Characterization techniques for nanostructured materials and their pitfalls

(ECONAM FP7 project)

Lecturer: Constantin R. Simovski

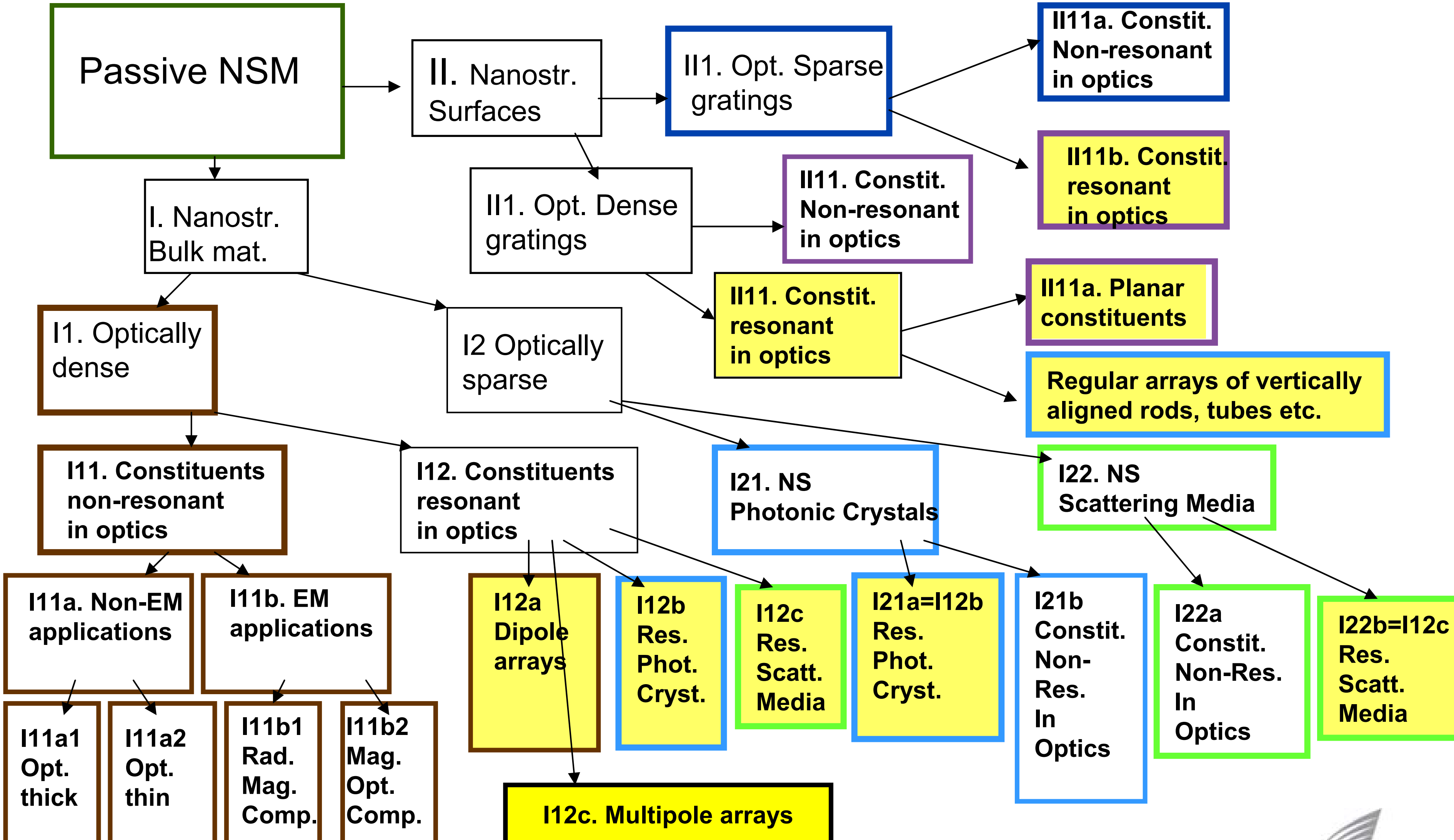
Dec. 10 2009

TKK

Classification of nanostructured materials (NSM) by their linear EM properties. Text

- Bulk passive structures **(N>4-5 Unit Cells)**
- **Optically dense bulk structures d<<λ**
- **Non-resonant materials:**
- **Non-EM applications, EM applications,**
- **Thick films, optically large samples, Thin films and island films,**
- **Radiofrequency Magnetic Media and Nanomagnets, Magneto-Optical Media**
- **Plasmonic and polaritonic MTM:**
- **Dipole arrays, Multipole arrays, Resonant Photonic Crystals, Resonant scattering media**
- **Optically sparse bulk structures d~>λ**
- **Nanostructured Photonic Crystals, Scattering media (resonant and non-resonant)**
- Surface passive structures **(N<4-5 Unit Cells)**
- **d<<λ Dense gratings d~>λ Diffraction gratings,**
- **Non-resonant, Resonant**
- **Planar MTM, Vertically Aligned Nanorods**
- Active nanostructures **(of quantum dots and wires, dye-doped nanoporous and liquid crystals matrices, etc). Out of scope**

Classification of NanoStructured Materials (NSM) by their linear EM properties. Chart



Explanation of the chart

Metamaterials

Scattering (non-transparent) media
Adopted optical characterization: QE, QA

Bulk uniform concentration media

Adopted optical characterization: ε, radio characterization: ε, μ .
(Bianisotropy is out of scope)

Photonic crystals/EBG
Adopted optical/ radio characterization: stopbands (bandgaps).
Additionally: Brillouin dispersion diagram, Fresnel isofrequency surfaces.

Diffraction gratings
Adopted optical characterization: $D(\lambda,m)$, $\Delta\lambda(m)$, $I_{norm.}(\lambda,m)$

Mesoscopic layers
Adopted optical characterization: QE, QA, $|R(\lambda)|$, $|T(\lambda)|$

Pitfalls (observations from literature survey)

- Referring a metamaterial to a wrong class. (Diffraction gratings, mesoscopic layers, photonic crystals described as a bulk medium sample)

  100s papers. A book

- Ignoring the anisotropy. (Treating a component of material parameter tensor as an isotropic ε or μ)

  10s papers. A book

Ignoring the bianisotropy. (Describing the bianisotropic material in terms of only ε and μ)

  Some papers

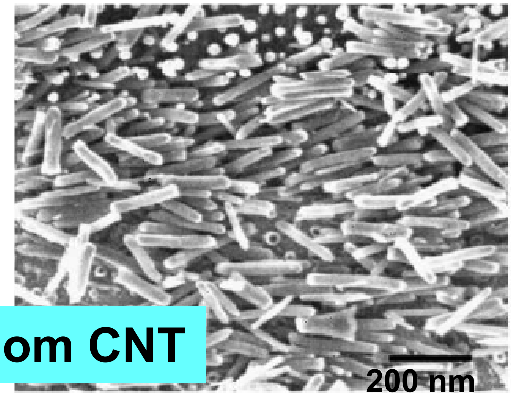
- Ignoring spatial dispersion effects in dipole-type bulk metamaterials

  10s papers. 2 books

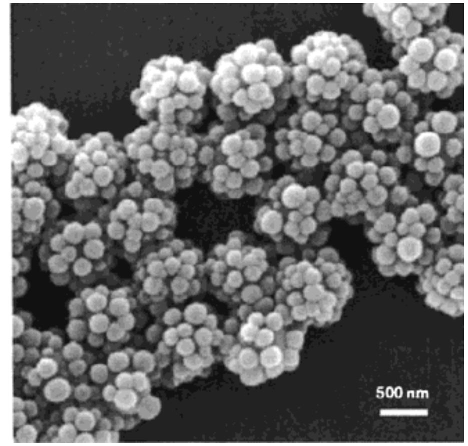
- Ignoring the problem of the spread boundary of bulk metamaterial samples 100s papers.

