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Spectroscopy of Nanomaterials II sem – part 8

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Photonic band-gap structures and metamaterials: manipulating light with artificial materials

OUTLOOK

The idea of realizing artificial materials through ordered, or controlled, assembly of sub-units has always been one of the most investigated possibilities in materials science

There are very many vivid and interesting examples of such artificial materials: two of them (at least, two!) involve interaction with e.m. waves, including optics:

- Photonic Band Gap (PBG) materials
- MetaMaterials (MMs)

Here we will restrict ourselves to a very short and qualitative description of their properties, basic operating principles, examples

Today's menu:

- Mixed appetizers of iridiscence and Bragg reflection/ diffraction
- First dish: photonic band gap in ordered artificial crystals, similarities with semiconductors, simple considerations
- Main course of metamaterials, with spicy potential
- Dessert: few drops of open possibilities



ALREADY SEEN IN THE INTRODUCTION



nano-scale. mage: University of Southampton



Iridiscence related to spatial organization of (scattering) material at the small scale (micro, rather than nano)



BRAGG FROM MULTIPLE INTERFACES



Bragg "diffraction", i.e., interference between multiple scattered beams (coherent each other) is at the basis of X-Ray Diffraction



The same applies in optics, involving reflections from multiple (at least 2) dielectric/dielecric interfaces _____





1-D BRAGG INTERFERENCE I

Starting point consists of Fresnel equations (continuity of field components at interface)

r and *t* represent the reflection and transmission coefficients for the electric field

For a **single** interface one gets:

$$egin{aligned} r_{\mathrm{s}} &= rac{n_1\cos heta_{\mathrm{i}} - n_2\cos heta_{\mathrm{t}}}{n_1\cos heta_{\mathrm{i}} + n_2\cos heta_{\mathrm{t}}} = t_{\mathrm{s}} - 1, & & \ \mathrm{TE} \ \mathrm{or} & & \ \mathrm{s-polarization} \ t_{\mathrm{s}} &= rac{2n_1\cos heta_{\mathrm{i}}}{n_1\cos heta_{\mathrm{i}} + n_2\cos heta_{\mathrm{t}}} = r_{\mathrm{s}} + 1, & \ r_{\mathrm{p}} &= rac{n_2\cos heta_{\mathrm{i}} - n_1\cos heta_{\mathrm{t}}}{n_1\cos heta_{\mathrm{t}} + n_2\cos heta_{\mathrm{i}}}, & & \ \mathrm{TM} \ \mathrm{or} & & \ \mathrm{p-polarization} \ t_{\mathrm{p}} &= rac{2n_1\cos heta_{\mathrm{t}} + n_2\cos heta_{\mathrm{i}}}{n_1\cos heta_{\mathrm{t}} + n_2\cos heta_{\mathrm{i}}}. & & \ \mathrm{TM} \ \mathrm{or} & & \ \mathrm{p-polarization} \ \end{array}$$

We will restrict to 1-D case
$$\rightarrow \theta = 0$$

We will consider multiple interfaces







1-D BRAGG INTERFERENCE II

For $\theta = 0$: $|r| = \left| \frac{n_2 - n_1}{n_2 + n_1} \right|$

Destructive interference will occur whenever dephasing between multiple reflection will be equal to $m\pi$ with *m* integer

$$k\Delta z = \frac{2\pi}{\lambda} n\Delta z = m\pi \to n\Delta z = m\frac{\lambda}{2}$$

Note, however, that the **contrast** of the interference pattern will be small, being small the reflectivity at any interface, as a consequence to the typically small n_2 - n_1 \rightarrow Peaks and zeros are broadened 100 90 80 n_H t_H t n, 70 Reflectance (%) tн n n t 60 : N pairs, 50 2N layers 27 pairs 40 18 pairs 30 10 pairs 20 10 n 950 1000 1050 1100 1150 1200 Wavelength (nm) NANO_16_08_0 http://www.df.unipi.it/~fuso/dida 6/38

