Review article

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Metamaterial superconductors

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Abstract: Searching for natural materials exhibiting larger electron-electron interactions constitutes a traditional approach to high-temperature superconductivity research. Very recently, we pointed out that the newly developed field of electromagnetic metamaterials deals with the somewhat related task of dielectric response engineering on a sub-100-nm scale. Considerable enhancement of the electron-electron interaction may be expected in such metamaterial scenarios as in epsilon near-zero (ENZ) and hyperbolic metamaterials. In both cases, dielectric function may become small and negative in substantial portions of the relevant four-momentum space, leading to enhancement of the electron pairing interaction. This approach has been verified in experiments with aluminum-based metamaterials. Metamaterial superconductor with $T_c = 3.9$ K have been fabricated, which is three times that of pure aluminum ($T_c = 1.2$ K), which opens up new possibilities to improve the T_c of other simple superconductors considerably. Taking advantage of the demonstrated success of this approach, the critical temperature of hypothetical niobium, MgB_2 - and H_2S -based metamaterial superconductors is evaluated. The MgB_2 -based metamaterial superconductors are projected to reach the liquid nitrogen temperature range. In the case of an H_2S -based metamaterial, the projected T_c appears to reach ~ 250 K.

Keywords: superconductivity; electromagnetic metamaterials; dielectric properties; epsilon near-zero metamaterial; hyperbolic metamaterial.

1 Introduction

One of the most important goals of condensed matter physics is reliably designing new materials with enhanced superconducting properties. Recently, an electromagnetic metamaterial strategy, consisting of deliberately engineering the dielectric properties of a nanostructured “metamaterial superconductor” that results in an enhanced electron pairing interaction that increases the value of the superconducting energy gap and the critical temperature, T_c , was suggested to achieve this goal [1, 2]. Our recent experimental work [3–5] has conclusively demonstrated that this approach can indeed be used to increase the critical temperature of a composite superconductor-dielectric metamaterial. For example, we have demonstrated the use of Al_2O_3 -coated aluminum nanoparticles to form epsilon near-zero (ENZ) core-shell metamaterial superconductors with a T_c that is three times that of pure aluminum [4]. This deep and non-trivial connection between the fields of electromagnetic metamaterials and superconductivity research stems from the fact that superconducting properties of a material, such as electron-electron pairing interaction, the superconducting critical temperature T_c , etc. may be expressed via the effective dielectric response function $\varepsilon_{\text{eff}}(q, \omega)$ of the material [6]. For example, considerable enhancement of attractive electron-electron interaction may be expected in such actively studied metamaterial scenarios as ENZ [7] and hyperbolic metamaterials [8], since in both cases, $\varepsilon_{\text{eff}}(q, \omega)$ may become small and negative in substantial portions or the four-momentum (q, ω) space. Such an effective dielectric response-based macroscopic electrodynamics description is valid if the material may be considered as a homogeneous medium on the spatial scales below the superconducting coherence length. Since this length (the size of the Cooper pair) equals ~ 100 nm in a typical BCS superconductor, the metamaterial unit size must fall within the window between the ~ 0.3 -nm (given by the atomic scale) and the ~ 100 -nm scale of a typical Cooper pair for the metamaterial approach to remain valid.

The metamaterial superconductor approach takes advantage of the recent progress in plasmonics [9] and electromagnetic metamaterials [10] to engineer an artificial medium or “metamaterial”, so that its effective

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dielectric response function $\varepsilon_{\text{eff}}(q, \omega)$ conforms to almost any desired behavior. It appears natural to use this newly found freedom to engineer and maximize the electron pairing interaction in such an artificial superconductor via engineering its dielectric response function $\varepsilon_{\text{eff}}(q, \omega)$. In this article, we will review the comparative advantages and shortcomings of various electromagnetic metamaterial strategies to achieve this goal. For example, the ENZ approach based on the plasmonic core-shell nanostructures [4] seems to be the most efficient way to achieve the highest T_c values. However, the core-shell metamaterial superconductor geometry exhibits poorer transport properties compared to its parent (aluminum) superconductor. A natural way to overcome this issue is the implementation of the layered hyperbolic metamaterial geometry, which is based on parallel periodic layers of metal separated by layers of dielectric. This geometry ensures excellent transport properties in the plane of the layers. As noted in [11], typical high- T_c superconductors (such as BSCCO) exhibit hyperbolic behavior in a substantial portion of the far infrared and terahertz frequency ranges. Indeed, it was demonstrated that the artificial hyperbolic metamaterial geometry may also lead to a considerable enhancement of superconducting properties [5].

We should also mention that very recently, other approaches to artificial metamaterial superconductor engineering have been proposed by several groups, such as suggestions to create better superconductors by phonon spectrum modification via periodic nanostructuring of thin film [12] and bulk [13] superconductors. It was also proposed to modify natural hyperbolic superconductors (such as $\text{HgBa}_2\text{CuO}_{4+y}$) via inhomogeneous charge density waves (CDWs) [14]. Together with our electromagnetic metamaterial approach these strategies open up new areas in superconductivity research at the unconventional intersection of nanophotonics and solid-state physics, which may potentially reach the scientific dream of achieving room temperature superconductivity [15].

2 Macroscopic electrodynamic description of superconductivity

Electromagnetic properties are known to play a very important role in the pairing mechanism of superconductors [6]. According to the BCS theory, a Cooper pair is formed from two electrons with opposite spins and momenta that are loosely bound. This mechanism may be described as an attractive interaction of electrons that results from the polarization of the ionic lattice which

these electrons create as they move through the lattice. Based on this interpretation, Kirzhnits et al. [6] formulated their description of superconductivity in terms of the dielectric response function of the superconductor. They demonstrated that the electron-electron interaction in a superconductor may be expressed in the form of an effective Coulomb potential,

$$V(\vec{q}, \omega) = \frac{4\pi e^2}{q^2 \varepsilon_{\text{eff}}(\vec{q}, \omega)} = V_c \frac{1}{\varepsilon_{\text{eff}}(\vec{q}, \omega)}, \quad (1)$$

where V_c is the Fourier-transformed Coulomb potential in vacuum and $\varepsilon_{\text{eff}}(q, \omega)$ is the linear dielectric response function of the superconductor treated as an effective medium. While the thermodynamic stability condition implies that $\varepsilon_{\text{eff}}(0, 0) > 0$, the dielectric response function at higher frequencies and momenta may become large and negative, which accounts for the weak net attraction and pairing of electrons in the superconducting condensate. Based on this approach, Kirzhnits et al. derived explicit expressions for the superconducting gap Δ and critical temperature, T_c , of the superconducting transition as a function of the dielectric response function, and demonstrated that their expressions agree with the BCS result.

The key observation made in Refs. [1, 2] was that the “homogeneous medium” approximation may remain valid even if the basic structural elements of the material are not simple atoms or molecules. It was suggested that artificial “metamaterials” may be created from much bigger building blocks, and the electromagnetic properties of these fundamental building blocks may be engineered in such a way that the attractive pairing interaction described by Eq. (1) is maximized. The two potential solutions described in [1, 2] require minimization of $\varepsilon_{\text{eff}}(q, \omega)$ within a substantial portion of the relevant four-momentum spectrum ($|\vec{q}| \leq 2k_F$, $\omega \leq$ BCS cutoff around the Debye energy), while keeping the real part of $\varepsilon_{\text{eff}}(q, \omega)$ negative. These solutions involve either the epsilon-near-zero (ENZ) [7] or hyperbolic metamaterial [8] scenarios, which naturally lead to broadband small and negative $\varepsilon_{\text{eff}}(q, \omega)$ behavior in substantial portions of the relevant four-momentum spectrum. In the isotropic ENZ scenario, the effective pairing interaction is described by Eq. (1), where $\varepsilon_{\text{eff}}(q, \omega)$ is assumed to characterize the macroscopic electrodynamic properties of the composite metamaterial. On the other hand, in the hyperbolic metamaterial scenario the effective Coulomb potential from Eq. (1) assumes the form

$$V(\vec{q}, \omega) = \frac{4\pi e^2}{q_z^2 \varepsilon_z(\vec{q}, \omega) + (q_x^2 + q_y^2) \varepsilon_1(\vec{q}, \omega)}, \quad (2)$$

where $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_1$ and $\varepsilon_{zz} = \varepsilon_2$ have opposite signs. As a result, the effective Coulomb interaction of two electrons may become attractive and very strong along spatial directions where

$$q_z^2 \varepsilon_2(\vec{q}, \omega) + (q_x^2 + q_y^2) \varepsilon_1(\vec{q}, \omega) \approx 0, \quad (3)$$

which indicates that the superconducting order parameter must be strongly anisotropic. This situation resembles the hyperbolic character of such high- T_c superconductors as BSCCO [11]. However, engineering such ENZ or hyperbolic metamaterials constitutes a much more challenging task compared to typical applications of superconducting metamaterials suggested so far [16], which only deal with metamaterial engineering on scales which are much smaller than the microwave or RF wavelengths. Since the superconducting coherence length (the size of the Cooper pair) is $\xi \sim 100$ nm in a typical BCS superconductor [17], the metamaterial unit size must fall within the window between ~ 0.3 nm (given by the atomic scale) and $\xi \sim 100$ -nm scale of a typical Cooper pair. Moreover, the coherence length of the metamaterial superconductor must be determined in a self-consistent manner. The coherence length will decrease with increasing T_c of the metamaterial superconductor since the approach of Kirzhnits et al. gives rise to the same BCS-like relationship between the superconducting gap Δ and the coherence length ξ [17]:

$$\left(\frac{\xi}{V_F}\right) \Delta \sim \hbar, \quad (4)$$

where V_F is the Fermi velocity. Therefore, the metamaterial structural parameter (such as the interlayer or interparticle distance, etc.), which must remain smaller than the coherence length, defines the limit of critical temperature enhancement. Demonstration of the superconductivity enhancement in electromagnetic metamaterials opens up numerous new possibilities for metamaterial enhancement of T_c in such practically important simple superconductors as niobium and MgB_2 .

3 Epsilon near-zero superconductors: theory and experiment

Let us demonstrate that tuning electron-electron interaction is indeed possible using the epsilon-near-zero (ENZ) metamaterial approach, which is based on intermixing metal and dielectric components in the right proportions.

Following [18], a simplified dielectric response function of a metal may be written as

$$\varepsilon_m(q, \omega) = \left(1 - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma - \omega_p^2 q^2 / k^2}\right) \left(1 - \frac{\Omega_1^2(q)}{\omega^2 + i\omega\Gamma_1}\right) \dots \left(1 - \frac{\Omega_n^2(q)}{\omega^2 + i\omega\Gamma_n}\right) \quad (5)$$

where ω_p is the plasma frequency, k is the inverse Thomas-Fermi radius, $\Omega_n(q)$ are dispersion laws of various phonon modes, and Γ_n are the corresponding damping rates. Zeroes of the dielectric response function of the bulk metal (which correspond to various bosonic modes) maximize electron-electron pairing interaction given by Eq. (1). In the discussion below we will limit our consideration to the behavior of $\varepsilon_m(q, \omega)$ near $\omega = \Omega_1(q)$ in the vicinity of the Fermi surface, so that a more complicated representation of $\varepsilon_m(q, \omega)$ by the Lindhard function, which accurately represents $\varepsilon_m(q, \omega)$ in the $q \rightarrow 0$ and $\omega \rightarrow 0$ limit [18], does not need to be used. We are going to use only the fact that ε_m changes sign near $\omega = \Omega_1(q)$ by passing through zero. Expression for $\varepsilon_m(q, \omega)$ given by Eq. (5) does exhibit this behavior.

