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Contribution of the electric quadrupole resonance in optical metamaterials

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Optical metamaterials can exhibit negative index of refraction when both the effective permittivity and permeability are negative. The negative permeability is usually considered to be associated with a magnetic dipole resonance and the contribution from electric quadrupoles is neglected. Here, we show by simulation that the electric quadrupole contribution is actually comparable to that from magnetic dipoles. We propose an experimental scheme to determine the relative contributions from the electric dipole, magnetic dipole, and electric quadrupole of a metallic nanostructure. This can be important in the design of metamaterials.

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Optical metamaterials are artificial structures composed of nanoscale units with unit dimensions smaller than the optical wavelength. They can be described as effectively continuous media and exhibit electromagnetic behavior not available in natural materials. A focus of research has been on metamaterials with negative index of refraction. It was first demonstrated in the microwave range[1–6] and later extended to infrared and optical frequencies.[7–20] To achieve a negative refractive index, both the effective permittivity (ε) and permeability (μ) have to be negative at the desired frequency.[1,21,22] It is straightforward to obtain a negative ε, which occurs naturally for metals at optical frequencies. However, negative μ is nonexistent in nature. Only recently, it was achieved in artificial metamaterials using strong magnetic resonances in suitably designed metal plasmonic nanostructures.[7–10,14–19] Similar to the magnetic dipole radiation, the electric quadrupole radiation can also be greatly enhanced by plasmon resonances and it is typically of comparable strength at optical frequencies. Therefore, one might expect electric quadrupoles to play as important a role as that of magnetic dipoles. However, in most previous studies, electric quadrupole contributions to the plasmon resonance were not carefully investigated.[16,17]

In this Rapid Communication, we study the effect of electric quadrupoles on the effective permeability of a metamaterial consisting of a pair of coupled metal nanostructures. We numerically calculate the internal field and current distribution in individual nanostructures and deduce the multipole components. It is shown that electric quadrupole ($\vec{Q}$) radiation has similar strength compared to that of magnetic dipole ($\vec{M}$) radiation. We also propose that by measuring the angle-resolved far-field radiation pattern, different multipole radiations can be distinguished and their strengths determined experimentally. Furthermore, we show that the electric quadrupole contributes to the effective μ rather than ε. Therefore it plays a central role in achieving negative permeability, the more challenging part for negative refraction.

Several metamaterial designs have been proposed for achieving negative refraction in the optical range. Many are variants of the parallel metallic nanobar structure (Fig. 1).[14–19] The incident electric field polarized along the bar can resonantly induce symmetric [Fig. 1(b)] or asymmetric [Fig. 1(c)] electron oscillations depending on the driving frequency. As illustrated in Fig. 1, the symmetric mode is characterized by a net electric dipole ($\vec{P}$), while the asymmetric mode, arising from a current distribution with the currents in the two metal bars out of phase, is a mode of mixed magnetic dipole and electric quadrupole character. Generally, however, a structure may have separate resonance modes with dominating magnetic dipole and electric quadrupole characters.

We calculate the scattering intensity spectrum and the internal electric field of a single unit of parallel bar structure using the discrete dipole approximation (DDA) method.[23,24] In this method, the interaction of the incoming light with the structure is described by an assembly of point dipoles distributed throughout the volume of the structure. The dipoles are induced by the local field, which is the sum of the incident field and the field created by the induced dipoles themselves. This generates a set of linearly coupled equations

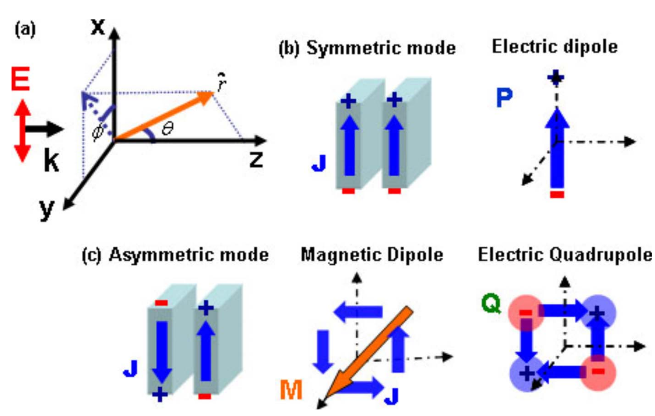

FIG. 1. (Color online) Coordinates and plasmon resonances of a pair of bars: (a) Relative coordinates of incident light with respect to the pair of bars. The incident light propagates on the z axis and is linearly polarized along the x axis being parallel to the long axes of the bars. (b) Symmetric electron oscillation is characterized as a net electric dipole (P). (c) Asymmetric electron oscillation is characterized as a sum of magnetic dipole (M) and electric quadrupole (Q). The arrows refer to currents and the "+" and "−" signs to the charge distribution.