CONCEPT OF OPTICAL BAND-GAP

There are wavelength ranges for which light is not reflected (or not transmitted)

This can be interpreted as the occurrence of *forbidden wavelengths* or **photonic band-gaps**

More in general:

- a photonic band-gap (PBG) system features a **periodic modulation** of the refractive index, that is of the dielectric constant (real-valued and positive, considering dielectrics)
- the periodic modulation resembles that of a crystal
- the occurrence of interference creates the band-gap (in the optical energy range, for our purposes)



Structures with 1-D, 2-D, 3-D periodicity of ε can be envisioned leading to 1-D (Bragg reflector), 2-D, 3-D PBGs



ELECTRONS IN A LATTICE

Kroenig-Penney model for an electron in a lattice



Steady-state Schroedinger equation

$$-\frac{\hbar^2}{2m}\nabla^2\psi(\vec{r}) + V(\vec{r}) = E\psi(\vec{r})$$

$$V(\vec{r}) = V(\vec{r} + \vec{R})$$

Bloch's theorem

$$\psi_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}(\vec{r}) \exp(i\vec{k}\cdot\vec{r})$$

with $u_{n,\vec{k}}(\vec{r}) = u_{n,\vec{k}}(\vec{r}+\vec{R})$

In 1-D, the solution of the Schroedinger equation leads to dispersion relation showing the occurrence of a band-gap for the electron energy



ELECTRON BAND-GAPS



In semiconductor crystals, band-gaps appear as a consequence of the **periodicity** in the potential energy due to the regular arrangement of the lattice



Main similiarities:

- band-gaps are related to the periodicity
- one can share many methods and tools (Bloch theorem, Brillouin zone, etc.)

Main differences:

- dispersion relations have different shapes because of massless photons
- the size scales (lattice parameters) and involved energies are markedly different



RELEVANT EQUATIONS I



$$\vec{\nabla} \times \vec{\nabla} \times \vec{H} = \varepsilon \varepsilon_0 \frac{\partial}{\partial t} \vec{\nabla} \times \vec{E} = -\mu_0 \varepsilon \varepsilon_0 \frac{\partial^2 \vec{H}}{\partial t^2} \quad \text{with } \vec{H}(t) \propto \exp(-i\omega t)$$

$$\rightarrow \vec{\nabla} \times \frac{1}{\varepsilon} \vec{\nabla} \times \vec{H} = \mu_0 \varepsilon_0 \omega^2 \vec{H} = \left(\frac{\omega}{c}\right)^2 \vec{H}$$

We choose:

 $\varepsilon = \varepsilon(\vec{r}) = \varepsilon(\vec{r} + \vec{R})$ with \vec{R} primitive vector of the unit cell

Using the Bloch theorem we can search for:

$$\vec{H}(\vec{r}) = \exp(-i\vec{k}\cdot\vec{r})\vec{H}_{n,\vec{k}}(\vec{r})$$

with $\vec{H}_{n,\vec{k}}$ periodic envelope function satisfying
 $(\vec{\nabla}+i\vec{k}) \times \frac{1}{\varepsilon}(\vec{\nabla}+i\vec{k}) \times \vec{H}_{n,\vec{k}} = \left(\frac{\omega_n(\vec{k})}{c}\right)\vec{H}_{n,\vec{k}}$
with ω_n eigenvalues

Formally, this is exactly the same problem encountered in semiconductor crystals!

The periodic dielectric constant plays the role of the potential for the electrons



RELEVANT EQUATIONS II

Eigenvalues $\omega_n(k)$ are continuous functions of k leading to dispersion relation showing bandgaps in ω (that is in energy)

Eigenfunctions are periodical in the reciprocal space



Figure 2: Left: Dispersion relation (band diagram), frequency ω versus wavenumber k, of a uniform one-dimensional medium, where the dashed lines show the "folding" effect of applying Bloch's theorem with an artificial periodicity a. Right: Schematic effect on the bands of a physical periodic dielectric variation (inset), where a gap has been opened by splitting the degeneracy at the $k = \pm \pi/a$ Brillouin-zone boundaries (as well as a higher-order gap at k = 0).

