One-Dimensional Epsilon-Near-Zero Crystals

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Alternating multilayer architectures are an ideal framework to tailor the properties of light. In photonic crystals, dielectrics with different refractive indices are periodically arranged to provide a photonic bandgap. Herein, it is shown that a periodic arrangement of metal/insulator layers gives rise to an Epsilon-Near-Zero (ENZ) crystal with distinct bands of vanishing permittivity. The analogy of metal/insulator/metal (MIM) cavities to wave mechanics that describes them as quantum-wells for photons is elaborated, and the Kronig–Penney (KP) model is applied to MIM multilayers. This KP modeling allows to extract the density of states for ENZ crystals appealing for lasing applications. The ENZ bandwidth can be tuned by the thickness of the metal layers and can span the entire visible range, and the interactions between bands of two different cavity subsystems in more complex ENZ crystals enable more elaborate ENZ band engineering. Finally, the difference between the ENZ crystals and hyperbolic metamaterials is elucidated and the conditions that separate these two regimes are quantified. The ENZ crystals constitute a new paradigm in the study of metal/insulator multilayers, and showcase a promising platform for light–matter interaction in photonic and plasmonic technologies.

1. Introduction

The interplay between light and matter is governed by a complex quantity called dielectric permittivity \( \varepsilon(\lambda) \) that refers to the material in which the propagation takes place.\[13\] In general, this quantity varies significantly with the wavelength of light. At wavelengths where the real part of the dielectric permittivity crosses zero, accompanied by a reasonably low imaginary part, the fascinating Epsilon-Near-Zero (ENZ) wave propagation regime occurs.\[2–4\] The vanishing permittivity enables a large variety of interesting optical properties such as nonlinear effects,\[5–8\] adiabatic frequency shifting,\[9\] ultrafast optical switching,\[10,11\] negative refraction,\[12\] intraband optical conductivity,\[13\] phase singularity engineering,\[14\] appearance of Casimir forces\[15\] and metatronics.\[16\] The ENZ regime occurs naturally in some materials. Silver is a well-studied example, where the real part of its dielectric permittivity crosses zero around 325 nm with a sufficiently low imaginary part \( (\varepsilon^\prime = 0.6) \).\[17\] Highly doped semiconductors and polaritonic materials show such a feature as well, with the advantage that their ENZ wavelength can be tuned by varying their doping level.\[18–21\]

Among them, indium tin oxide (ITO) is by far the most studied.\[22–26\] However, the ENZ wavelength of ITO is in the near-infrared spectral range (around 1530 nm), and moving it to the visible would require doping well beyond the solubility limits. Moreover, obtaining a broad ENZ response in highly doped semiconductors is still very challenging. One approach to overcome this drawback is to design waveguides and to exploit their cutoff wavelength.\[18,27–29\] This approach has pioneered the experimental demonstration of an ENZ dispersion, but it relies on a guided geometry that puts stringent constraints in terms of acceptance angle, coupling losses, and hinders the integration in nanostructured devices.\[20,21\] An ENZ response can also result from a hyperbolic (or “indefinite”) dispersion, which occurs in some materials such as graphite,\[30\] hexagonal boron nitride,\[31,32\] and tetradymites.\[33\] However, such “natural” hyperbolic materials manifest an ENZ permittivity only at a fixed wavelength that is defined by their bulk properties. Hyperbolic metamaterials (HMMs) are artificially designed structures where deep subwavelength patterns result in a hyperbolic dispersion. One archetypical architecture of HMMs consists in deeply subwavelength metal/dielectric multilayers that manifests strong optical anisotropy together with a hyperbolic dispersion that is customizable via the design of the metal/dielectric fill fraction.\[34–36\] HMMs usually manifest a single ENZ wavelength, and can be treated by the effective medium approximation.
(EMA) that describes the optical properties of the multilayer stack within the quasistatic limit. Therefore, the wavelength must be much larger than the layer thicknesses (roughly by a factor of 50). This has the consequence that no optical cavity resonances can be sustained in the layers.\cite{37} HMMs have been recently described by a Kronig–Penney (KP) modeling approach that considered the propagation of strictly evanescent waves in both the metallic and dielectric layers.\cite{48}

