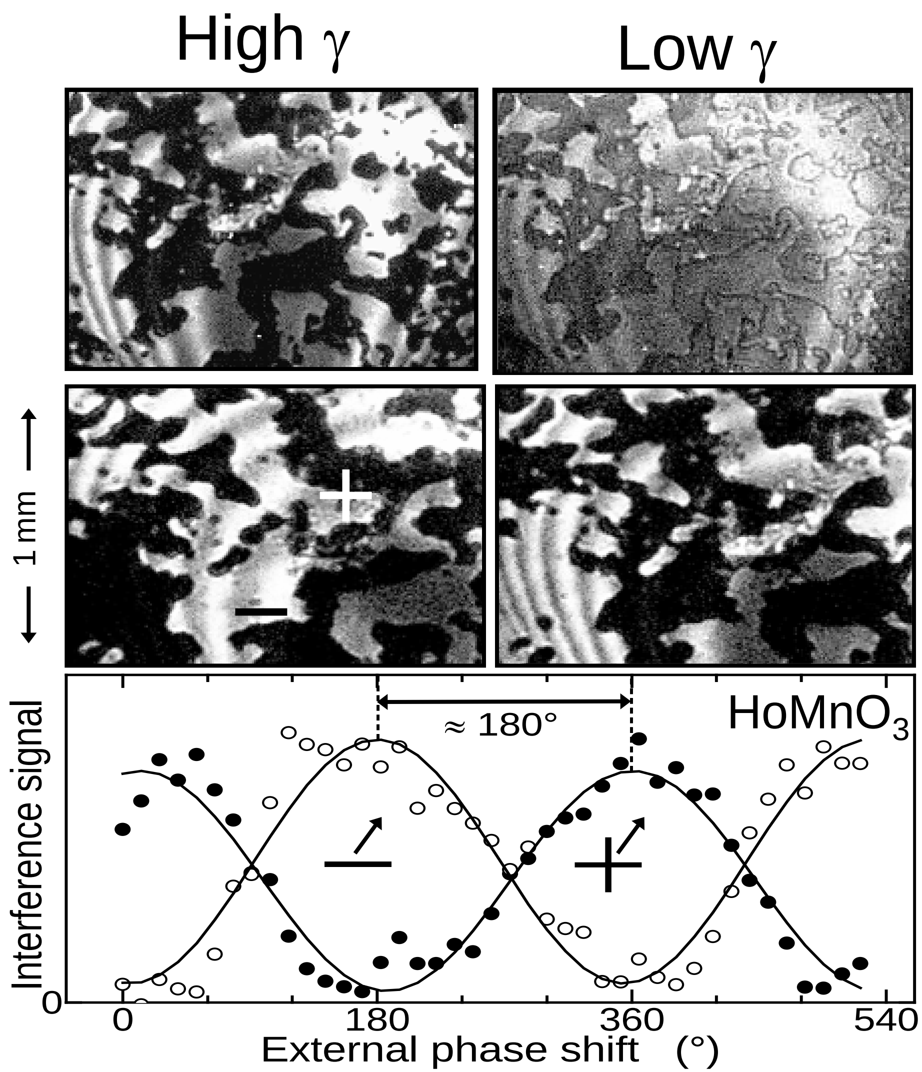
Coherence: $|\gamma|$

Visibility:

$$V = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \frac{2\sqrt{I_1 I_2}|\gamma|}{I_1 + I_2}$$

For $I_1 = I_2 \Rightarrow V = |\gamma|$

|γ| > 99% possible!



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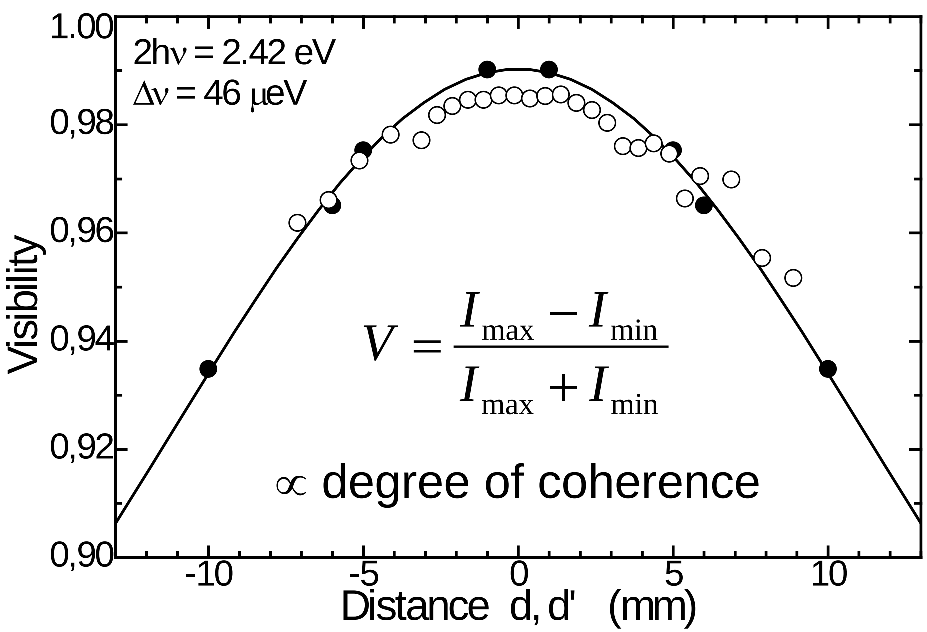
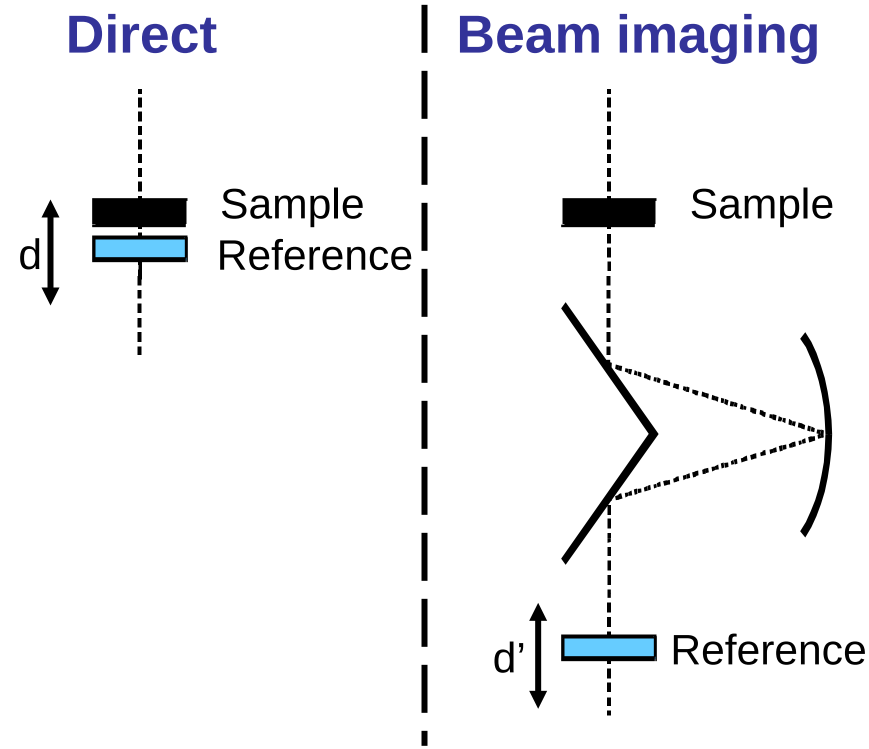
Phase-Resolved SH Imaging (Results)





Visibility
almost 100%

Loss of (spatial)
coherence
fully compensated!

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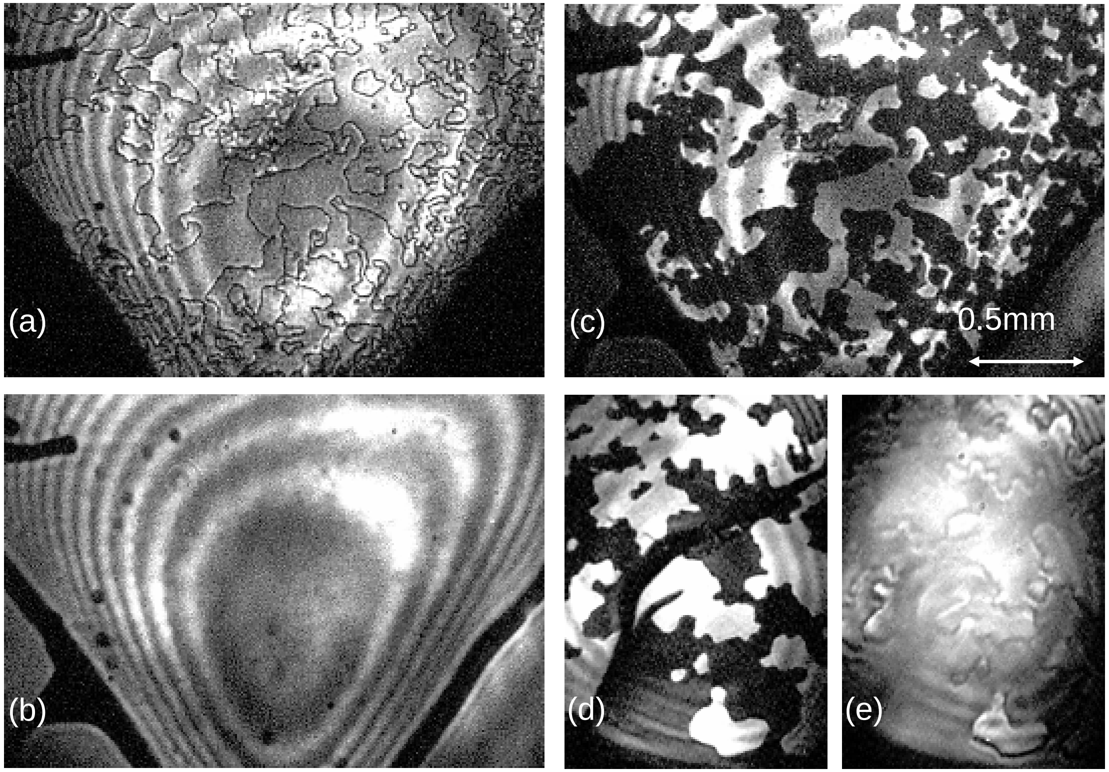
Phase-Resolved SH Imaging (Results)