100s papers. 3 books

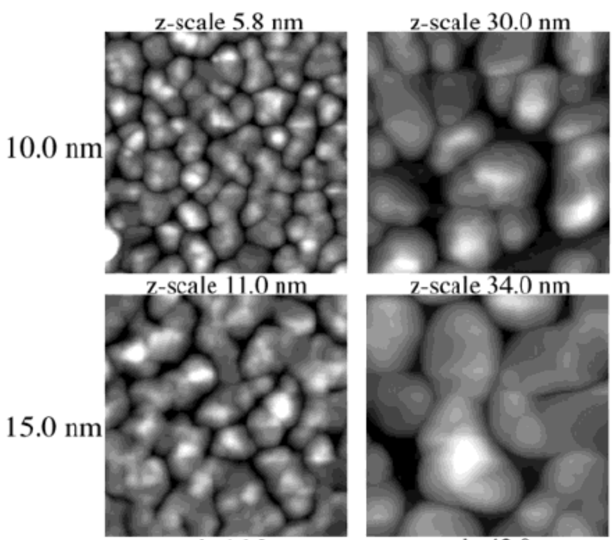
Scattering media (incl. Plasmonic)



Random CNT

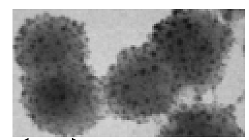


SiO2 Rasp-berries



Clusters of nanoislands and nanoparticles

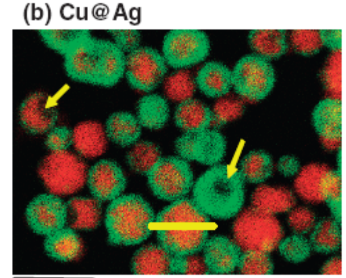
Clusters of nanoclusters



100 nm

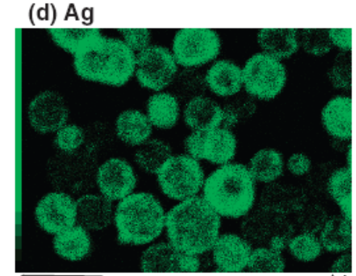
Au Nano-Particles /Si core

(b) Cu@Ag



200 nm

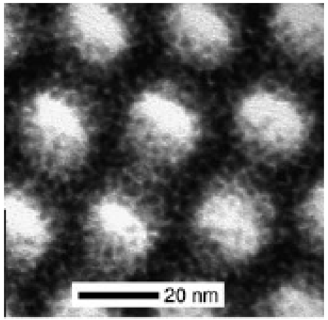
(d) Ag



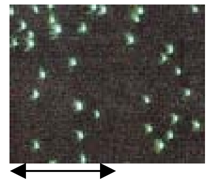
200 nm

Bulk plasmonic, d<<λ
1)g~d Dipole materials. 2 g<<d Photonic crystals

Regular **Random**



Dipole MTM (modest resonant slow-wave factor)

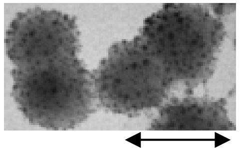


200 nm

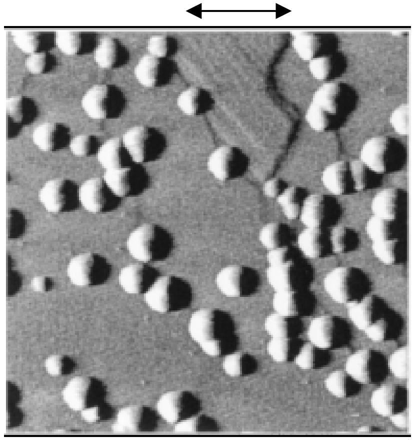
Colloids of Au (Ag) NanoParticles

Bulk lattices: Au particles 15 nm

Colloids of Au Core-shell Nanoclusters

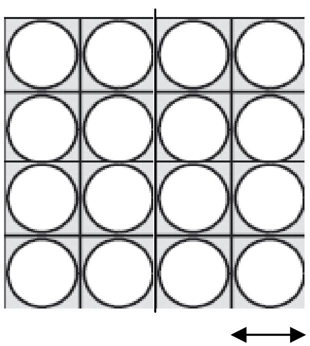


100 nm



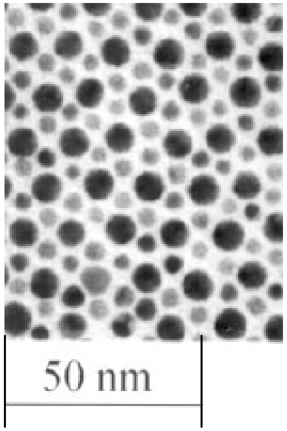
Multilayer/random Ag or Au NanoParticles

Scattering Media with Resonant Absorption



50 nm

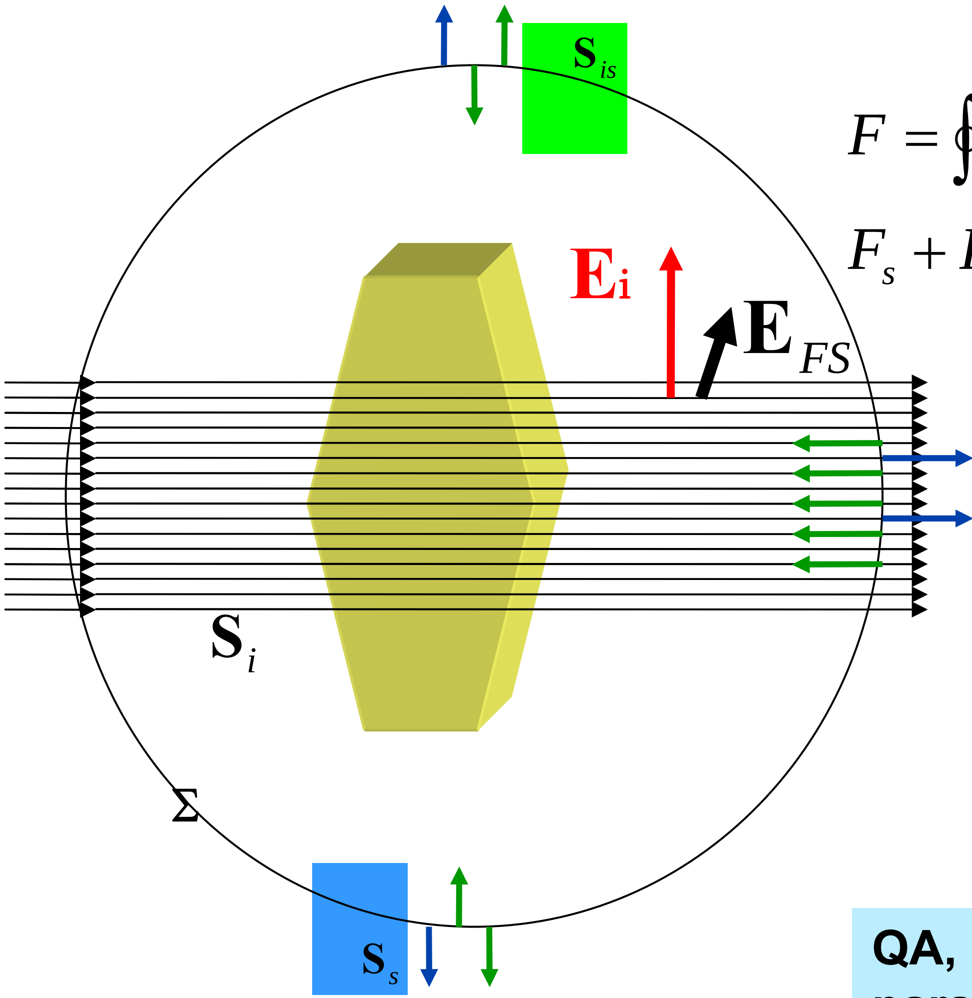
Bulk porous lattice (Ag matrix)



Alternating Ag Particles 10+5 nm

Plasmonic Photonic Crystals (High resonant slow wave factor)

Scattering sample's characterization: absorption, extinction, scattering cross sections



$$F = \oint \mathbf{S} \cdot d\boldsymbol{\Sigma}, \quad F = F_s + F_i + F_{is} = F_s + F_{is},$$

$$F_s + F_{is} - W_a = 0, \quad F_{is} \propto \mathrm{Im}(\mathbf{E}_{FS} \cdot \mathbf{E}^*{}_i)$$

$$QA = \frac{W_a}{E^2{}_i} = \frac{F}{E^2{}_i}, \quad QS = \frac{W_s}{E^2{}_i}$$

$$QE = \propto \frac{\mathrm{Im}(\mathbf{E}_{FS} \cdot \mathbf{E}_i)}{E_i{}^2} = \frac{W_a + W_s}{E_i{}^2}$$

