Application of metamaterial nano-engineering for increasing the superconducting critical temperature

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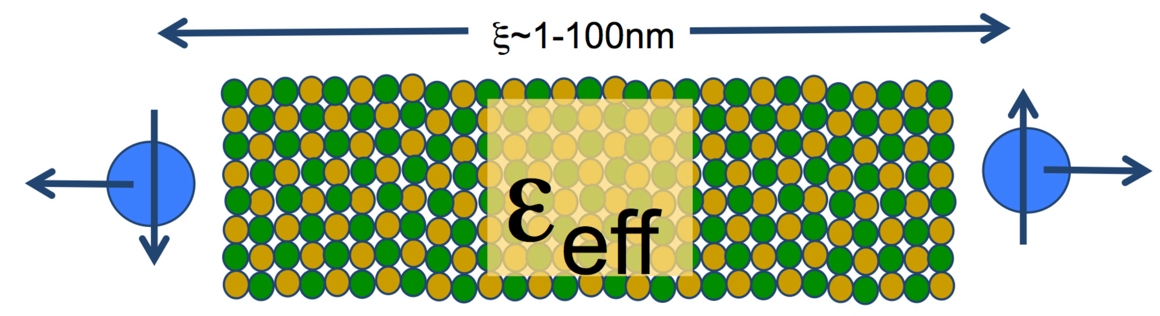
We have demonstrated that the metamaterial approach to dielectric response engineering increases the critical temperature of a composite superconductor-dielectric system in the epsilon near zero (ENZ) and hyperbolic regimes. To create such metamaterial superconductors three approaches were implemented: 1) mixtures of tin and barium-titanate and strontium-titanate nanoparticles, 2) Al_2O_3-coated aluminium nanoparticles, and 3) thin Al/Al_2O_3 heterostructures that form a hyperbolic metamaterial superconductor. IR reflectivity measurements confirmed the predicted metamaterial behavior. These results suggest the possibility of considerable T_c enhancement in other superconductors.

MIT Technology Review

How Metamaterials Could Hold the Key to High Temperature Superconductivity

Metamaterial

- Material engineered to have a property that is not found in nature.
- Made from assemblies of multiple elements fashioned from composite materials.
- Length scales that are smaller than those of the phenomena they influence (e. g. wavelength for optical).
- Derive their properties not from the properties of the base materials, but from their newly designed structures.
- The relevant length scale for superconductors is the coherence length, ξ.



T_c determined by nanostructure properties

If ε_{eff}<0 and small then V and T_c will be large.
Epsilon near zero (ENZ)

Positive ε
Negative ε

The effective Coulomb potential in a superconductor (D.A. Kirzhnits, *et al.*, J. Low Temp. Phys. 10, 79 (1973)):

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

T_c is defined by solving integral equation for the superconducting condensate:

$$\Phi(\boldsymbol{p})=-\int\frac{d^3k}{(2\pi)^3}\frac{4\pi e^2}{(\boldsymbol{p}-\boldsymbol{k})^2}\frac{\tanh\left(\frac{\xi_k}{2T_c}\right)}{2\xi_k}\left[1-2\int_0^\infty\frac{dE\rho(\boldsymbol{p}-\boldsymbol{k},E)}{E+|\xi_k|+|\xi_p|}\right]\Phi(\boldsymbol{k})$$

Where ρ(q,E) is the inverse dielectric response function:

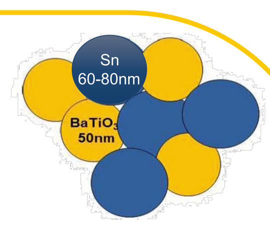
$$\rho(q,E)=-\left(\frac{1}{\pi}\right)\mathrm{Im}\left[\frac{1}{\epsilon(\boldsymbol{q},E)}\right]$$

Evaluation of the maximum critical temperature T_c^{max} produced an optimistic T_c^{max}~300K estimate at E_F~10eV.

- The effective medium consideration assumes a "homogeneous system" so that "the influence of the lattice periodicity is taken into account only to the extent that it may be included into ε_{eff}(q,ω)".
- The "homogeneous system" approximation remains valid even if the basic structural elements of the material are not simple atoms or molecules.
- Artificial "metamaterials" may be created from much bigger building blocks, and the electromagnetic properties of these fundamental building blocks may be engineered at will.

