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Jacob B. Khurgin
Johns Hopkins University

Greg Sun
University of Massachusetts Boston, greg.sun@umb.edu

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In search of the elusive lossless metal

J. B. Khurgin[1,a)] and G. Sun[2,b)]
[1]*Department of Electrical and Computer Engineering, The Johns Hopkins University, Baltimore, Maryland 21218, USA*
[2]*Department of Physics, University of Massachusetts Boston, Boston, Massachusetts 02125, USA*

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We show that when one looks beyond the Drude model of metal conductivity, the metals that may be extremely lossy for low frequency electromagnetic waves can become perfectly lossless in the mid-IR region or higher, while retaining the essential metallic characteristic of negative permittivity even at those frequencies. We identify that the transition to the lossless regime occurs when the interatomic distances in the lattice exceed certain values, typically a factor of two larger than those occurring in nature. We believe that advances in nanoassembly may render lossless metals feasible with revolutionary implications for the fields of plasmonics and metamaterials. © *2010 American Institute of Physics*. [doi:10.1063/1.3425890]

Recent years have seen an exponential growth in works dedicated to the study of various plasmonic and metamaterial schemes based on the interaction of optical waves with metals that are structured, typically, on a subwavelength scale and thus are capable of exhibiting prescribed optical properties that are unattainable in other materials.[1–3] Although interest in this problem is growing at an explosive rate, the main looming challenge to the practical implementation of anything containing metals in the optical frequency range remains unchanged and unmoved since the 1960s (if not earlier) when it was realized that all-dielectric structures, such as waveguides and fibers, potentially have much lower loss than metals. While a number of ways to reduce the losses in metals have been proposed by designing the structures with little metal penetration such as long-range surface plasmon polaritons[4] and others,[5,6] the reduction of loss always comes at the expense of commensurate, if not higher, reduction in the degree of optical field confinement, and, consequently, in the range in which optical properties of the metallic structures can be engineered.

The futility of attempts to reduce the losses of plasmonic and metamaterial structures by geometrical means is rather obvious from this straightforward argument. All the interesting effects in the metal-containing structures occur when the field becomes confined on a subwavelength scale which, according to Maxwell's equations, implies that the magnetic field becomes vanishingly small as we approach the so-called "electrostatic limit." Then, as we follow the evolution of the energy contained in the medium, when the phase is 0 or π the energy is entirely in the form of potential energy of charges and potentials but when the phase changes to $\pi/2$ or $3\pi/2$ the energy has nowhere to go but into the kinetic energy of moving electrons, and the electrons in the metal do get scattered by defects and phonons. Thus in a truly subwavelength in all three dimensions structure, or in a propagating plasmon with a wave vector much larger than wave vector in dielectric, about half of the time all the energy is contained in the kinetic motion of electrons. Hence, on average, the energy loss rate is about one half of the energy loss rate in the metal, with little regard to geometry.

Thus the only way to reduce the loss in subwavelength plasmonic and metamaterial structures is to reduce the loss of the metal itself while keeping it metallic, i.e., conductive and having a negative dielectric constant—a rather daunting task. The heavy impact of metal losses on the performance of metamaterials has been a subject of lively discussion in the literature[7–10] but to the best of our knowledge, that discussion did not go back to the basic physics of metals. The goal of this paper is to move the discussion to this basic level, which may yield unforeseen and potentially valuable results.

According to the Drude theory, the loss (imaginary part of the dielectric constant ε) of the metal is associated with the scattering of conduction electrons by defects, surface states, and lattice vibrations. Consequently, the most apparent path toward reduced loss is improving the quality of the metal to avoid defects but this method does not reduce scattering by the lattice vibrations. The latter can be mitigated only by lowering the temperature, and having practical devices operating at cryogenic temperatures is hardly an option. Furthermore, in small nanoparticles there is always a disproportionate contribution by surface states that is difficult to reduce. The alternative of adding optical gain to compensate the loss[11–13] requires very high gain material, complicates the fabrication, and leads to excess noise.[14] Therefore, within the constraints of Drude theory the prospect of ever finding or synthesizing a low loss metallic material appears to be doomed.