Sample

Reference



Sample
+
Reference

imaging direct

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Phase-Resolved SH Imaging (Summary)

- Large working distances (~1 m)
- More experimental freedom
- High signal contrast
- Improved image quality
- Allows use of broadband laser sources with poor beam quality

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Part III - Experimental Techniques

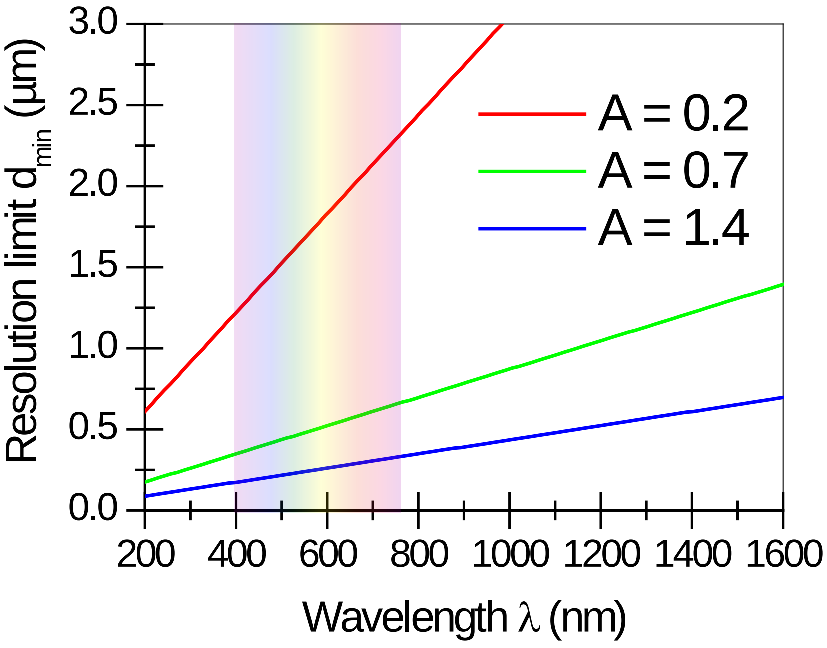
Nonlinear imaging & the problem of optical resolution

Limit of Optical Resolution

Optical resolution is limited by diffraction:

$$d_{min} = 0.61 \lambda / A$$

with numerical aperture $A = n \sin \varphi$

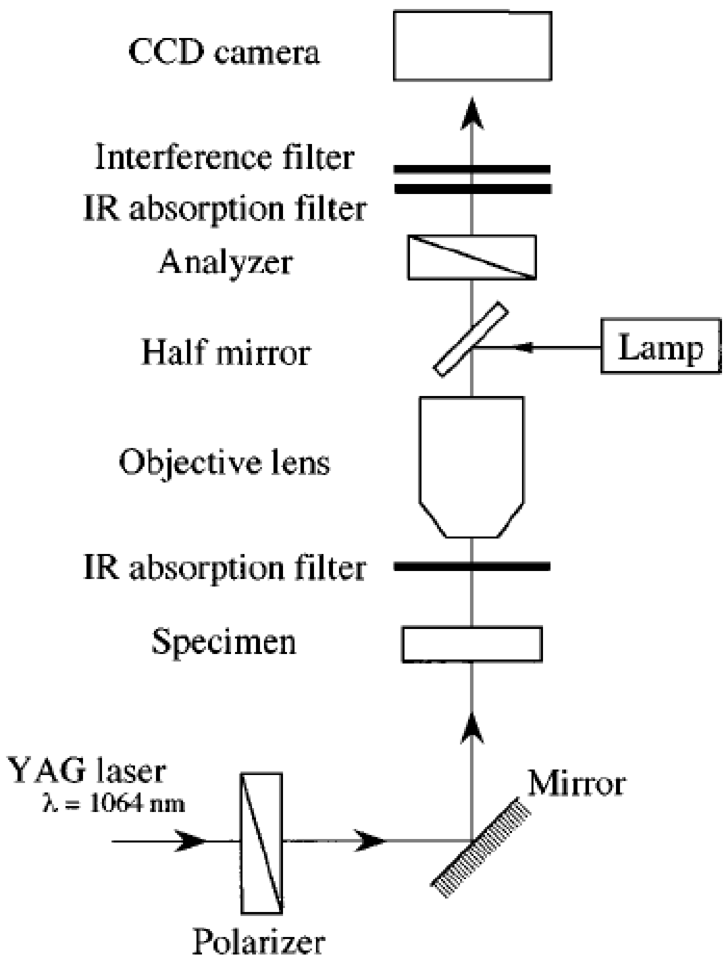


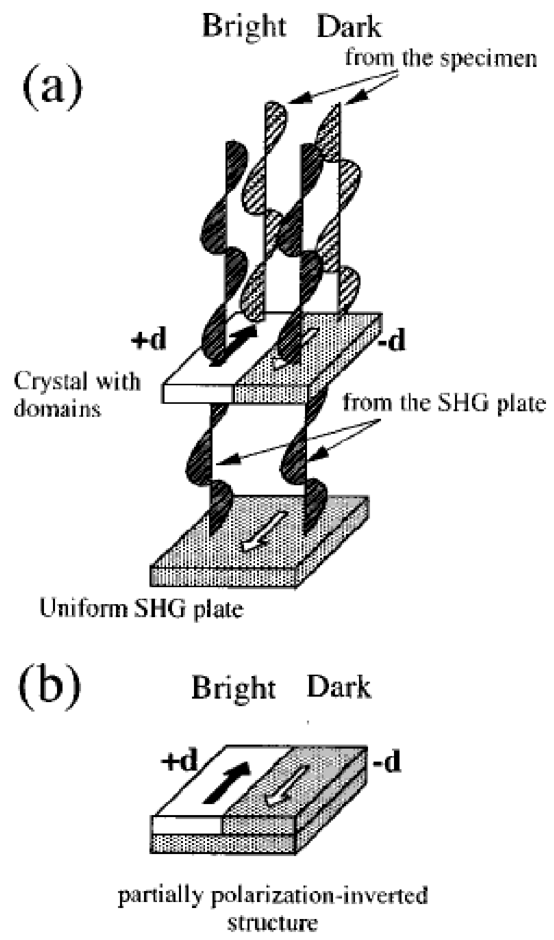
<u>Typical values of A:</u>

- Standard lens (f=200mm, ∅=50mm): A ≈ 0.2
- Photo lens: A ≈ 0.7
- Microscope objective up to A = 1.4

⇒ Resolution limit down to some hundred nm

SHG Microscopy





S. Kurimura & Y. Uesu J. Appl. Phys. 81, 369 (1997)

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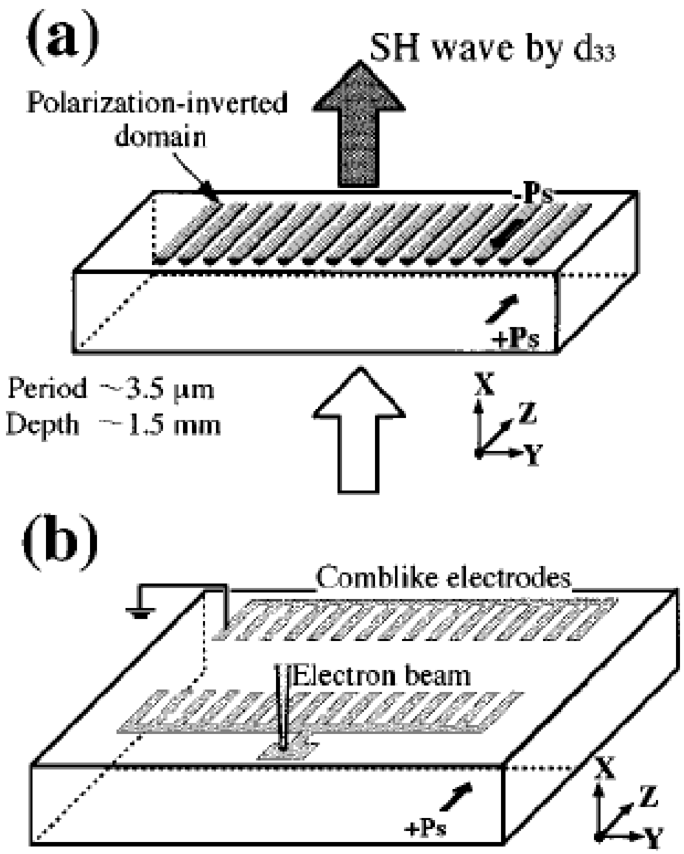
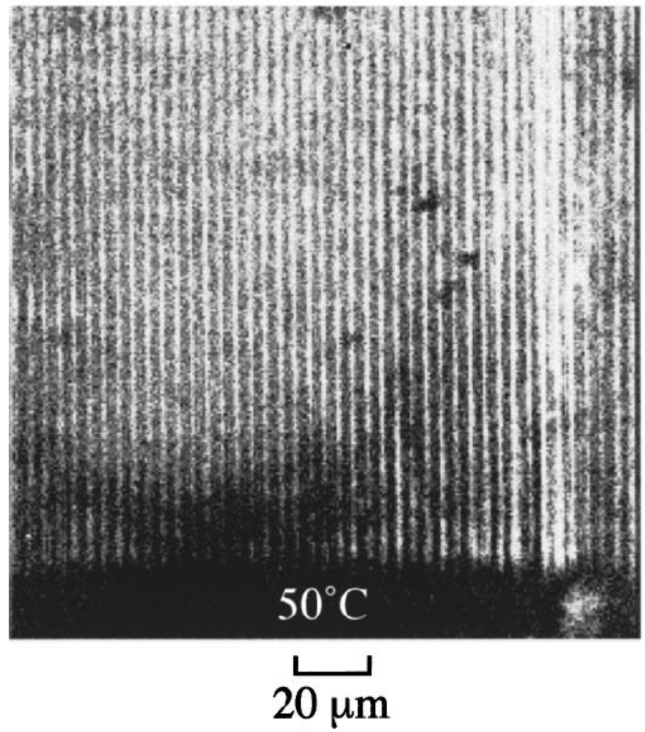
SHG Microscopy