Metal/insulator/metal (MIM) nanocavities, where the dielectric layers act as optical cavities, are an interesting alternative as design-flexible ENZ materials to their natural counterparts and HMMs.\cite{38–41} The optical response of these layered systems can be described by an effective permittivity that can be directly measured by spectroscopic ellipsometry. As a strong point, their ENZ wavelength can be straightforwardly tuned by changing the thickness of the dielectric layer. We recently demonstrated that the optical properties of MIM nanocavities can be understood by a semiclassical model built on the analogy between wave optics and quantum mechanics.\cite{42–44} This model was extended to coupled MIM cavity systems, providing an accurate description of the resonances and modal dispersion, including the mode hybridization in the double-cavity MIMIM system, whose dynamics resemble those of molecular orbitals.\cite{42, 45–47}

In this article, we demonstrate that a periodic arrangement of MIM cavities forms an ENZ crystal in analogy to the periodic arrays of atoms in solid-state crystals. We investigate MIM systems of one up to ten stacked photonic cavities and measure their optical response by spectroscopic ellipsometry. The optical properties of the ENZ crystals can be described in the framework of a KP model adapted to metal/insulator multilayers. In this scenario, we show that the waves propagating within the ENZ crystal represent Bloch waves. The KP model allows us to derive the dispersion relation $k(E)$ of the crystal wave vector $k$ as a function of the energy $E$, and to introduce the concept of density of ENZ states in the crystal that, in analogy to solid-state crystals, strongly increases toward the band edges. One interesting feature is the dispersion with negative slope of the high energy (HE) band related to the antibonding mode that translates to a negative group velocity of the propagating wave. We demonstrate via COMSOL-based simulations that in the frequency range corresponding to this antibonding band, negative refraction occurs. The ENZ crystal can be seen as to consist of MIM cavities as unit cells. This is instructive, since the center wavelength of the bands is defined by the dielectric layer thickness as in the MIM, and also the angular dispersion of the resonances is maintained. Furthermore, the width of the ENZ band depends on the thickness of the metal layer, in analogy to the resonance splitting in MIMIM systems.\cite{46} By controlling the metal layer thickness, we were able to engineer ENZ bands with $\approx$475 nm bandwidth, covering almost the entire visible range. The concept of ENZ crystals can be extended to more complex architectures that include two subsets of MIM cavity unit cells with different dielectric layer thickness, which allows to investigate coupling of resonances with different frequencies. We note that our KP approach, in which we consider photonic cavities that allow for standing waves, is substantially different from the study of Li and Khurgin,\cite{48} where HMMs were treated in a plasmonic picture with fully evanescent waves, and also from photonic crystals, where the photonic band gap originates from Bragg reflection.\cite{49–52}

Finally, we put the MIM nanocavities in perspective to layered HMMs. Both systems are formed by alternating metal and dielectric layers, but HMMs consist of layers with deep subwavelength thicknesses, whereas the dielectric layers in the MIM nanocavities are sufficiently thick to act as optical cavities. Here, the smallest thickness below which the dielectric layer in the MIM does not sustain cavity modes constitutes the boundary between ENZ crystals and HMMs.

2. Results and Discussion

2.1. Concept of ENZ Bands

A single MIM cavity sustains at least one resonant mode provided that the thickness of the dielectric layer is sufficient. An insightful way to describe the MIM cavity is to homogenize its optical response via an effective dielectric permittivity that can be directly measured by ellipsometry.\cite{48} We recently demonstrated that in correspondence of the cavity modes, the real part of the measured effective permittivity of the MIM crosses zero whereas the imaginary part is sufficiently low to allow resonant tunneling, and therefore, these modes can be classified as ENZ resonances.\cite{45} We note that the ENZ dispersion arising at the cavity mode of a MIM is substantially different from that of a waveguide working at its cutoff frequency, as discussed in Section 1 of the Supporting Information.

