Negative Effective Refractive Index Metamaterials at Optical Frequencies Based on Superlattices of Noble Metals and Excitonic Semiconductors

Andrea Vallecchi and ***Matteo Albani***

Department of Information Engineering, University of Siena, Via Roma 56, Siena, 53100 Italy.

Email: andrea.vallecchi@unisi.it; matteo.albani@dii.unisi.it

Abstract

Super lattices of engineered spherical nanoparticles are considered as model structures exhibiting dielectric and magnetic resonances at optical frequencies. We first show that a lattice of excitonic semiconductor nanoparticles can be used to realize a magnetic medium. Then, either we form a binary superlattice combining the magnetic crystal with an electric one of metal nanospheres, or we coat the nanospheres of the magnetic crystal with a metal layer and consider a single lattice of coated nanospheres. Both these approaches are shown to represent effective routes to realization of three-dimensional (3D) isotropic negative index metamaterials in the visible.

1 Introduction

Negative index metamaterials (NIMs) are usually constructed by combining a "magnetic" sublattice (one which exhibits negative permeability) of miniaturized RLC circuits, e.g. split-ring resonators (SRRs), with an "electric" one (exhibiting negative permittivity) of thin metallic wires. Excellent progress of research on this type of metamaterials have been accomplished at microwave frequencies, but few of these developments can find immediate application at infrared and optical frequencies where simpler structures are needed. For instance, SRRs, which can provide a negative effective permeability, have a detailed geometry which becomes difficult to fabricate on a nanometer scale.

A different design approach has been recently suggested where the electric and magnetic sublattices are occupied by units of less elaborate geometry such as cylinders or spheres made from resonant materials. The Mie resonances of the inclusions provide a mechanism for the creation of magnetic or electric resonances based on displacement currents, and offer a simpler and versatile route for the fabrication of isotropic metamaterials operating at higher frequencies. For example, negative index composites at infrared frequencies have been reported using two interpenetrating lattices of polaritonic and Drude material spheres, providing negative permeability and negative permittivity, respectively [1]. Another method to realize isotropic NIMs based on Mie resonances is using only one kind of micron-scale non-magnetic coated spheres. In [2] spheres with a core of a polaritonic crystal $LiTaO_3$ coated with a thin layer of a semiconductor following a Drude model dispersion were used to demonstrate isotropic negative refraction.

In this work we consider lattices of spherical nanoparticles as model structures exhibiting dielectric and/or magnetic resonances at optical frequencies. Since dielectric and magnetic resonances do not usually show up at the same frequency in a spherical homogeneous nanoparticle, binary composites of metallic and dielectric nanospheres are considered to design a NIM. In particular, to accomplish negative permeability at optical frequencies we exploit the large electric permittivity stemming from intrinsic material resonances of certain semiconductors with strong excitonic oscillation strength [3]. Once a crystal exhibiting negative permeability is at hand, in order to achieve a NRI behavior we combine the magnetic crystal with an electric crystal, made of noble metal nanoparticles, showing a negative permittivity so as to form a binary particle superlattice.

As an alternative, we coat the spheres of the magnetic crystal with a metal layer in a way that the coated unit exhibits an electric resonance at the same spectral region of the magnetic one [2]. The underlying physical mechanisms correspond to a negative effective permeability response due to the excitonic spherical core, while a negative effective permittivity effect results from an electric-dipole resonance of the metal coating. Since the metal permittivity is negative, the electric field is evanescent within the sphere and the

978-1-4244-6051-9/11/$26.00

electric dipole resonance is a surface resonance in contrast to the volume effect of the magnetic resonance. Therefore, the coating can be designed to have a negative permittivity.