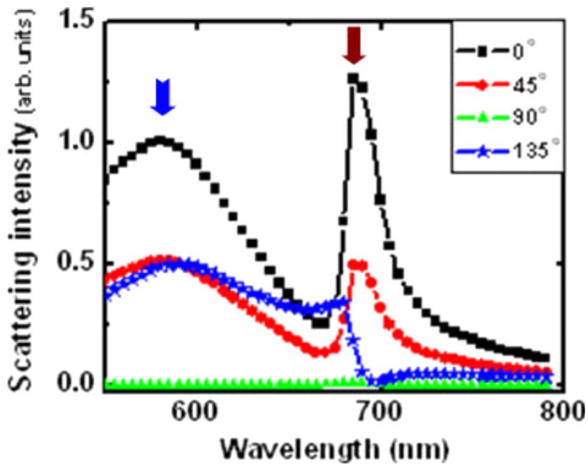

FIG. 2. (Color online) Scattering intensity spectra on the x-z plane ($\phi=0$) for $\theta=0°$, 45°, 90°, and 135° of a pair of parallel silver bars. The scattering geometry is depicted in Fig. 1, where θ is the angle between the incident light and the scattered light propagation directions. Each bar is 135 nm high, 80 nm wide, and 30 nm thick. The separation between bars is 25 nm. The arrow at 580 nm denotes the symmetric mode resonance; the arrow at 685 nm denotes the asymmetric mode resonance.

which are solved self-consistently. Solution of the equations yields both the local electric field distribution and the far-field scattering intensity in different directions. We consider two silver bars in air with a cross section of $135\times 80\ \text{nm}^2$ and a thickness of 30 nm and with the bars separated by a 25-nm-thick SiO_2 layer. The optical constants of silver were taken from Ref. 25. We show in Fig. 2 the light-scattering spectra along several directions on the x-z plane ($\phi=0$). The beam geometry is illustrated in Fig. 1. The spectra exhibit two resonances at 580 and 685 nm, corresponding to symmetric and asymmetric modes, respectively. The calculated local-field distribution inside the metal structure allows us to obtain the current-density distribution and the multipole components of $\vec{P}$, $\vec{M}$, $\overleftrightarrow{Q}$, etc., on the structure. We can then calculate separately the complex far fields $\tilde{E}_P$, $\tilde{E}_M$, and $\tilde{E}_Q$, generated by $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$, and compare their relative strengths.[26] For the 580 nm resonance, we found that the currents in the two bars are in phase and the electric dipole radiation $\tilde{E}_P$ dominates. For the 685 nm resonance, the currents are largely out of phase as expected from an asymmetric mode. The corresponding field ratio in the forward direction ($\theta=0$) is $|\tilde{E}_{P_0}|:|\tilde{E}_{M_0}|:|\tilde{E}_{Q_0}|=1:0.81:0.62$. As the wavelength moves away from 685 nm, $|\tilde{E}_{M_0}|$ and $|\tilde{E}_{Q_0}|$ decrease rapidly, while $|\tilde{E}_{P_0}|$ changes only slightly. Therefore we attribute the electrical dipole field $\tilde{E}_{P_0}$ to the nonresonant contribution from the tail of the 580 nm resonance. The relative magnitudes of $\tilde{E}_{M_0}$ and $\tilde{E}_{Q_0}$ show that the contribution of the electric quadrupole is comparable to that of the magnetic dipole.

One may question whether other multipoles also contribute significantly to the far-field radiation. The answer from our calculation is negative. This can be seen by comparing