The argument of nonexistence of low loss metal holds well for low frequency electromagnetic radiation, defined here by $\hbar\omega < k_B T$. At these frequencies the dielectric properties of metal are determined entirely by the motion of conduction electrons near the Fermi surface. The imaginary part of the dielectric constant is associated with a transition between two states near the Fermi surface separated by energy $\hbar\omega_1$ [Fig. 1(a)], and momentum conservation requires that some scattering process associated with phonons or defects took place (dotted lines). At low frequencies there are always plenty of unoccupied final states slightly above the Fermi levels. Both real ε_r and imaginary ε_i parts of ε are proportional to the density of states on the Fermi level ρ_f, and the Drude theory remains mostly correct for both parts of ε.

a)Electronic mail: jakek@jhu.edu.
b)Electronic mail: greg.sun@umb.edu.

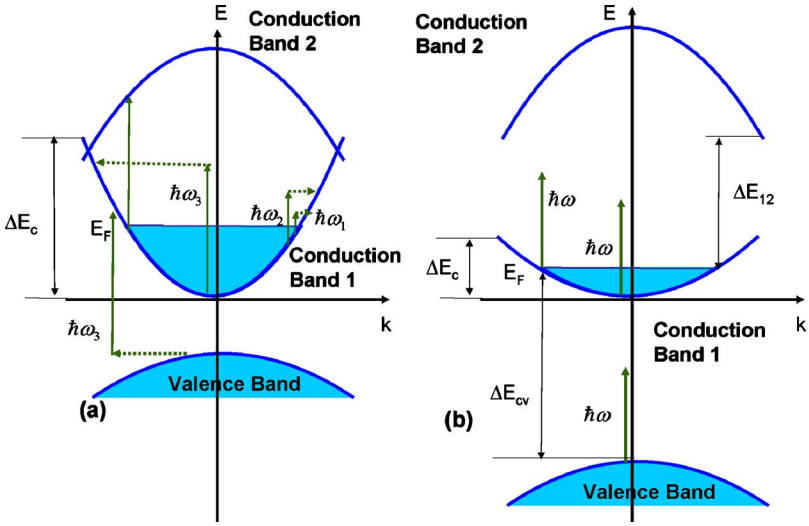

FIG. 1. (Color online) Absorption of electromagnetic waves in metal. (a) The low frequency $\hbar\omega_1, \hbar\omega_2$ radiation is absorbed by free carriers inside the lowest conduction band, while the higher frequency $\hbar\omega_3$ radiation is also absorbed by interconduction band transitions. (b) If the photon energy falls into the gap between two conduction bands the absorption cannot take place, while the dielectric constant can still be negative.

As frequencies increase, toward the near-IR and visible range shown as $\hbar\omega_3$, additional absorption channels open up that are associated with transitions from the lowest to the second conduction band and also from the deep valence band to the states above the Fermi level. These interband processes do not require (although do not preclude) scattering. It is well known that, at the onset of the interband transitions, the Drude theory loses validity for both ε_r and ε_i. What is perhaps less known is that Drude theory for the imaginary part of ε loses its validity even for the processes entirely contained within the conduction band as the frequency increases to the intermediate values $\hbar\omega_2$. As one can see from Fig. 1(a), energy conservation requires the free carrier absorption to take place between two real states separated by energy $\hbar\omega_2$ (the "Fermi golden rule"). Hence $\varepsilon_i(\omega_2)$ depends on the density of all the possible initial and final states in the conduction band. One can modify the Drude formula by making the scattering rate γ a function of frequency. At the same time, formally speaking, the real part of ε remains associated with virtual transitions occurring between a given partially filled state with wave vector $\mathbf{k}$ near Fermi surface and itself. (This can be best seen using the $\mathbf{A}.\mathbf{p}$ gauge for electron-photon interaction). Hence ε_r depends only on ρ_f, and one can write, using the Lindhard formula,[15]

$$\varepsilon(\omega) = \varepsilon_{ib}(\omega) - \omega_p^2/[\omega^2 + j\omega\gamma(\omega)] \approx \varepsilon_{ib}(\omega) - \frac{\omega_p^2}{\omega^2} + j\frac{\gamma(\omega)}{\omega^3}, \quad (1)$$

where $\varepsilon_{ib}(\omega)$ is the dielectric constant due to interband transitions,

$$\omega_p^2 = e^2\rho_f v_f^2/3\varepsilon_0, \quad (2)$$

is the plasma frequency, and v_f is the average velocity at the Fermi surface. It is important to emphasize that $\varepsilon_r(\omega_2)$ is practically unrelated to $\varepsilon_i(\omega_2)$ and only related via the Kramers–Kronig formula to the huge absorption at low frequencies $\varepsilon_i(0)$ [second term in Eq. (1)] and the interband absorption at higher frequencies [first term in Eq. (1)].