Resonances in multiple stacked MIM cavities connected via thin metallic layers split due to mode coupling. This concept, which is at the base of our approach toward systems sustaining ENZ bands, and which shares many analogies with the mode splitting of the electronic orbitals in an array of interacting atoms, is shown in Figure 1. For the metal/dielectric cavities under discussion, the mode splitting occurs due to strong coupling between the cavity modes, and the coupling strength depends mainly on the thickness of the intermediate metal layers.\cite{45, 46}

If the single MIM, that can be seen as a unit cell of the ENZ crystal, shows one ENZ mode, the associated multilayer shows one single ENZ band (Figure S2, Supporting Information). However, if the MIM unit cell is sufficiently thick to sustain multiple modes (Figure 1a), several ENZ bands are formed, where each band can be associated to a specific mode of the MIM unit cell. In analogy to a band structure, these ENZ bands are separated by a bandgap (Figure 1b).

Following the approach outlined in Figure 1, we fabricated metal/insulator stacks consisting of Ag (35 nm) and ITO (60 nm) layers with different numbers of cavities. Here, ITO was chosen as the dielectric, due to its high refractive index and transparency in the visible spectral range, and because of its straightforward deposition via DC magnetron sputtering (we note that our approach works equally well with, for example, Al$_2$O$_3$ as dielectric, as demonstrated in the Supporting Information). Silver was selected as metal, due to its optimal refractive index that fulfills the hermiticity requirements described in our previous work.\cite{53} Figure 2a shows the s-polarized reflectance measured by ellipsometry at an incidence angle $\theta = 30^\circ$ for up to ten stacked cavities. The p-polarized spectra show very
similar behavior and are plotted in Figure S2 of Section 2, Supporting Information. As demonstrated in our earlier work on MIM and MIMIM systems,\textsuperscript{[46]} the minima in reflectance that correspond to maxima in transmission (see also Figure 2e), can be classified as ENZ resonances of the multistack. For up to five cavities, the different ENZ resonances can be clearly discerned, as highlighted by black circles in Figure 2a. For larger cavity number, modes start to overlap and form a continuous dip in reflectance so that for ten cavities, a band of around 140 nm bandwidth is formed (380–520 nm). The experimental data is in excellent agreement with the scattering matrix method (SMM) simulations shown in Figure 2b.

The optical response of metal/insulator systems can be described by a homogenized dielectric permittivity that can be measured via spectroscopic ellipsometry. The real and imaginary part of the effective dielectric permittivity of multilayers up to three cavities are shown in Figure 2c, d, respectively. The (near) zero-crossings that coincide with a small imaginary part fulfill the ENZ condition and are highlighted by the vertical dashed lines. These wavelengths coincide with the minima in reflectance (\(R\)) curves and the maxima in transmission (\(T\)) plotted in Figure 2e. With the absorbance (\(A\)) as \(A = 1 - T - R\), we obtain also maxima in absorbance (Figure 2e) at these wavelengths, and we consider this coincidence of maxima absorbance and transmission, that...
is a signature of resonant tunneling, as the ENZ criterium. A detailed investigation of the effective permittivity of ENZ crystals is given in Section 3, Supporting Information, where we also elucidate that modeling of the zero-crossing of the real effective permittivity for modes at the band edges is challenging, although these still preserve the ENZ properties.