QA, QS,QE – mesoscopic parameters

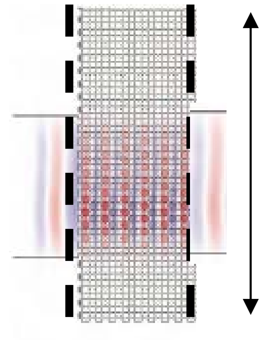
Photonic crystals experimental characterization

Usually - validation of simulations!

|R|

Detector (Spectrometer)

beamwidth~(2-5)λ



Detector (Spectrometer), rarely- interferometer

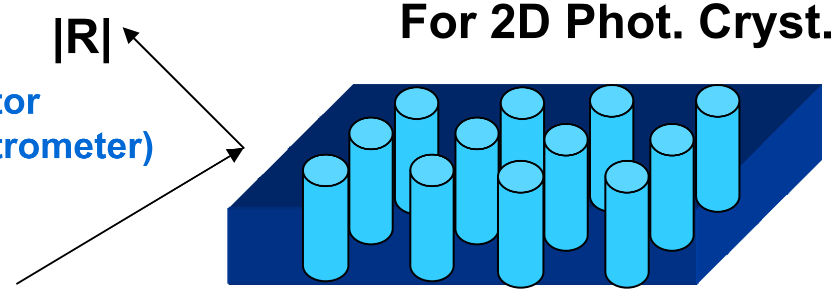
|T|, rarely- phase(T)

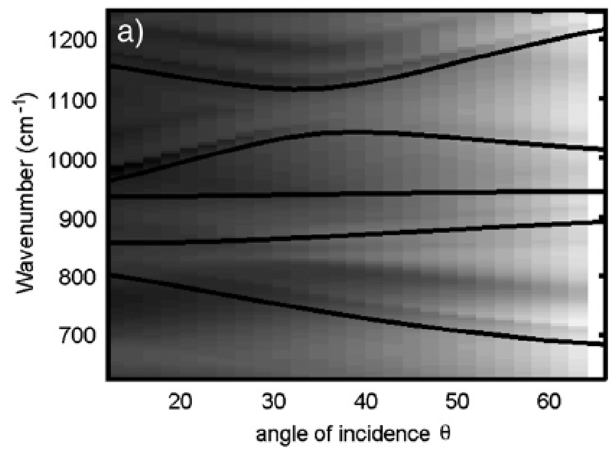
1. **Band-gaps detection [56].**
2. **For low-loss structures: phase(T) – dispersion along ΓX [57]**

For 2D Phot. Cryst.

|R|

Detector (Spectrometer)





Band-gaps detection [58]

Photonic crystals treated as media

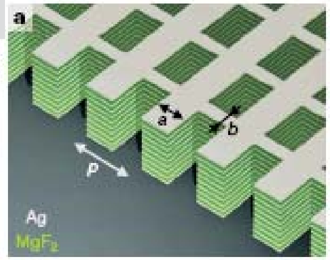
doi:10.1038/nature07247

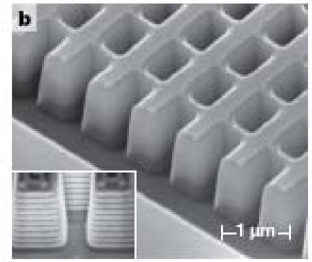
nature LETTERS

Not acceptable!

Three-dimensional optical metamaterial with a negative refractive index

Jason Valentine[1]*, Shuang Zhang[1]*, Thomas Zentgraf[1]*, Erick Ulin-Avila[1], Dentcho A. Genov[1], Guy Bartal[1] & Xiang Zhang[1,2]





unit cell of $p = 860$ nm, λ of 1,475 nm, the index of refraction is approaching zero

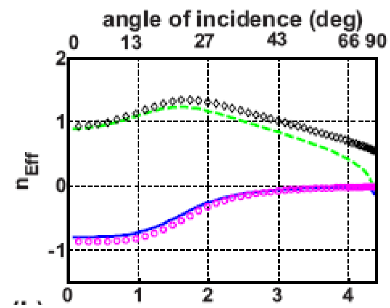
PHYSICAL REVIEW B 78, 155102 (2008)

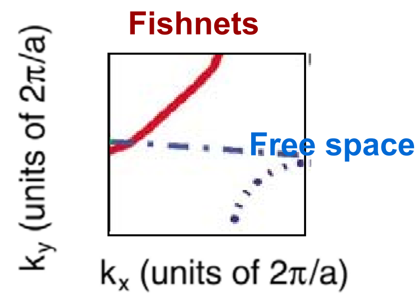
Light propagation in a fishnet metamaterial

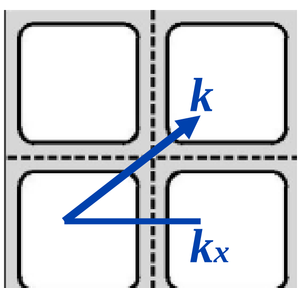
Analytical theory of wave propagation through stacked fishnet metamaterials

R. Marqués,[1]* L. Jelinek,[1] F. Mesa,[2] and F. Medina[1]

6 July 2009 / Vol. 17, No. 14 / OPTICS EXPRESS 11582







Cladding
(ε_c=10+*i*1)

Acceptable

PHYSICAL REVIEW B 67, 035109 (2003)

Photonic approach to making a material with a negative index of refraction

Gennady Shvets

$$\epsilon_{\rm eff}=\left(\frac{1}{\chi_p}+\frac{1-\cos\chi_v b}{\chi_v \sin\chi_v b}\right)\left(\frac{1}{\epsilon_c\chi_p}+\frac{1-\cos\chi_v b}{\chi_v\sin\chi_v b}\right)^{-1},$$

$$\chi_v=\sqrt{\omega^2/c^2-k_x^2},\quad \chi_p=\sqrt{k_x^2-\epsilon_c\omega^2/c^2}$$

$$\mu_{\rm eff}=1-\frac{c^2\chi_x}{\omega^2\sin\chi_v b}\left(\frac{1}{\epsilon_c\chi_p}+\frac{1-\cos\chi_v b}{\chi_v\sin\chi_v b}\right)^{-1},$$

$$Z\neq\sqrt{\mu_{eff}/\varepsilon_{eff}}$$

ABC are required

Photonic crystal mimics the homogeneous medium only under

- **2 conditions:**
- **Geom. isotropic lattice**
- **Special environment**

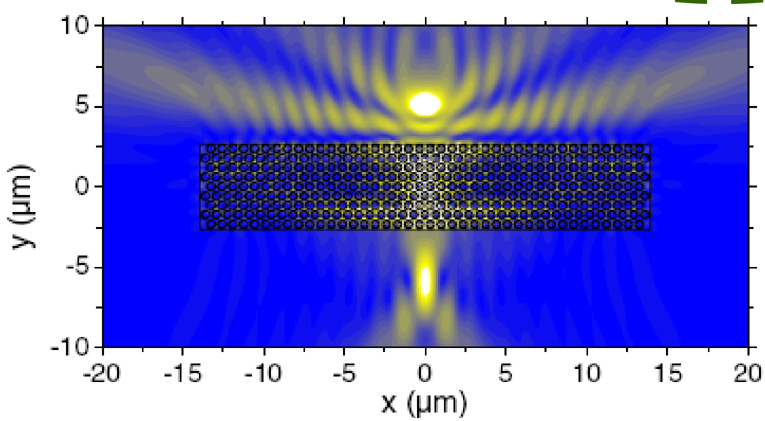
PRL **97**, 073905 (2006)

Photonic Crystal Lens: From Negative Refraction and Negative Index to Negative Permittivity and Permeability

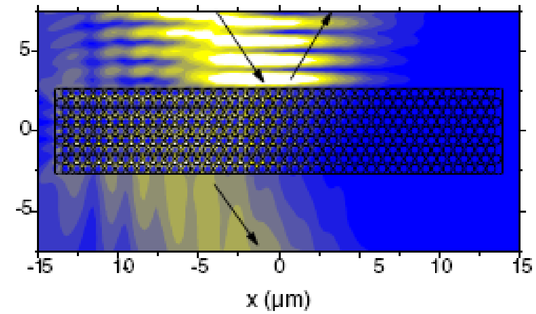
T. Decoopman,[1,2] G. Tayeb,[1] S. Enoch,[1] D. Maystre,[1] and B. Gralak[1]

electric field when the structure is surrounded by a homogeneous material with $\varepsilon = 5.7$ and $\mu = 0.175$ (both positive), i.e., a material having the same impedance as in

our interpretation is that in our case the photonic crystal mimics a homogeneous material with $\mu_{\rm eff} = 1/\varepsilon_{\rm eff} \neq -1$.