Once the real and imaginary parts of ε are decoupled, it becomes apparent that the road to small ε_i goes through reducing the density of the final states to which the transition can be made. And it follows, that, in the presence of a gap between two conduction bands, once the energy $h\omega$ is high enough that it is significantly (by at least the phonon energy) larger than the width of conduction band ΔE_c, as shown in Fig. 1(b), the density of possible final states becomes 0 and the free carrier absorption is eliminated. Now, in order to avoid interband absorption the photon energy should be also smaller than the gap ΔE_{12} between the Fermi level and the minimum of the second conduction band and the gap ΔE_{cv} between the top of the valence band and the Fermi level. When all three conditions are satisfied, the material does become lossless but the question remains whether the material remains a metal, i.e., whether $\varepsilon_r(\omega)$ as defined by Eq. (1) is still negative.

To answer this question, we shall now examine the reason why the natural metals do not have the lossless region, and, by doing so, we shall formulate the conditions that might open the possibility of reduced loss. First we use the tight-binding approach and apply it to the simplest of atoms, sodium, in which the lowest conduction band is formed by the half filled $3s$ orbitals and the next conduction band is formed by unfilled $3p$ orbitals, separated by about 2.1 eV. Na crystallizes in the bcc lattice with a lattice constant a; its reciprocal lattice is fcc. Introducing the coupling energy between two neighboring atoms $V_{ss} \sim V_0 \exp(-a\sqrt{3}/2a_0)$, where a_0 is the Bohr radius, we obtain the full width of the conduction band $\Delta E_c = 16V_{ss}$, Fermi wave vector $k_f = 6^{1/3}\pi^{2/3}a^{-1}$, and Fermi velocity $v_f \approx 1.16\hbar^{-1}V_{ss}a$. Given that $\rho_f = \hbar^{-1}\pi^{-2}v_f^{-1}k_f^2$ and substituting it all into Eq. (2) we obtain,

$$\hbar^2\omega_p^2 \approx 0.6e^2V_{ss}/a\varepsilon_0. \quad (3)$$

Therefore, now the lossless metal condition that $\varepsilon_r(\omega) < 0, \varepsilon_i(\omega) \to 0$ becomes,

$$16V_{ss} = \Delta E_c < \hbar\omega < \hbar\omega_p\varepsilon_{ib}^{-1/2} = [0.6e^2V_{ss}/a\varepsilon_0\varepsilon_{ib}]^{1/2}. \quad (4)$$

For such a lossless metallic region to exist the plasma energy should the width of the band by some margin of K, meaning

$$\hbar^2\omega_p^2 \approx 0.6e^2V_{ss}/a\varepsilon_0\varepsilon_{ib} = K^2\Delta E_c^2 = 256K^2V_{ss}^2, \quad (5)$$

which immediately results in

$$V_{ss} = 4 \times 10^{-3}e^2/K^2a\varepsilon_0\varepsilon_{ib} \approx 1.2a_0/aK^2\varepsilon_{ib}(\text{eV}). \quad (6)$$

Now, given the exponential dependence of coupling energy on the lattice constant, Eq. (6) can always be satisfied for the a reasonably large lattice constant. In Fig. 2 we show the dependence of the energy spread in the $3s$ and $3p$ con-

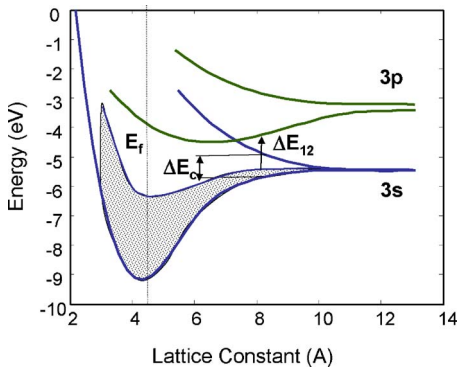

FIG. 2. (Color online) Energy bands in the bcc Na as functions of lattice constant.

duction bands as a function of the lattice constant according to Slater,[16] and one can see that $\Delta E_c = 16V_{ss}$ decreases rapidly once the lattice constant increases by only a few angstrom from the equilibrium value of 4.3 A. Therefore, Eq. (4) becomes,

$$19.2a_0/aK^2\varepsilon_{ib} < \hbar\omega < 19.2a_0/aK\varepsilon_{ib}. \quad (7)$$

At the same time, one can see that the splitting between the $3s$ and $3p$ bands appears only at $a > 7A$. So to assure that $\hbar\omega_p < \Delta E_{12}$ it is reasonable to take $a > 8A$ which results in the relation $\hbar\omega_p \approx 1.12\ \text{eV}/K\varepsilon_{ib}$.