2.2. KP Model for ENZ Crystals

In a previous work, we have demonstrated that the MIM nanocavity can be treated with a semiclassical approach as a quantum well for photons.\(^{[45]}\) In this view, the metal plays the role of a potential barrier whose height is given by the square of the imaginary part of its refractive index, \(\kappa^2\). The dielectric layer corresponds to the potential well of depth \(-n^2\), where \(n\) is the real part of the refractive index.\(^{[45]}\) In this scenario, the multilayer stack can be seen as a 1D series of quantum wells (Figure 3a), to which the KP model can be applied.\(^{[53–57]}\) For a potential well width of \(t_w\) and a barrier width of \(t_m\), the KP model yields the dispersion relation

\[
f(\alpha t_m, \beta t_d) = \frac{\alpha^2 - \beta^2}{2\alpha \beta} \sinh(\alpha t_m) \sin(\beta t_d) + \cosh(\alpha t_m) \cos(\beta t_d) = \cos(\kappa L)
\]  

\[
\kappa = k_0 \kappa_m
\]  

\[
\beta = k_0 n_d
\]

in the barrier (corresponding to the metal), and in the dielectric that corresponds to the well. Here, \(k_0 = 2\pi/\lambda\).

Substitution of Equations (2) and (3) into Equation (1) gives the dispersion relation for the ENZ crystal

\[
\kappa L = \frac{\kappa_m^2}{\kappa_m n_d} \sinh(k_0 \kappa_m t_m) \sin(k_0 n_d t_d) + \cosh(k_0 \kappa_m t_m) \cos(k_0 n_d t_d) = \cos(kL)
\]  

(4)

Since the right term in Equation (4) is a cosine, light propagation inside the ENZ crystal is only allowed in the spectral range where \(f(\alpha t_m, \beta t_d)\) falls between \(-1\) and \(1\). This range constitutes the ENZ band. Outside of this range, wave propagation is suppressed and, therefore, this region represents the bandgap.
to the well-known Ferrell–Berreman mode,[58–62] and for wavelengths smaller than 327 nm Ag does not behave like metal. Therefore, the description of periodic potential wells does not work in this regime in which the system does not sustain any resonances. Starting from the dispersion relation reported in Equation (4), it is possible to derive the dependence of the wave vector \( k \) on the wavelength \( \lambda \). It is, however, convenient to refer to a quantity \( k_{\text{norm}} = k(\lambda) \cdot \lambda / \pi \). The dispersion of \( k_{\text{norm}}(\lambda) \) is plotted in Figure 3d and corresponds to the more broadly used \( E(k) \) band diagram of a crystal, as shown in the inset. By differentiating \( k_{\text{norm}} \) with respect to the energy \( E \), we can express the density of epsilon-near-zero states (DoES) for the ENZ crystals (Figure 3e).\(^{[53]} \) In fact, the spectral distribution of the modes in the ENZ crystal is not homogeneous, but manifests a larger number of modes near the band edges, as shown in Figure 1b and calculated for the decane molecule in Figure S4g, Supporting Information. A detailed discussion on the DoES is presented in Section 3, Supporting Information.

For the particular system described in Figure 3, the slope of the \( E(k_{\text{norm}}) \) curve is always positive. However, if the thickness of the dielectric is increased, new allowed bands appear in the visible range, related to higher-order modes. This is the case, for example, for the ten-cavity-ENZ crystal in Figure 1. The MIM unit cell cavity shows two modes, at \( \approx 680 \text{ nm} \) and \( \approx 375 \text{ nm} \), respectively. Stacking ten of these cavities on top of each other leads to the formation of two bands that are centered at the wavelengths of the two unit-cell modes, as shown in Figure 4a–e.