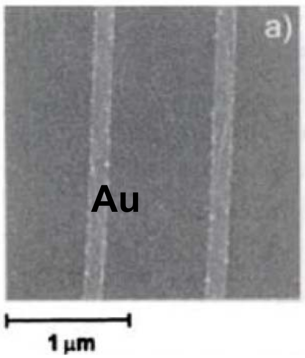
λ=2.5 μm

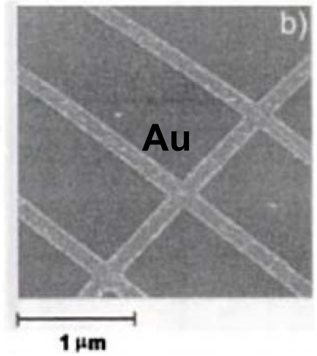


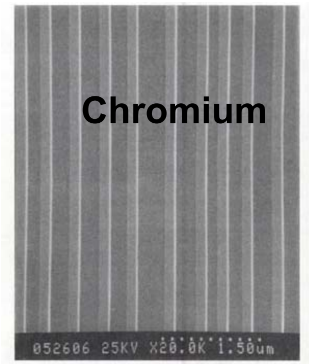
Vacuum surround. Negative refraction but no subwavelength effects

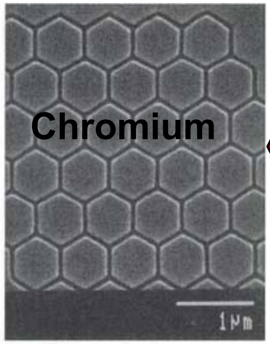
Special medium surround: a weakly subwavelength image arises

Diffraction gratings

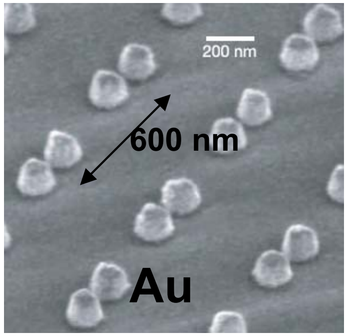


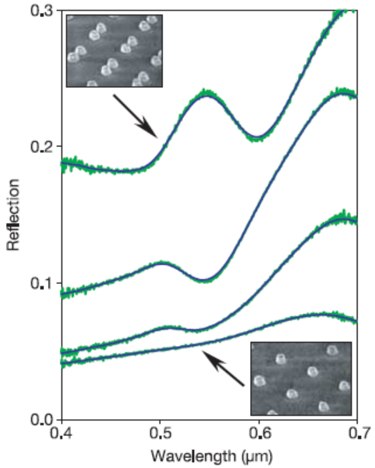




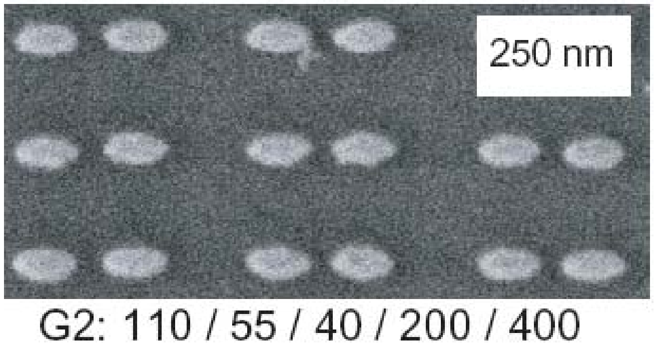


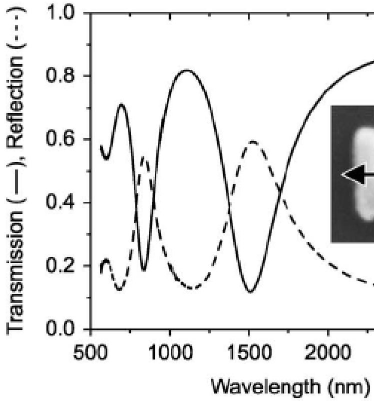
Handbook of microscopy for nanotechnology (N. Yao, Z.L. Wang 2005 Kluwer)





(Grigorenko 2005)

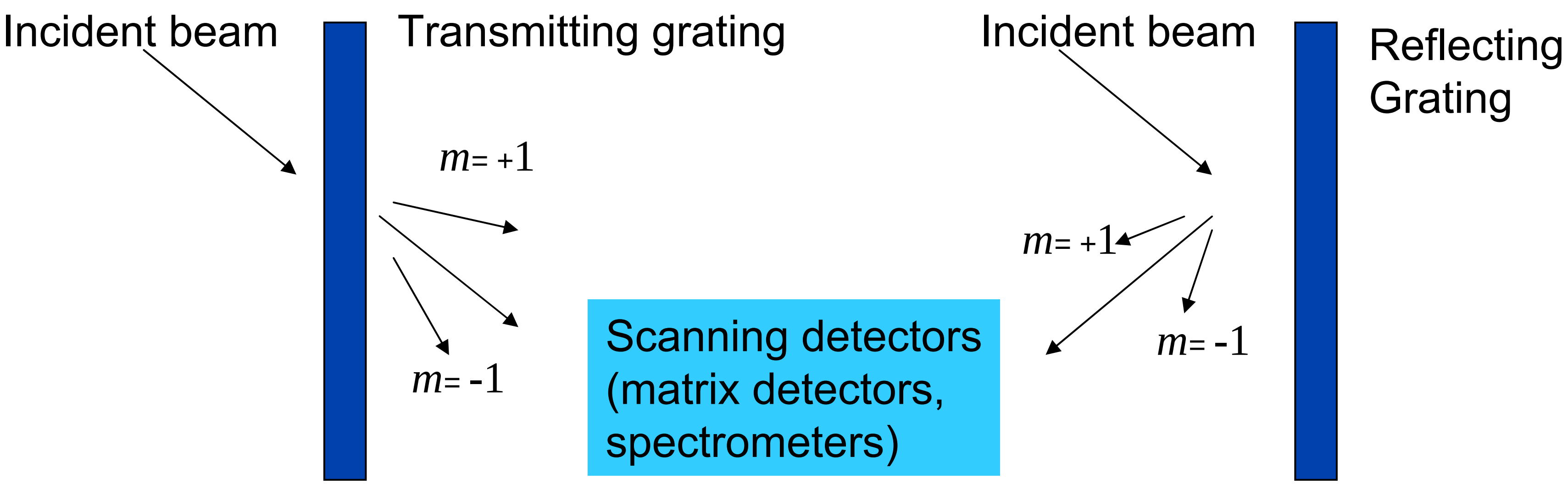




(Shalaev, 2003)

Characterization of diffraction gratings

- Normal incidence $\lambda > d$, oblique incidence $\lambda > 2d$:
- $|R|$ or $|T|$ (λ). Plasmonic gratings: absorption at Wood anomalies $Wa = 1 - |R|^2 - |T|^2$.
- Normal incidence $\lambda < d$, Oblique incidence $\lambda < 2d$:
- Angular dispersion $D(\lambda, m)$, where $m = \pm 1 .. \pm [d/\lambda]$ grating spectral orders.
- 3. Free intervals of dispersion $\Delta\lambda(m)$. 4. Normalized intensity distribution $I_{max}(\lambda, m)$.