 $\vec{H}_{n,\vec{k}}(\vec{k}) = \vec{H}_{n,\vec{k}}(\vec{k} + \vec{G})$

with \vec{G} reciprocal lattice vector

The treatment leads to results very much similar to those of semiconductor physics

For instance, in the 1-D case a band-gap is opened at the border of the Brillouin zone

The band-gap stems from the periodicity of the considered system

The band-gap width depends on the periodicity and, mostly, on the dielectric constant variation, that is on the contrast of the refractive index

http://ab-initio.mit.edu/photons/tutorial/photonic-intro.pdf



PHYSICAL PICTURE (REVISED)



Standing waves will occur in the 1-D PBG structure

An integer number of half-wavelengths will stay within the structure periodicity

We will have standing waves for the electric field described by $sin(\pi x/a)$ and $cos(\pi x/a)$ functions in order to cope with the boundary conditions

The sin function will be peaked in the low refractive index dielectric, the cos in the high refractive index medium

If we keep the wavelength constant in the different media, we will have to assume different (angular) frequencies, according to $\omega = kc/n = 2\pi c/(n\lambda)$

Being the energy proportional to ω , we will find different energies according to *n*: the sin function, peaked in the low refractive index dielectric, will correspond to the permitted higher energy, the cos function vice versa



2-D (AND 3-D) PBG CRYSTALS

In order for a complete band gap to arise in two or three dimensions, two additional hurdles must be overcome. First, although in each symmetry direction of the crystal (and each \vec{k} point) there will be a band gap by the one-dimensional argument, these band gaps will not necessarily overlap in frequency (or even lie between the same bands). In order that they overlap, the gaps must be sufficiently large, which implies a minimum ε contrast (typically at least 4/1 in 3d). Since the 1d mid-gap frequency $\sim c\pi/a\sqrt{\varepsilon}$ varies inversely with the period a, it is also helpful if the periodicity is nearly the same in different directions—thus, the largest gaps typically arise for hexagonal lattices in 2d and fcc lattices in 3d. which have the most nearly circular/spherical Brillouin zones. Second, one must take into account the vectorial boundary conditions on the electric field: moving across a dielectric boundary from ε to some $\varepsilon' < \varepsilon$, the inverse "potential" $\varepsilon |\vec{E}|^2$ will decrease discontinuously if \vec{E} is parallel to the interface (\vec{E}_{\parallel} is continuous) and will *increase* discontinuously if \vec{E} is perpendicular to the interface ($\varepsilon \vec{E}_{\perp}$ is continuous). This means that, whenever the electric field lines cross a dielectric boundary, it is much harder to strongly contain the field energy within the high dielectric, and the converse is true when the field lines are parallel to a boundary. Thus, in order to obtain a large band gap, a dielectric structure should consist of thin, continuous veins/membranes along which the electric field lines can run—this way, the lowest band(s) can be strongly confined, while the upper bands are forced to a much higher frequency because the thin veins cannot support multiple modes (except for two orthogonal polarizations). The veins must also run in all directions, so that this confinement can occur for all \vec{k} and polarizations, necessitating a complex topology in the crystal.

Ultimately, however, in two or three dimensions we can only suggest rules of thumb for the existence of a band gap in a periodic structure, since no rigorous criteria have yet been determined. This made the design of 3d photonic crystals a trial and error process, with the first example by Ho *et al.* of a complete 3d gap coming three years after the initial 1987 concept. As is discussed by the final section below, a small number of families of 3d photonic crystals have since been identified, with many variations thereof explored for fabrication.