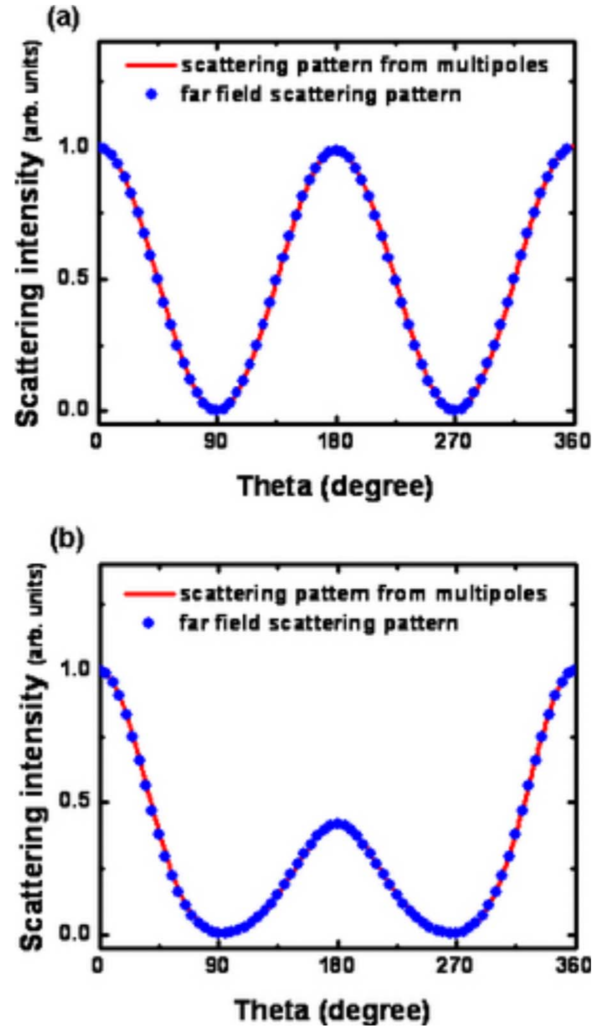

FIG. 3. (Color online) Comparison of the far-field scattering patterns on the x-z plane calculated from multipoles ($\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$) and directly from DDA calculation: (a) symmetric mode at 580 nm; (b) asymmetric mode at 685 nm. The solid curve corresponds to the scattering intensity calculated from $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$. The dots are the scattering intensities calculated directly from the DDA simulation. θ is the angle between the incident light and the scattered light propagation directions. The excellent agreement between curves and dots shows that the radiation from the parallel bar structure is dominated by $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$.

the coherent sum of radiation from $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$ with that directly obtained from the DDA simulation, which inherently includes radiation from all orders of multipoles. Figure 3 shows the comparison for scattered radiation at 580 and 685 nm on the x-z plane versus angle θ. The curves are the sums of radiation calculated from $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$ and the dots are directly from the DDA simulation. The agreement is almost perfect. Apparently, higher-order multipoles have much weaker radiation strengths that are negligible for these nanoscale structures. It is then possible to deduce $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$ unambiguously from the polarization-dependent and angle-resolved scattering spectra.

In practice, for nanostructures with certain symmetry, the multipole components can be easily determined by measuring the far-field radiation pattern along specific planes. For example, for the parallel bar structure in Fig. 1, the far fields generated from $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$ and propagating along $\hat{r}$ on the x-z plane are $\vec{E}_{P_0}\cos\theta$, $\vec{E}_{M_0}$, and $\vec{E}_{Q_0}\cos 2\theta$, respectively, with $\vec{E}_{P_0}$, $\vec{E}_{M_0}$, and $\vec{E}_{Q_0}$ being complex. The total scattered electric field is $\vec{E}_{\text{total}}=(|\vec{E}_{P_0}|\cos\theta+|\vec{E}_{M_0}|e^{i\phi_M}+|\vec{E}_{Q_0}|e^{i\phi_Q}\cos 2\theta)\hat{\theta}$, where the phases ϕ_M and ϕ_Q are relative to $\vec{E}_{P_0}$. The measured scattering spectra with their polarization dependence can be fitted by the total intensity $|\vec{E}_{\text{total}}|^2=||\vec{E}_{P_0}|\cos\theta+|\vec{E}_{M_0}|e^{i\phi_M}+|\vec{E}_{Q_0}|e^{i\phi_Q}\cos 2\theta|^2$ to obtain $\vec{E}_{P_0}$, $\vec{E}_{M_0}$, and $\vec{E}_{Q_0}$ and hence $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$. To demonstrate this, we fit the far-field scattering pattern directly obtained from DDA method to retrieve $|\tilde{E}_{P_0}|:|\tilde{E}_{M_0}|:|\tilde{E}_{Q_0}|=1:0.88:0.67$, whereas explicit calculation of $\vec{P}$, $\vec{M}$, and $\overleftrightarrow{Q}$ gives $|\tilde{E}_{P_0}|:|\tilde{E}_{M_0}|:|\tilde{E}_{Q_0}|=1:0.81:0.62$. The agreement shows that indeed it is possible to deduce separately the multipole contributions in a scattering experiment.

Now we have seen that since $\overleftrightarrow{Q}$ can be significant for the asymmetric resonance of a metallic nanostructure, it is important to examine its possible contribution to the effective ε and μ of a metamaterial. For an array of nanostructures, interactions between nanostructure units can affect the plasmon resonances. However, the multipole resonant characteristics should remain, and we expect electric quadrupole contribution to still be important at an asymmetric resonance. For the parallel bar structure, $\tilde{E}_M$ and $\tilde{E}_Q$ have the same phase in the forward and backward directions at the asymmetric resonance, and may appear indistinguishable for light propagation in the corresponding metamaterial. Therefore, one may anticipate that electrical quadrupole $\overleftrightarrow{Q}$ plays a similar role as that of magnetic dipole $\vec{M}$ and both contribute to the effective μ.