In particular, the multiple hybridization of the MIM mode at 675 nm gives origin to a low energy band (LE), whereas the mode at 375 nm gives rise to a HE band in Figure 4a, where the KP function for such an ENZ crystal is plotted. The spectral region separating the allowed bands can be defined as the “bandgap” of the ENZ crystal. The fact that the HE band stems from the hybridization of HE modes furthermore excludes backfolding of the LE dispersion into the first Brillouin zone due to superlattice effects as the origin of the HE band.\(^{[63]} \) Figure 4b shows the SMM calculated reflectance at normal incidence. Two valleys are visible in correspondence of the two ENZ bands, demonstrating that the light can be coupled in the ENZ crystal only within the ENZ band, whereas in the spectral regions of bandgap, the reflectance of the ENZ crystal is very high. Moreover, the reflectance valley in the LE band shows several dips, which are the hybridized LE modes of the ten cavity ENZ crystal, and their spectral superposition composes the band. Thus, in analogy with the electronic states in solid-state crystals, the band is made of a large number of discrete allowed states. If the spectral superposition of the modes in the band is sufficient, the band appears as a continuum, as in the case of the HE band, that results in a smooth valley in reflectance. The \( k_{\text{norm}} \) vector for this system is shown in Figure 4c. In Figure 4d, the \( dE/dk \) diagram shows that the DoES increases at the band edges, in very good agreement with the SMM simulation results in Figure 1. The \( k_{\text{norm}}(\lambda) \) diagram for the ideal (infinite) ENZ crystal shown in Figure 4c can be reversed to obtain the more common \( E(k_{\text{norm}}) \) band diagram shown in Figure 4e. Interestingly, the HE band in Figure 4e shows a negative \( E(k_{\text{norm}}) \) dispersion. More generally, we can say that if a band derives from the hybridization of symmetric modes, its slope is positive, whereas it is negative if the band comes from the hybridization of antisymmetric ones. From the \( E(k_{\text{norm}}) \) dispersion, the group velocity of the propagating wave in the ENZ crystal can be derived as\(^{[53]} \)

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**Figure 4.** ENZ crystal with HE and LE bands. a) KP function, b) reflectance at normal incidence, c) \( k_{\text{norm}} \), and d) \( dE/dk \) for a 20/120 nm Ag/ITO ENZ crystal made of ten stacked MIM cavities. e) \( E(k_{\text{norm}}) \) band diagram of the corresponding ENZ crystal. f,g) Amplitude of electric field for a monochromatic plane wave incident at an angle of 30° on the ten cavity structure, with wavelength in the center of the HE band, f) at 360 nm, and at the LE band edge of it g), at 420 nm. The field is plotted on log-scale, on top of which the Poynting vector is traced by black arrows. The data are calculated via COMSOL Multiphysics.
For the HE band, \( \frac{dE}{\hbar k_{\text{norm}}} \) is negative and, consequently, also the group velocity. Since the group velocity is associated to the energy propagation in the crystal, a negative group velocity leads to negative refraction, a phenomenon that has been predicted to occur in the so-called left-handed materials. Figure 4f,g show a COMSOL Multiphysics based simulation of the amplitude of the modulus of the electric field inside the ten cavities ENZ crystal. We considered illumination at an angle of incidence of \( \theta = 30^\circ \), and at two wavelengths: \( \lambda = 360 \text{ nm} \), at the center of the HE band (Figure 4f) with clearly negative slope, and \( \lambda = 420 \text{ nm} \) for which a high DoESs together with an almost flat slope are found. The dashed arrows in Figure 4f,g indicate the Poynting vector outside and inside the ENZ crystal, calculated via COMSOL-based simulations, and highlight the signature of negative refraction at 360 nm wavelength. Interestingly, since at 420 nm, the slope of the \( E(k_{\text{norm}}) \) dispersion is almost flat, the group velocity approaches zero, fulfilling the slow-light confinement typical of ENZ modes. Therefore, the phase velocity approaches infinity, leading to an almost vertical Poynting vector within the ENZ crystal. Such a feature is typical for ENZ materials and corresponds to the propagation of a wave with an almost infinite wavelength.