As summarized in [19], the critical temperature of a superconductor in the weak coupling limit is typically calculated as

$$T_c = \theta \exp\left(-\frac{1}{\lambda_{\text{eff}}}\right), \quad (6)$$

where θ is the characteristic temperature for a bosonic mode mediating electron pairing (such as the Debye temperature θ_D in the standard BCS theory, or $\theta_{\text{ex}} = \hbar\omega_{\text{ex}}/k$ or $\theta_{\text{pl}} = \hbar\omega_{\text{pl}}/k$ in the theoretical proposals which suggest excitonic or plasmonic mediation of the electron pairing interaction), and λ_{eff} is the dimensionless coupling constant defined by $V(q, \omega) = V_c(q) \varepsilon^{-1}(q, \omega)$ and the density of states ν (see for example [20]):

$$\lambda_{\text{eff}} = -\frac{2}{\pi} \nu \int_0^\infty \frac{d\omega}{\omega} \langle V_c(q) \text{Im} \varepsilon^{-1}(\vec{q}, \omega) \rangle, \quad (7)$$

where V_c is the unscreened Coulomb repulsion and the angle brackets denote average over the Fermi surface.

Compared to the bulk metal, zeroes of the effective dielectric response function $\varepsilon_{\text{eff}}(q, \omega)$ of the metal-dielectric metamaterial are observed at shifted positions compared to the zeroes of $\varepsilon_m(q, \omega)$ [2], and additional zeros may also appear. According to the Maxwell-Garnett approximation [21], mixing of nanoparticles of a superconducting

“matrix” with dielectric “inclusions” (described by the dielectric constants ε_m and ε_d , respectively) results in the effective medium with a dielectric constant ε_{eff} , which may be obtained as

$$\left(\frac{\varepsilon_{\text{eff}} - \varepsilon_m}{\varepsilon_{\text{eff}} + 2\varepsilon_m} \right) = (1-n) \left(\frac{\varepsilon_d - \varepsilon_m}{\varepsilon_d + 2\varepsilon_m} \right), \quad (8)$$

where n is the volume fraction of metal ($0 \leq n \leq 1$). The explicit expression for ε_{eff} may be written as

$$\varepsilon_{\text{eff}} = \frac{\varepsilon_m ((3-2n)\varepsilon_d + 2n\varepsilon_m)}{(n\varepsilon_d + (3-n)\varepsilon_m)}, \quad (9)$$

and it is easy to verify that

$$\varepsilon_{\text{eff}}^{-1} = \frac{n}{(3-2n)\varepsilon_m} + \frac{9(1-n)}{2n(3-2n)} \frac{1}{(\varepsilon_m + (3-2n)\varepsilon_d/2n)} \quad (10)$$

For a given value of the metal volume fraction n , the ENZ conditions ($\varepsilon_{\text{eff}} \approx 0$) may be obtained around $\varepsilon_m \approx 0$ and around

$$\varepsilon_m \approx -\frac{3-2n}{2n} \varepsilon_d \quad (11)$$

Since the absolute value of ε_m is limited by some value $\varepsilon_{m,\text{max}}$ [see Eq. (5)], the latter zero of ε_{eff} disappears at small n as $n \rightarrow 0$ at some critical value of the volume fraction $n = n_{\text{cr}} = 1.5\varepsilon_d/\varepsilon_{m,\text{max}}$. Let us evaluate $\text{Im}(\varepsilon_{\text{eff}}^{-1}(q, \omega))$ near this zero of ε_{eff} at $n > n_{\text{cr}}$. Based on Eq. (10),

$$\text{Im}(\varepsilon_{\text{eff}}^{-1}) \approx \frac{9(1-n)}{2n(3-2n)\varepsilon_m''} \quad (12)$$

where $\varepsilon_m' = \text{Re}\varepsilon_m$ and $\varepsilon_m'' = \text{Im}\varepsilon_m$. Assuming that $\nu \sim n$ (which is justified by the fact that there are no free charges in the dielectric phase of the metamaterial) and using Eq. (7), we may obtain the resulting expression for λ_{eff} as a function of λ_m and n :

$$\lambda_{\text{eff}} \approx \frac{9(1-n)}{2(3-2n)} \lambda_m, \quad (13)$$

where λ_m is also determined by Eq. (7) in the limit $\varepsilon \rightarrow \varepsilon_m$, and we have assumed the same magnitudes of ε_m'' for the metamaterial zero described by Eq. (11) and for the $\varepsilon_m \approx 0$ conditions. This assumption will be re-evaluated in Section 5 and confronted with experimental data for aluminum-based ENZ metamaterial, which indicate that ε_m'' changes by $\sim 11\%$. Figure 1A shows the predicted behavior of $\lambda_{\text{eff}}/\lambda_m$ as a function of n . Based on this prediction, we may expect enhancement of superconducting properties

Figure 1: Theoretical modeling of ENZ metamaterial superconductors. (A) Predicted behavior of $\lambda_{\text{eff}}/\lambda_m$ as a function of metal volume fraction n in a metal-dielectric metamaterial. (B) Plots of the hypothetical values of T_c as a function of metal volume fraction n , which would originate from either Eq. (13) or Eq. (15) in the absence of each other. The experimentally measured data points from [4] are shown for comparison on the same plot. The vertical dashed line corresponds to the assumed value of n_{cr} . Note that the theoretical curves contain no free parameters.

of the metal-dielectric metamaterial in the $n_{\text{cr}} < n < 0.6$ range. For comparison, Figure 1A also shows the behavior of λ_{eff} near the $\varepsilon_m \approx 0$ pole of the inverse dielectric response function of the metamaterial. According to Eq. (9), near $\varepsilon_m \approx 0$ the effective dielectric response function of the metamaterial behaves as

$$\varepsilon_{\text{eff}} \approx \frac{3-2n}{n} \varepsilon_m \quad (14)$$

Therefore, near this pole

$$\lambda_{\text{eff}} \approx \frac{n^2}{(3-2n)} \lambda_m \quad (15)$$

Let us apply the obtained simple estimates to the case of Al-Al₂O₃ core-shell metamaterial studied in [4]. Assuming the known values $T_{\text{cbulk}} = 1.2$ K and $\theta_D = 428$ K of bulk

aluminum [8], Eq. (6) results in $\lambda_m = 0.17$, which corresponds to the weak coupling limit. In order to make the mechanism behind the enhancement of T_c in the Al-Al₂O₃ core-shell metamaterial superconductor abundantly clear, we have plotted the hypothetical values of T_c as a function of metal volume fraction n , which would originate from either Eq. (13) or Eq. (15) in the absence of each other. The corresponding values calculated as

$$T_c = T_{c\text{bulk}} \exp\left(\frac{1}{\lambda_m} - \frac{1}{\lambda_{\text{eff}}}\right) \quad (16)$$

are shown in Figure 1B. The vertical dashed line corresponds to the assumed value of n_{cr} .

The experimentally measured data points from Ref. [4] are shown for comparison on the same plot. The match between the experimentally measured values of enhanced T_c and the theoretical curve obtained based on Eq. (13) is quite impressive, given the fact that Eqs. (13) and (16) do not contain any free parameters. Such a good match unambiguously identifies metamaterial enhancement as the physical mechanism of critical temperature tripling in the Al-Al₂O₃ core-shell metamaterial superconductor. It is impressive that such simple and well-known nanophotonics tools as the effective medium theory may be used to considerably enhance the critical temperature of simple superconductors.

The proof of principle experiments conducted with both random [3] and core-shell [4] ENZ metal-dielectric metamaterials indeed validates the effective medium-based theory outlined above. Our initial superconducting metamaterial samples [3] were prepared using commercially available tin and barium titanate nanoparticles obtained from the US Research Nanomaterials, Inc. The nominal diameter of the BaTiO₃ nanoparticles was 50 nm, while tin nanoparticle size was specified as 60–80 nm. Both nanoparticle sizes fall substantially below the superconducting coherence length in pure tin $\xi_{\text{Sn}} \sim 230$ nm [17]. Our choice of materials was based on results of numerical calculations of the real part of the dielectric constant of the Sn/BaTiO₃ mixture shown in Figure 2. These calculations were based on the measured dielectric properties of Sn [22] and BaTiO₃ [23], respectively, and on the Maxwell-Garnett expression, Eq. (9), for the dielectric permittivity of the mixture. These calculations indicated that it was possible to achieve broadband ENZ conditions in the 30–50% range of the volume fraction of BaTiO₃ in the frequency range of relevance around $h\nu \sim kT_c$ of pure tin.

The Sn/BaTiO₃ superconducting metamaterials were fabricated by combining the given amounts of Sn and BaTiO₃ nanoparticle powders by volume into a single test

Figure 2: Numerical calculations of the real part of the dielectric constant of the Sn/BaTiO₃ mixture as a function of volume fraction of BaTiO₃ performed with 10% steps.

tube filled with de-ionized water. The resulting suspensions were sonicated and magnetically stirred for 30 min, followed by water evaporation. The remaining mixtures of Sn and BaTiO₃ nanoparticles were compressed into test pellets using a hydraulic press. A typical scanning electron microscopy (SEM) image of the resulting Sn/BaTiO₃ composite metamaterial is shown in Figure 3. The original compressed nanoparticles are clearly visible in the image. The resulting average metamaterial composition has been verified after fabrication using an SEM with energy-dispersive X-ray spectroscopy (EDS). The compositional analysis of an area of the samples of about 1 μm in diameter is consistent with this nominal composition. Such EDX spectra were used to establish the homogeneous character of the fabricated composite metamaterials.

The superconducting critical temperature T_c of various Sn/BaTiO₃ metamaterials was measured via the onset of diamagnetism for samples with different volume fractions of BaTiO₃ using a MPMS SQUID magnetometer. The zero-field-cooled (ZFC) magnetization per unit mass for several samples with varying concentrations of BaTiO₃ is plotted in Figure 4A. The temperatures of the onset of the superconducting transition and the temperatures of the midpoint of the transition are plotted in Figure 5. The T_c increased from the pure Sn value of 3.68 K with increasing BaTiO₃ concentration to a maximum $\Delta T_c \sim 0.15$ K or 4% compared to the pure tin sample for the 40% sample followed by T_c decreasing at higher volume fractions. A pure tin sample was prepared from pressed tin nanoparticles of the same diameter using the same method of preparation. The value of T_c agreed with expected value of pure Sn. The magnetization of the composite samples in the superconducting state is comparable in magnitude with the pure tin sample. The increase of T_c and its dependence on effective dielectric constant determined by the concentration

Figure 3: Random mixture metamaterials.

