

Seminar to the electronic properties of graphene:

Optical absorption of a single graphene layer

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Motivation

- Interaction of an electromagnetic field with a material is of fundamental interest
- Excitation of massless electrons in comparison to massive electrons
- Transmissivity, reflectivity and absorption of an atomically thin material
- Prediction of the behavior of the optical conductivity over a large region of the electromagnetic spectrum

Electromagnetic scattering problem

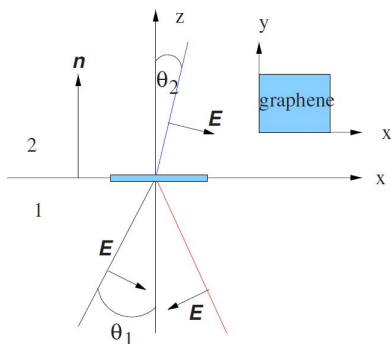


Figure: Scattering geometry.

- Single graphene layer between two media with ϵ_1 and ϵ_2 .
- Incident p polarized electromagnetic wave with $\mathbf{k} = (k_x, 0, k_z)$ and $\mathbf{E} = (E_x, 0, E_z)$.
- Boundary conditions:

$$\mathbf{n} \cdot (\mathbf{D}_2 - \mathbf{D}_1) = \rho, \quad (1)$$

$$\mathbf{n} \times (\mathbf{E}_2 - \mathbf{E}_1) = 0, \quad (2)$$

where ρ is the graphene charge density.

With the incident, reflected and transmitted Field E_i , E_r and E_t the boundary conditions hold

$$(E_i - E_r) \cos \theta_1 - E_t \cos \theta_2 = 0, \quad (3)$$

$$\epsilon_1 \epsilon_0 (E_i + E_r) \sin \theta_1 - \epsilon_2 \epsilon_0 E_t \sin \theta_2 = \rho. \quad (4)$$

Due to the given polarisation current can only flow in x -direction, thus the charge density is directly connected to the current density via the **continuity equation**

$$\frac{\partial}{\partial x} j_x(\mathbf{r}) = -\frac{\partial}{\partial t} \rho(\mathbf{r}) \quad \xrightarrow{F.T.} \quad \rho(\omega) = j_x(\omega) \cdot \frac{k_x}{\omega}, \quad (5)$$

and **Ohm's law** reads

$$j_x(\omega) = \sigma(\omega) \cdot E_x = \sigma(\omega) \cdot E_t \cos \theta_2, \quad (6)$$

where $\sigma(\omega)$ is the complex optical conductivity, and we can write

$$\sigma(\omega) = \sigma_{xx}(\omega). \quad (7)$$

Combining the boundary conditions, the continuity equation and Ohm's law [(3)-(6)] with the expression for the transmissivity T and the reflectivity R given by

$$T = \sqrt{\frac{\epsilon_2}{\epsilon_1}} \frac{\cos \theta_2}{\cos \theta_1} \left| \frac{E_t}{E_i} \right|^2 \quad \text{and} \quad R = \left| \frac{E_r}{E_i} \right|^2,$$

one gets for normal incidence

$$T(\theta_1 = 0) = \sqrt{\frac{\epsilon_2}{\epsilon_1}} \cdot \frac{4(\epsilon_1 \epsilon_0)^2}{\left| (\sqrt{\epsilon_1 \epsilon_2} + \epsilon_1) \epsilon_0 + \frac{\sqrt{\epsilon_1} \sigma_{xx}(\omega)}{c} \right|^2}, \quad (8)$$

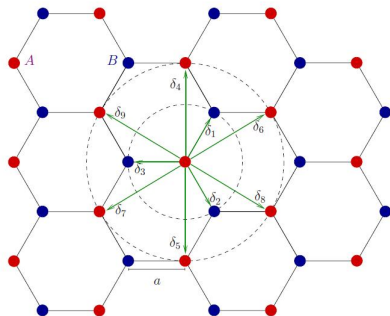
$$R(\theta_1 = 0) = \frac{\left| (\sqrt{\epsilon_1 \epsilon_2} - \epsilon_1) \epsilon_0 + \sqrt{\epsilon_1} \frac{\sigma_{xx}(\omega)}{c} \right|^2}{\left| (\sqrt{\epsilon_1 \epsilon_2} + \epsilon_1) \epsilon_0 + \sqrt{\epsilon_1} \frac{\sigma_{xx}(\omega)}{c} \right|^2}. \quad (9)$$

⇒ Real and imaginary part of the optical conductivity $\sigma_{xx}(\omega)$ have to be determined!