To be more rigorous, we examine the effective ε and μ of a metamaterial with reference to the Maxwell equations. It is known that at optical frequencies, ε and μ are not uniquely defined.[27–30] For instance, one can lump all material responses into a wave vector $\vec{k}$–dependent ε and set μ as 1. In the case of metamaterials, one often uses $\vec{k}$-independent effective ε and μ to describe electric dipole and magnetic dipole contributions of the responses, respectively. The question is whether in the presence of non-negligible electric quadrupole contribution it is still possible to have a description with $\vec{k}$-independent effective ε and μ so that simple Fresnel coefficients for transmission and reflection are still valid. This issue has not yet been addressed.

We consider the simple case of an isotropic bulk metamaterial. In this case, the electric quadrupole tensor is described by $Q_{ij}=i\alpha_Q(k_iE_j+k_jE_i)$, where α_Q is a constant and k_i and E_j are the components of wave vector $\vec{k}$ and incoming electric field $\vec{E}$. The macroscopic Maxwell equations are typically written in the form

$$\nabla\cdot\vec{D}=0,\qquad \nabla\cdot\vec{B}=0,$$

$$\nabla\times\vec{E}=-\frac{1}{c}\frac{\partial\vec{B}}{\partial t},\qquad \nabla\times\vec{H}=\frac{1}{c}\frac{\partial\vec{D}}{\partial t},$$

where $\vec{D}=\vec{E}+4\pi(\vec{P}-\nabla\cdot\overleftrightarrow{Q})\equiv\varepsilon(k)\vec{E}$ and $\vec{H}=\vec{B}-4\pi\vec{M}\equiv\mu\vec{B}$ are the electric displacement and magnetic field, respectively.

However, as we mentioned above, $\vec{D}$ and $\vec{H}$ are not uniquely defined.[27–30] The macroscopic Maxwell equations are invariant if we replace $\vec{D}$ and $\vec{H}$ with $\vec{D}'=\vec{E}+4\pi\vec{P}$ and $\vec{H}'=\vec{B}-4\pi(\vec{M}+\vec{M}_Q)$ with $\nabla\times\vec{M}_Q=-(1/c)[\partial(\nabla\cdot\overleftrightarrow{Q})/\partial t]$. For an isotropic material, we find $\vec{M}_Q=(\omega/c)^2\alpha_Q\vec{B}$. Together with the materials response relations of $\vec{P}=\chi_E\vec{E}$ and $\vec{M}=\chi_M\vec{B}$, it yields $\varepsilon=1+4\pi\chi_E$ and $\mu^{-1}=(1-4\pi\chi_M)-4\pi(\omega/c)^2\alpha_Q$, where both ε and μ are $\vec{k}$ independent and the latter contains an electric quadrupole contribution. This electric quadrupole contribution can be viewed as a resonance enhanced spatial dispersion in the metamaterial.

We show in the supplementary material[31] that the same conclusion can be reached by considering inclusion of electric quadrupole contributions in the derivation of transmission and reflection coefficients and matching them with the known Fresnel coefficients in terms of ε and μ. In this derivation, boundary conditions have to be treated with great care.[30]

Although our description is shown to be valid for an isotropic material, it also holds true for light propagation in high-symmetry directions in nonisotropic materials, which is often the experimental case. For instance, it applies to normal incidence of light in a fishnet metamaterial, where a negative refractive index has been reported.

In summary, we have shown that metamaterials consisting of a pair of metal bars or similar nanostructures may have electric quadrupole resonances comparable to magnetic dipole resonances in strength at the resonant frequency. Light-scattering spectroscopy on a unit nanostructure should allow separate determinations of the different multipole components at various resonant frequencies and hence determination of the nature of the resonances. In an isotropic metamaterial or anisotropic metamaterial with waves propagating along high-symmetry directions, the non-negligible electric quadrupole appears to contribute to the effective μ. This implies that electric quadrupole contribution may also yield a negative μ near its resonance in a metamaterial. Generally, electric quadrupole resonance can appear at a different frequency from the magnetic dipole resonance and may alone give rise to negative μ. This component may facilitate the design of resonance properties of future metamaterials.

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[31] See EPAPS Document No. E-PRBMDO-78-R04836 for derivation of the permittivity and permeability including the electric quadrupole contribution by considering the transmission and reflection coefficients from a dielectric-metamaterial interface. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.