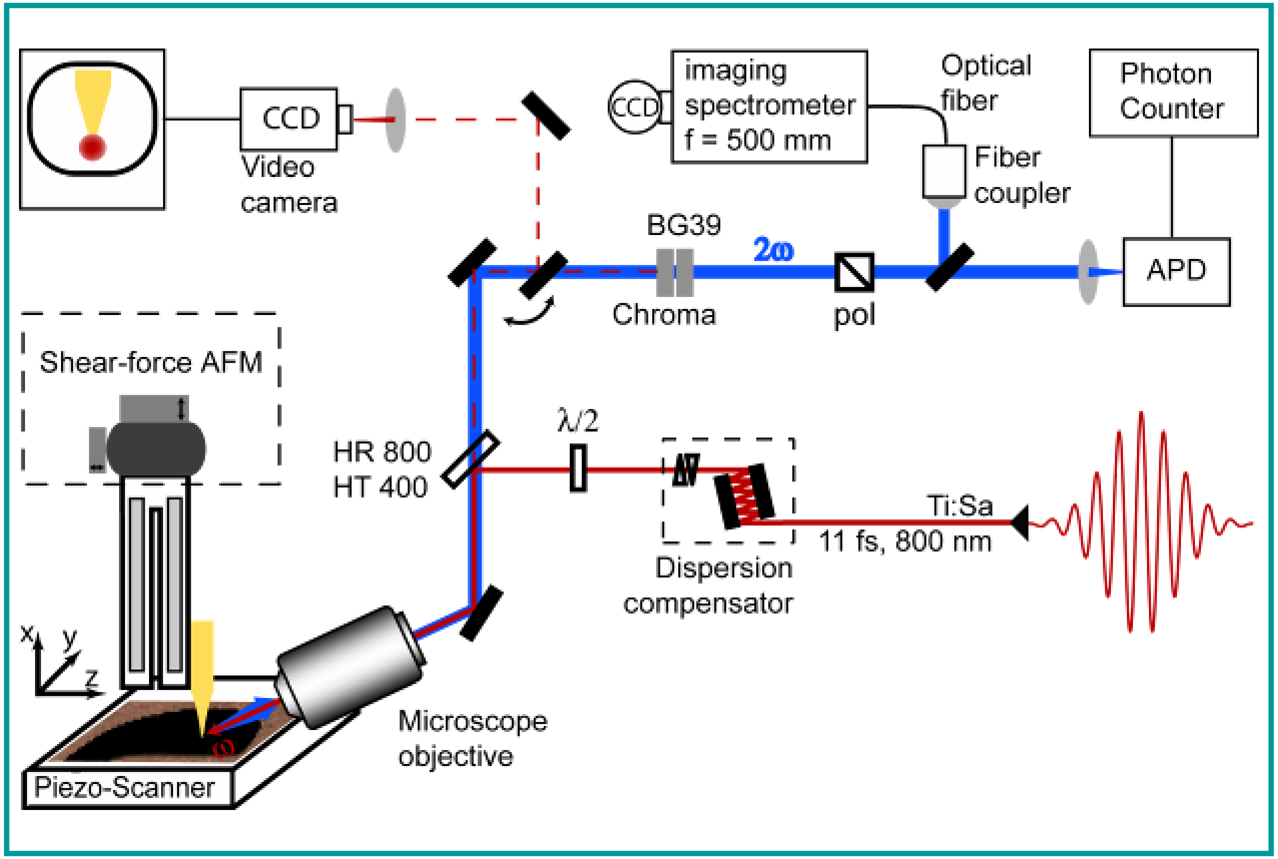
Ferroelectric stripe domains in a $LiTaO_3$ QPM device

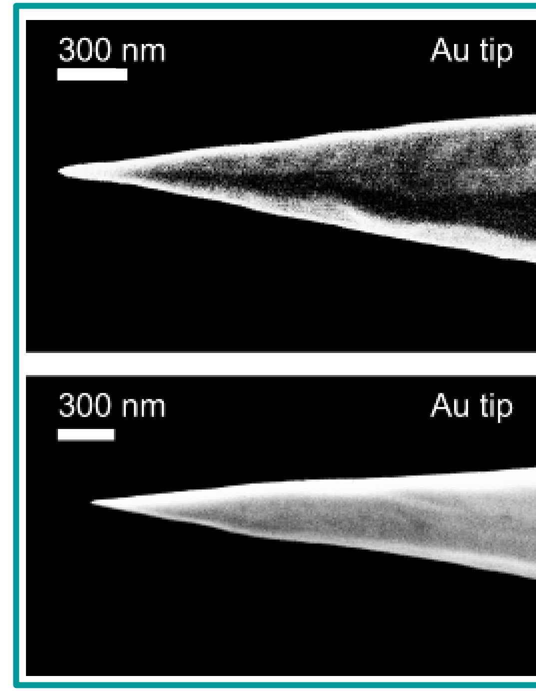


S. Kurimura & Y. Uesu J. Appl. Phys. 81, 369 (1997)

Going Beyond the Optical Resolution Limit

Tip- enhanced near-field microscope





SEM micrographs
of Au tips: R ~ 10 nm

[Neacsu, Reider, and Raschke, Phys. Rev. B **71**, 201402 (2005)]

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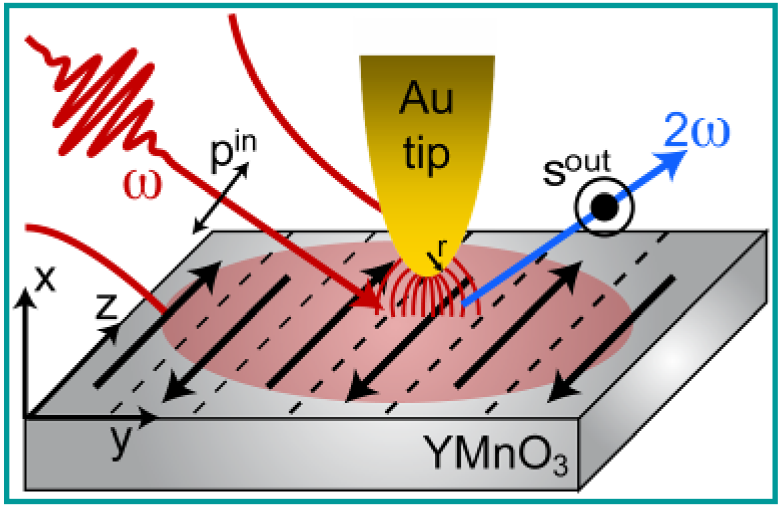
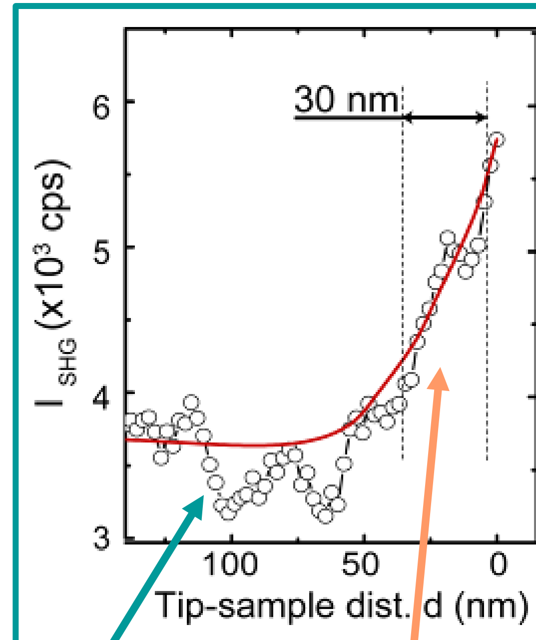
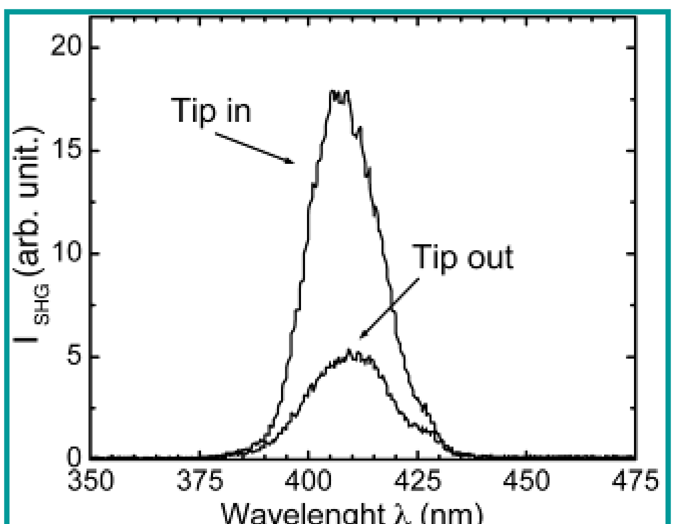
Imaging of FEL Domains in $YMnO_3$