(A) SEM image of the composite Sn/BaTiO₃ metamaterial with 30% volume fraction of BaTiO₃ nanoparticles. Individual compressed nanoparticles are clearly visible in the image. (B) Schematic diagram of the metamaterial sample geometry.

of BaTiO₃ agrees qualitatively with the Maxwell-Garnett theory-based calculations described above (see Figure 2). Moreover, the decrease in T_c at higher volume fraction of BaTiO₃, which is apparent from Figure 5 also agrees well with the Maxwell-Garnett theory, since $\epsilon_{\text{eff}}(q, \omega)$ changes sign to positive for higher BaTiO₃ concentrations.

To verify the reproducibility of these results, our measurements were repeated for several sets of nanocomposite samples fabricated using strontium titanate nanoparticles (instead of barium titanate) using the same fabrication technique described above. The superconducting critical temperature T_c of the Sn/SrTiO₃ metamaterial samples was measured for samples with different volume fractions of SrTiO₃ nanoparticles as shown in Figure 4B producing volume fraction dependencies, which are similar to those obtained for Sn/BaTiO₃ samples. These results established that the metamaterial approach to dielectric response engineering can indeed increase the critical temperature of a composite superconductor-dielectric metamaterial. However, despite this initial success, the observed critical

Figure 4: Temperature dependence of zero-field-cooled magnetization per unit mass for several samples with varying concentration of (A) BaTiO₃ and (B) SrTiO₃ measured in magnetic field of 10 G.

Figure 5: Temperatures of the onset of the superconducting transition (blue squares) and of the midpoint of the transition (red circles) plotted as a function of volume fraction of BaTiO₃. The line is a guide to the eye.

temperature increase was modest. It was argued in [2] that the random nanoparticle mixture geometry may not be ideal because simple mixing of superconductor and dielectric nanoparticles results in substantial spatial variations of $\varepsilon_{\text{eff}}(q, \omega)$ throughout a metamaterial sample. Such variations lead to considerable broadening and suppression of the superconducting transition.

To overcome this issue, it was suggested that an ENZ plasmonic core-shell metamaterial geometry, which has been developed to achieve partial cloaking of macroscopic objects [24], should be implemented [2]. The cloaking effect relies on mutual cancellation of scattering by the dielectric core (having $\varepsilon_d > 0$) and plasmonic shell (with $\varepsilon_m < 0$) of the nanoparticle, so that the effective dielectric constant of the nanoparticle becomes very small and close to that of vacuum (a plasmonic core with a dielectric shell may also be used). This approach may be naturally extended to the core-shell nanoparticles having negative ENZ behavior, as required in the superconducting application. Synthesis of such individual ENZ core-shell nanostructures followed by nanoparticle self-assembly into a bulk ENZ metamaterial (as shown in Figure 6) appears to be a viable way to fabricate an extremely homogeneous metamaterial superconductor.

The design of an individual core-shell nanoparticle is based on the fact that scattering of an electromagnetic field by a sub-wavelength object is dominated by its electric dipolar contribution, which is defined by the integral sum of its volume polarization [24]. A material with

$\varepsilon > 1$ has a positive electric polarizability, while a material with $\varepsilon < 1$ has a negative electric polarizability (since the local electric polarization vector, $P = (\varepsilon - 1)E/4\pi$, is opposite to E). As a result, the presence of a plasmonic shell (core) cancels the scattering produced by the dielectric core (shell), thus providing a cloaking effect. Similar consideration for the negative ENZ case leads to the following condition for the core-shell geometry:

$$r_c^3 \varepsilon_c \approx -(r_s^3 - r_c^3) \varepsilon_s, \quad (17)$$

where r_c and r_s are the radii, and ε_c and ε_s are the dielectric permittivities of the core and shell, respectively. Eq. (17) corresponds to the average dielectric permittivity of the core-shell nanoparticle being approximately equal to zero. Working on the negative side of this equality will ensure negative ENZ character of each core-shell nanoparticle. A dense assembly of such core-shell nanoparticles will form a medium that will have small negative dielectric permittivity. Moreover, in addition to obvious advantage in homogeneity, a core-shell based metamaterial superconductor design enables tuning of the spatial dispersion of the effective dielectric permittivity $\varepsilon_{\text{eff}}(q, \omega)$ of the metamaterial, which would further enhance its T_c [2]. Spatial dispersion of a metamaterial is indeed well known to originate from plasmonic effects in its metallic constituents. In a periodic core-shell nanoparticle-based ENZ metamaterial spatial dispersion is defined by the coupling of plasmonic modes of its individual nanoparticles. This coupling enables propagating plasmonic Bloch modes and hence nonlocal effects.

The successful realization of such an ENZ core-shell metamaterial superconductor using compressed Al_2O_3 -coated aluminum nanoparticles has been reported in [4], leading to tripling of the metamaterial critical temperature compared to the bulk aluminum. This material is ideal for the proof of principle experiments because the critical temperature of aluminum is quite low ($T_{c, \text{Al}} = 1.2 \text{ K}$ [17]), leading to a very large superconducting coherence length $\xi = 1600 \text{ nm}$ [17]. Such a large value of ξ facilitates the metamaterial fabrication requirements while Al_2O_3 exhibits very large positive values of dielectric permittivity up to $\varepsilon_{\text{Al}_2\text{O}_3} \sim 200$ in the terahertz frequency range [25]. These results provide an explanation for the long known, but not understood, enhancement of the T_c of granular aluminum films [26, 27].

The 18-nm-diameter Al nanoparticles for these experiments were acquired from the US Research Nanomaterials, Inc. Upon exposure to the ambient conditions, a $\sim 2\text{-nm}$ -thick Al_2O_3 shell is known to form on the aluminum nanoparticle surface [28], which is comparable to the

Figure 6: Schematic geometry of the ENZ metamaterial superconductor based on the core-shell nanoparticle geometry. The nanoparticle diameter is $d = 18 \text{ nm}$. The inset shows typical dimensions of the fabricated bulk aluminum-based core-shell metamaterial.

9-nm radius of the original Al nanoparticle. Further aluminum oxidation may also be achieved by heating the nanoparticles in air. The resulting core-shell Al_2O_3 -Al nanoparticles were compressed into macroscopic, ~ 1 -cm diameter, ~ 0.5 -mm-thick test pellets using a hydraulic press, as illustrated in the inset in Figure 6.

The IR reflectivity of such core-shell metamaterial samples was measured in the long-wavelength IR (LWIR) (2.5–22.5 μm) range using an FTIR spectrometer, and compared with reflectivity spectra of Al and Al_2O_3 , as shown in Figure 7. While the reflectivity spectrum of Al is almost flat, the spectrum of Al_2O_3 exhibits a very sharp step-like behavior around 11 μm that is related to the phonon-polariton resonance, which results from coupling of an infrared photon with an optic phonon of Al_2O_3 [29]. The step in reflectivity is due to the negative sign of $\epsilon_{\text{Al}_2\text{O}_3}$ near resonance. This step-like behavior may be used to characterize the volume fraction of Al_2O_3 in the core-shell metamaterial. In the particular case shown in Figure 7, the volume fraction of Al_2O_3 in the core-shell metamaterial may be estimated, based on the Maxwell-Garnett approximation, as $\sim 39\%$, which corresponds to $(r_s - r_c) \sim 0.18r_c$. At $r_c \sim 9$ nm, the corresponding thickness of Al_2O_3 appears to be $(r_s - r_c) \sim 1.6$ nm, which matches expectations based on [28].

The Kramers-Kronig analysis of the FTIR reflectivity spectra of the Al- Al_2O_3 sample also allows us to evaluate $\epsilon_{\text{eff}}(0, \omega)$ for the metamaterial in the LWIR spectral range. Plots of the real part of ϵ for pure Al and for the Al- Al_2O_3 core-shell metamaterial based on the Kramers-Kronig analysis of the data in Figure 7 are plotted in Figure 8. The

Figure 7: Comparison of the FTIR reflectivity spectrum of a typical core-shell Al_2O_3 -Al metamaterial sample with reflectivity spectra of bulk Al and Al_2O_3 samples.

The step in reflectivity around 11 μm may be used to characterize the volume fraction of Al_2O_3 in the core-shell metamaterial. The increased noise near 22 μm is related to the IR source cutoff.

Figure 8: Plots of the real part of ϵ for pure Al and for the Al- Al_2O_3 core-shell metamaterial based on the Kramers-Kronig analysis of the FTIR reflectivity data from Figure 2.

(A) Comparison of ϵ' for pure Al and for the Al- Al_2O_3 metamaterial clearly indicates that $\epsilon_{\text{Al-}\text{Al}_2\text{O}_3} \ll \epsilon_{\text{Al}}$. (B) Real part of ϵ for two different Al- Al_2O_3 core-shell metamaterials based on the Kramers-Kronig analysis. While both metamaterials shown in (B) exhibit much smaller ϵ compared to the bulk aluminum, the metamaterial prepared using less oxidized aluminum nanoparticles exhibits considerably larger negative ϵ .

plot in Figure 8A clearly demonstrates that $\epsilon_{\text{Al-}\text{Al}_2\text{O}_3} \ll \epsilon_{\text{Al}}$ so that the ENZ condition was achieved in the sense that the initial dielectric constant of aluminum was reduced by a factor ~ 1000 . On the other hand, Figure 8B demonstrates that the dielectric constant of the Al- Al_2O_3 core-shell metamaterials remains negative and relatively small above 11 μm . In particular, the large negative contribution to ϵ from the aluminum cores is compensated by the large positive contribution from the Al_2O_3 shells leading to the upturn of $\epsilon_{\text{Al-}\text{Al}_2\text{O}_3}$ that is observed near 20 μm in Figure 8B, which is caused by the large positive value of $\epsilon_{\text{Al}_2\text{O}_3}$ in this spectral range. Note that while both metamaterials shown in Figure 8B exhibit much smaller ϵ compared to the bulk aluminum, the metamaterial prepared using less

oxidized aluminum nanoparticles exhibits considerably larger negative ϵ . The relatively large noise observed in the calculated plot of ϵ_{Al} in Figure 8A is due to the fact that the aluminum reflectivity is close to 100% above $7\ \mu\text{m}$ so that the Kramers-Kronig-based numerical analysis of the reflectivity data does not work reliably for pure aluminum samples in this spectral range. Another limitation on the accuracy of the analysis is the use of the finite spectral range ($2.5\text{--}22.5\ \mu\text{m}$) of the FTIR spectrometer rather than the infinite one assumed by the rigorous Kramers-Kronig analysis. These limitations notwithstanding, we note that our result for pure aluminum is in good agreement with the tabulated data for ϵ_{Al} reported in [30]. Therefore, these results reliably confirm the ENZ character of the core-shell Al-Al₂O₃ metamaterial. It is also interesting to note that the same FTIR technique applied to the tin-BaTiO₃ nanocomposite metamaterials studied in [3] also confirms their expected ENZ character, as illustrated in Figure 9. In both

Figure 9: Plots of the real part of ϵ for pure tin and for the ENZ tin-BaTiO₃ nanocomposite metamaterial studied in [3]. (A) Comparison of ϵ' for compressed tin nanoparticles and for the tin-BaTiO₃ nanocomposite metamaterial. (B) Real part of ϵ for the tin-BaTiO₃ nanocomposite metamaterial.

cases, the goal of metamaterial engineering was to create an effective superconducting medium with negative ENZ response. While both Figures 8 and 9 confirm that this goal has been achieved, the core-shell geometry of the developed Al-Al₂O₃ metamaterial has a clear advantage. The core-shell geometry guarantees a homogeneous spatial distribution of the effective dielectric response function, leading to tripling of T_c for the Al-Al₂O₃ core-shell metamaterial, compared to $\sim 5\%$ increase of T_c of the tin-BaTiO₃ random nanocomposite metamaterial developed in [3].