2.3. ENZ Crystals with Two MIM Cavity Subsystems and Analogy to Molecular Orbitals

The ENZ multilayer inherits the spectral characteristics from its fundamental MIM components, as well as the coupling dynamics between adjacent cavities. Therefore, the center position of the bands can be tuned via the thickness of the dielectric layers similarly to the cavity resonance in a MIM system. The bandwidth of an ENZ crystal can be varied via the thickness, and at two wavelengths: \( \lambda = 360 \text{ nm} \), at the center of the HE band (Figure 4f) with clearly negative slope, and \( \lambda = 420 \text{ nm} \) for which a high DoESs together with an almost flat slope are found. The dashed arrows in Figure 4f,g indicate the Poynting vector outside and inside the ENZ crystal, calculated via COMSOL-based simulations, and highlight the signature of negative refraction at 360 nm wavelength. Interestingly, since at 420 nm, the slope of the \( E(k_{\text{norm}}) \) dispersion is almost flat, the group velocity approaches zero, fulfilling the slow-light confinement typical of ENZ modes. Therefore, the phase velocity approaches infinity, leading to an almost vertical Poynting vector within the ENZ crystal. Such a feature is typical for ENZ materials and corresponds to the propagation of a wave with an almost infinite wavelength.

For systems where the two resonance frequencies approach each other, the coupling dynamics can be explored by fixing the thickness of the dielectric layer \( t_\text{d-fix} = 100 \text{ nm} \) in one subsystem and varying that of the second one \( t_\text{d-var} = 200 \text{ nm} \). Sweeping the width of the dielectric layer of the variable subsystem allows to tune this band across that of the fixed subsystem. As discussed earlier, the coupling dynamics between the cavities can be seen in analogy to the hybridization of atomic orbitals. Atomic orbitals with very different energies weakly interact if superimposed, thus causing only small variations in both character and energy of the molecular orbitals. Orbitals with similar energies couple strongly, giving rise to larger energy splitting and character mixing. Therefore, when the thicknesses of the two subsets of cavities are very different (and, therefore, the resonances are far in energy), interactions between neighboring cavities become negligible, and the ENZ bands arise mostly from interactions between cavities of the same thickness.

As in the case of molecular orbitals, the interaction between the modes of the ENZ crystal considered in Figure 5d becomes stronger as the resonance of the varying cavity approaches that of the fixed one. When the dielectric layer thicknesses of two subsystems are the same, the resonances of the modes belonging to each of the two ENZ bands strongly interact, giving rise to avoided crossings of the resonances. This leads to the splitting of the energy levels, which is evident in Figure 5e, where the transmittance spectrum of the complete ENZ crystal, calculated via SMM simulations, is depicted. At the crossing point, the transmittance of the ENZ crystal manifests a minimum, where the single MIM component has its resonance and, therefore, shows maximum transmittance. The inset of Figure 5e shows the reflectance of the system at the anticrossing point, at a magnified scale, manifesting a maximum where the single MIM would be at resonance with minimum reflectance. We note that the matching of minimum in reflectance with maximum in transmission highlights the ENZ nature of the modes (see Section 8. Supporting Information for a full range plot of the reflectance). The ENZ crystal consisting of two different cavity subsets can be included in the framework of the ENZ KP model by taking a constant function \( f_\text{fix}(\alpha m, \beta d) \) associated to the fixed subsystem, and a function \( f_\text{var}(\alpha m, \beta d-\text{var}) \) for the one with
The function of the total ENZ crystal becomes

\[ f_{\text{tot}}(\alpha_t, \beta_t) = f_{\text{fix}}(\alpha_t, \beta_t) \times f_{\text{var}}(\alpha_t, \beta_{t\text{--var}}) \]  

Equation (6)

Figure 5f shows the wavelengths at which \( f_{\text{tot}}(\alpha_t, \beta_t) \) crosses 1 and \(-1\), and the obtained pattern follows the band edges in Figure 5e.

2.4. Differentiating ENZ Crystal and HMM Regimes

ENZ crystals are formed if the dielectric layers are sufficiently thick to sustain optical resonances. Beyond this limit, for layer thicknesses that are much smaller than the wavelength of light, metal–insulator stacks can act as HMMs, and the EMA can be used for modeling the optical response if the thickness of the layers is deeply subwavelength.\(^\text{35,36,69,70}\) In this approach, HMMs can be described as a uniaxial crystal in which the
in- and out-of-plane optical constants can be expressed as follows:\cite{36,67,68}

\begin{align}
\varepsilon_{||} &= \frac{\varepsilon_d t_d + \varepsilon_m t_m}{t_d + t_m} \tag{7} \\
\varepsilon_{\perp} &= \frac{\varepsilon_d \varepsilon_m (t_d + t_m)}{\varepsilon_d t_d + \varepsilon_m t_m} \tag{8}
\end{align}