Epsilon near zero (ENZ) composite

V. N. Smolyaninova, *et al.*, Sci. Rep 4, 7321 (2014).



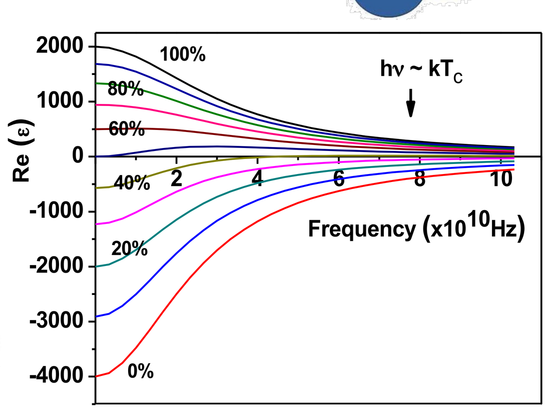
Sn/$BaTiO_3$ mixture:

Sn: Drude model $\qquad \varepsilon_m=\varepsilon_{m\infty}-\frac{\omega_p^2}{\omega(\omega+i\gamma)}$

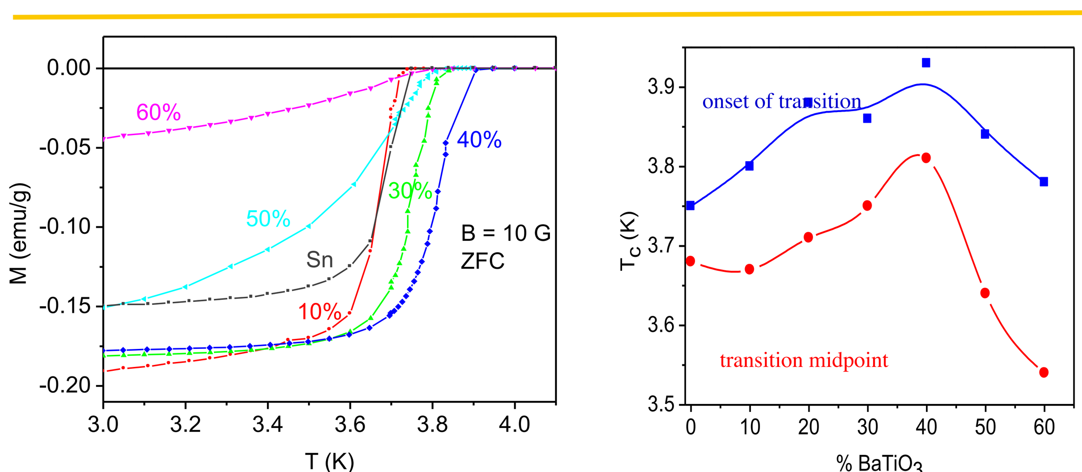
$BaTiO_3$: Debye model $\qquad \mathrm{Re}\,\varepsilon_i=\frac{\varepsilon_i(0)}{1+\omega^2\tau^2}$

Maxwell-Garnett approximation:

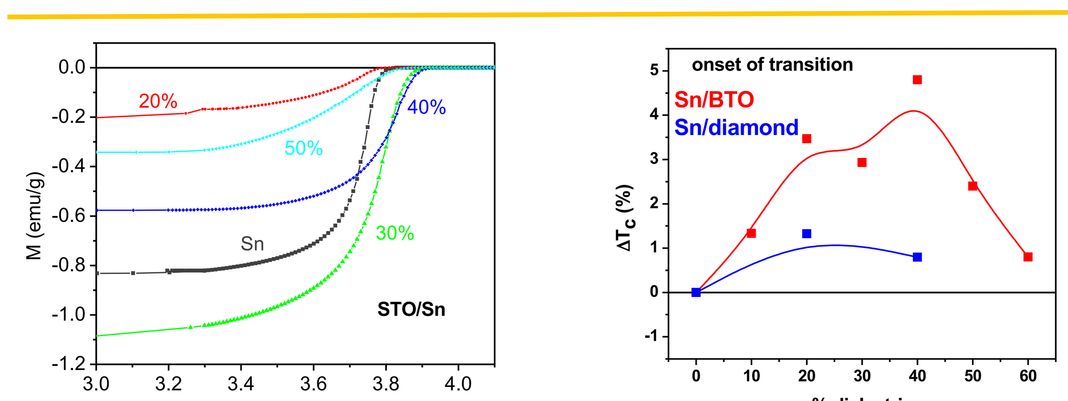
$$\varepsilon_{eff}=\varepsilon_m\frac{(2\varepsilon_m+\varepsilon_i)-2\delta_i(\varepsilon_m-\varepsilon_i)}{(2\varepsilon_m+\varepsilon_i)+\delta_i(\varepsilon_m-\varepsilon_i)}$$