The T_c of various Al-Al₂O₃ core-shell metamaterials was determined via the onset of diamagnetism for samples with different degrees of oxidation using a MPMS SQUID magnetometer. The ZFC magnetization per unit mass versus temperature for several samples with various volume fractions of Al₂O₃ is plotted in Figure 10A, whereas the corresponding

Figure 10: Measured parameters of the core-shell metamaterial superconductors.

(A) Temperature dependence of ZFC magnetization per unit mass for several Al-Al₂O₃ core-shell metamaterial samples with increasing degree of oxidation measured in magnetic field of 10 G. The highest onset of superconductivity at $\sim 3.9\ \text{K}$ is marked by an arrow. This temperature is 3.25 times larger than $T_c = 1.2\ \text{K}$ of bulk aluminum. (B) Corresponding FTIR reflectivity spectra of the core-shell metamaterial samples. Decrease in reflectivity corresponds to decrease of the volume fraction of aluminum.

reflectivity data are shown in Figure 10B. Even though the lowest achievable temperature with our MPMS SQUID magnetometer was 1.7 K, we were able to observe a gradual increase of T_c that correlated with an increase of the Al_2O_3 volume fraction as determined by the drop in reflectivity shown in Figure 10B. The reliability of the MPMS SQUID magnetometer at $T > 1.7$ K was checked by measurements of the T_c of bulk tin at $T_c = 3.7$ K, as described in Ref. [3], in excellent agreement with the textbook data [17].

The observed increase in T_c also showed good correlation with the results of the Kramers-Kronig analysis shown in Figure 8B: samples exhibiting smaller negative ϵ demonstrated higher T_c increase. The highest onset temperature of the superconducting transition reached 3.9 K, which is more than three times as high as the critical temperature of bulk aluminum, $T_{c\text{Al}} = 1.2$ K [17]. All of the samples exhibited a small positive susceptibility that increased with decreasing temperature, consistent with the presence of small amounts of paramagnetic impurities. The discussed T_c values were determined by the beginning of the downturn of $M(T)$, where the diamagnetic superconducting contribution starts to overcome paramagnetic contribution, making this temperature the lower limit of the onset of superconductivity. Further oxidation of aluminum nanoparticles by annealing for 2 h at 600°C resulted in a T_c less than 1.7 K, our lowest achievable temperature. Based on the reflectivity step near 11 μm (see Figure 10B), the volume fraction of Al_2O_3 in this sample may be estimated as $\sim 50\%$, which corresponds to $(r_s - r_c) \sim 0.26r_c$. For $r_c \sim 9$ nm, the corresponding thickness of Al_2O_3 was $(r_s - r_c) \sim 2.4$ nm.

Thus, the theoretical prediction of a large increase of T_c in ENZ core-shell metamaterials shown in Figure 1 has been confirmed by direct measurements of $\epsilon_{\text{eff}}(0, \omega)$ of the fabricated metamaterials and the corresponding measurements of the increase of T_c . These results strongly suggest that increased aluminum T_c 's that were previously observed in very thin (< 50 -nm thickness) granular aluminum films [26, 27] and disappeared at larger film thicknesses were due to changes in the dielectric response function rather than quantum size effects and soft surface phonon modes [27]. As clearly demonstrated by the experimental data and the discussion above, the individual Al nanoparticle size is practically unaffected by oxidation, thus excluding the size effects as an explanation of giant T_c increase in our bulk core-shell metamaterial samples. The developed technology enables efficient nanofabrication of bulk aluminum-based metamaterial superconductors with a T_c that is three times that of pure aluminum and with virtually unlimited shapes and dimensions. These results open up numerous new possibilities of considerable T_c increase in other simple superconductors.

4 Hyperbolic metamaterial superconductors: theory and experiment

While the T_c increase observed in ENZ metamaterial superconductors is impressive, the core-shell metamaterial superconductor geometry exhibits poor transport properties compared to its parent (aluminum) superconductor. A natural way to overcome this issue is the implementation of the hyperbolic metamaterial geometry (Figure 11A), which has been suggested in [1, 2]. Hyperbolic metamaterials are extremely anisotropic uniaxial materials, which behave like a metal ($\text{Re}\epsilon_{xx} = \text{Re}\epsilon_{yy} < 0$) in one direction and

Figure 11: Geometry and basic properties of hyperbolic metamaterial superconductors.

(A) Schematic geometry of a “layered” hyperbolic metamaterial. (B) Electron-electron pairing interaction in a hyperbolic metamaterial is strongly enhanced near the cone in momentum space defined as $q_z^2 \epsilon_2 + (q_x^2 + q_y^2) \epsilon_1 = 0$.

like a dielectric ($\text{Re}\epsilon_{zz} > 0$) in the orthogonal direction. Originally introduced to overcome the diffraction limit of optical imaging [8], hyperbolic metamaterials demonstrate a number of novel phenomena resulting from the broadband singular behavior of their density of photonic states. The “layered” hyperbolic metamaterial geometry shown in Figure 11A is based on parallel periodic layers of metal separated by layers of dielectric. This geometry ensures excellent transport properties in the plane of the layers. Let us demonstrate that the artificial hyperbolic metamaterial geometry may also lead to a considerable enhancement of superconducting properties.

The first successful realization of an artificial hyperbolic metamaterial superconductor has been reported in [5]. The metamaterial was made of aluminum films separated by thin layers of Al_2O_3 . This combination of materials is ideal for the proof of principle experiments because it is easy to controllably grow Al_2O_3 on the surface of Al, and because the critical temperature of aluminum is quite low ($T_{c\text{Al}} = 1.2\text{ K}$ [17]), leading to a very large superconducting coherence length $\xi = 1600\text{ nm}$ [17]. Such a large value of ξ facilitates the metamaterial fabrication requirements since the validity of macroscopic electrodynamic description of the metamaterial superconductor requires that its spatial structural parameters must be much smaller than ξ . It appears that the $\text{Al}/\text{Al}_2\text{O}_3$ hyperbolic metamaterial geometry is capable of superconductivity enhancement, which is similar to that observed for a core-shell metamaterial geometry [4], while having much better transport and magnetic properties compared to the core-shell superconductors. The multilayer $\text{Al}/\text{Al}_2\text{O}_3$ hyperbolic metamaterial samples for these experiments (Figure 12) were prepared using sequential thermal evaporation of thin aluminum films followed by oxidation of the top layer for 1 h in air at room temperature. The first layer of aluminum was evaporated onto a glass slide surface. Upon exposure to ambient conditions a $\sim 2\text{-nm}$ -thick Al_2O_3 layer is known to form on the aluminum film surface [28]. Further aluminum oxidation may also be achieved by heating the sample in air. The oxidized aluminum film surface was used as a substrate for the next aluminum layer. This iterative process was used to fabricate thick multilayer (up to 16 metamaterial layers) $\text{Al}/\text{Al}_2\text{O}_3$ hyperbolic metamaterial samples. A transmission electron microscopy (TEM) image of the multilayer metamaterial sample is shown in Figure 12. During TEM experiments samples were coated with gold and platinum to ensure conductivity of the surface during sample preparation. A focused ion beam (FIB) microscope was used to prepare a sample for transmission electron microscopy (TEM). Samples were analyzed using a JEOL 2200 FS TEM, acquiring bright-field and high-resolution

Figure 12: TEM image of a 16-layer metamaterial sample. During the imaging experiments, samples were coated with gold and platinum to ensure conductivity of the surface during sample preparation. The inset shows that the interfacial layers are amorphous, between polycrystalline grains of Al, which, in cross-section, exhibit Moiré cross-hatching.

images. Figure 12 shows an image from the hyperbolic stack, showing polycrystalline Al grains, with 1- to 2-nm-thick amorphous Al_2O_3 spacing layers, corresponding with the designed structure. Some Al_2O_3 layers are difficult to discern due to slight sample warping from the preparation process. The inset shows that the interfacial layers are indeed amorphous, between polycrystalline grains of Al, which, in cross-section, exhibit Moiré cross-hatching.

To demonstrate that these multilayer samples exhibit hyperbolic behavior, we studied their transport and optical properties (Figures 13–15). The temperature dependence of the sheet resistance of a 16-layer 10-nm/layer $\text{Al}/\text{Al}_2\text{O}_3$ hyperbolic metamaterial and a 100-nm-thick Al film are shown in Figure 13A. As illustrated in the logarithmic plot in the inset, the electronic conductivity of the metamaterial approaches conductivity values of bulk aluminum (indicated by the arrow) and is far removed from the parameter space characteristic for granular Al films [27], which is indicated by the gray area in the inset. These results were corroborated by measurements of IR reflectivity of these samples, shown in Figure 13B. The IR reflectivity of the hyperbolic metamaterial samples was measured in the long wavelength IR (LWIR) (2.5–22.5 μm) range using an FTIR spectrometer, and compared with reflectivity spectra of Al and Al_2O_3 . While the reflectivity spectrum of bulk Al is almost flat, the spectrum of Al_2O_3 exhibits a very sharp step-like behavior around 11 μm that is related to the phonon-polariton resonance, which results from coupling of an infrared photon with an optical

Figure 13: Measurements of DC and AC (optical) conductivity of the aluminum layers of the fabricated hyperbolic metamaterials. (A) Temperature dependence of the sheet resistance of a 16-layer 10-nm/layer $\text{Al}/\text{Al}_2\text{O}_3$ hyperbolic metamaterial and a 100-nm-thick Al film. As illustrated in the logarithmic plot in the inset, the conductivity of the metamaterial approaches conductivity values of bulk aluminum and is far removed from the parameter space characteristic for granular Al films which is indicated by the gray area. (B) IR reflectivity of bulk aluminum, 3- and 8-layer hyperbolic metamaterial, and the core-shell metamaterial samples measured in the long-wavelength IR (LWIR) (2.5–22.5 μm) range using an FTIR spectrometer. The step-in reflectivity around 11 μm is related to the phonon-polariton resonance (PPR) and may be used to characterize the spatial distribution of Al_2O_3 in the metamaterial samples.

phonon of Al_2O_3 [29]. The step in reflectivity is due to the negative sign of $\epsilon_{\text{Al}_2\text{O}_3}$ near the resonance. The absence of this step in our multilayers indicates that the aluminum layers in these samples are continuous and not intermixed with aluminum oxide. Such a step is clearly observed in reflectivity data obtained from a core-shell $\text{Al}/\text{Al}_2\text{O}_3$

Figure 14: Calculated plots of the real parts of $\epsilon_{x,y}$ (A) and ϵ_z (B) of the multilayer $\text{Al}/\text{Al}_2\text{O}_3$ metamaterial. The metamaterial consists of 13-nm-thick Al layers separated by 2 nm of Al_2O_3 in the LWIR spectral range. The calculations were performed using Eqs. (18) and (19) based on the Kramers-Kronig analysis of the FTIR reflectivity of Al and Al_2O_3 in Ref. [4]. The metamaterial appears to be hyperbolic except for a narrow LWIR spectral band between 11 and 18 μm .

sample shown in Figure 13B where the aluminum grains are separated from each other by Al_2O_3 . On the other hand, this step is completely missing in reflectivity spectra of the hyperbolic metamaterial samples (the step at 9 μm observed in the spectrum of a three-layer sample is due to phonon-polariton resonance of the SiO_2 substrate). Thus, the transport and optical measurements confirm excellent DC and AC (optical) conductivity of the aluminum layers of the fabricated hyperbolic metamaterials.