Hamiltonian and current density operator

Hamiltonian in tight-binding form for nearest neighbors in second quantisation:

$$H = -t \sum_{\mathbf{r}, s} \sum_{\delta=\delta_1-\delta_3} [a_s^\dagger(\mathbf{r}) b_s(\mathbf{r} + \delta) + b_s^\dagger(\mathbf{r} + \delta) a_s(\mathbf{r})] \quad (10)$$



- $a_s^\dagger(\mathbf{r})$ and $b_s^\dagger(\mathbf{r} + \delta)$ create an electron in sublattice A and B
- $t \approx 3\text{eV}$ is the next-nearest neighbor hopping parameter
- $\delta_1 = \frac{a}{2} (1, \sqrt{3})$,
 $\delta_2 = \frac{a}{2} (1, -\sqrt{3})$,
 $\delta_3 = -a(1, 0)$
- a is the carbon-carbon distance

Figure: Graphene lattice structure.

Transformation of the Hamiltonian to the momentum space to implicate an electromagnetic field:

$$a_s^\dagger(\mathbf{r}) = \frac{1}{\sqrt{A_s}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} a_{\mathbf{k},s}^\dagger \quad \text{and} \quad b_s^\dagger(\mathbf{r}) = \frac{1}{\sqrt{A_s}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} b_{\mathbf{k},s}^\dagger,$$

where A_s is the sample area, lead to

$$H = -\frac{t}{A_s} \sum_{\mathbf{r},s,\delta} \left[\sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{r}} a_{\mathbf{k},s}^\dagger \sum_{\mathbf{k}'} e^{i\mathbf{k}'\cdot(\mathbf{r}+\delta)} b_{\mathbf{k}',s} + \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot(\mathbf{r}+\delta)} b_{\mathbf{k},s}^\dagger \sum_{\mathbf{k}'} e^{i\mathbf{k}'\cdot\mathbf{r}} a_{\mathbf{k}',s} \right],$$

and one gets the final result

$$H = -t \sum_{\mathbf{k},s,\delta} \left[e^{i\mathbf{k}\cdot\delta} a_{\mathbf{k},s}^\dagger b_{\mathbf{k},s} + e^{-i\mathbf{k}\cdot\delta} b_{\mathbf{k},s}^\dagger a_{\mathbf{k},s} \right]. \quad (11)$$

In presence of an electromagnetic field:

$$\mathbf{p} \rightarrow \mathbf{p} + e\mathbf{A} \quad \text{or} \quad \mathbf{k} \rightarrow \mathbf{k} + \frac{e}{\hbar}\mathbf{A}, \quad (12)$$

where \mathbf{A} is the vector potential, is leading to

$$H = -t \sum_{k,s,\delta} \left[e^{i(\mathbf{k} + \frac{e}{\hbar}\mathbf{A}) \cdot \delta} a_{k,s}^\dagger b_{k,s} + e^{-i(\mathbf{k} + \frac{e}{\hbar}\mathbf{A}) \cdot \delta} b_{k,s}^\dagger a_{k,s} \right], \quad (13)$$

giving the "**Peierls Substitution**"

$$t \rightarrow t \cdot e^{i\frac{e}{\hbar}\mathbf{A} \cdot \delta}. \quad (14)$$

Transformation back to real space leads to

$$H = -t \sum_{\mathbf{r},s,\delta} \left[e^{i\frac{e}{\hbar}\mathbf{A} \cdot \delta} a_s^\dagger(\mathbf{r}) b_s(\mathbf{r} + \delta) + e^{-i\frac{e}{\hbar}\mathbf{A} \cdot \delta} b_s^\dagger(\mathbf{r} + \delta) a_s(\mathbf{r}) \right]. \quad (15)$$