ENZ conditions are projected to occur around 30-50% volume fraction of $BaTiO_3$

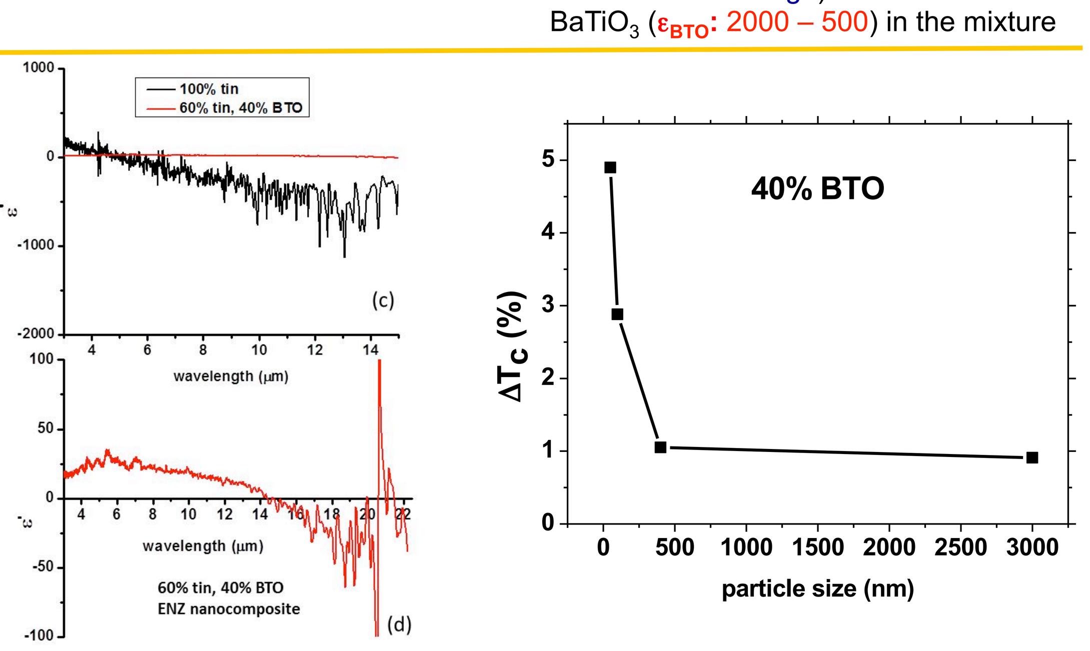


- An increase of the critical temperature of the order of ΔT_C ~ 0.15 K compared to tin sample (compressed nanoparticles
- Location of T_C maximum is consistent with Maxwell-Garnett analysis.



Also works for 60 nm Sn/100 nm $SrTiO_3$

Significantly smaller T_C increase observed if diamond ($\varepsilon_{diamond}$=5.6 from MHz to visible range) is used instead of $BaTiO_3$ (ε_{BTO}: 2000 – 500) in the mixture



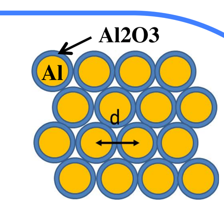
Kramers-Kronig analysis of FTIR reflectivity spectra: evaluate $\varepsilon_{eff}(0,\omega)$

Effect is significantly reduced when nanoparticle size exceeds 240 nm coherence length in Sn