In more than 1-D the occurrence of band-gaps is much less straightforward to be ascertained

Spatial arrangement of material properties (dielectric constant) should enable identifying "veins" (with constant ε) supporting electric field lines

Particular symmetry and geometry requirements must be applied, that can be verified only with numerical calculation methods

2-D (and 3-D) PBG structures have a non-trivial topology, but they can be demonstrated to exist leading to photonic band-gaps

http://ab-initio.mit.edu/photons/tutorial/photonic-intro.pdf



2-D PBG CRYSTALS (HEXAGONAL)



Figure 4: Band diagrams and photonic band gaps for hexagonal lattices of high dielectric rods ($\varepsilon = 12$, r = 0.2a) in air (top), and air holes (r = 0.3a) in dielectric (bottom), where a is the center-center periodicity. The frequencies are plotted around the boundary of the irreducible Brillouin zone (shaded triangle, left center), with solid-red/dashed-blue lines denoting TE/TM polarization (electric field parallel/perpendicular to plane of periodicity). The rods/holes have a gap the TM/TE bands.

http://ab-initio.mit.edu/photons/tutorial/photonic-intro.pdf

For instance, in 2-D a regular arrangement of (high) dielectric rods in air, or vice versa, leads to a photonic band-gap

The band-gap width depends on spacing: $\Delta \omega_{BG} \sim c/a$

The spacing, or PBG lattice parameter, must be a fraction of the wavelength

Hundreds of nm is the typical size scale for the lattice parameter in PBGs



EXAMPLE OF 3-D PBG CRYSTAL



structure exhibits a 21% omnidirectional band gap.

3-D PBGs can be designed with complicated geometries Large dielectric differences are needed to obtain large band-gaps

http://ab-initio.mit.edu/photons/tutorial/photonic-intro.pdf



PBG FABRICATION I

Required, in general:

- Ability to produce voids in dielectrics
- Or ability to modify the shape of dielectrics
- Or ability to grow regular (and controlled) patterns of dielectrics

In principle, this should be replicated in several dimensions



Few problems with 1-D and 2-D (planar) structures built in materials of interest for microelectronics





PBG FABRICATION II



Since dielectrics can be made of polymers (hence taking advantage of the broad range of phyiscal properties achievable in such materials), specific in-plane fabrication methods for polymers can be used

For instance, NanoImprint Lithography (NIL), and its variants can be used

PBG FABRICATION III

2-D/3-D opal and inverse opal structures can also be fabricated through self-assembly of polymer nanospheres (close-packing assembly)



PBG FABRICATION IV





The print head and/or bed is moved to the correct X/Y/Z position for placing the material

3-D printing can be applied to some materials, especially polymers (but accuracy is a concern, as well as integration with other materials)



PBG OPTICAL SENSING

A variety of optical sensors can be conceived exploiting PBG

A PBG (for instance, even a simple Bragg reflector) will have specific band-gaps, which can be modified when its surface, duly functionalized, is altered because of molecular adsorption

The devices can be easily integrated (on a chip) and achieve a large sensitivity



PBG APPLICATIONS I

While PBG typically consists of highly ordered structures, with a well controlled modulation of the refractive index, one of the most important application, especially from the "historical" point of view, entails **defective PBG** (intended as PBG structures including defects in predefined positions)

For instance, in a 2-D PBG consisting of equispaced dielectric cylinders, on cylinder in a row is missing

- \rightarrow The conditions for the band gap are modified
- \rightarrow If correctly designed, the PBG can support **propagation** of light with energy in the (unperturbed) band gap along the defective row
- \rightarrow A waveguide can be obtained





PBG APPLICATIONS II





PBG APPLICATIONS III





Already commercially well-available are the **photonic crystal fibers:** technologies exist to produce 2-D PBG on bendable materials, with a waveguiding core consisting of a defect (distributed all along the fiber length)



Main advantages with respect to ordinary fibers:

- Low attenuation for any desired wavelength
- No limitation for the entrance angle (no need for total reflection!)
- Can be bent at large angles withour degrading the waveguiding properties
- Can be implemented in sophisticated and highly sensitive sensors



PBG APPLICATIONS IV



A 2-D PBG is integrated with a laser

The hole induces a defect where lasing action is achieved:

- Spontaneous emission is in the band gap, hence inhibited
- Stimulated emission is permitted in the defective region
- Quality factor of the resulting cavity is enhanced and low-threshold miniaturized laser is obtained

Scherer et al., UCLA

A very demanding (but very appealing!) application of PBGs foresees their integration with laser sources in order to realize extremely-high quality optical cavities (maybe, in 3-D!) leading to extremely-high gain and negligible threshold conditions for the lasing action



Exciting perspectives are open for photonic devices using PBGs (but technological issues are open, as well)



METAMATERIALS I

In general terms, a **metamaterial** is a material system specifically engineered in order to obtain "superior" properties, virtually of any kind

The term material requires that the individual components, or subsystem, can be described by a kind of **macroscopically averaged** approach

 \rightarrow The system components must be "small" compared to the size scale of interest

In recent years (in the last decade, or so), **metamaterials** have been introduced and developed where the "superior" properties are found in interaction with e.m. waves

- The size scale of interest is the wavelength
- It is much simpler, in general, to build a so-conceived metamaterial operating in the radiofrequency range, typically up to the THz range (even hundreds of THz, that is near-IR)
- Truly "optical" metamaterials are still in the research stage

Within this frame, the macroscopically-averaged quantities are magnetic (and dielectric) constants, i.e., magnetic (and electrical) permeabilities or permittivities, e.g., μ_R (and ϵ_R)



METAMATERIALS II



The MM approach is different with respect to PBG, where the periodic modulation of ε_R is first treated at the microscopic level, but then leads to a wave equation ruling the macroscopic behavior (eigenfunctions, eigenstates)

There are, however, similarities, since PBG are artificial materials as well!



MANIPULATING THE MAGNETIC PERMEABILITY

We have seen how, in certain conditions, one can get $Re{\epsilon_R} < 0$ (for a certain ω range)

This is the case of **plasmon resonances**, e.g., plasmon oscillations in the Drude model

$$\varepsilon_{R} = 1 - \frac{\omega_{p}^{2}}{\omega^{2} + i\gamma\omega}$$

Within the frame of MM, a material showing one negative coefficient is called **single negative (SNG)**

Systems can be built leading to $\text{Re}\{\mu_R\} < 0$ (for a certain ω range, typically in the microwave or THz ranges)

An example is the Split Ring Resonantor (SRR)

When immersed in a variable external magnetic field (e.g., perpendicular to the slide plane), current is induced by Faraday effect **and** charge is accumulated at the split borders

SRR can be modeled by using RLC circuits and related techniques





REMINDERS OF RLC CIRCUITS



A magnetic dipole moment p_m can be attributed to a circuit concerned by a current *I* (in the simplest case, it is just $p_m \sim I$)

In the linear, isotropic approximation, the magnetization field *M*, hence the permeability, can be related to the *individual (averaged)* magnetic dipole moment

 → Currents induced in the SRR are responsible for magnetic properties of the MM (intended as a collection of individual components)

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}) = \mu_0 (\vec{H} + \chi_m \vec{H}) = \mu_0 \mu_R \vec{H}$$
$$\rightarrow \mu_R = 1 + \chi_m$$
$$\vec{M} = \chi_m \vec{H} = \frac{\Delta N}{\Lambda V} < \vec{p}_m >$$



SRR-BASED MM MAGNETIC PERMEABILITY

The actual behavior of a real SRR can require a complicated model

It can be shown that, in most SRR-based materials, one gets: $E\omega^2$

$$\mu_R \sim 1 + \frac{F\omega}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

with F a (geometrical) factor





In properly designed systems, the size of the individual SRR can be made smaller than the wavelength and **arrays** of individual resonators can be put together in order to have a **metamaterial**

Metamaterial consists of array(s) of individual resonators → Macroscopically averaged quantities can be derived

Padilla et al., Materials Today 9, 28 (2006)