Here, \( \varepsilon_m \) and \( \varepsilon_d \) are the dielectric permittivities of the metal and of the dielectric, respectively, and \( t_m \) and \( t_d \) their thicknesses. In order for the multilayer to manifest an indefinite (hyperbolic) dispersion, the sign of \( \varepsilon_{||} \) and \( \varepsilon_{\perp} \) must be opposite: with \( \varepsilon_{||} < 0 \) and \( \varepsilon_{\perp} > 0 \), the HMM has a Type I anisotropy, whereas for the opposite case it is a Type II anisotropy. This approximation assumes that either the electric field (concerning \( \varepsilon_{||} \)) or the displacement field (concerning \( \varepsilon_{\perp} \)) is continuous at the metal/dielectric interfaces.\cite{71} However, an upper limit for the layer thicknesses has not been quantified, and it is interesting to establish how much smaller the layer thicknesses have to be with respect to the operating wavelength for precise modeling with the EMA. For example, several structures have been analyzed in the framework of the EMA neglecting the description of optical features, such as reflectance dips (transmittance peaks) occurring in spectral regions characterized by EMA-calculated dispersions defined as "effective dielectric" or "Type I."\cite{72,73}

From Equation (7), we see that the EMA associates the same optical constants to all systems with equal metal and dielectric layer thicknesses. These systems are known to manifest the so-called ENZ and Pole HMMs, to which many fascinating properties, from super-collimation to laser emission, are associated.\cite{72,74,75}

**Figure 6a** shows the in- and out-of-plane effective permittivity derived by EMA for a metal/dielectric multilayer made of Ag and ITO with equal thickness. In particular, two different Ag/ITO multilayers of 20/20 nm and 80/80 nm metal/dielectric layer thickness are shown. The effective dielectric permittivities of these two systems, calculated via the EMA, are identical since, in this case, \( t_m \) and \( t_d \) cancel out, which leads to one single \([\varepsilon_{||}, \varepsilon_{\perp}]\) pair of curves. However, the scattering response of the two systems is very different as is shown in Figure 6b by the Absorbance \((1 - (\text{Transmittance} + \text{Reflectance}))\) of the two multilayers. The 80/80 nm Ag/ITO multilayer (blue curve) manifests a pronounced absorption band between 506 and 535 nm (highlighted with blue shading). This behavior is neglected by EMA that predicts such a system to be highly reflective, thus in the deep Type II hyperbolic regime. However, our ENZ KP representation shown in Figure 6c captures this absorption band by the condition \(-1 < f(ab, \beta a) < 1\) that is fulfilled in the range between 506 and 535 nm (Figure 6c blue curve). Interestingly, the LE band edge related to the 20/20 nm Ag/ITO system is very close to the Type I/Type II transition predicted by the EMA. Figure 6d reports the HE and LE band edges as a function of the dielectric layer thickness, together with the topological transition obtained from EMA. We find that the topological transition converges with the LE band edge for \( t_d < 7\) nm, which coincides with the smallest dielectric layer thickness at which a single MIM cavity (in the Ag/ITO material system) can sustain a mode. This lower limit can be found by analyzing the exact dispersion of the MIM cavity.
\[
\tan \left( \frac{2\pi}{\lambda} \left( n_d - \frac{1}{2} \right) \right) = \frac{\epsilon_m}{\epsilon_d}
\]  

Equation (8) is geometrically solved in Figure 6e, as a function of the dielectric layer thickness. Below \( t_d = 7 \) nm (green curve in Figure 6e), there is no intersection between the left and the right terms of Equation (8), and therefore, no cavity mode can be excited. In this regime, the propagation in the metal/insulator multilayer is sustained only by evanescent waves and the EMA can describe the system with very good precision (this is also the regime discussed by a KP approach in the study by Li and Khurgin). Above this regime, the optical response of the multilayer system cannot be precisely described by the local EMA, and this thickness delimits the boundary between HMMs and ENZ crystals. We note that the value of this thickness limit depends on the dielectric material, for example, with \( \text{Al}_2\text{O}_3 \) as dielectric we obtain \( t_d = 13 \) nm (see Section 9, Supporting Information).