The Kramers-Kronig analysis of the FTIR reflectivity spectra of Al and Al_2O_3 measured in [4] also allowed us to calculate the ϵ_1 and ϵ_2 components of the $\text{Al}/\text{Al}_2\text{O}_3$ layered films in the LWIR spectral range using the Maxwell-Garnett approximation as follows:

Figure 15: Ellipsometry and polarization reflectometry of Al/Al₂O₃ hyperbolic metamaterials.

(A) Comparison of measured pseudo-dielectric function using ellipsometry and theoretically calculated $\text{Re}\epsilon_1$ and $\text{Im}\epsilon_1$. Theoretical data points are based on the real and imaginary parts of ϵ_{Al} tabulated in [30]. (B) Data points are measured p- and s-polarized reflectivities of the metamaterial sample at 2.07 eV (600 nm) and 2.88 eV (430 nm). Dashed lines are fits using Eqs. (20–23). ϵ_1 and ϵ_2 obtained from the fits confirm hyperbolic character of the metamaterial.

$$\epsilon_1 = n\epsilon_m + (1-n)\epsilon_d \quad (18)$$

$$\epsilon_2 = \frac{\epsilon_m \epsilon_d}{(1-n)\epsilon_m + n\epsilon_d} \quad (19)$$

where n is the volume fraction of metal, and ϵ_m and ϵ_d are the dielectric permittivities of the metal and dielectric, respectively [31]. Results of these calculations for a multilayer metamaterial consisting of 13-nm-thick Al layers separated by 2 nm of Al₂O₃ are shown in Figure 14. The metamaterial appears to be hyperbolic except for a narrow LWIR spectral band between 11 and 18 μm . A good match

between the Maxwell-Garnett approximation [Eqs. (18) and (19)] and the measured optical properties of the metamaterial is demonstrated by ellipsometry (Figure 15A) and polarization reflectometry (Figure 15B) of the samples.

Variable angle spectroscopic ellipsometry with photon energies between 0.6 and 6.5 eV on the Al/Al₂O₃ metamaterial have been performed using a Woollam variable angle spectroscopic ellipsometer (W-VASE). For a uniaxial material with optic axis perpendicular to the sample surface and in plane of incidence, ellipsometry provides the pseudo-dielectric function which, in general, depends both on ϵ_1 and ϵ_2 . However, as demonstrated by Jellison and Baba [32], the pseudo-dielectric function in this measurement geometry is dominated by the in-plane dielectric function ϵ_1 and is independent of the angle of incidence. The measured results for the real and imaginary parts of the pseudo-dielectric function in Figure 15A show good agreement with the model for the in-plane dielectric function [Eq. (18)]. The calculated data points are based on the real and imaginary parts of ϵ_{Al} tabulated in [30]. The measured sign of the real part of the pseudo-dielectric function is negative, which suggests metallic in-plane transport. The sign of the real part of ϵ_2 (and therefore, the hyperbolic character of our samples) was determined by polarization reflectometry, since ellipsometry data are less sensitive to ϵ_2 [32]. Polarization reflectometry also confirmed the negative sign of the real part of ϵ_1 consistent with ellipsometry data. The metamaterial parameters were extracted from the polarization reflectometry data as described in detail in [33]. Reflectivity for s-polarization is given in terms of the incident angle θ by

$$R_s = \left| \frac{\sin(\theta - \theta_{\text{ts}})}{\sin(\theta + \theta_{\text{ts}})} \right|^2, \quad (20)$$

where

$$\theta_{\text{ts}} = \arcsin\left(\frac{\sin\theta}{\sqrt{\epsilon_1}}\right). \quad (21)$$

Reflectivity for p-polarization is given as

$$R_p = \left| \frac{\epsilon_1 \tan\theta_{\text{tp}} - \tan\theta}{\epsilon_1 \tan\theta_{\text{tp}} + \tan\theta} \right|^2, \quad (22)$$

where

$$\theta_{\text{tp}} = \arctan \sqrt{\frac{\epsilon_2 \sin^2 \theta}{\epsilon_1 \epsilon_2 - \epsilon_1 \sin^2 \theta}}. \quad (23)$$

We measured the p- and s-polarized absolute reflectance on the metamaterial sample using the reflectance

mode of the ellipsometer. The reflectance was measured at two photon energies, 2.07 (600 nm) and 2.88 eV (430 nm), as shown in Figure 15B, and was normalized to the measured reflectance of a 150-nm gold film. The absolute reflectance of the gold film was obtained from ellipsometry measurements. The estimated uncertainty in the absolute reflectance of the Al/Al₂O₃ metamaterial is one percent. In order to obtain the dielectric permittivity ϵ_1 and ϵ_2 values, we fit the s-polarized reflectance first and get the in-plane dielectric function ϵ_1 . We then use the in-plane dielectric function to fit the p-polarized reflectance to obtain the out-of-plane dielectric function, ϵ_2 . The data analysis was done using W-VASE software. At 2.07 eV (600 nm), $\epsilon_1 = -7.17 + 1.86i$ and $\epsilon_2 = 1.56 + 0.21i$, and at 2.88 eV (430 nm), $\epsilon_1 = -2.15 + 0.50i$ and $\epsilon_2 = 1.30 + 0.09i$. It is clear that the real part of the out-of-plane dielectric function is positive while the real part of the in-plane dielectric function is negative, which confirms the dielectric nature along z-axis and metallic nature in the xy-plane, i.e. a hyperbolic metamaterial.

The T_c and critical magnetic field, H_c , of various samples (Figures 16 and 17) were determined via four-point resistivity measurements as a function of temperature and magnetic field, H , using a Physical Property Measurement System (PPMS) by Quantum Design. Even though the lowest achievable temperature with our PPMS system was 1.75 K, which is higher than the critical temperature $T_{c, Al} = 1.2$ K of bulk aluminum, we were able to observe a pronounced effect of the number of layers on T_c of the hyperbolic metamaterial samples. Figure 16A shows measured resistivity as a function of temperature for the 1-, 3- and 8-layer samples each having the same 8.5-nm layer thickness. While the superconducting transition in the 1-layer sample was below 1.75 K and could not be observed, the 3- and 8-layer metamaterial samples exhibited progressively higher critical temperature, which strongly indicates the role of hyperbolic geometry in T_c enhancement. A similar set of measurements performed for several samples having 13-nm layer thickness is shown in Figure 16B.

The measurements of H_c in parallel and perpendicular fields are shown in Figure 17. Figure 17A shows measured resistivity as a function of temperature for a 16-layer 13.2 nm layer thickness hyperbolic metamaterial sample. The critical temperature of this sample appears to be $T_c = 2.3$ K, which is about two times higher than the T_c of bulk aluminum (another transition at $T_c = 2.0$ K probably arise from one or two decoupled layers or edge shadowing effects where the thickness of the films is not uniform). The inset in Figure 17A illustrates the measurements of H_c^{parallel} for this sample. The critical field appears

Figure 16: Effect of the number of layers on T_c of the Al/Al₂O₃ hyperbolic metamaterial samples.

(A) Measured resistivity as a function of temperature is shown for the 1-, 3- and 8-layer samples each having the same 8.5-nm-layer thickness. (B) Measured resistivity as a function of temperature for the 1-, 3-, 8- and 16-layer samples each having the same 13-nm layer thickness.

to be quite large (~ 3 T), which is similar to the values of H_c^{parallel} observed previously in granular aluminum films [34]. However, it is remarkable that such high critical parameters are observed for the films, which are much thicker than granular Al films.

Measurements of the perpendicular critical field H_c^{perp} for the same metamaterial sample, which are shown in Figure 17B allowed us to evaluate the Pippard coherence length

$$\xi = \sqrt{\frac{\phi_0}{2\pi H_{c2}}}. \quad (24)$$

Figure 17: Evaluation of the Pippard coherence length of the Al/Al₂O₃ hyperbolic metamaterial. (A) Measured resistivity as a function of temperature for a 16-layer 13.2-nm-layer thickness metamaterial sample. The critical temperature appears to be $T_c = 2.3$ K. The inset shows the resistivity of this sample as a function of parallel magnetic field at $T = 1.75$ K. (B) Resistivity of the same sample as a function of perpendicular magnetic field at $T = 1.75$ K. Assuming $H_{c2}^{perp} = 100$ G (based on the measurements shown in the inset), the corresponding coherence length appears to be $\xi = 181$ nm, which is much larger than the layer periodicity.

Assuming $H_{c2}^{perp} = 100$ G (based on the inset in Figure 17B), the corresponding coherence length appears to be $\xi = 181$ nm, which is much larger than the layer periodicity. Other measured samples also exhibit the coherence length around 200 nm. Therefore, our use of effective medium approach is validated and our multilayer samples should obey the metamaterial theory.

We have also studied changes in T_c as a function of Al layer thickness in a set of several 8-layer Al/Al₂O₃ metamaterial samples, as shown in Figure 18A. The quantitative

Figure 18: Effect of the aluminum volume fraction n on T_c of the Al/Al₂O₃ hyperbolic metamaterial samples. (A) Resistivity as a function of temperature for the 8-layer samples having different aluminum layer thicknesses. (B) Experimentally measured behavior of T_c as a function of n (which is defined by the Al layer thickness) correlates well with the theoretical fit (red curve) based on the hyperbolic mechanism of T_c enhancement. Experimental data points shown in black correspond to 8-layer samples, while blue ones correspond to 16-layer samples.

behavior of T_c as a function of n may be predicted based on the hyperbolic enhancement of the electron-electron interaction [Eq. (2)] and the density of electronic states, ν , on the Fermi surface which experience this hyperbolic enhancement. Using Eqs. (18) and (19), the effective Coulomb potential from Eq. (2) may be rewritten as

$$V(\vec{q}, \omega) = \frac{4\pi e^2}{q^2 \left(\frac{q_z^2}{q^2} \frac{\epsilon_d \epsilon_m}{((1-n)\epsilon_m + n\epsilon_d)} + \frac{q_x^2 + q_y^2}{q^2} (n\epsilon_m + (1-n)\epsilon_d) \right)}. \quad (25)$$

Let us assume once again (see Ref. [15] and the theoretical discussion in the previous section) that the dielectric response function of the metal used to fabricate the hyperbolic metamaterial shown in Figure 11 may be described by Eq. (5), and the critical temperature of a metamaterial superconductor may be found using Eq. (6) via the density of states in Eq. (7).