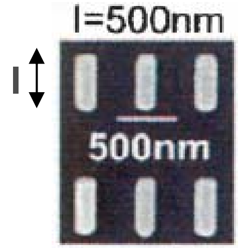
Diffraction gratings treated as bulk media

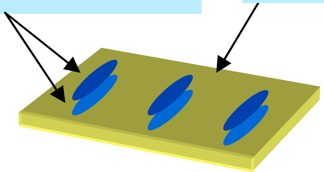
3198 OPTICS LETTERS / Vol. 30, No. 23 / December 1, 2005

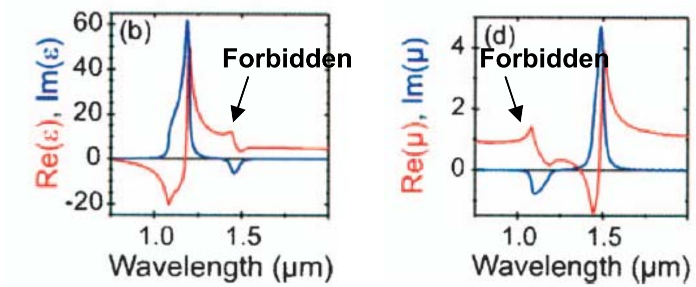
Cut-wire pairs and plate pairs as magnetic atoms for optical metamaterials

G. Dolling, C. Enkrich, and M. Wegener
Institut für Angewandte Physik, Universität Karlsruhe (TH), Wolfgang-Gaede-Strasse 1, D-76131 Karlsruhe, Germany

J. F. Zhou and C. M. Soukoulis*





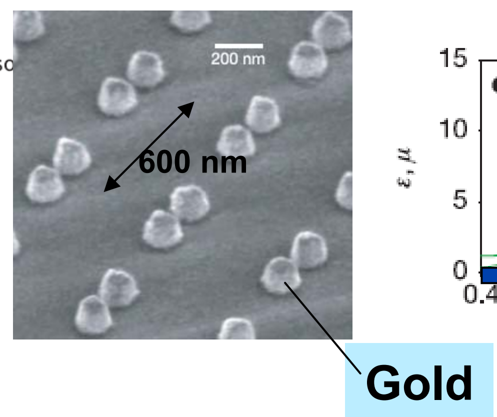


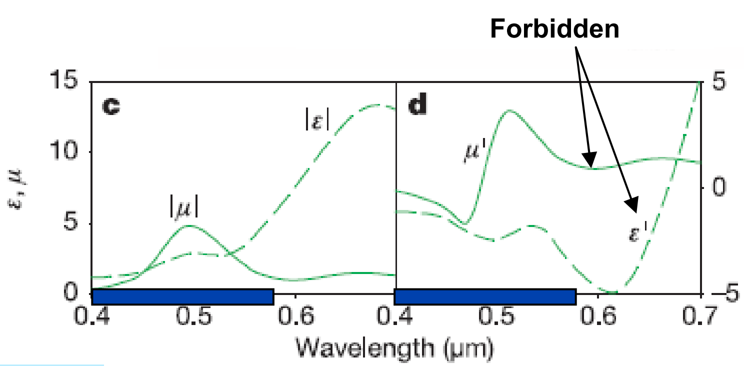
nature

Nanofabricated media with negative permeability at visible frequencies

A. N. Grigorenko[1], A. K. Geim[1], H. F. Gleeson[1], Y. Zhang[1], A. A. Firso

Vol 438|17 November 2005|**doi:10.1038/nature04242**





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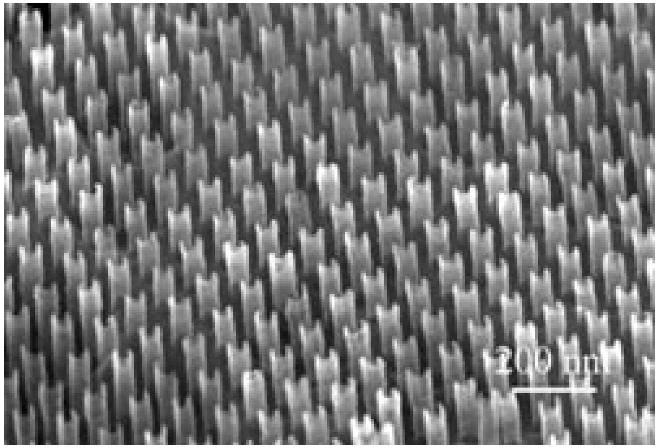
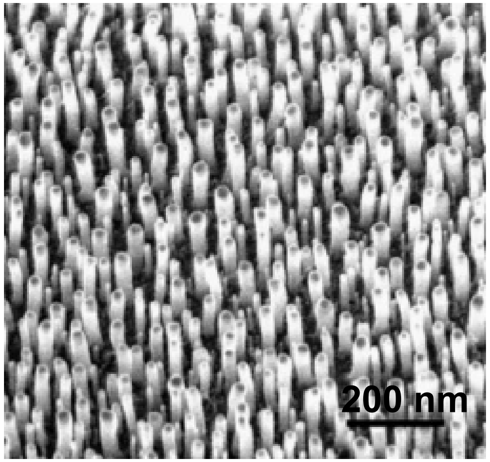
Vertically aligned nanorods



Plasmonic (gold) nanorods



CNT

Other vertically aligned Nanorods (InP, TiO2 etc)

Modest slow-wave factor

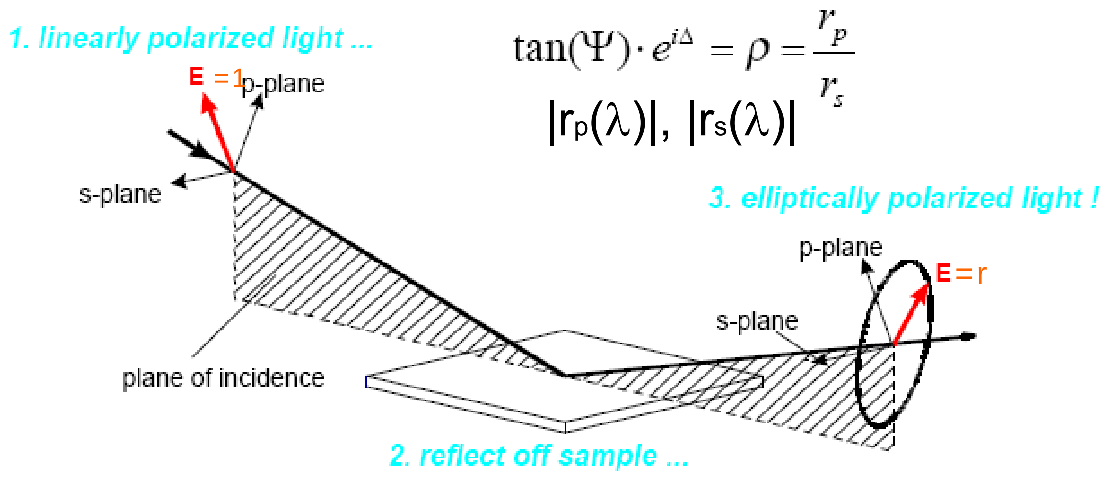
Can be treated as uniaxial dielectric if period<<λ

Huge slow-wave factor (>100)

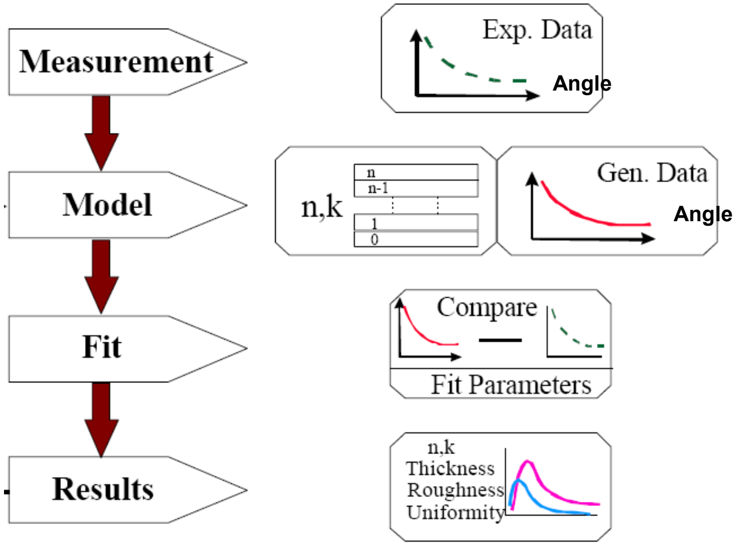
Wire medium
ABC are obviously required

VASE

Variable-Angle-Spectrometric Ellipsometry



Basic configuration for reflection ellipsometry.