ENZ scenario verified

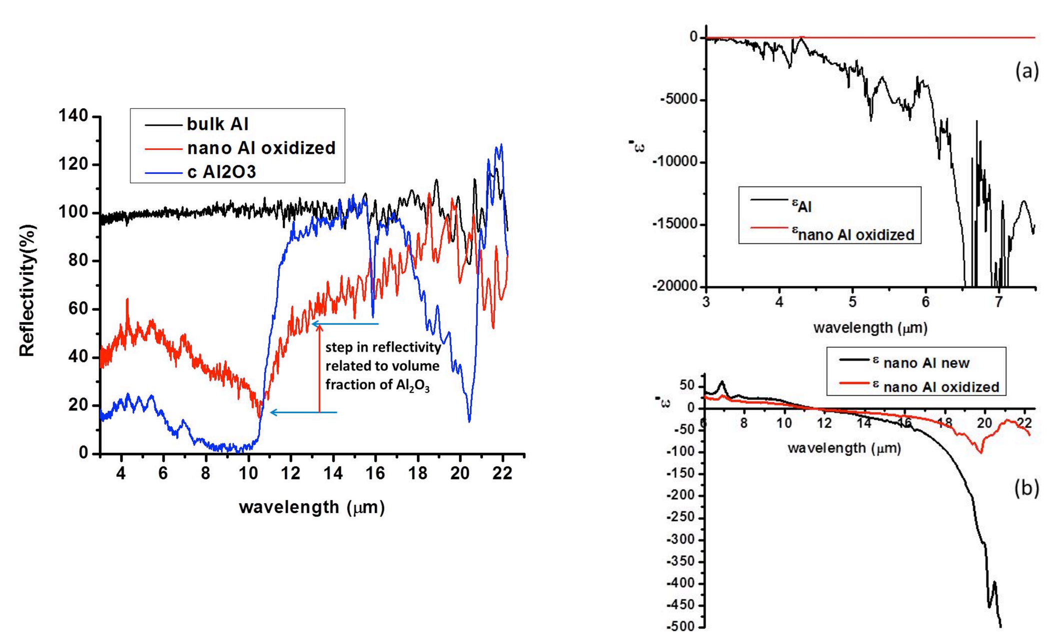
Epsilon near zero (ENZ) core-shell

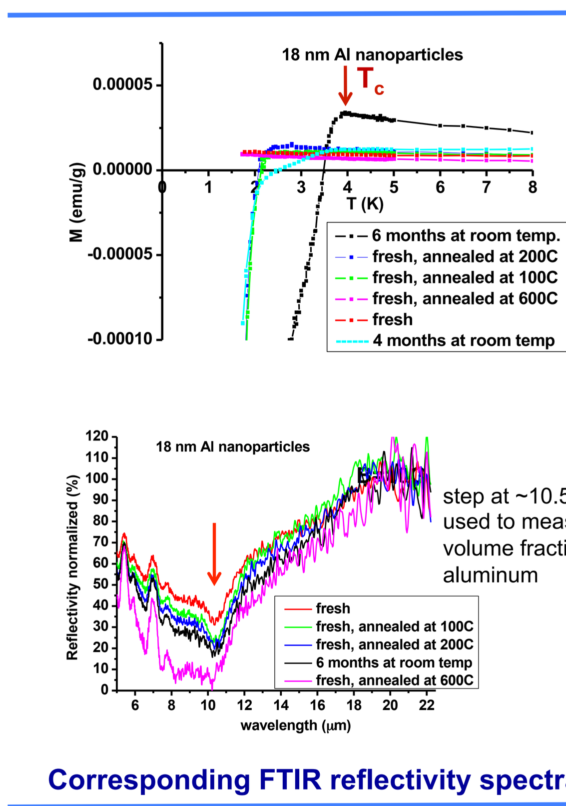
V. N. Smolyaninova, *et al.*, , Sci. Rep. **5**, 15777 (2015).



compressed Al_2O_3-coated aluminum nanoparticles

- 18 nm diameter Al nanoparticles (T_c=1.2K, ξ=1600 nm)
- Exposure to the ambient conditions: ~ 2 nm thick Al_2O_3 shell on surface
- Al_2O_3 exhibits very large positive values of dielectric permittivity up to ε_{Al2O3}~200 in the THz range
- Comparable to the 9 nm radius of the original Al nanoparticle
- Further Al oxidation may also be achieved by heating the nanoparticles in air