Let us consider the region of four-momentum (q, ω) space, where $\omega > \Omega_1(q)$. While $\varepsilon_m = 0$ at $\omega = \Omega_1(q)$, $\varepsilon_m(q, \omega)$ is large in a good metal and negative just above $\Omega_1(q)$.

near $n=1$. Due to the complicated angular dependence in Eq. (27), it is convenient to reverse the order of integration in Eq. (7) and perform the integration over $d\omega$ first, followed by angular averaging. Following the commonly accepted approach, while integrating over $d\omega$ we take into account only the contributions from the poles given by Eq. (27), and assume the value of $\text{Im}\varepsilon_m = \varepsilon_m''$ to be approximately the same at both poles. The respective contributions of the poles to $d(\nu V)/dx$ may be written as

$$\frac{d(\nu V)}{dx} \approx \frac{2\pi e^2 \left((1-n) \left(\left(1 - \frac{1}{2n(1-n)(1-x^2)} \right) \pm \sqrt{\left(1 - \frac{1}{2n(1-n)(1-x^2)} \right)^2 - 1} \right) + n \right)}{q^2 \varepsilon_m'' (1-n)(1-x^2) \sqrt{\left(1 - \frac{1}{2n(1-n)(1-x^2)} \right)^2 - 1}} \quad (30)$$

Based on Eq. (25), the differential of the product νV may be written as

$$\begin{aligned} d(\nu V) &= \frac{4\pi e^2 n \sin\theta d\theta}{q^2 \left(\frac{\varepsilon_d \varepsilon_m}{((1-n)\varepsilon_m + n\varepsilon_d)} \cos^2\theta + (n\varepsilon_m + (1-n)\varepsilon_d) \sin^2\theta \right)} = \\ &= -\frac{4\pi e^2 n dx}{q^2 \left((n\varepsilon_m + (1-n)\varepsilon_d) - \frac{n(1-n)(\varepsilon_m - \varepsilon_d)^2}{(n\varepsilon_d + (1-n)\varepsilon_m)} x^2 \right)} \end{aligned} \quad (26)$$

where $x = \cos\theta$, and θ varies from 0 to π . The latter expression has two poles at

$$\varepsilon_m = \left(\left(1 - \frac{1}{2n(1-n)(1-x^2)} \right) \pm \sqrt{\left(1 - \frac{1}{2n(1-n)(1-x^2)} \right)^2 - 1} \right) \varepsilon_d \quad (27)$$

As the volume fraction, n , of metal is varied, one of these poles remains close to $\varepsilon_m = 0$, while the other is observed at larger negative values of ε_m :

$$\varepsilon_m^+ \approx -n(1-n)(1-x^2)\varepsilon_d, \quad (28)$$

$$\varepsilon_m^- \approx -\frac{\varepsilon_d}{n(1-n)(1-x^2)}. \quad (29)$$

This situation is similar to calculations of T_c for ENZ metamaterials. Since the absolute value of ε_m is limited [see Eq. (5)], the second pole disappears near $n=0$ and

Near $n=0$ and $n=1$, these expression may be approximated as

$$\frac{d(\nu V)^+}{dx} \approx \frac{4\pi e^2 n^2}{q^2 \varepsilon_m''} \quad (31)$$

and

$$\frac{d(\nu V)^-}{dx} \approx \frac{4\pi e^2}{q^2 \varepsilon_m'' (1-x^2)}, \quad (32)$$

respectively. Note that at the $\omega = \Omega_1(q)$ zero of the dielectric response function of the bulk metal the effective Coulomb potential inside the metal may be approximated as

$$V_m(\vec{q}, \omega) = \frac{4\pi e^2}{q^2 \varepsilon_m(q, \omega)} \approx -\frac{4\pi e^2}{q^2 \varepsilon_m''}, \quad (33)$$

so that the coupling constant λ_{eff} of the hyperbolic metamaterial obtained by angular integration of the sum of Eqs. (31) and (32) may be expressed via the coupling constant λ_m of the bulk metal:

$$\lambda_{\text{eff}} \approx \lambda_m \left(n^2 + \alpha \ln \left| \frac{1+x_0}{1-x_0} \right| \right), \quad (34)$$

where α is a constant of the order of 1 and x_0 is defined by the maximum negative value of ε_m , which determines if the second pole [Eq. (29)] exists at a given n . Based on Eq. (29),

$$x_0^2 \approx 1 + \frac{\varepsilon_d}{n(1-n)\varepsilon_{m,\text{max}}} \quad (35)$$

If the second pole does not exist, then $x_0 = 0$ may be assumed. Based on Eq. (6), the theoretically predicted value of T_c for the hyperbolic metamaterial is calculated as

$$T_c = T_{\text{cbulk}} \exp\left(\frac{1}{\lambda_m} - \frac{1}{\lambda_{\text{eff}}}\right) = T_{\text{cbulk}} \exp\left(\frac{1}{\lambda_m} \left(1 - \frac{1}{n^2 + \alpha \ln \left| \frac{1+x_0}{1-x_0} \right|}\right)\right), \quad (36)$$

assuming the known values $T_{\text{cbulk}} = 1.2$ K and $\lambda_m = 0.17$ for bulk aluminum [15]. The predicted behavior of T_c as a function of n is plotted in Figure 18B. This figure demonstrates that the experimentally measured behavior of T_c as a function of n (which is defined by the Al layer thickness) correlates well with the theoretical fit, which was obtained using Eq. (36) based on the hyperbolic mechanism of T_c enhancement.

The observed combination of transport and critical properties of the Al/Al₂O₃ hyperbolic metamaterials is very far removed from the parameter space typical of the granular aluminum films [27, 34]. Together with the number of layer and layer thickness dependence of T_c and H_c shown in Figures 16–18, these observations strongly support the hyperbolic metamaterial mechanism of superconductivity enhancement. The developed technology enables efficient nanofabrication of thick film aluminum-based hyperbolic metamaterial superconductors with a T_c that is two times that of pure aluminum and with excellent transport and magnetic properties. While the observed T_c increase is slightly smaller than the one observed in ENZ metamaterials [4], the hyperbolic metamaterial geometry exhibits superior transport and magnetic properties compared to the ENZ core-shell metamaterial superconductors. In addition, our theoretical model is applicable to previous experiments performed in NbN/AlN [35] and Al/Si [36] multilayer geometries. We should also note that unlike recent pioneering work on quantum metamaterials [37], which are based on superconducting split-ring resonators and quantum circuits, our work aims at engineering of metamaterials with enhanced superconducting properties.

5 What next? How to further increase critical temperature in a metamaterial superconductor

While theoretical plots in Figure 1B unambiguously identify the physical mechanism of T_c enhancement in the

Al-Al₂O₃ core-shell metamaterial superconductor, it must be understood that a complete theory should take into account simultaneous contributions of both poles of Eq. (10) to λ_{eff} of the metamaterial. It is also clear that according to Eq. (5) the metamaterial pole occurs at a slightly different frequency compared to the $\varepsilon_m \approx 0$ pole, and therefore it must have slightly different value of $\varepsilon_m'' = \text{Im}\varepsilon_m$ compared to the value of ε_m'' for pure aluminum at $\text{Re}\varepsilon_m \approx 0$. In order to obtain more precise values, let us consider the behavior of ε_m in more detail. Since

$$\left(1 - \frac{\Omega_1^2(q)}{\omega^2 + i\omega\Gamma_1}\right) = \frac{(\omega + \Omega_1)(\omega - \Omega_1) + i\omega\Gamma_1}{\omega^2 + i\omega\Gamma_1}, \quad (37)$$

let us assume that near $\omega = \Omega_1(q)$ Eq. (5) may be approximated as

$$\varepsilon_m \approx -E_m(\omega - \Omega_1) + i\varepsilon_m''(\omega), \quad (38)$$

where E_m is a positive constant. Based on Eq. (11), the corresponding frequency of the “metamaterial” pole is

$$\omega = \Omega_1 + \frac{(3-2n)\varepsilon_d}{2nE_m}, \quad (39)$$

which is slightly higher than Ω_1 , and therefore, a slightly larger value of $\text{Im}(\varepsilon_m) = \varepsilon_m''(\Omega_1 + (3-2n)\varepsilon_d/2nE_m)$ may be expected at the metamaterial pole at this higher frequency. As a result, by taking into account simultaneous contributions from both poles [by adding the contributions to λ_{eff} from the “metal” and the “metamaterial” poles given by Eqs. (13) and (15), respectively], the final expression for λ_{eff} is

$$\begin{aligned} \lambda_{\text{eff}} &\approx \frac{n^2}{(3-2n)}\lambda_m + \frac{9(1-n)}{2(3-2n)}\frac{\varepsilon_m''}{\varepsilon_m''} \lambda_m \\ &= \lambda_m \left(\frac{n^2}{(3-2n)} + \frac{9(1-n)\alpha}{2(3-2n)} \right), \end{aligned} \quad (40)$$

where $\alpha = \varepsilon_m''/\varepsilon_m'' < 1$ is determined by the dispersion of ε_m'' . Substitution of Eq. (40) into Eq. (16) produces the following final expression for the critical temperature of the metamaterial:

$$T_c = T_{\text{cbulk}} \exp\left(\frac{1}{\lambda_m} \left(1 - \frac{1}{\left(\frac{n^2}{(3-2n)} + \frac{9(1-n)\alpha}{2(3-2n)}\right)}\right)\right) \text{ at } n > n_{\text{cr}}, \quad (41)$$

which now has a single fitting parameter α . We will consider it as a free parameter of the model, since we are not aware of any experimental measurements of dispersion of $\text{Im}\varepsilon_m$ for aluminum. Note that Eq. (41) depends on ε_d only

via n_{cr} and α . The calculated behavior of T_c as a function of n is presented in Figure 19A. The agreement appears to be very good. The best fit to experimental metamaterial data is obtained at $\alpha = 0.89$. We must emphasize that this model is quite insensitive to the particular choice of functional form of $\varepsilon_m(q, \omega)$ in the broad (q, ω) range. In our derivations, we are only using the fact that ε_m changes sign near $\omega = \Omega_1(q)$ by passing through zero, which is described by Eq. (38).

The apparent success of such a simple theoretical description in the case of Al-Al₂O₃ core-shell and hyperbolic metamaterial superconductors prompted us to apply the same theory to the tin-based ENZ metamaterials

Figure 19: Comparison between theory and experiment for ENZ metamaterials.