2 Composite of excitonic semiconductor spheres

The magnetic dipole response of a nonmagnetic composite is usually weak. This can be driven into resonance, however, by using materials with a large permittivity. Excitonic semiconductors can provide the required large dielectric constants in the visible range. The relative permittivity of excitonic materials can be described by the Lorentz dispersion relation

$$\varepsilon_r(\omega) = \varepsilon_b \left(1 + \frac{\omega_L^2 - \omega_T^2}{\omega_T^2 - \omega^2 - i\omega\gamma_e}\right) \tag{1}$$

where ε_b is the background dielectric constant, ω_T is the transverse exciton frequency, ω_L is the longitudinal exciton frequency, and γ_e is the damping constant. Among excitonic semiconductors, copper chloride (CuCl) possesses a high Z_3 exciton oscillation strength, that can be exploited to obtain a strong magnetic resonance. The appropriate values of the parameters in (1) for the Z_3 exciton of CuCl are those used in [4] to match with experimental data for CuCl microcrystals: $\varepsilon_b = 5$, $\omega_T = 4.8655 \times 10^{15}$ rad/s, $\omega_L = 4.8738 \times 10^{15}$ rad/s, $\gamma_e = 2.2637 \times 10^{12}$ rad/s. In particular, the value of the damping constant is larger than for bulk CuCl, in accordance with the broadening of the absorption linewidth for increasingly small CuCl microcrystals [5]. The magnetic permeability of CuCl is unity.

A straightforward characterization of the response of a collection of spheres in terms of the size and material properties of the constituent spheres can be achieved through the extended Maxwell Garnett theory [6]. This model incorporates elements of the Mie scattering theory [7] within the formulas of ε_r^{eff} and μ_r^{eff}, expanding their range of validity to arbitrary wavelengths and skin depths within the particles from the original static limit for the ordinary Maxwell Garnett formulas [8]. In particular, the effective permittivity and permeability are expressed in terms of the electric and magnetic dipole scattering coefficients a_1 and b_1 of the Mie multipole series expansion of the field scattered by a sphere as

$$\varepsilon_r^{eff} = \varepsilon_h \frac{k_h^3 + 4\pi i N a_1}{k_h^3 - 2\pi i N a_1}, \quad \mu_r^{eff} = \frac{k_h^3 + 4\pi i N b_1}{k_h^3 - 2\pi i N b_1} \tag{2}$$

where k_h denotes the wavenumber in the host medium, and N is the volume density of the spheres, which is connected to the volume filling fraction of the composite by $f = 4\pi N r_p^3/3$. The scattering coefficients a_1 and b_1 can be found in [7], and are functions of the size, and the relative permittivity and permeability of the spheres/scatterers. As shown in [3], the effective permeability of a collection of CuCl nanospheres exhibits a resonance near the exciton resonance frequency, in the range where the material permittivity grows quite large. The effective permeability becomes negative just above this resonance.

3 Binary composite of excitonic semiconductor and silver nanospheres

To realize a metamaterial possessing a negative refractive index over a certain frequency window, that is, simultaneous negative effective permittivity and negative effective permeability, we can form a periodic crystal wherein plasmonic and excitonic particles are arranged on two interpenetrating simple cubic lattices, respectively. The resulting structure would be a body centered cubic (bcc) lattice ignoring the differences between the spheres (Fig. 1(a)). The sublattice of excitonic spheres provides negative magnetic permeability in certain frequency regions, while the sublattice of plasmonic spheres provides negative electric permittivity. Both phenomena stem from the single sphere Mie resonances. By a suitable choice of materials and parameters, a common region can be found where both permittivity and permeability are negative and the structure exhibits a negative refractive index band. In the following, we consider such a binary multilayer structure, consisting of alternating planes of plasmonic and excitonic spheres, and prove by using the extended Maxwell Garnett effective medium theory that a NRI behavior can actually be accomplished.