Since all the other bands are split by large distances from the conduction bands we can assume that ε_{ib} is on the order of unity. Then taking $K \sim 1.5$ we obtain a plasma energy of about 0.75 eV ($\lambda_p \sim 1700$ nm), indicating that our hypothetical material still behaves like a metal without any significant loss in the range of 1700–2500 nm with real and imaginary parts of ε sketched in Fig. 3. One can see that the transparent region is bound on the long wavelength side at $\lambda_c = hc/\Delta E_c$ by the onset of free carrier absorption inside the $3s$-band and on the short wavelength side at $\lambda_{12} = hc/\Delta E_{12}$ by the onset of nominally forbidden (weak) interband absorption from the $3s$ to the $3p$ band. The dashed line shows the free carrier absorption using the Drude approximation with $\gamma = 10^{14}\ \text{s}^{-1}$ (scattering time of 10 fs). The actual absorption starts deviating from the Drude formula when the photon energies become commensurate with the conduction band width.

It is essential to stress here once again that, no matter how strong the scattering inside the band, there will be no absorption in the perfectly reflecting interband region because there are no states there. The situation is no different

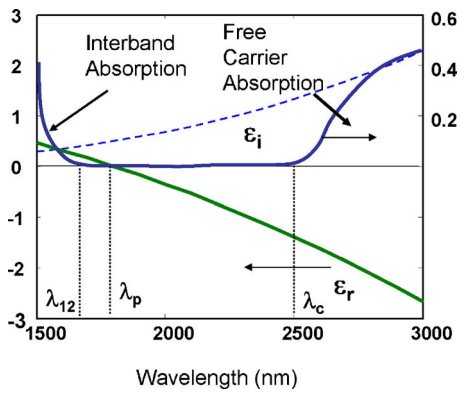

FIG. 3. (Color online) Real and imaginary parts of the dielectric constant for bcc Na with lattice constant of $8A$. The dashed curve shows ε_i in Drude approximation with a scattering constant of $\gamma = 10^{14}\ \text{s}^{-1}$.

from the one occurring in transparent dielectric and semiconductor materials (Urbach tail),[17,18] where far below the band gap the imaginary part of ε is much less than predicted by Lorentz formula. For instance, the scattering rate of valence electrons in optical glass is easily on a scale of only a few femtoseconds, and a simple application of Lorentz formula would yield a huge absorption in the mid-gap, on the order of 10 cm^{-1}. Yet, in reality the absorption is orders of magnitude less than that simply because there is no real states in the midgap, other than a few impurity states. Similarly and inevitably, there will be defect and surface states situated in the gap between two conduction bands in the real metal but their density is far less than the density of states inside the band and absorption will still be orders of magnitude less.

It goes without saying that naturally occurring metals typically crystallize with distances between neighboring atoms that are roughly half of the ones required to narrow the bands enough to render the metal lossless. One can argue that it happens because the interatomic electrostatic forces are just too strong for the lossless metal to occur. But what is important is that this limitation is (a), not fundamental and (b) is not by orders of magnitude. Thus the situation is thorny, yet not hopeless, as there remains a possibility that using modern methods of nanoassembly synthetic structures with larger interatomic distances can be built from scratch, perhaps by using closed shell atoms between the metal atoms to effectively screen the electrostatic field, for instance in aluminum monoxide AlO (Ref. 19) the Al atoms are separated by a full lattice space and it is still a metal since one of three Al valence electrons remains in the conduction band.

The solution may also be found in organometallic compounds or by going to lower dimensional structures. It is precisely to stimulate the research along these and other, yet unknown directions that we have presented our results here. Reducing the metal loss by orders of magnitude as outlined here is the key to making a practical field out of what has been largely a research enterprise in plasmonics and metamaterials, and it is our belief that eventually the quest for the elusive lossless metal will come to fruition.

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