Tip-sample distance dependence





$$\vec{E}(\omega) = (E_x(\omega), E_y(\omega), 0)$$

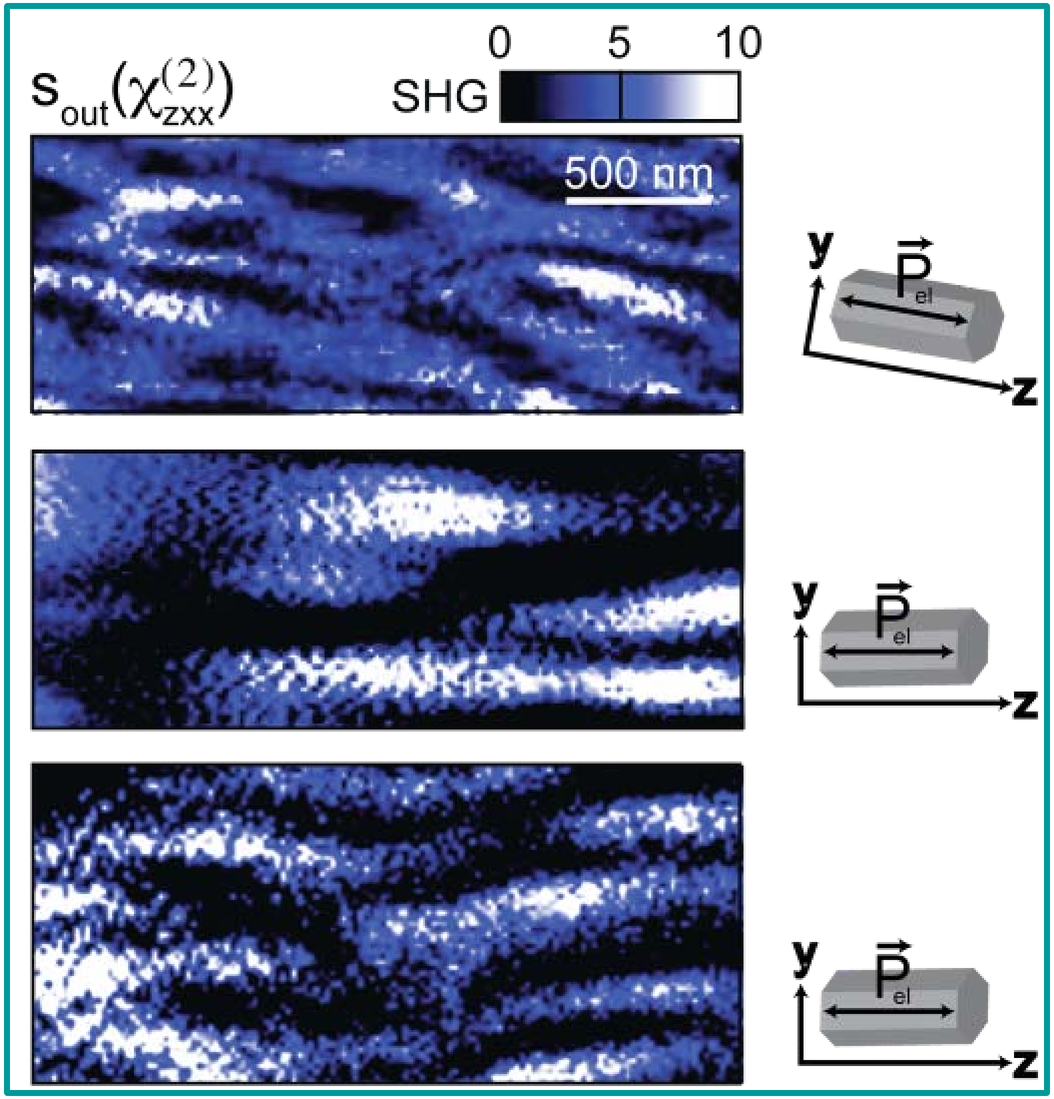
$$P_z^{(2)}(2\omega) \approx \chi_{zxx}^{(2)}[E_x + E_y]^2$$

Far-field self-homodyne reference

Near-field enhanced contribution

[Neacsu, Reider, and Raschke, Phys. Rev. B **71**, 201402 (2005)]

Imaging of FEL Domains in $YMnO_3$



[Neacsu et.al., Nature Materials, submitted]

Domain dimensions:
> 100 nm wide (y)
~ 1µm long (z)

Ferroelectric domains

Extended along
the hexagonal axis z

⇩

Parallel with $\mathbf{p}_z$

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Part III - Experimental Techniques

Surfaces & interfaces

First Magnetic SHG Experiment

VOLUME 67, NUMBER 20 PHYSICAL REVIEW LETTERS 11 NOVEMBER 1991

Effects of Surface Magnetism on Optical Second Harmonic Generation

J. Reif, J. C. Zink, C.-M. Schneider, and J. Kirschner

Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, W-1000 Berlin 33, Germany

(Received 21 May 1991)

We report on the first experiments showing the influence of surface magnetization on optical second harmonic generation in reflection at a Fe(110) surface. The magneto-optical Kerr effect modifies the hyperpolarizability of the surface in the optical field, leading to a dependence of the second harmonic yield on the direction of magnetization relative to the light fields. For the clean surface an effect of 25% was determined, which decays exponentially with surface contamination by the residual gas, thus demonstrating the high surface sensitivity of this technique.

2878

PACS numbers: 75.30.Pd, 78.20.Ls, 78.65.Ez

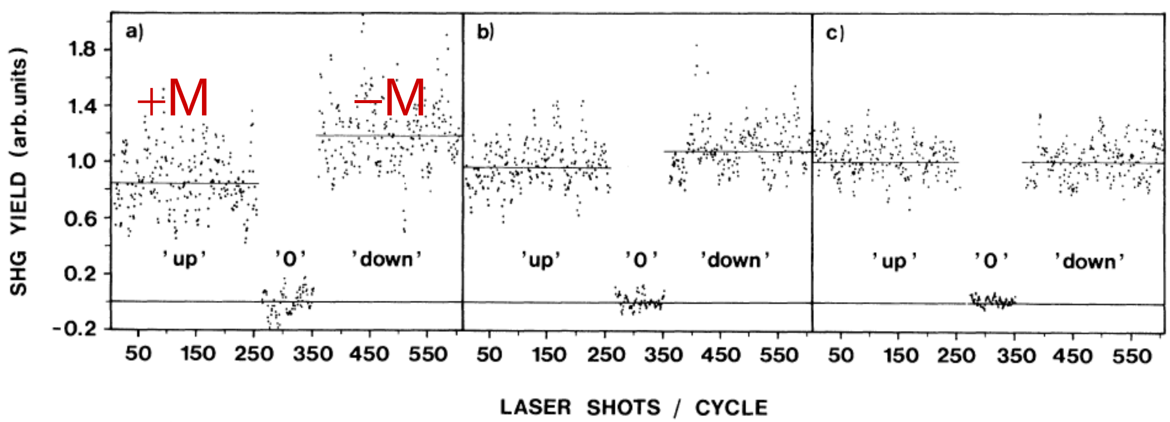
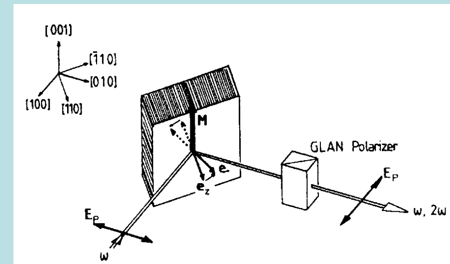


FIG. 2. Relative magnetization dependence of second harmonic signal for three different times elapsed since sample preparation [(a) ≈45 min, (b) ≈60 min, (c) ≥180 min]. Shown is, in each panel, an averaged [superposition of (a) 220, (b) 550, and (c) 750 cycles] experimental cycle, consisting of 250 pulses with magnetization "up," 100 pulses with no SHG signal (obtained by means of a UV blocking glass filter), and 250 pulses with magnetization "down." All signals are normalized to the expected value without influence of magnetization [cf. Eq. (1)]. The solid lines represent the average of the respective regions of interest.

Observation of a second harmonic contribution which depends on the magnetization of a Fe(001) surface

Small signal, but with high contrast → typical for SHG!



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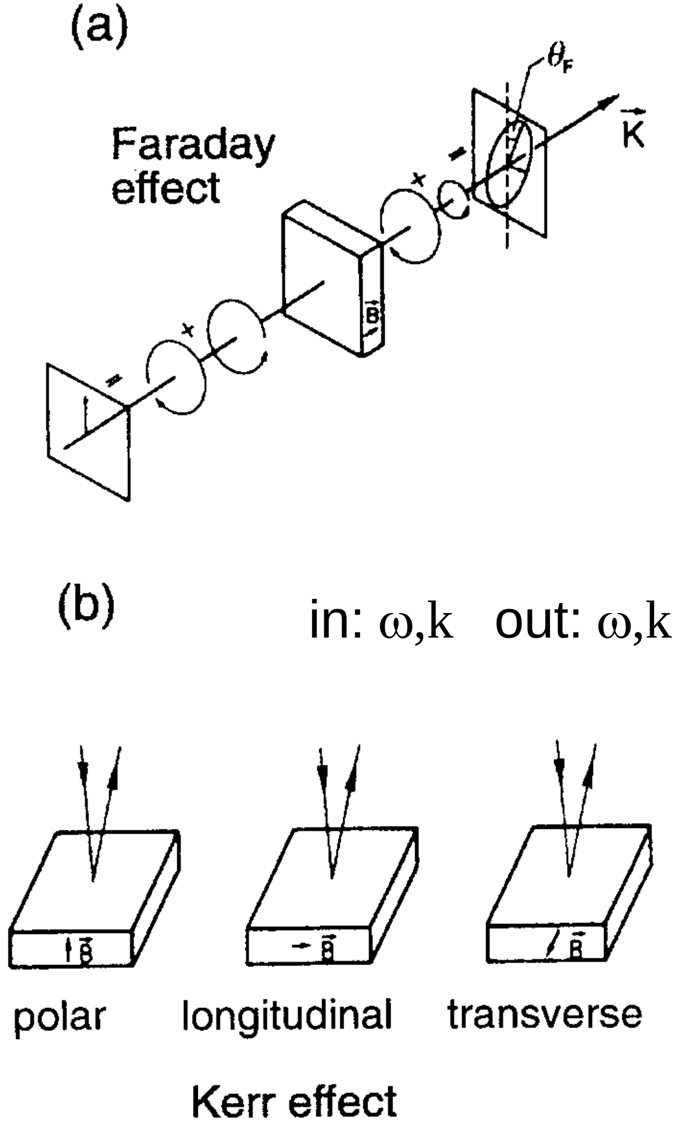
Linear Magneto-Optical Effects



Dielectric function :

$$\tilde{\boldsymbol{\varepsilon}} = \varepsilon \begin{pmatrix} 1 & iQ & 0 \\ -iQ & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

- Rotation of plane of polarization upon transmission/reflection on magnetized medium
- Described by non-diagonal elements of 3×3 matrix
- $Q \ll 1 \;\; \Rightarrow$ **small effect ($10^{-2}...10^{-5}$)**