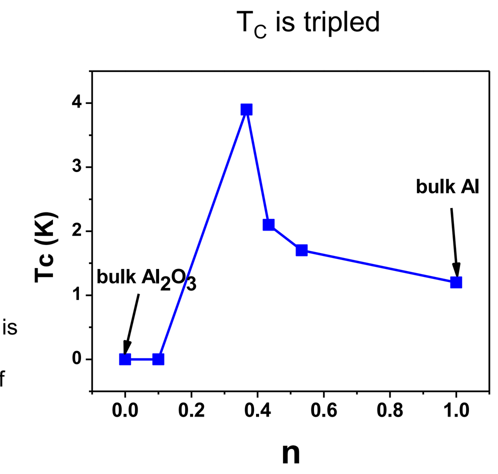


step at ~10.5 μm is used to measure volume fraction of aluminum

Corresponding FTIR reflectivity spectra

bulk Al: T_C = 1.2 K
Al-Al_2O_3 core-shell: T_C = 3.9 K

T_C is tripled



Decrease in reflectivity corresponds to decrease of the volume fraction of aluminium.

Maxwell-Garnett approximation:

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

n - the volume fraction of superconductor

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

metal pole $\qquad$ additional pole

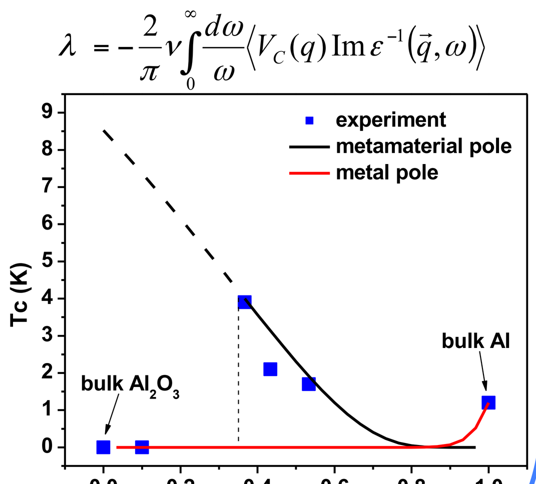
$$\lambda_{eff}\approx\frac{n^2}{(3-2n)}\lambda_m \qquad \lambda_{mm}\approx\frac{9(1-n)}{2(3-2n)}\lambda_m$$

$$T_c=T_{Cbulk}\exp\left(\frac{1}{\lambda_m}-\frac{1}{\lambda_{eff}}\right)$$

Weak coupling approximation:

$$T_c=\theta\,\exp\left(-\frac{1}{\lambda}\right)$$

$$\lambda=-\frac{2}{\pi}\nu\int_0^\infty\frac{d\omega}{\omega}\left\langle V_C(q)\,\mathrm{Im}\,\varepsilon^{-1}(\vec{q},\omega)\right\rangle$$

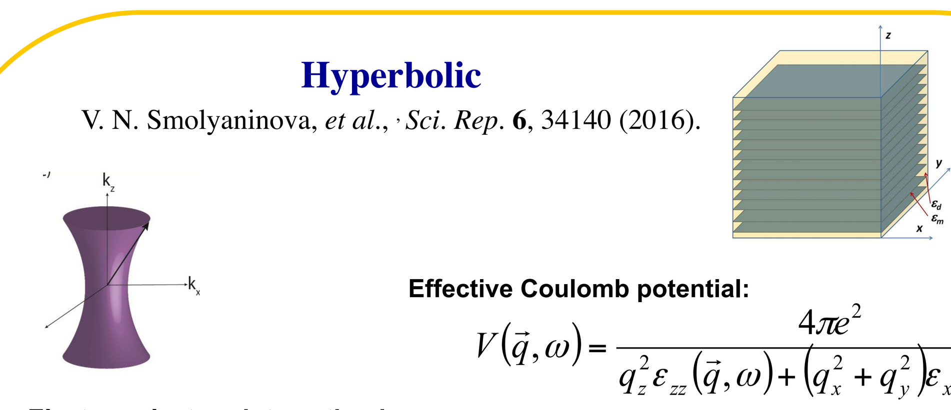


no free parameters! $\qquad$ n

PRB 93, 184510 (2016)