NEGATIVE MAGNETIC PERMEABILITY



MANIPULATING THE REFRACTIVE INDEX

In optics, we typically consider $n = \sqrt{\epsilon_R}$ since we assume that a material of interest for optics shows $\mu_R = 1$

However, the wave equation reads

$$\nabla^{2}\vec{E} = \mu_{0}\mu_{R}\varepsilon_{0}\varepsilon_{R}\frac{\partial^{2}\vec{E}}{\partial t^{2}} = \frac{1}{c^{2}/n^{2}}\frac{\partial^{2}\vec{E}}{\partial t^{2}}$$
$$\rightarrow n = \frac{1}{\sqrt{\varepsilon_{R}\mu_{R}}}$$

In case of **complex** ε_R and μ_R , the square root can be **negative**!!



DOUBLE NEGATIVE MATERIALS (DNG)



MMs IN OPTICS (EXAMPLE)

An array of gold structures arranged in paired nanorods is realized

When interacting with an e.m. wave:

- The electric field induces a current (symmetric plasmon) oscillation along every rod axis
- The magnetic field, considered to cross the surface delimited by the nanorod pair, induces antiparallel currents in the nanorods (antisymmetryc plasmon)

→ A magnetic dipole moment is created parallel to the incident magnetic field, whose direction depends on being above (parallel) or below (anti-parallel) the resonance

> "Magnetic" properties can be attributed to surface plasmons arranged according to specific geometries



Designed to operate for $\lambda \sim 1.2 \ \mu m$

Shalaev, et al., Opt. Lett. 30, 3356 (2005)

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THE POTENTIAL OF NEGATIVE REFRACTION





EXAMPLES I





Refraction angle from a MM wedge and comparison with a reference wedge (made of teflon)



Shelby, et al., Science (2001)

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Refractive index (real and imaginary parts) in the near-IR range [in (b) depurated by the substrate contribution]



EXAMPLES II



Examples at different wavelengths exist

Truly "optical" MMs not yet completely established

Great interest for their further development



Padilla et al., Materials Today 9, 28 (2006)

Smith, D. R., et al., Phys. Rev. Lett. (2000) 84, 4184
Wiltshire, M. C. K., et al., Science (2001) 291, 849

10. Enkrich, C., et al., Phys. Rev. Lett. (2005) 95, 203901

Yen, T. J., et al., Science (2004) 303, 1494
Linden, S., et al., Science (2004) 306, 1351

A STRIKING APPLICATION (ENVISIONED) I





Pendry (1999)

A STRIKING APPLICATION (ENVISIONED) II



Pendry (1999) http://www.df.unipi.it/~fuso/dida



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CONCLUSIONS

- ✓ Obtaining artificial materials through controlled assembly of specific sub-units is one of the major goals of materials science since from foundations
- Many possibilities exist for giving such artificial materials superior, or exotic, properties pertaining their interaction with e.m. waves
- Photonic band-gap crystals can be designed and realized, providing specific (and tailored) transmission/reflection properties: in 1-D they are very well known and simple to attain, extension to higher dimensions is cumbersome, but very appealing
- Metamaterials address a similar issue, but with a different approach, based on the possiblity to achieve exotic magnetic and electric properties, possibly leading to a negative refractive index
- Once technical and technological issues will be completely handled, breakthroughs can be expected from the application of such materials in the field of optics, nano-optics, optoelectronics, photonics



FURTHER READING

A recent textbook covering both PBG and MM (chapter 5 and 3, respectively):

D.L. Andrews, Nanophotonic Structures and Materials, Wiley, Hoboken (2015).

A freely downloadable text on PBGs, very similar to chapter 5 above, can be found at:

http://ab-initio.mit.edu/photons/tutorial/photonic-intro.pdf

(Johnson and Joannopoulos, MIT)

A seminal paper on PBG, by Yablonovitch (J. Phys: Codens. Matter 5, 2443 (1993): http://iopscience.iop.org/article/10.1088/0953-8984/5/16/004/pdf

A short review on MM: W. Padilla, et al., Materials Today 9, 28 (2006).