R. Vollmer in "Nonlinear Optics in Metals", Clarendon (1998)

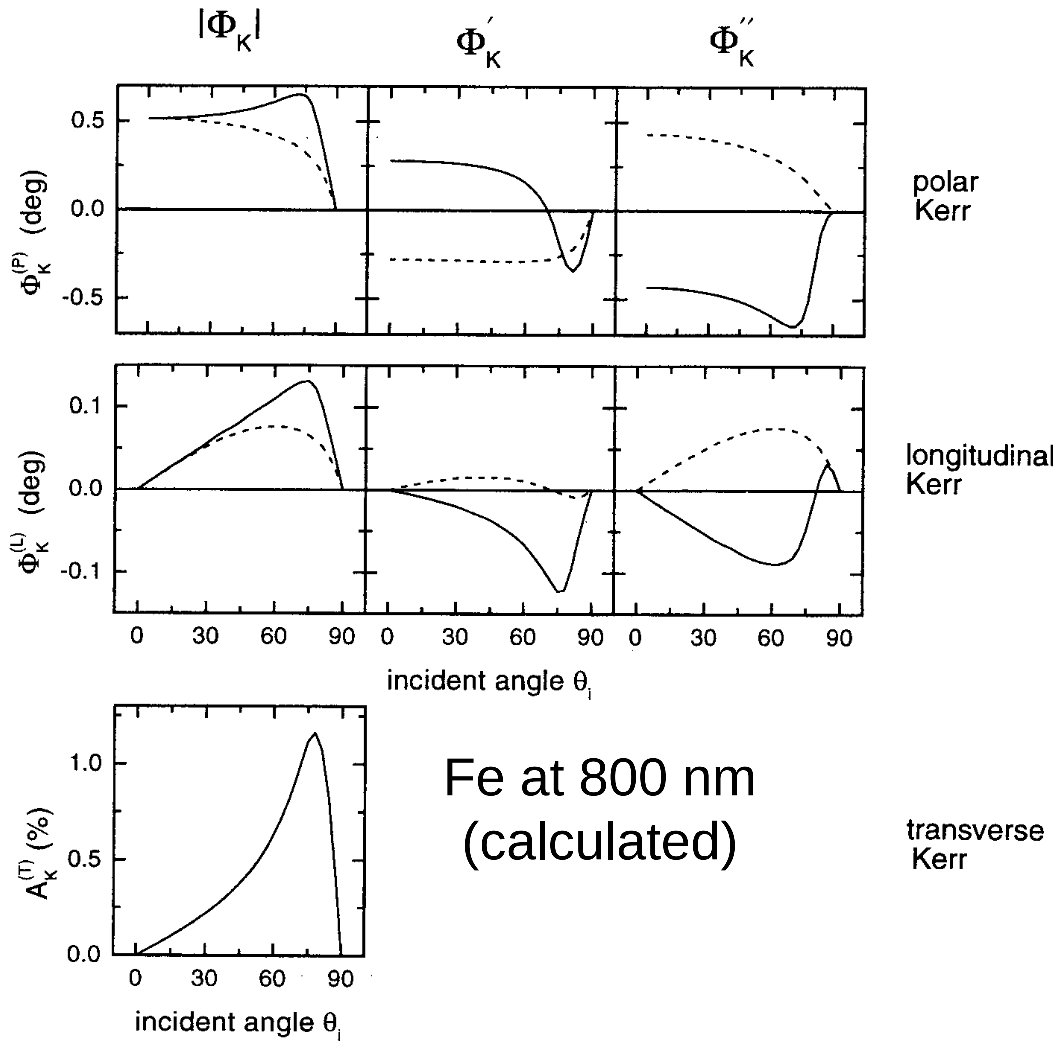
Linear Magneto-Optical Effects

Kerr rotation

and ellipticity

$$\Phi_{Ks} = \Phi'_{Ks} + i\Phi''_{Ks} = \frac{E_p^{(r)}}{E_s^{(r)}}$$

$$\Phi_{Kp} = \Phi'_{Kp} + i\Phi''_{Kp} = \frac{E_s^{(r)}}{E_p^{(r)}}$$



Fe at 800 nm (calculated)

R. Vollmer in "Nonlinear Optics in Metals", Clarendon (1998)

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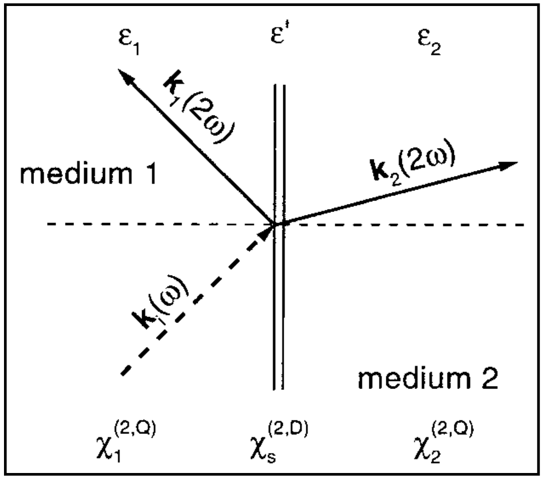
Nonlinear Magneto-Optical Effects



Generation of reflected SH wave:

$$P_i(2\omega) = \chi^{(2)}_{ijk}(M)\, E_j(\omega)\, E_k(\omega)$$

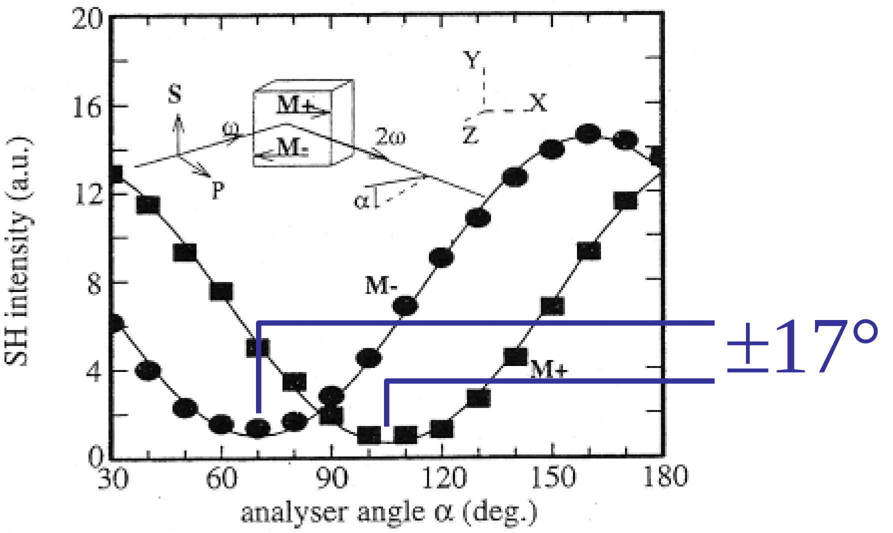
with $\chi^{(2)}(-M) = -\chi^{(2)}(+M)$

$\Rightarrow$ $\chi^{(2)}$ is 3rd-rank c-tensor

NOMOKE:

NOnlinear **M**agneto-**O**ptical **K**err-**E**ffect

Hugh effects of several tenth of degrees!



B. Koopmans et al. Phys. Rev. Lett. 74, 3692 (1995)

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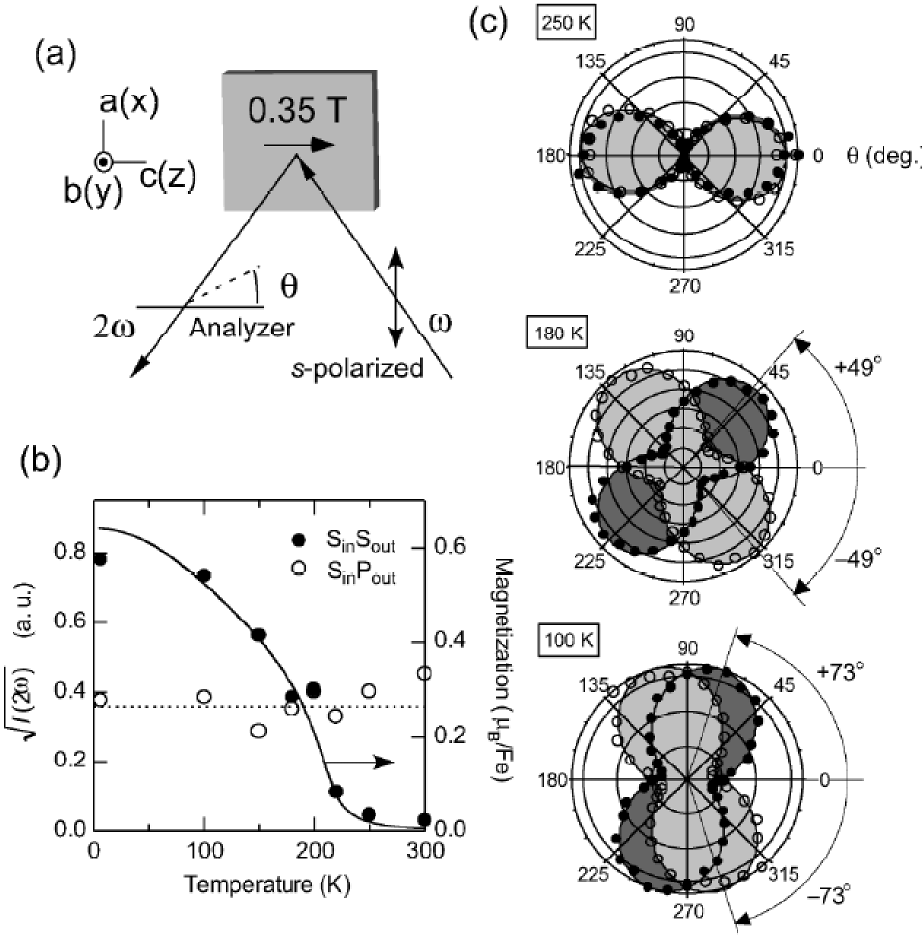
NOMOKE on a Polar Ferromagnet

$GaFeO_3$:

- Pyroelectric
- Ferromagnetic T_C = 205 K

Crystallographic
+ magnetic SHG:

$$\vec{P}(2\omega) = \epsilon_0 \begin{pmatrix} \chi^{m}_{xxx} \\ \chi^{cry}_{yxx} + \chi^{m}_{yxx} \\ 0 \end{pmatrix} E_x^2(\omega).$$



Ogawa, et.al., Phys. Rev. Lett. 92, 047401 (2004)