For two-component composite materials, when the volume fraction of the inclusions is smaller than that of host and the interaction of the two kinds of particles can be neglected, the total electric and magnetic polarizations can be assumed to be proportional to $\sum_{i=A,B} N_i \alpha_i^{e,m}$, where N_i and $\alpha_i^{e,m}, i = A, B$, represent the number densities and the electric and magnetic polarizabilities of the particles of type A or B. Under these assumptions, by applying the Clausius-Mossotti equation to the binary composite comprising two different kinds of spheres embedded in a matrix the effective permittivity of the composite can be simply expressed as

$$\varepsilon_r^{eff} = \varepsilon_h \frac{k_h^3 + 3i\left(\dfrac{f_A a_1^A}{r_A^3} + \dfrac{f_B a_1^B}{r_B^3}\right)}{k_h^3 - \dfrac{3i}{2}\left(\dfrac{f_A a_1^A}{r_A^3} + \dfrac{f_B a_1^B}{r_B^3}\right)} \tag{3}$$

where k_h is the wavenumber in the host medium, a_1^A and a_1^B are the Mie electric dipole scattering coefficients of the two type of constituent particles, and $f_i = 4\pi N_i r_i^3/3, i = A, B$ represent their respective filling fractions. A relation similar to (3) can be obtained for the effective magnetic permeability of the binary composite in terms of the Mie magnetic dipole scattering coefficients b_1^A and b_1^B.

The effective parameters for a binary composite consisting of CuCl and silver nanospheres calculated by