Hyperbolic

V. N. Smolyaninova, *et al.*, Sci. Rep. **6**, 34140 (2016).



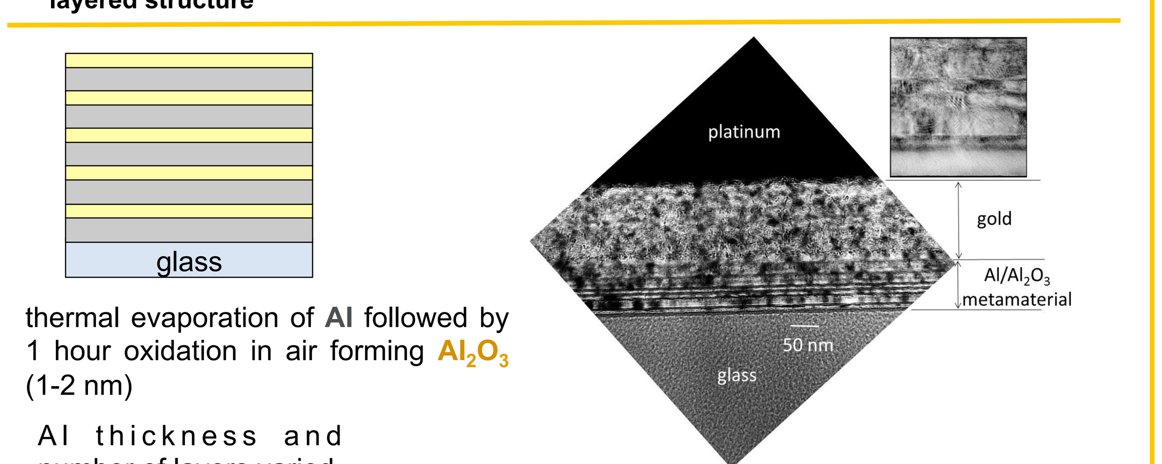
Effective Coulomb potential:

$$V(\vec{q},\omega)=\frac{4\pi e^2}{q_z^2\varepsilon_{zz}(\vec{q},\omega)+(q_x^2+q_y^2)\varepsilon_{xx}(\vec{q},\omega)}$$

diverges at: $\quad q_z^2\varepsilon_{zz}(\vec{q},\omega)+(q_x^2+q_y^2)\varepsilon_{xx}(\vec{q},\omega)\approx 0$

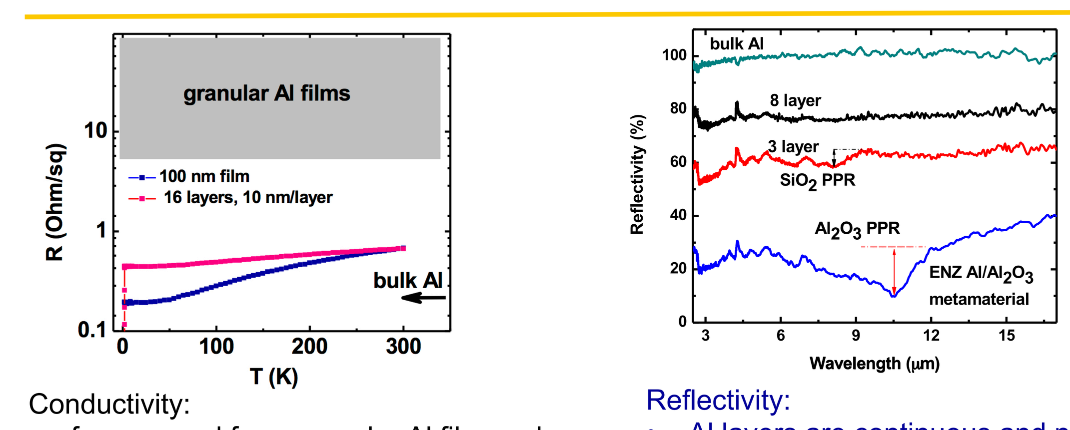
- Electron-electron interaction is strongly enhanced in hyperbolic metamaterials
- The best choice of geometry appears to be metal/dielectric layered structure

Smolyaninov, Smolyaninova, PRB 91, 094501 (2015)



thermal evaporation of Al followed by 1 hour oxidation in air forming Al_2O_3 (1-2 nm)