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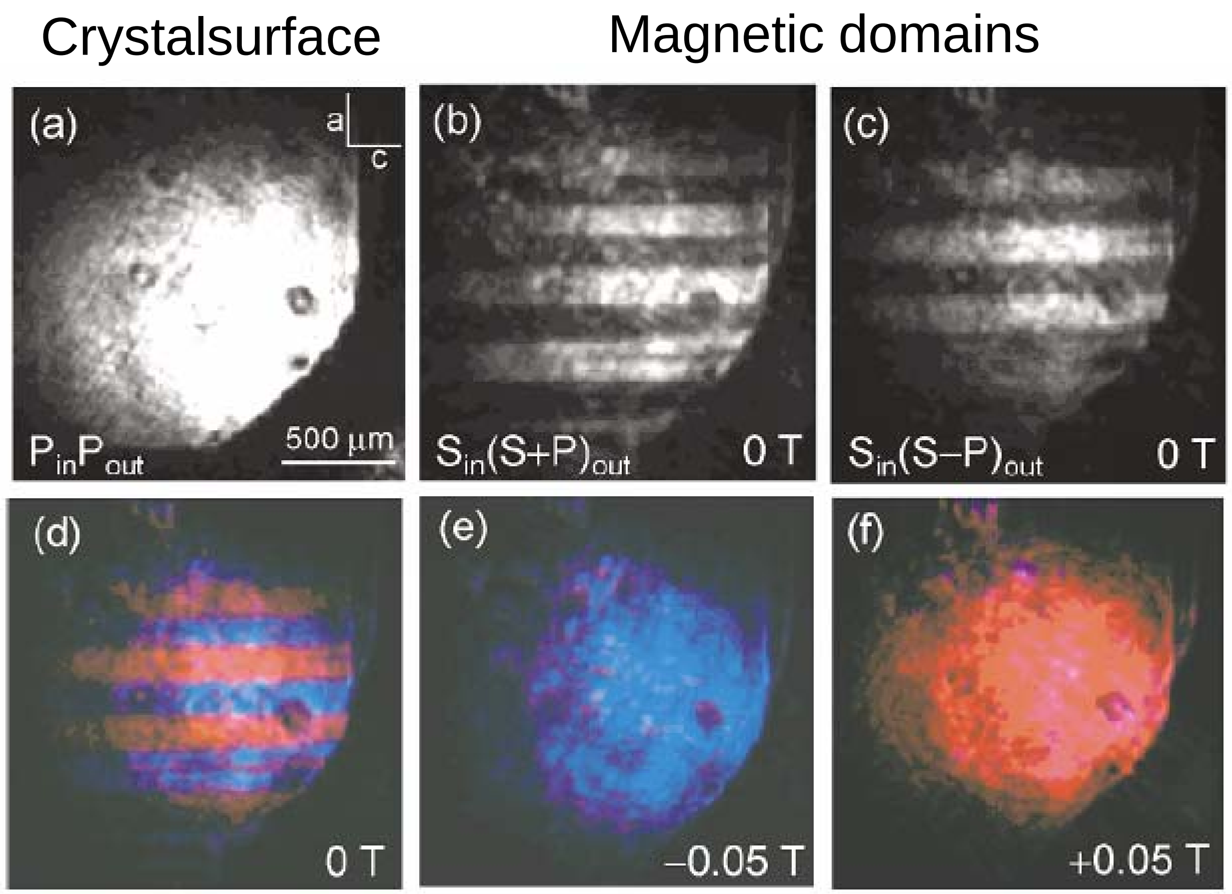
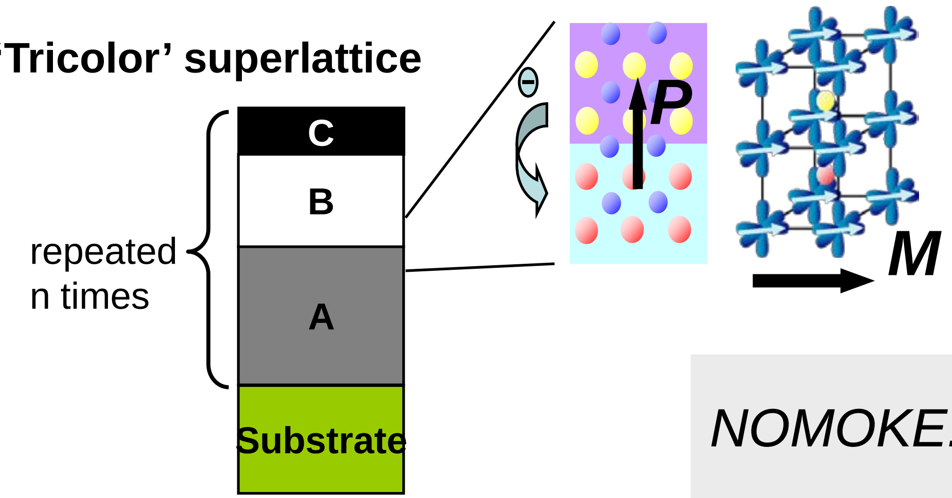
Magnetic Domain Imaging



Ogawa, et.al., Phys. Rev. Lett. 92, 047401 (2004)

Interface Sensitivity

'Tricolor' superlattice



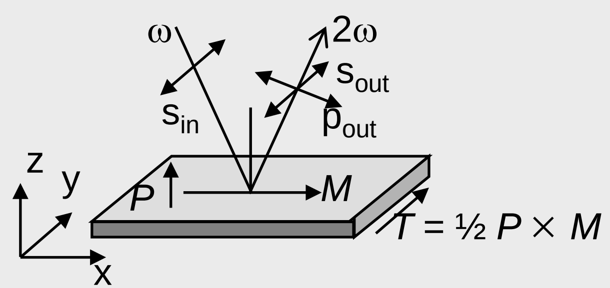
Transition metal oxide superlattices:

Charge transfer ⇒ **polarization**

orbital ordering ⇒ **magnetization**

NOMOKE:

$$\tan\phi = \frac{P_s^m}{P_p^{nm}\tan\Theta}$$



Time & spatial inversion symmetry only broken at AB-interface ⇒ **SHG**

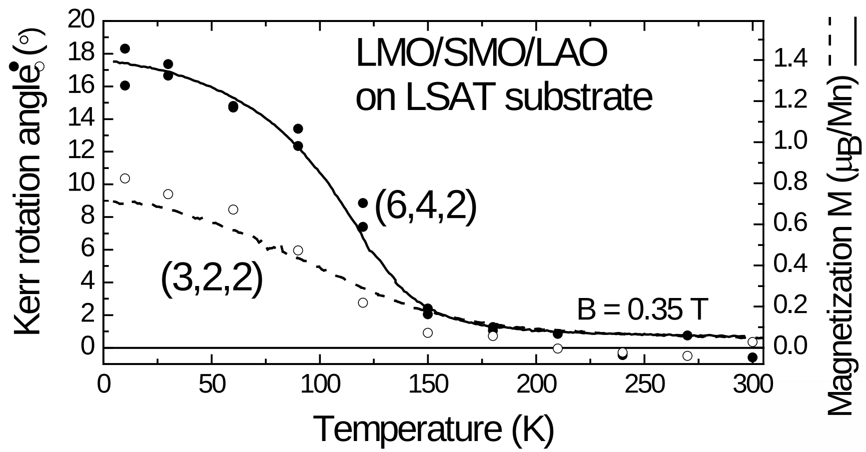
Polarization SHG ∝ *P*

$$P_p^{nm}(2\omega) \propto \chi^{nm} E_s(\omega) E_s(\omega)$$

Magnetic SHG ∝ *T=P×M*

$$P_s^m(2\omega) \propto \chi^m E_s(\omega) E_s(\omega)$$

$\chi^m := \chi^m$(B)



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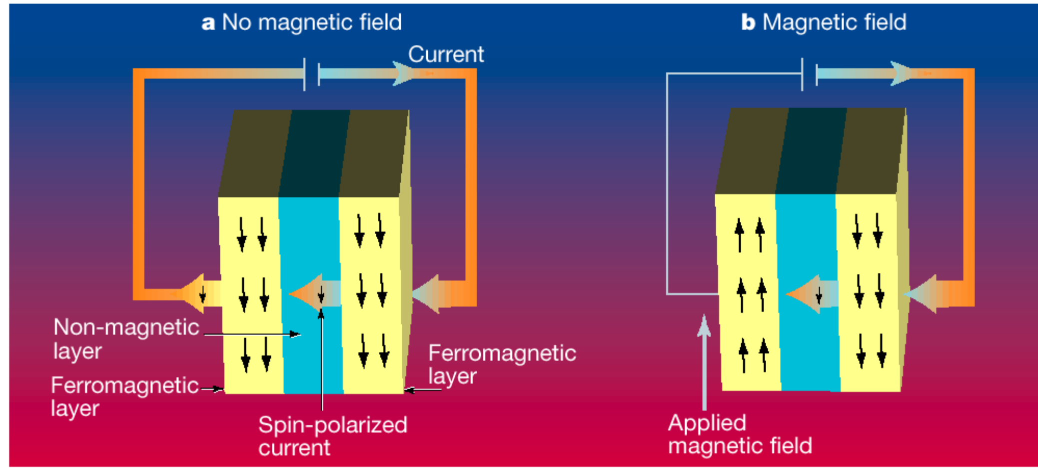
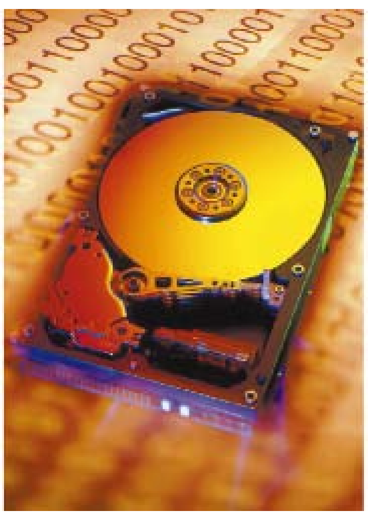
Part III - Experimental Techniques

Ultrafast nonlinear optics

Technological Needs

- data storage
- data transfer
- etc.





Where are the physical limits?