3. Conclusion

We demonstrated that the multiple hybridization of ENZ modes in stacked multilayers of MIM resonators leads to ENZ bands that can be described in analogy to the electronic band structure in solid-state crystals. In this frame, the metal and dielectric multilayers form a periodic potential for photons to which the KP formalism can be applied, implying that waves traveling in the ENZ crystal are Bloch waves. This approach leads to an \( E(\kappa_{\text{norm}}) \) band diagram where bands with positive and negative slope are present. Consequently, the DoES can be defined in the ENZ band, manifesting a sharp increase at the band edges. The combination of the increased spectral bandwidth of the resonating cavity in ENZ crystals, together with the increased density of states at the band edge, provides highly promising conditions for lasing if a gain material is embedded in the system [76, 77].

Furthermore, our approach yields a negative dispersion for the ENZ band stemming from antisymmetric modes, which relates to a negative group velocity in the ENZ crystal, resulting in negative refraction. We predict that, by reducing the thickness of the metal layers, an ENZ bandwidth of about 475 nm can be engineered, covering almost the entire visible range. Our semiclassical model of metal/insulator multilayer structures also elucidates the boundary between ENZ crystals and HMMs as the minimum thickness of the dielectric layer at which cavity modes can occur. For thicker dielectric layers that sustain cavity modes, EMA fails to describe the effective dielectric permittivity accurately and does not discern the influence of the layer thickness for systems with equal metal and dielectric layers. These properties are captured by our KP approach, which therefore provides an insightful perspective on the physics behind metal/insulator multilayers, and represents a versatile toolbox for the design of functional metamaterials.

4. Experimental Section

**DC Magnetron Sputtering Deposition:** Ag and ITO were deposited via a DC magnetron sputtering (Table 1). The parameters are as follows.

| Material      | Power Rate [W] | Pre-sputtering chamber pressure [mBar] | Sputtering chamber pressure [mBar] |
|---------------|----------------|----------------------------------------|------------------------------------|
| Ag            | 20             | \( 3 \times 10^{-3} \)                | \( 4.6 \times 10^{-2} \)            |
| ITO           | 40             | \( 3 \times 10^{-3} \)                | \( 4.6 \times 10^{-2} \)            |

**Ellipsometry:** Spectroscopic ellipsometry was conducted on each deposited layer and all the multilayers using an M2000 ellipsometer from Woollam. The resolution had been kept at the maximum allowed by the instruments, that is, on average, of 1.5 nm. Spectroscopic ellipsometry of multilayers was performed at each angle of interest. P- and S-polarization reflectance was recorded with the same resolution on the same setup.

**Scattering Matrix Method Simulations:** A standard SMM code adapted from the study by Rumpf in MATLAB had been used to theoretically confirm, design, and investigate the properties of the multilayered system. We used the experimentally obtained dispersions for the dielectric and metal layers reported in Section 10, Supporting Information. The code had been upgraded to calculate all the spectroscopic parameters, as illustrated in Section 3, Supporting Information.

**COMSOL Multiphysics Modeling:** Full-field simulations were conducted by exciting with a monochromatic plane wave via a user-defined port, on the back of which suitably meshed Perfectly Matched Layers had been applied. At the lateral boundaries, continuity boundary conditions were implemented to simulate infinite domains.

**Molecular Orbitals’ Modeling:** The orbitals were computed via an SCF procedure using the OpenMolcas software, and a nonrelativistic Atomic-Natural-Orbitals Double Zeta Polarized basis set was used.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

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