Known fitting procedure implies:

1. **Bulk medium (at least 5-6 molecules across)**
2. **Not metamaterials (μ=1)**

Characterization techniques for plasmonic and CNT nanostructured surfaces

Reported experiments:

MTM with planar plasmonic elements, N=1-2: a) **Used method: NRW. Results: Not adequate.**

b) Used method: spectroscopy. Results: Incomplete.

1. Grids of verticaly aligned plasmonic nanorods. Spectroscopy. Incomplete. Verticaly aligned CNT. No results

Reported theory:

1. Holloway et al.: surface electric and magnetic tensor susceptbility. Simovski: electric and magnetic grid impedance.

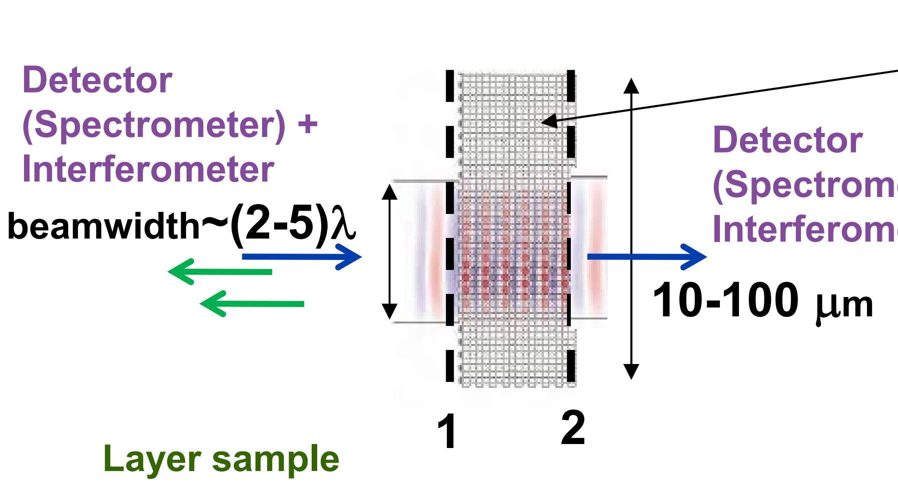
Not sufficiently developed and never checked

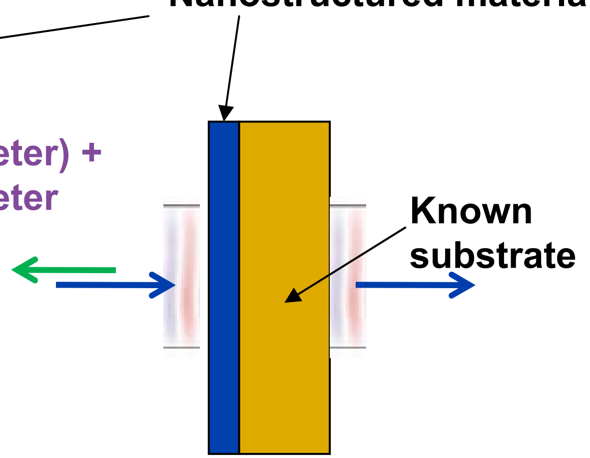
2. Plasmonic nanowires and CNT.

Wire medium models with tensor $\varepsilon(q)$. Insufficiently developed: (no additional boundary conditions)

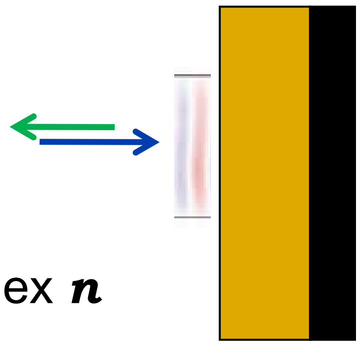
Nicholson-Ross-Weir (NRW) technique in optics

Complex **R, T** ➡ n, $Z = \sqrt{\mu/\varepsilon}$





1952, Schopper

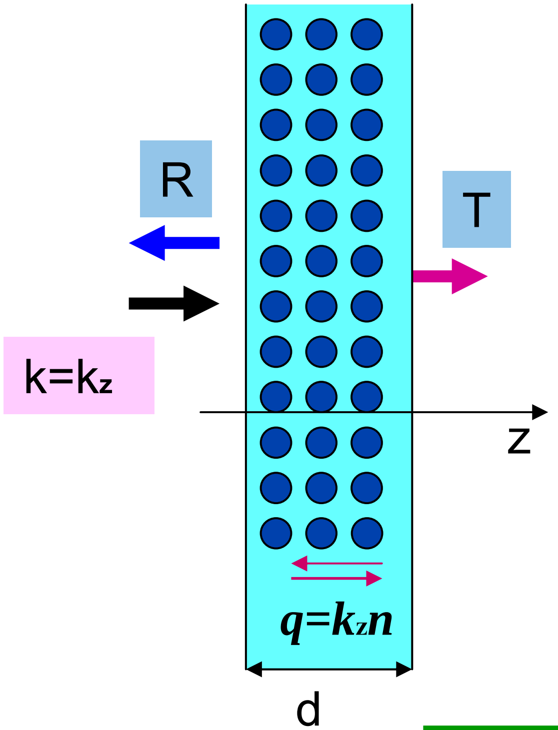


Complex **R** ➡ Complex n

Weakly dispersive n (see O. Heavens, Optics of Thin Films)

NRW method (theory for uniform slabs)

Replace the finite-thickness lattice by an "equivalent" continuous layer



$$T = \left[\cos(nk_z d) - \frac{i}{2}\left(Z + \frac{1}{Z}\right)\sin(nk_z d)\right]^{-1} e^{-ik_z d},$$

$$R = \frac{-i}{2}\left(Z - \frac{1}{Z}\right)\sin(nk_z d)\,T\,e^{ik_z d},$$

Then:

$$n = \pm\cos^{-1}\left(\frac{1 - r^2 - t^2}{2t}\right),$$

$$Z = \pm\left[\frac{(1+r)^2 - t^2}{(1-r)^2 - t^2}\right]^{1/2},$$

where $r = R$ and $t = T\,e^{ik_z d}$

$$\epsilon_{eff} = n/z$$

$$\mu_{eff} = nz$$

However, remember that

NRW was developed NOT for metamaterials!
Equivalence for a given case≠adequacy

Being applied for

1) **Non-bulk (surface) structures**
2) **Nanostructured photonic crystals**

and even

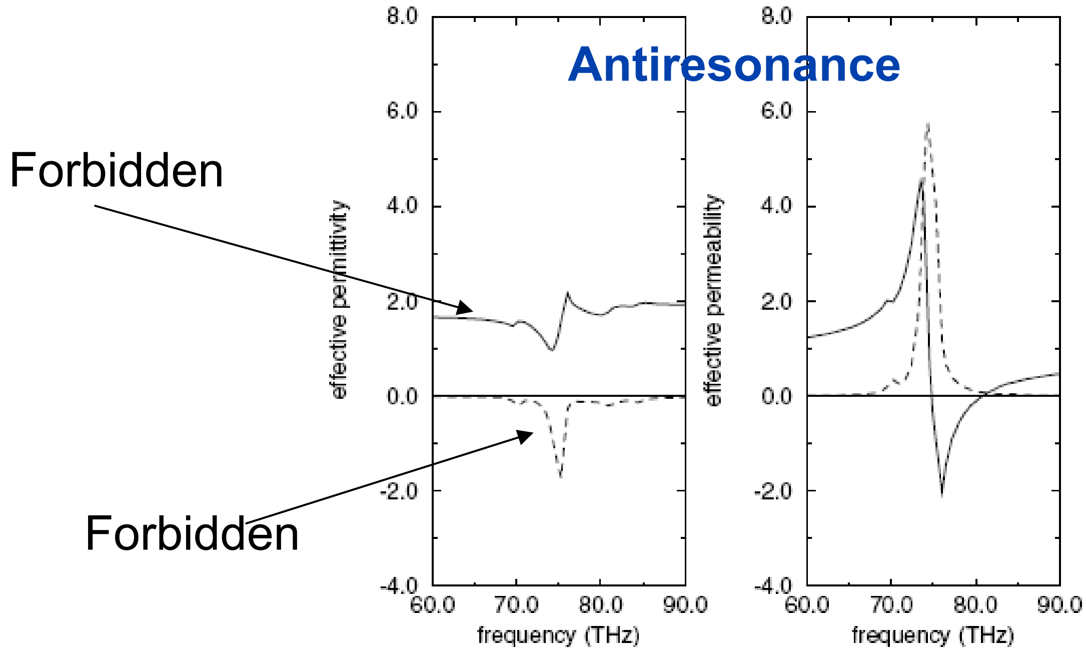
3) **Bulk nanostructured media with resonant constituents**

these method lead to ”beating the physical limits”= violation of physical laws.