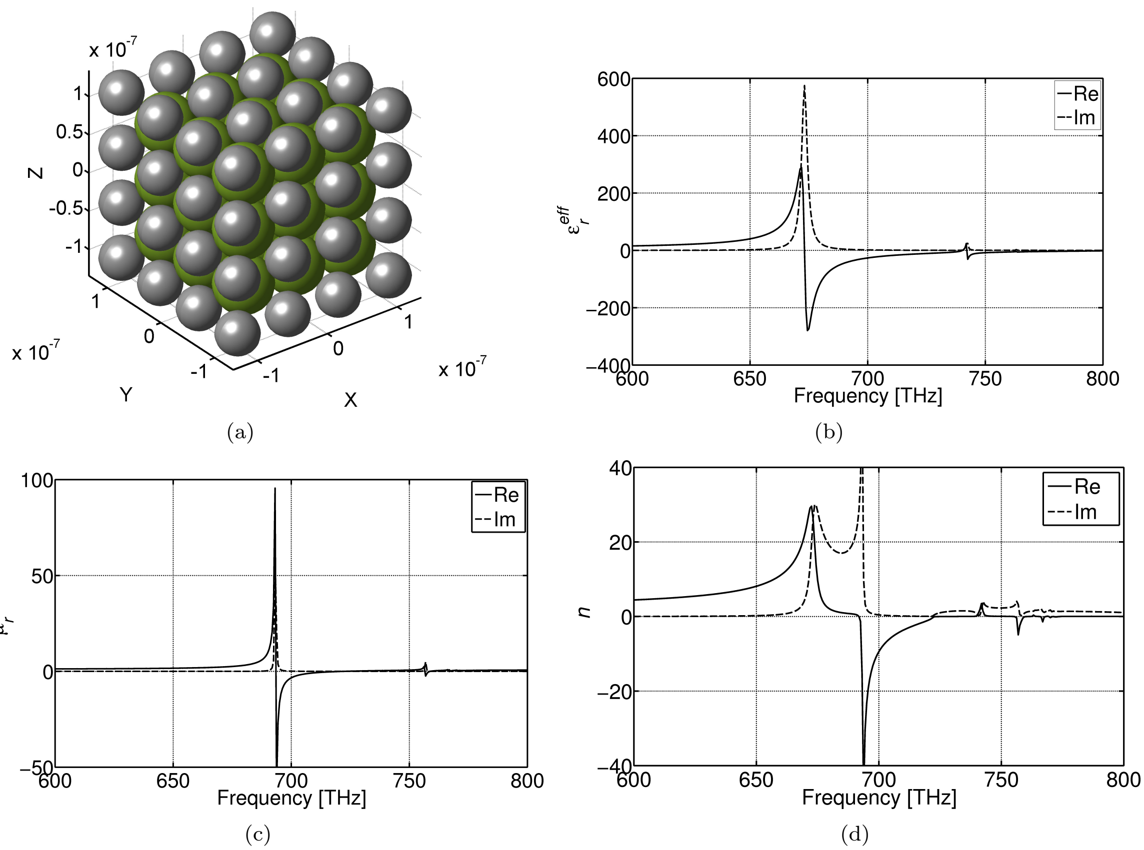

Figure 1: Binary bcc lattice consisting of alternating layers of excitonic and silver nanoparticles arranged on two interpenetrating simple cubic sublattices. (a) View of the resulting superlattice with a total filling fraction $f \approx 0.73$; (b) effective permittivity, (c) permeability, and (d) refractive index of such a composite. The radius of CuCl spheres is 36 nm, whereas the radius of silver spheres is 26.35 nm.

(3) and the analogous formula for the permeability are plotted in Fig. 1. The radius of CuCl nanospheres is $r_A = 36$ nn, whereas silver particle radius is $r_B = 26.35$ nn. The two types of nanospheres are arranged periodically in a bcc lattice with a unit cell size of 72 nm, corresponding to a total filling fraction $f \approx 0.73$. The effective refractive index $n^{eff} = \sqrt{\varepsilon_r^{eff} \mu_r^{eff}}$, shown in Fig. 1(d), is calculated so that its imaginary part is positive since we are dealing with passive materials (with a $\exp(-i\omega t)$ time harmonic dependence).

As apparent, the magnetic resonance falls within the negative region of the effective permittivity. As a result, both the effective permittivity and permeability of the binary lattice assume negative values in a frequency region around 700 THz, and in this frequency range a negative refractive index is achieved. The imaginary part of the effective parameters is proportional to the attenuation, which is an inevitable consequences of the underlying resonances. However, losses rapidly decrease away from the resonances, and there is a broad frequency range where simultaneous negative permittivity and permeability values can be exploited with negligible losses.

4 Acknowledgments

This work was supported from the European Commission 7$^{\text{th}}$ Framework Program FP7/2008, "Nanosciences, Nanotechnologies, Materials and New Production Technologies (NMP)" theme, research area "NMP-2008-2.2-2 Nanostructured meta-materials", grant agreement number 228762.

5 References

1. V. Yannopapas and A. Moroz, "Negative refractive index metamaterials from inherently non-magnetic materials for deep infrared to terahertz frequency ranges," *J. Phys.: Condens. Matter*, **17**, 2005, p. 3717.

2. M. S. Wheeler, J. S. Aitchison, and M. Mojahedi, "Coated nonmagnetic spheres with a negative index of refraction at infrared frequencies," *Phys. Rev. B*, **73**, Jan. 2006, p. 045105.

3. V. Yannopapas and N. V. Vitanov, "Photoexcitation-induced magnetism in arrays of semiconductor nanoparticles with a strong excitonic oscillator strength," *Phys. Rev. B*, **74**, Nov 2006, p. 193304.

4. Y. Masumoto, T. Wamura, and T. Kawamura, "Anomalous change of extinction spectra of CuCl microcrystals," *Appl. Phys. Lett.*, **58**, 1991, pp. 2270–2272.

5. T. Wamura, Y. Masumoto, and T. Kawamura, "Size-dependent homogeneous linewidth of Z_3 exciton absorption spectra in CuCl microcrystals," *Appl. Phys. Lett.*, **59**, 1991, pp. 1758–1760.

6. R. Ruppin, "Evaluation of extended maxwell-garnett theories," *Optics Communications*, **182**, 2000, pp. 273–279.

7. C. F. Bohren and D. R. Huffman, *Absorption and scattering of light by small particles*, Bohren, C. F. & Huffman, D. R., Ed. New York: Wiley, 1983.

8. P. C. Waterman and N. E. Pedersen, "Electromagnetic scattering by periodic arrays of particles," *J. Appl. Phys.*, **59**, 1986, pp. 2609–2618.