(A) Theoretical plot of T_c versus volume fraction n of aluminum in the Al-Al₂O₃ core-shell metamaterial calculated using Eq. (41). The best fit to experimental data is obtained at $\alpha = 0.89$. (B) Theoretical plot of T_c versus volume fraction n of tin in the tin-BaTiO₃ ENZ metamaterial [3] calculated using Eq. (41). The best fit to experimental data is obtained at $\alpha = 0.83$. The experimental data points are taken from Ref. [3].

studied in [3]. Assuming the known values $T_{cbulk} = 3.7$ K and $\theta_D = 200$ K of bulk tin [17, 18], Eq. (6) results in $\lambda_m = 0.25$, which also corresponds to the weak coupling limit. The calculated behavior of T_c as a function of n is presented in Figure 19B, which also shows experimental data points measured in [3]. The agreement also appears to be very good, given the spatial inhomogeneity of the fabricated metamaterials [3] (note also the difference in temperature scales in Figure 19A and B). The best fit to experimental metamaterial data is obtained at $\alpha = 0.83$. It appears that a smaller increase in metamaterial T_c in this case is due to larger value of permittivity ε_d of the dielectric component of the metamaterial, which according to Eq. (11) limits the range $n_{cr} < n < 0.6$ where the metamaterial T_c enhancement may occur. Larger value of ε_d also leads to smaller value of α [see Eq. (39)], which also reduces the metamaterial pole contribution to λ_{eff} .

We should also note that the appearance of an additional “metamaterial” pole in the Maxwell-Garnett expression [Eq. (9)] for a metal-dielectric mixture does not rely on any particular spatial scale, as long as it is smaller than the coherence length. In fact, the Maxwell-Garnett approximation may be considered as a particular case of the Clausius-Mossotti relation [21], which traces the dielectric constant of a mixture to the dielectric constants of its constituents, and it is only sensitive to the volume fractions of the constituents. Therefore, the same concept is supposed to be applicable at much smaller spatial scales compared to the two metamaterial cases studied in Refs. [3] and [4]. We anticipate that similar T_c enhancements may be observed in metamaterials based on other higher temperature superconductors, which have smaller coherence length, such as niobium and MgB₂.

First, let us consider the case of niobium, which has $T_{cbulk} = 9.2$ K and $\theta_D = 275$ K in the bulk form [17, 18]. Enhancing the superconducting properties of niobium is a very important task, since niobium alloys, such as Nb₃Sn and NbTi are widely used in superconducting cables and magnets. Based on Eq. (6), niobium has $\lambda_m = 0.29$, which also corresponds to the weak coupling limit. The coherence length of niobium is $\xi = 38$ nm [17, 18], which would complicate nanofabrication requirements for a niobium-based metamaterial. However, given the current state of nanolithography, which operates on a 14 nm node [38], these requirements still look quite realistic. Alternatively, smaller than 38-nm-diameter nanoparticles would need to be used in nanoparticle-based ENZ metamaterial geometries.

The calculated behavior of T_c of a niobium-based ENZ metamaterial as a function of n is presented in Figure 20A for different values of the α ratio in Eq. (41). The vertical

Figure 20: T_c projections for hypothetical niobium and MgB₂ based metamaterials. (A) Theoretical plots of T_c versus volume fraction n of niobium in a hypothetical niobium-based ENZ metamaterial calculated using Eq. (41) for different values of the α ratio. The experimental data points for bulk Nb and Nb₃Sn are shown in the same plot for comparison. (B) Theoretical plots of T_c versus volume fraction n of MgB₂ in a hypothetical MgB₂-based ENZ metamaterial calculated using Eq. (41) for different values of the α ratio. In both cases the vertical dashed lines correspond to the same value of n_{cr} as in the Al-Al₂O₃ core-shell metamaterial superconductor.

dashed line in the plot corresponds to the same value of n_{cr} as in the Al-Al₂O₃ core-shell metamaterial superconductor. It is interesting to note that the general range of predicted T_c enhancement matches well with the observed enhancement of T_c in various niobium alloys [17]. The corresponding experimental data point for Nb₃Sn is shown in the same plot for comparison (it is assumed that $n=0.75$ for Nb₃Sn). As we have mentioned above, our model is based on the Maxwell-Garnett approximation, which traces the dielectric constant of a mixture to the dielectric constants of its

constituents. The spatial scale of mixing is not important within the scope of this model. Therefore, our model may be applicable to some alloys. We should note that the additional “metamaterial” pole described by Eq. (11) may also be present in the case of a mixture of a normal metal with the superconductor. However, unlike the previously considered case of a dielectric mixed with a superconductor, the additional “metamaterial” pole is observed at $\omega < \Omega_1$, where the dielectric constant of the superconductor ϵ_s is positive [see Eq. (38)], while the dielectric constant of the normal metal ϵ_m is negative (it is assumed that the critical temperature of the normal metal is lower than the critical temperature of the superconductor). Indeed, under these conditions, an additional pole in the inverse effective dielectric response function of the metamaterial does appear in [Eq. (10)], and similar to Eq. (11), it is defined as

$$\epsilon_s \approx -\frac{3-2n}{2n}\epsilon_m \quad (42)$$

This pole will result in the enhanced T_c of the metamaterial (or alloy), which may be calculated using the same Eq. (41). However, since this additional pole occurs at $\omega < \Omega_1$, it is expected that $\text{Im}\epsilon_s$ will be smaller at this frequency, resulting in factor α being slightly larger than one. This conclusion agrees well with the position of Nb₃Sn data point on Figure 20A.

Next, let us consider the case of MgB₂, which has $T_{c\text{bulk}} = 39$ K and $\theta_D = 920$ K in the bulk form [39]. The coherence length of MgB₂ remains relatively large: the π and σ bands of electrons have been found to have two different coherence lengths, 51 and 13 nm [40]. Both values are large enough to allow metamaterial fabrication, at least in principle. Based on Eq. (6), MgB₂ has $\lambda_m = 0.32$, which still remains within the scope of the weak coupling limit. The calculated behavior of T_c of a MgB₂-based ENZ metamaterial as a function of n is presented in Figure 4B for different values of the α ratio in Eq. (41). Similar to Figure 20A, the vertical dashed line in the plot corresponds to the same value of n_{cr} as in the Al-Al₂O₃ core-shell metamaterial superconductor. It appears that the critical temperature of MgB₂-based ENZ metamaterial would probably fall in the liquid nitrogen temperature range. A good choice of the dielectric component of such a metamaterial could be diamond: 5-nm-diameter diamond nanoparticles are available commercially, see for example Ref. [3].

Unfortunately, superconductors having progressively higher T_c are not well described by Eq. (6), which is valid in the weak coupling limit only. Thus, it is interesting to evaluate what kind of metamaterial enhancement may be expected in such system as H₂S, which superconducts at 203 K at very high pressure [41]. While simple theoretical

description developed in our work may not be directly applicable to this case as far as T_c calculations are concerned (because of the very large values of $\theta_D \sim 1200$ K and $\lambda \sim 2$ in this material [42]), adding a suitable dielectric or normal metal to H_2S will still result in an additional “metamaterial” pole in its inverse dielectric response function. Eqs. (8–12) will remain perfectly applicable in this case. Therefore, adding such a pole will enhance superconducting properties of H_2S . Based on Eq. (10), we may predict that the enhancement of superconducting properties will be observed at $n \sim 0.6$, as it also happened in the cases of aluminum and tin-based metamaterials considered in this paper. As far as the choice of a dielectric is concerned, based on Eqs. (8–12), it appears that readily available nanoparticles of diamond (off the shelf 5-nm-diameter diamond nanoparticles were used in [3]) could be quite suitable, since diamond has rather low dielectric constant $\epsilon_{dia} \sim 5.6$, which stays almost constant from the visible to RF frequency range. Low permittivity of the dielectric component ensures smaller value of n_{cr} defined by Eq. (11), and hence larger metamaterial enhancement. It is not inconceivable that 5-nm-diameter diamond nanoparticles could be added to H_2S in the experimental chamber used in [41].

Unfortunately, in the strong coupling limit, the expected T_c enhancement may not be as drastic as in the weak coupling limit described by Eq. (6). In the $\lambda \gg 1$ limit of the Eliashberg theory, the critical temperature of the superconductor may be obtained as [43]

$$T_c = 0.183\theta_D \sqrt{\lambda}. \quad (43)$$

Therefore, enhancement of λ by the largest possible factor of 1.5 calculated based on the Maxwell-Garnett theory for the effective dielectric response function of the metamaterial (see Figure 1A) will lead to T_c enhancement by factor of $(1.5)^{1/2}$, which means that a critical temperature range ~ 250 K (or $\sim -20^\circ\text{C}$) may potentially be achieved in a H_2S -based metamaterial superconductor. Such a development would still be of sufficient interest, since this would constitute an almost room temperature superconductivity.

Considerable increase of T_c of the metamaterial superconductors may also be achieved by optimizing the metamaterial geometry. Historically, the suggestion to use highly polarizable dielectric side chains or layers in order to increase T_c of a 1D or 2D electronic system can be traced back to the pioneering papers by Little [44] and Ginzburg [45]. Using modern language, the superconducting systems proposed in these works could be called “superconducting metamaterials”. While these proposals never led to hypothesized room temperature superconductivity, experimental attempts to realize such superconductors

were limited by modest polarizability of natural materials. Recent development of high- ϵ metamaterials gives these proposals another chance [2]. An example of the high-index metamaterial, which may be used in the modern day versions of either 1D or 2D superconducting geometries proposed by Little and Ginzburg is shown in Figure 21 [2].

Figure 21: High-index metamaterials.

(A) Unit cell structure of the high-index metamaterial, which may be used in the modern day version of the 1D or 2D superconducting geometries proposed by Little [44] and Ginzburg [45]. The metamaterial is made of a thin “I”-shaped metallic patch symmetrically embedded in a dielectric material. The 3D structure of this metamaterial may be described as an array of subwavelength capacitors, in which the gap width defined by $g = L - a$ and the interlayer spacing d (exaggerated for clarity) define the capacitor values. (B) Real and imaginary parts of ϵ_{eff} numerically calculated for the metamaterial geometry shown in (A) for the following values of geometrical parameters: $L = 98$ nm, $g = 14$ nm, $w = 28$ nm. The metamaterial exhibits broadband high ϵ behavior, while metamaterial losses remain modest below 50 THz.

In another recent development, fractal metamaterial superconductor geometry has been suggested and analyzed based on the theoretical description of critical temperature increase in ENZ metamaterial superconductors [46]. Considerable enhancement of critical temperature has been predicted in such fractal metamaterials due to appearance of large number of additional poles in the inverse dielectric response function of the fractal. Indeed, relatively large value of the superconducting coherence length $\xi = 1600$ nm of bulk aluminum [17] leaves a lot of room for engineering an aluminum-based fractal metamaterial superconductor according to the procedure shown schematically in Figure 22A.