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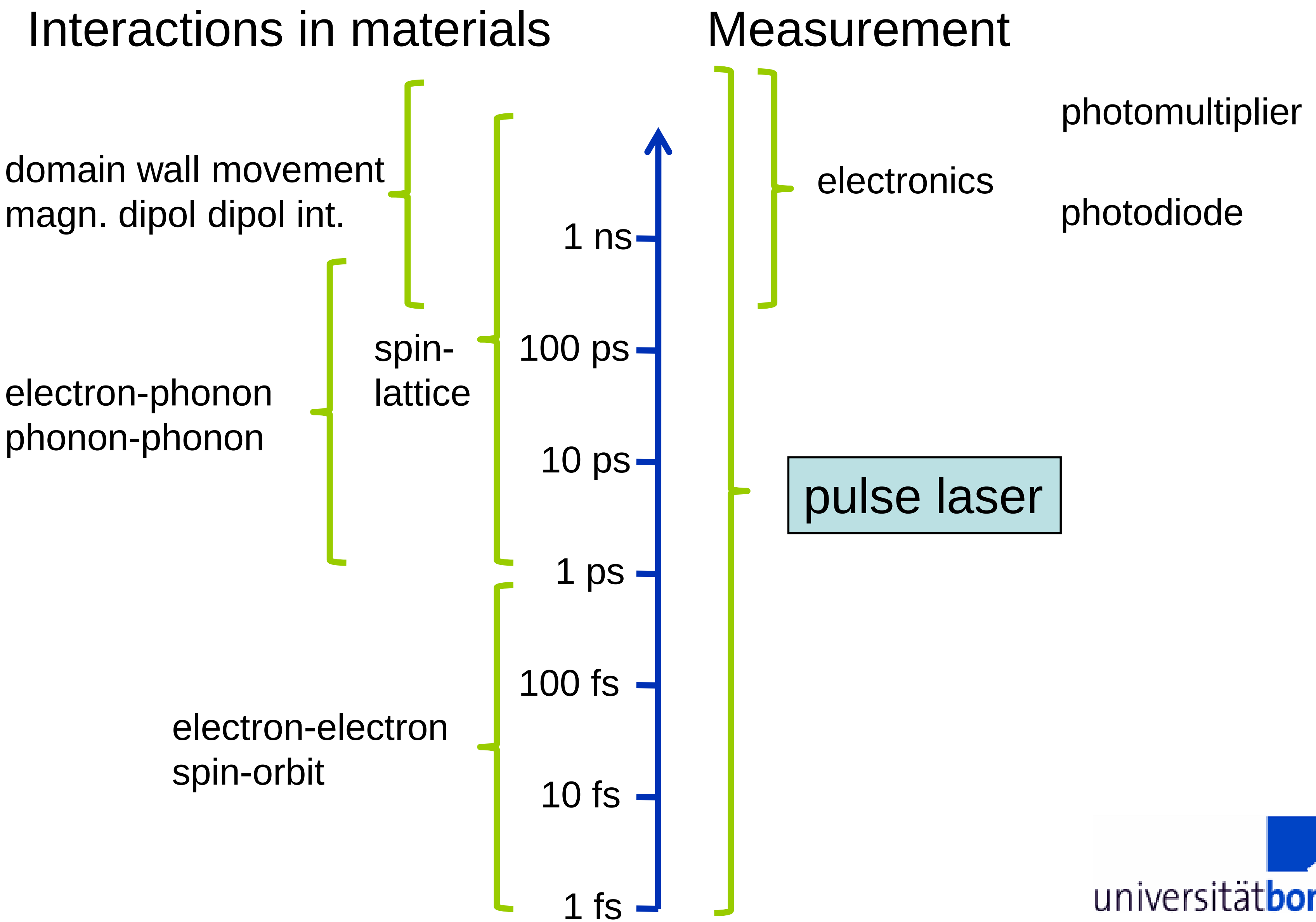
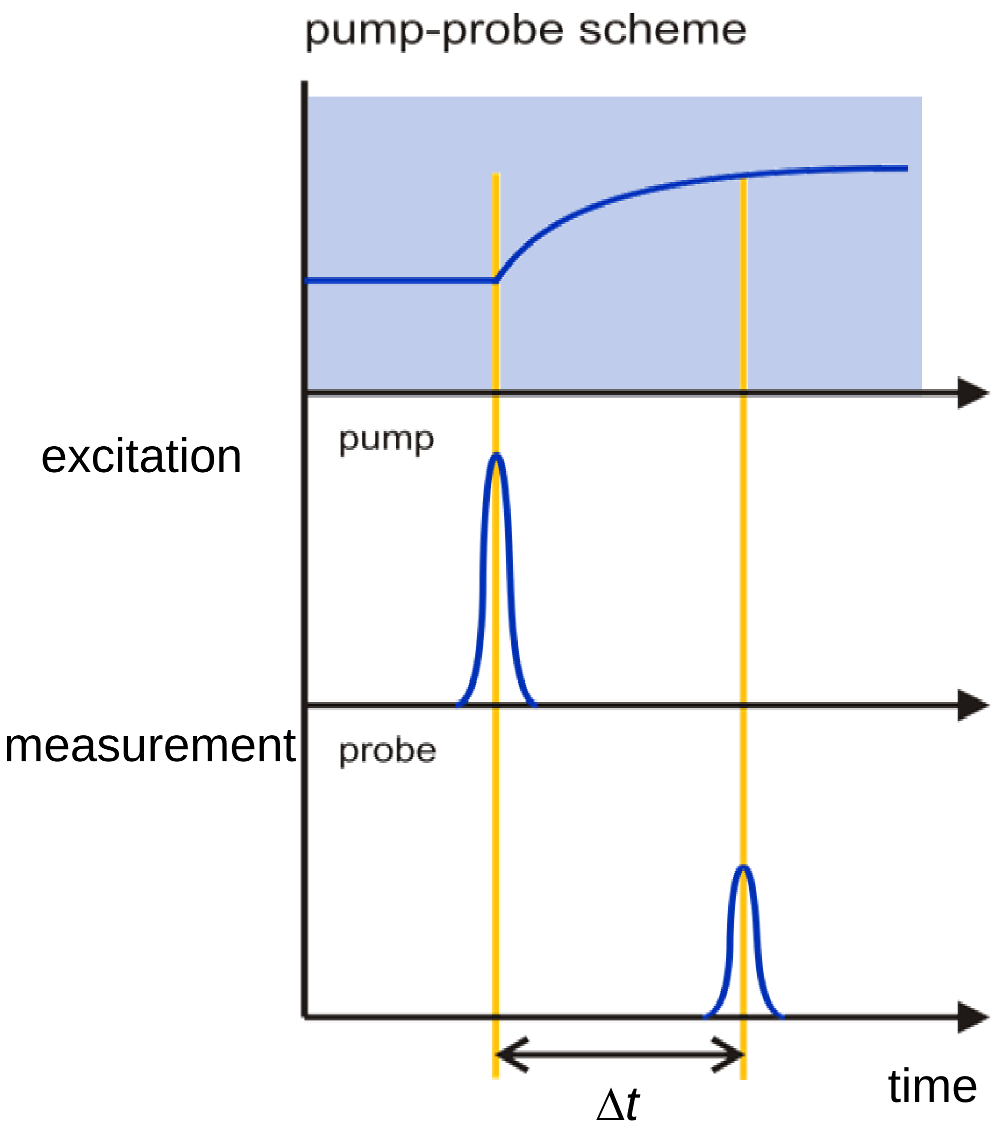
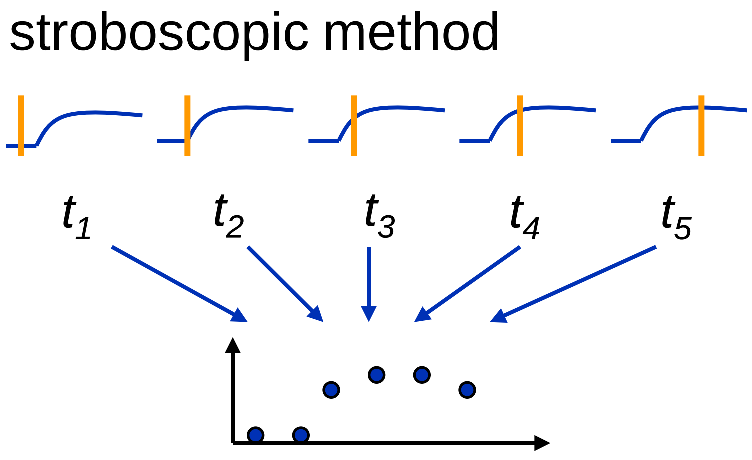
Timescales


Interactions in materials
Measurement
photomultiplier
domain wall movement
magn. dipol dipol int.
electronics
photodiode
1 ns
spin-
lattice
100 ps
electron-phonon
phonon-phonon
10 ps
pulse laser
1 ps
100 fs
electron-electron
spin-orbit
10 fs
1 fs

Time Resolved Pump-Probe Experiments





Excitation

- optic
- magnetic
- etc.

Measurement

linear/**nonlinear** optical effects

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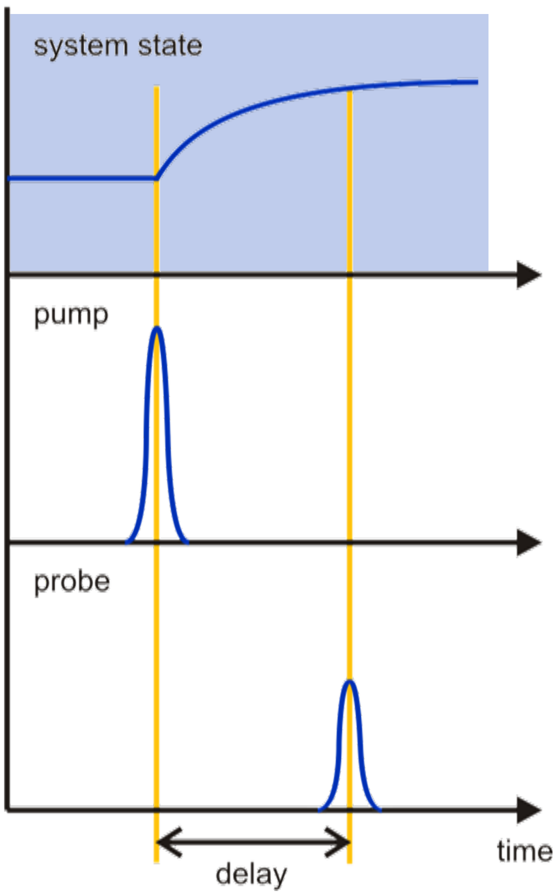
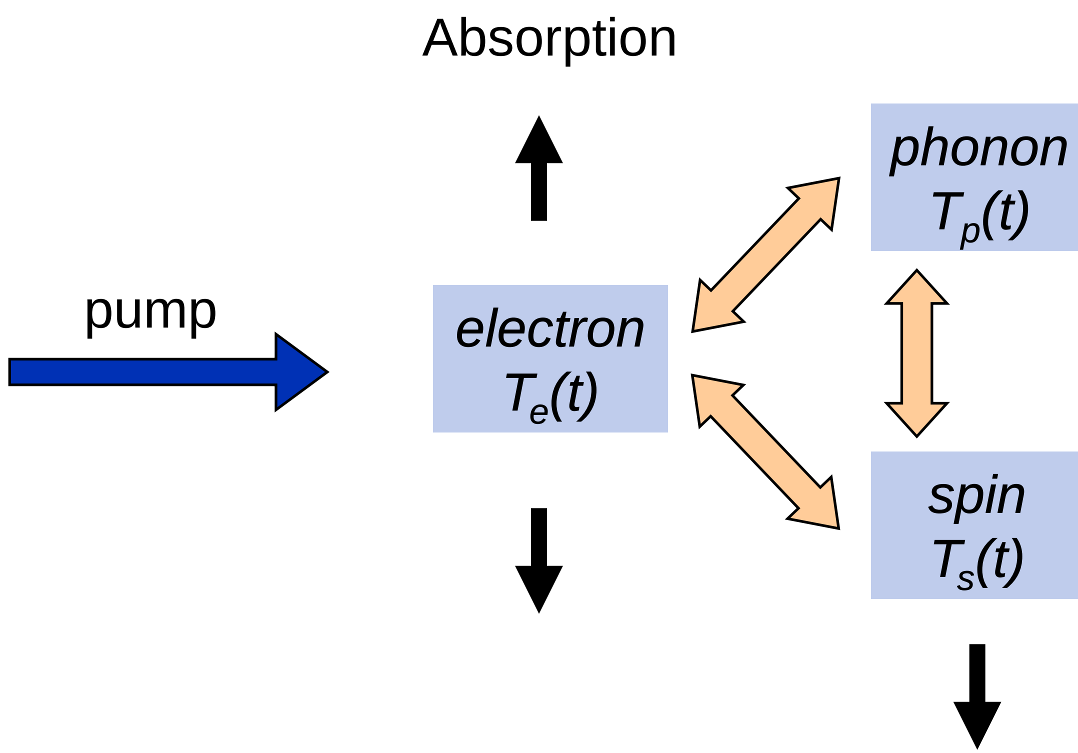
Three-Temperature Modell