Al thickness and number of layers varied



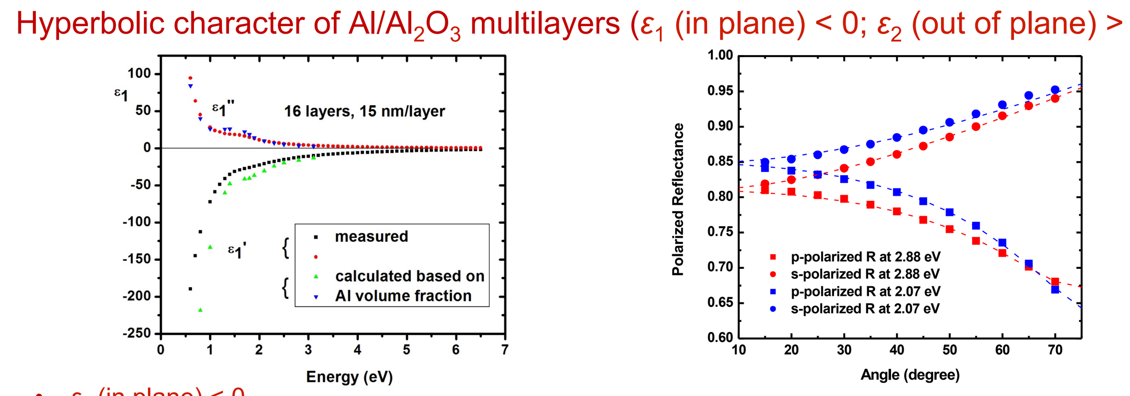
Conductivity:

- far removed from granular Al films values
- approaches conductivity values of bulk Al

Reflectivity:

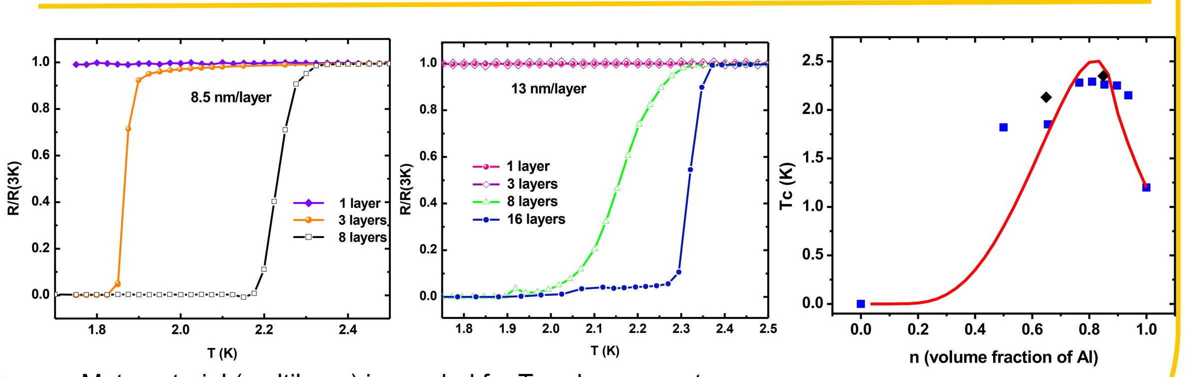
- Al layers are continuous and not intermixed with aluminum oxide

Hyperbolic character of Al/Al_2O_3 multilayers (ε_1 (in plane) < 0; ε_2 (out of plane) > 0)



- ε_1 (in plane) < 0
- good agreement with calculated values based on Al volume fraction

ε_1 = -7.17 and ε_2 = 1.56, at 2.07 eV (600 nm)
ε_1 = -2.15 and ε_2 = 1.30 at 2.88 eV (430 nm)



Metamaterial (multilayer) is needed for T_c enhancement

Curve is fit to weak coupling BCS model with Maxwell-Garnett approx. for ε_{eff}

Summary

- A Macroscopic electrodynamics-based approach to superconductivity (Kirzhnits *et al.*) sets a very large limit on T_C
- Electron-electron interaction is strongly enhanced in ENZ and hyperbolic metamaterials
- Our proof of principle experiments demonstrate validity of the metamaterial approach

This work was supported in part by NSF grant DMR-1104676.