Let us consider the central image (the second fractal order) from Figure 22A. We may use the Maxwell-Garnett approximation [Eq. (8)] in order to determine the effective dielectric permittivity of such metamaterial. However, this time, we will assume that the “first-order metamaterial”

Figure 22: Fractal metamaterial superconductors.

(A) Schematic geometry of a metal-dielectric fractal metamaterial superconductor. For the first fractal order (second panel), the volume fraction of the superconductor is $n = 0.56$. (B) The first few poles of the inverse dielectric response function of a fractal metal-dielectric metamaterial plotted as a function of n for the case of $\varepsilon_d = 3$. The fractal order is marked near the curve for each pole. The vertical dashed line corresponds to the critical value of the metal volume fraction n_{cr} observed in the case of the Al-Al₂O₃ core-shell superconductor. It is used to determine $n_{cr}^{(k)}$ for the next fractal orders, as indicated by the horizontal dashed line.

described by Eq. (9) plays the role of the “matrix”. The volume fraction of the new matrix is n , and it is diluted with the same dielectric ε_d with volume fraction $(1-n)$. Mixing of these components results in the effective medium with a dielectric constant $\varepsilon_{eff}^{(2)}$, which may be obtained as [compare to Eq. (9)]:

$$\varepsilon_{eff}^{(2)} = \frac{\varepsilon_{eff}^{(1)}((3-2n)\varepsilon_d + 2n\varepsilon_{eff}^{(1)})}{(n\varepsilon_d + (3-n)\varepsilon_{eff}^{(1)})}. \quad (44)$$

It is easy to verify that in addition to the pole at $\varepsilon_m \approx 0$ and the first-order pole described by Eq. (11), the inverse dielectric response function of the “second order” fractal metamaterial has additional poles at

$$\varepsilon_m = -\varepsilon_d \frac{(3-2n)(3+n)}{8n^2} \left(1 \pm \sqrt{1 - \frac{16n^3}{(3-2n)(3+n)^2}} \right). \quad (45)$$

These additional poles may be expressed in the recurrent form as

$$\varepsilon_m^{(2)} = \varepsilon_m^{(1)} \frac{(3+n)}{4n} \left(1 \pm \sqrt{1 - \frac{16n^3}{(3-2n)(3+n)^2}} \right). \quad (46)$$

The latter equation, which expresses $\varepsilon_m^{(k+1)}$ as a function of $\varepsilon_m^{(k)}$, may be used to determine all the poles of the fractal metamaterial structure using an iterative procedure. The first few poles determined in such a way are plotted in Figure 22B as a function of n for the case of $\varepsilon_d = 3$. This plot makes it clear that most of the poles in each iteration [which correspond to the minus sign in Eq. (46)] stay near $\varepsilon_m \approx 0$, while one pole in each iteration (corresponding to the plus sign) may be written as

$$\varepsilon_m^{(k+1)} \approx \varepsilon_m^{(k)} \frac{(3+n)}{2n}. \quad (47)$$

The vertical dashed line in Figure 22B corresponds to the critical value of the metal volume fraction n_{cr} observed in the case of the Al-Al₂O₃ core-shell superconductor [3]. As indicated in Figure 22B, this value may be used as a guideline to evaluate how many additional poles may be observed in a real fractal metamaterial at a given volume fraction n . The additional poles of the inverse dielectric response function of the fractal metamaterial defined by Eq. (47) may be described as the plasmon-phonon modes of the metamaterial, which participate in the Cooper pairing of electrons in a fashion, which is quite similar to the conventional BCS mechanism.

Let us evaluate what kind of critical temperature increase may be expected in a fractal metamaterial

superconductor because of the appearance of all these additional poles in $\varepsilon_{\text{eff}}^{-1}(q, \omega)$. We already have demonstrated that the additional poles of the inverse dielectric response function may be found using an iterative procedure. A similar iterative expression may be derived for $\text{Im}\varepsilon_{\text{eff}}^{-1}(q, \omega)$ near these poles. Based on Eq. (10), we may write the following expression for the imaginary part of the inverse dielectric response function of the first-order material near the metamaterial pole:

$$\text{Im}((\varepsilon_{\text{eff}}^{(1)})^{-1}) \approx \frac{9(1-n)}{2n(3-2n)} \alpha \text{Im}((\varepsilon_{\text{eff}}^{(0)})^{-1}), \quad (48)$$

where $\text{Im}((\varepsilon_{\text{eff}}^{(0)})^{-1}) = 1/\varepsilon_m''$, and $\alpha \sim 1$ near $n \sim 1$. Since the magnitude of ε_m is finite (see Figure 22B), in a real fractal metamaterial geometry, a large number of poles may be expected only at values of n close to 1. Therefore, from now on we will assume that $\alpha = 1$. An expression similar to Eq. (48) may be applied iteratively to the next fractal orders. As far as the density of states ν in Eq. (7) is concerned, as illustrated by Figure 22A, with each iteration, the density of states of the metamaterial is multiplied by a factor of n . Thus, we may now sum up contributions of all the fractal poles to λ_{eff} . It may be obtained as a sum of a geometrical progression:

$$\lambda_{\text{eff}} \approx \left(n^{K-1} \left(\frac{9(1-n)}{2(3-2n)} \right) + n^{K-2} \left(\frac{9(1-n)}{2(3-2n)} \right)^2 + \dots + \left(\frac{9(1-n)}{2(3-2n)} \right)^K \right) \lambda_m, \quad (49)$$

$$\lambda_m = n^{K-1} \left(\frac{9(1-n)}{2(3-2n)} \right) \left(\frac{1 - \left(\frac{9(1-n)}{2n(3-2n)} \right)^K}{1 - \left(\frac{9(1-n)}{2n(3-2n)} \right)} \right) \lambda_m,$$

assuming that the metamaterial structure contains K fractal orders. The resulting λ_{eff} is plotted in Figure 23 for the first four fractal orders. The corresponding $n_{\text{cr}}^{(k)}$ for each fractal order (determined using Figure 22B) are marked by the vertical dashed lines in Figure 23. This figure clearly demonstrates that fractal structure promotes superconductivity by increasing λ_{eff} . For the case of Al-based metamaterial, the enhancement of T_c is expected for at least the first three fractal orders. Compared to a simple metal-dielectric ENZ metamaterial (described as a “first-order fractal” in Figure 23), the higher-order fractal metamaterial structures exhibit much stronger enhancement of the coupling constant λ_{eff} , which should lead to much larger T_c increase. Based on Figure 23, the enhancement of T_c ($\lambda_{\text{eff}}/\lambda_m > 1$) in a fractal metamaterial occurs starting at $n \sim 0.8$, which is close enough to $n \sim 1$ to validate our assumptions. The corresponding values of T_c calculated

Figure 23: Plot of the magnitude of λ_{eff} given by Eq. (49) as a function of n for the first four orders of a fractal metamaterial superconductor.

The corresponding $n_{\text{cr}}^{(k)}$ are marked by the vertical dashed lines.

using Eq. (16) based on the superconducting parameters of bulk aluminum for the first two fractal orders are shown in Figure 24. The calculated curves are terminated at the experimentally defined values of $n_{\text{cr}}^{(k)}$ for the respective fractal order, which are taken from Figure 22B. Eight-fold enhancement of T_c compared to the bulk aluminum is projected for the second-order fractal structure. The fractal enhancement of T_c may become even more pronounced for materials having larger values of $-\varepsilon_m$ compared to bulk aluminum.

Figure 24: Enhancement of T_c of the fractal metamaterial superconductor calculated as a function of n based on the superconducting parameters of bulk aluminum.

The second-order fractal structure demonstrates considerably higher T_c compared to the first-order structure.

Our results agree with the recent observations [47, 48] that fractal defect structure promotes superconductivity. In particular, it was observed that the microstructures of the transition-metal oxides, including high- T_c copper oxide superconductors, are complex. For example, the oxygen interstitials or vacancies (which strongly influence the dielectric properties of the bulk high- T_c superconductors [49]) exhibit fractal order [47]. These oxygen interstitials are located in the spacer layers separating the superconducting CuO_2 planes. They undergo fractal ordering phenomena that induce enhancements in the transition temperatures with no changes in the overall hole concentrations. Such ordering of oxygen interstitials in the $\text{La}_2\text{O}_{2+y}$ spacer layers of $\text{La}_2\text{CuO}_{4+y}$ high- T_c superconductors is characterized by a fractal distribution up to a maximum limiting size of 400 nm. It was observed [47], quite intriguingly, that these fractal distributions of dopants seem to enhance superconductivity at high temperature, which is difficult to explain since the superconducting coherence length in these compounds is very small $\xi \sim 1\text{--}2$ nm [47, 48]. Appearance of the plasmon-phonon modes of the fractal structure described above may resolve this issue, since such fractal phonon modes reside on a scale, which is much larger than several nanometers. We should also mention that such a mechanism may also explain observations of increased critical temperatures in fractal Pb thin films [50].

6 Conclusion

Unlike the traditional searches of higher T_c superconductors, which rely on choosing natural materials exhibiting larger electron-electron interactions, the metamaterial superconductor paradigm offers considerably extended range of search scenarios. The newly developed electromagnetic metamaterials offer the field of superconductivity research many novel tools, which enable intelligent engineering of electron pairing interaction. Considerable enhancement of the electron-electron interaction may be expected in such metamaterial scenarios as in ENZ and hyperbolic metamaterials, as well as in novel fractal metamaterial geometries. In all these cases, the dielectric function may become small and negative in substantial portions of the relevant four-momentum space, leading to enhancement of the electron pairing interaction. This approach has been verified in experiments with tin- and aluminum-based metamaterials. Aluminum-based metamaterial superconductor with $T_c = 3.9$ K have been

Table 1: Summary of the experimentally measured parameters of various metamaterial superconductors.

Composition	T_c (K)		Reference
	Bulk	Metamaterial	
ENZ			
Sn/BaTiO ₃	3.68	3.83	[3]
Sn/SrTiO ₃	3.68	3.80	[3]
Al/Al ₂ O ₃	1.2	3.9	[4]
Hyperbolic			
Al/Al ₂ O ₃	1.2	2.4	[5]
Sn/CaF ₂	3.68	3.92	To be published
Sn/MgF ₂	3.68	3.87	To be published

fabricated, that is three times that of pure aluminum ($T_c = 1.2$ K), which opens up new possibilities to considerably improve T_c of other simple superconductors. Experimental results obtained so far in various ENZ and hyperbolic metamaterial superconductor systems are summarized in Table 1.

Taking advantage of the demonstrated success of this approach, the critical temperature of hypothetical niobium, MgB_2 - and H_2S -based metamaterial superconductors has been evaluated. The MgB_2 -based metamaterial superconductors are projected to reach the liquid nitrogen temperature range. In the case of an H_2S -based metamaterial, the projected T_c appears to be as high as ~ 250 K, which almost reaches the room temperature range. We hope that our brief review clearly demonstrates that the future of metamaterial superconductors is bright, and we anticipate many novel exciting scientific and technical applications of these materials.

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