TKK

Results of wrong applying the NRW method

- **Violation of locality (passivity, causality, II law of thermodynamics)**
- **Extracted ε and μ are not applicable for oblique incidence, for narrow wave beams, for evanescent waves**
- **Polaritons are neglected**



Similar results:

100s papers and 3 books

Experimental characterization for bulk plasmonic dipole MTM and plasmonic photonic crystals

Reported experiments:

1. Dipole plasmonic MTM. Used method: NRW. Results: indequate
2. Plasmonic photonic crystals. Used method: NRW. Results: indequate
3. Plasmonic diffraction gratings. Used method: ellipsometry. Results: indequate

Reported self-consistent theories:

1 Dipole plasmonic MTM:

1.1 Bulk (Simovski): Not sufficiently developed, not checked 1.2 Planar (Holloway et al.): The same

2. Plasmonic photonic crystals:

2.1. Gralak et al. Weakly developed, 2.2 Shvets-Urzhumov: Insufficiently developed, not checked 2.3 Silveirinha: The same

Reported controversial theory:

Arbitrary resonant lattices (Felbaq et al.).

Difficult to accept. Not checked

Correct characterization of dipole-type bulk metamaterials (no experimental results yet)

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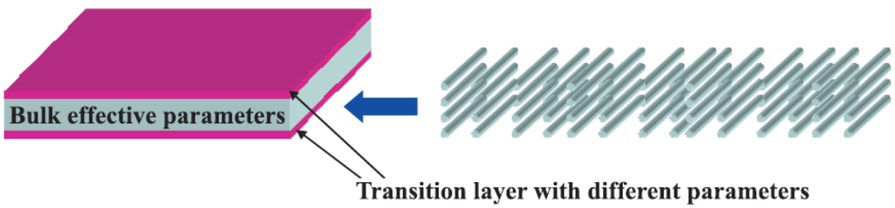
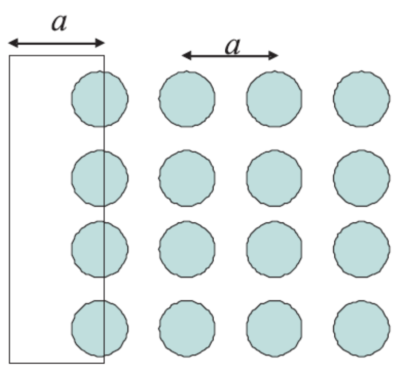
PHYSICAL OPTICS

Material Parameters of Metamaterials (a Review)

C. R. Simovski



Transition layers:
refraction index+ wave impedance



Same parameters as for the infinite lattice

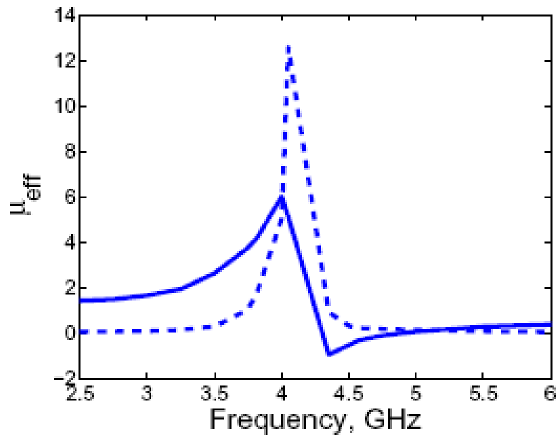
Resonant particles

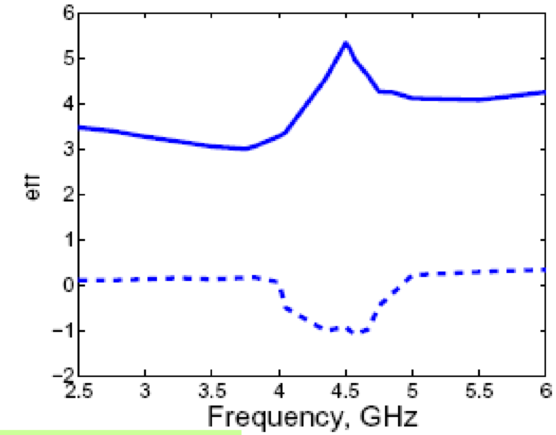
Antiresonance explanation

$$n^2 = \varepsilon_B \mu_B = \varepsilon_{stat.} \mu_L ,$$

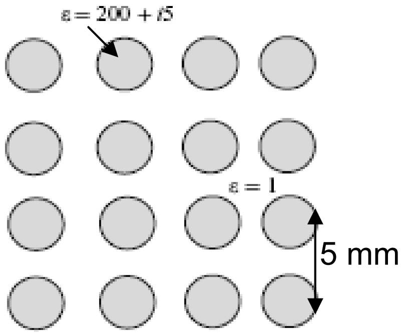
$$\varepsilon_B = \varepsilon_{stat.} \frac{1 + A\omega^2 / (\omega_0{}^2 - \omega^2 - i\Gamma\omega)}{1 + B\omega^2 / (\omega_0{}^2 - \omega^2 - i\Gamma\omega)},$$

$1 > B > A$ $\quad \varepsilon_B$ is "antiresonant"