pump-probe scheme





Crystallographic SHG

$P(t) \sim \chi^e[T_e(t)]\, E\, E$

Magnetic SHG

$\boldsymbol{P(t) \sim \chi^m[T_s(t)]\, E\, E}$

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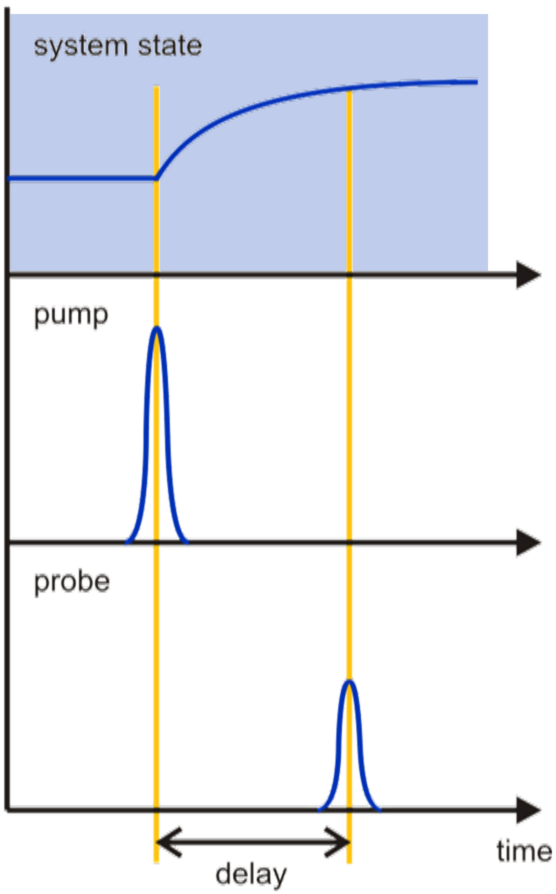
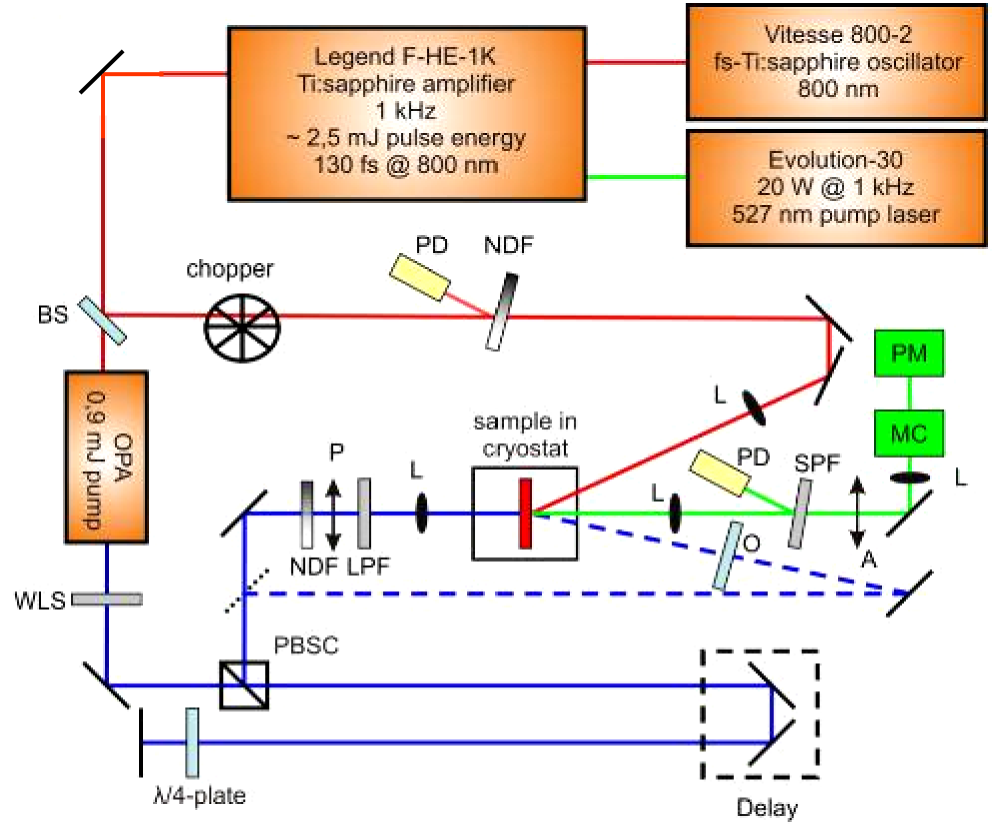
Experimental Setup

pump-probe scheme



Time



BS: Beamplitter
OPA: Optical Parametric Amplifier
WLS: Wavelength Separator
GT: Glan-Taylor-Prism
NDF: Neutral Density Filter
LPF: Long Pass Filter
SPF: Short Pass Filter
FM: Flip Mirror

P: Polarizer
A: Analyzer
L: Lens
PBSC: Polarizing Beamsplitter Cube
PD: Photodiode
MC: Monochromator
PM: Photomultiplier
O: identical optics to transmission

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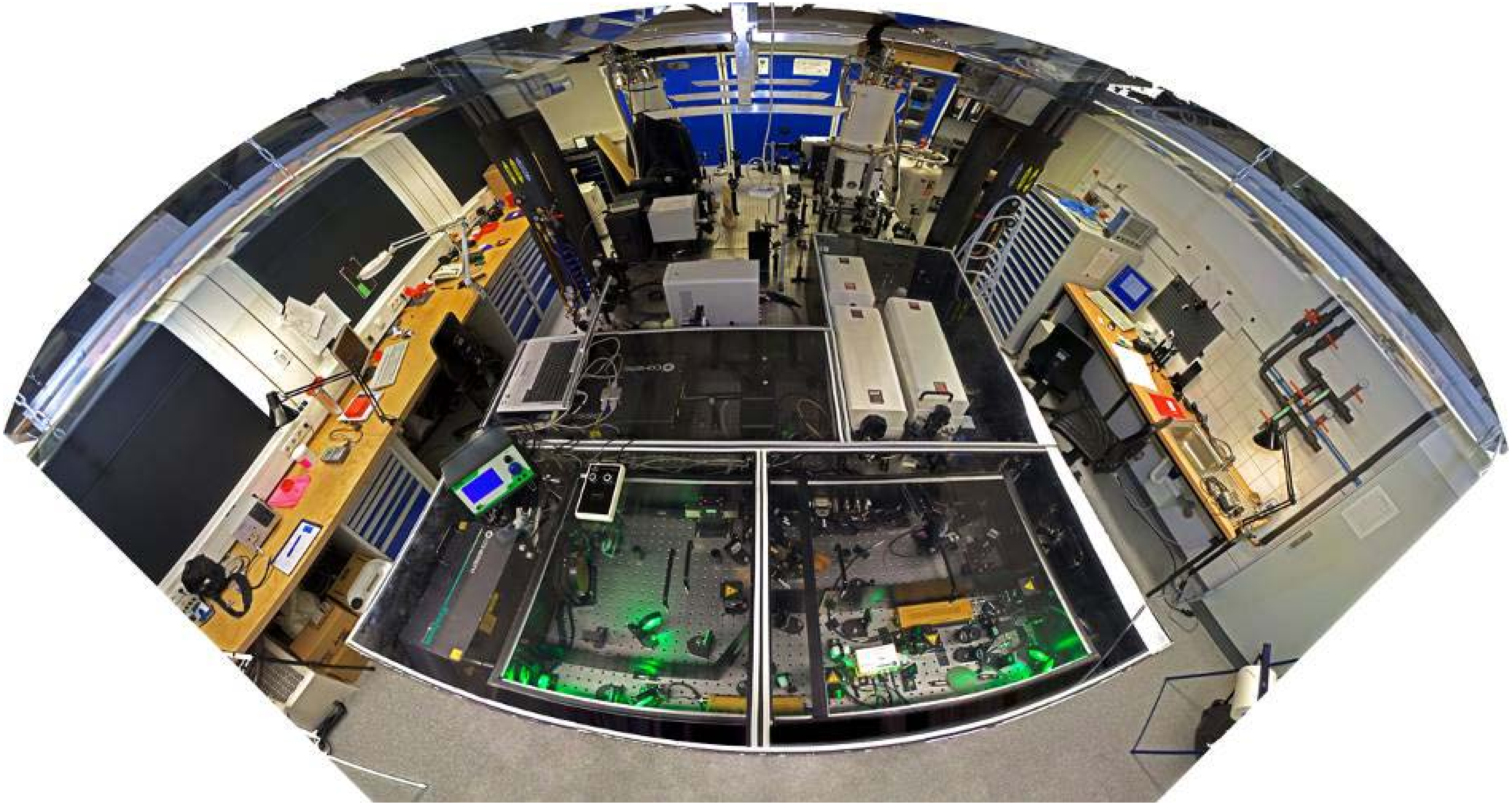
fs-Laser System



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