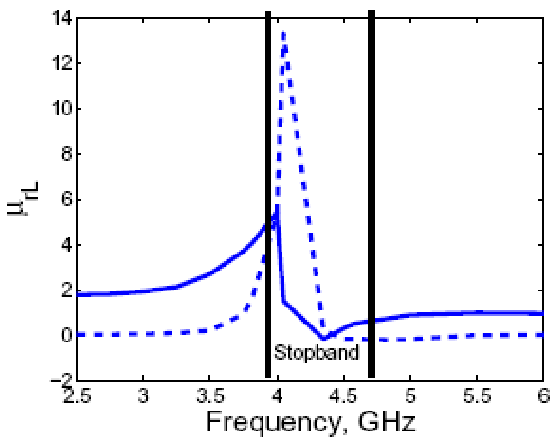


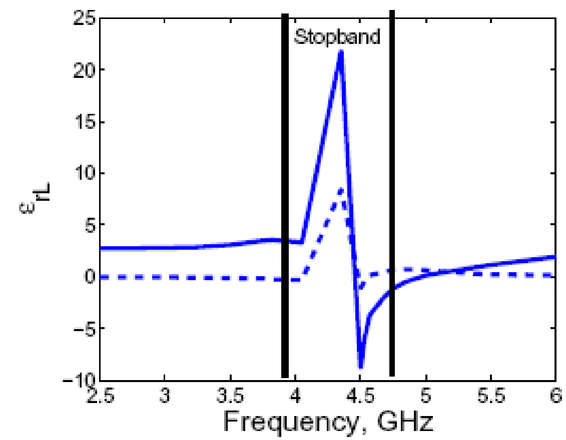


"EMP" extracted by NRW



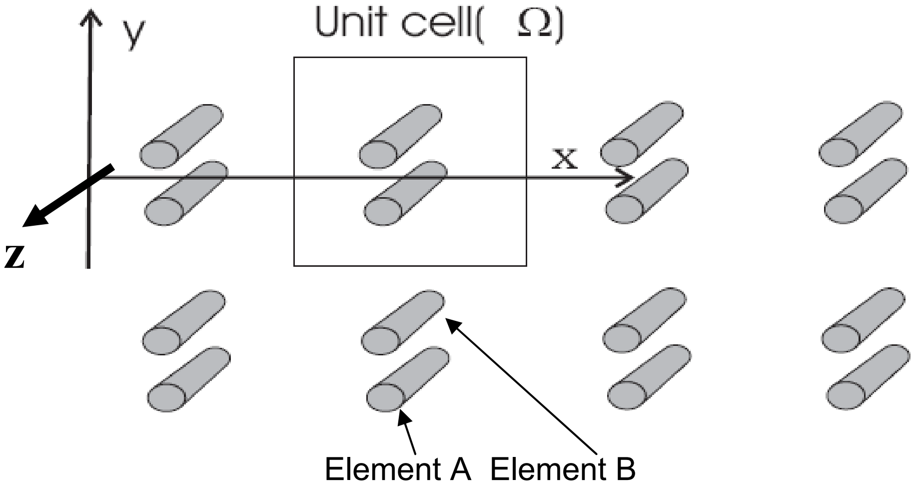
Magnetic Mie resonance

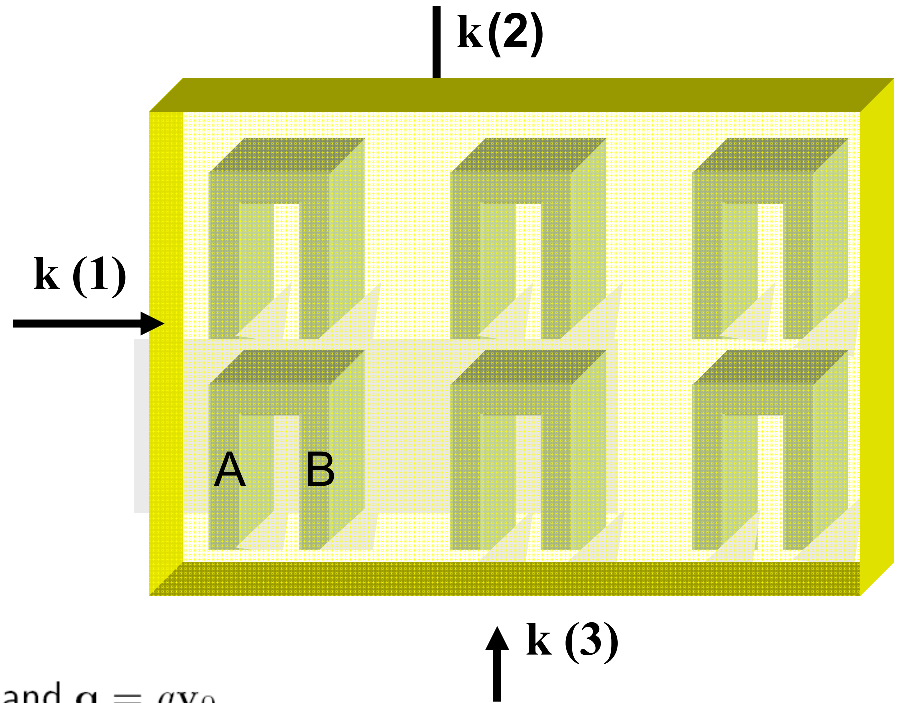




Local EMP

Bulk multipolar arrays





"Artificial magnetic" when and only when: $\omega = \omega_{\mathrm{mag}}$ and $\mathbf{q} = q\mathbf{y}_0$.
If $\mathbf{q} = q\mathbf{x}_0$, this is an artificial dielectric.

In all other cases – more material parameters are needed.

Never "artificial magnetic"

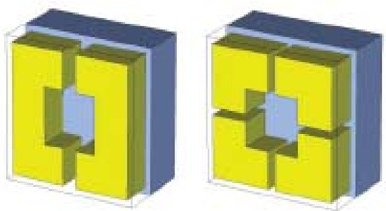
k(1) - M + Q

k(2) - another Q

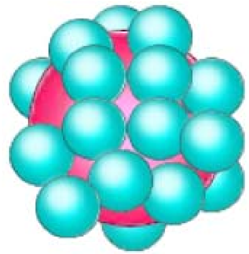
k(3) - third Q

Pitfall of artificial magnetism in multipolar media

- ”Magnetism” due to phase shift between two elements (A and B) of an open inlcusions – 100s papers
- Quadrupoles and octupoles can be neglected only for



Or for



In other cases (dual bars, U-shaped SRRs etc)

$$D_i = \varepsilon'_{ij} E_j + j\xi'_{ij} H_j + b_{ijkl} \nabla_k \nabla_l \mathbf{E}_j,$$

$$B_i = \mu'_{ij} H_j - j\xi'_{ji} \mathbf{E},$$

Or

$$D_i = \varepsilon_{ij}(\omega, \mathbf{q}) E_j, \quad \varepsilon_{ij}(\omega, \mathbf{q}) = \varepsilon^{(0)}_{ij}(\omega) + j\gamma_{ijk}(\omega) q_k + j\gamma_{ijkm}(\omega) q_k q_m + \dots$$

$$\mathbf{H} = \mu_0^{-1} \mathbf{B}.$$

In both cases ABC are required!

Handbook of Artificial Materials
Vol I: Phenomena and Theory

Material parameters and field energy in reciprocal composite media

C. Simovski and S. Tretyakov
Helsinki University of Technology

TKK

Metasurfaces (no experimental results, yet)

Electric and magnetic surface susceptibilities

ELSEVIER
Available online at www.sciencedirect.com
ScienceDirect
Metamaterials 3 (2009) 100–112
Metamaterials
www.elsevier.com/locate/metmat

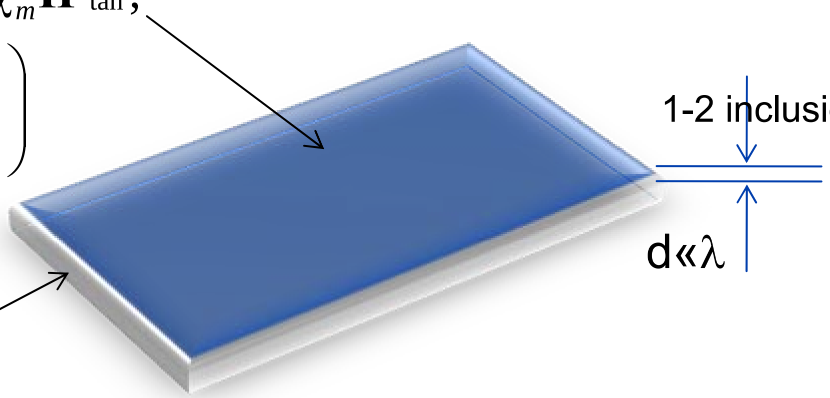
A discussion on the interpretation and characterization of metafilms/metasurfaces: The two-dimensional equivalent of metamaterials

Christopher L. Holloway[a,*], Andrew Dienstfrey[b], Edward F. Kuester[c], John F. O'Hara[d], Abul K. Azad[d], Antoinette J. Taylor[d]

MTM messcopic olayer (no cross-polarization and spatial dispersion)

$$\mathbf{J}_e = \chi_e \mathbf{E}^i_{\tan}, \quad \mathbf{J}_m = \chi_m \mathbf{H}^i_{\tan},$$

$$\chi_{e,m}^{TE,TM} = \begin{pmatrix} \chi_{xx} & \\ & \chi_{yy} \end{pmatrix}$$



TKK

Conclusions

- **There are many pitfalls in the NSM characterization**
- **Classification of NSM is very important to select the proper characterization parameters to retrieve**
- **To explain the physical meaning of retrieved parameters is very important**
- **There are self-consistent theories of NSM characterization, however**

not sufficiency developed and never experimentally checked!

- **For some NSM even no any theory yet!**
- **Inadequate characterization method (wrong interpretation) –**
- **impasses in the theory and insufficient practical achievements –**
- **metamaterials are compromised as such – no more support**