The current density operator j_x can be observed with the Hamilton mechanics:

$$j_x = -\frac{\partial H}{\partial A_x} \quad (16)$$

Expanding the exponential function in the Hamiltonian up to second order reading

$$e^{i\frac{e}{\hbar} A_x \delta_x} \simeq 1 + i\frac{e}{\hbar} A_x \delta_x, \quad (17)$$

is giving

$$j_x = j_x^P + A_x \cdot j_x^D, \quad (18)$$

with

$$j_x^P = \frac{ite}{\hbar} \sum_{\mathbf{r}, s, \delta} [\delta_x \cdot a_s^\dagger(\mathbf{r}) b_s(\mathbf{r} + \delta) - \delta_x \cdot b_s^\dagger(\mathbf{r} + \delta) a_s(\mathbf{r})], \quad (19)$$

and

$$j_x^D = -\frac{te^2}{\hbar^2} \sum_{\mathbf{r}, s, \delta} [\delta_x^2 \cdot a_s^\dagger(\mathbf{r}) b_s(\mathbf{r} + \delta) - \delta_x^2 \cdot b_s^\dagger(\mathbf{r} + \delta) a_s(\mathbf{r})]. \quad (20)$$

Optical conductivity

The optical conductivity $\sigma_{xx}(\omega)$ can be obtained from the **Kubo formula** (electromagnetic field as a linear perturbation to the system):

$$\sigma_{xx}(\omega) = \frac{\langle j_x^D \rangle}{iA_s \cdot (\omega + i\varepsilon)} + \frac{\Lambda_{xx}(\omega + i\varepsilon)}{i\hbar A_s \cdot (\omega + i\varepsilon)}, \quad (21)$$

where $\varepsilon \rightarrow 0^+$ the sample area can be written as $A_s = N_c A_c$, with

$$A_c = 3\sqrt{3}a^2/2 : \text{Area of the unit cell,}$$

N_c : number of unit cells.

The function $\Lambda_{xx}(\omega + i\varepsilon)$ is given in the Heisenberg picture by

$$\Lambda_{xx}(i\omega_n) = \int_0^{\hbar\beta} d\tau e^{i\omega_n\tau} \langle j_x^P(\tau) j_x^P(0) \rangle, \quad (22)$$

with

$$j_x^P(\tau) = e^{iH\tau} \cdot j_x^P \cdot e^{-iH\tau}. \quad (23)$$

With the identity

$$\lim_{\varepsilon \rightarrow 0} \int_{-\infty}^{\infty} \frac{f(\omega)}{\omega + i\varepsilon} d\omega = \lim_{\varepsilon \rightarrow 0} \int_{-\infty}^{-\varepsilon} \frac{f(\omega)}{\omega + i\varepsilon} d\omega + \lim_{\varepsilon \rightarrow 0} \int_{\varepsilon}^{\infty} \frac{f(\omega)}{\omega + i\varepsilon} d\omega - i\pi \int_{-\varepsilon}^{\varepsilon} \delta(\omega) f(\omega) d\omega, \quad (24)$$

the real part of the conductivity $\Re\sigma_{xx}(\omega)$ is given by

$$\Re\sigma_{xx}(\omega) = - \left(\frac{\langle j_x^D \rangle}{A_s \cdot \omega} + \pi \frac{\Re\Lambda_{xx}(\omega + i\varepsilon)}{\hbar \cdot A_s} \right) \cdot \delta(\omega) + \frac{\Im\Lambda_{xx}(\omega + i\varepsilon)}{\hbar \cdot \omega \cdot A_s}, \quad (25)$$

where $\delta(\omega)$ is the Dirac delta function, which can be set to zero, since we are interested in frequencies $\omega > 0$.

With the equations (18) and (20) and the graphene energy bands

$$E(\mathbf{k}) = \pm t \cdot |\phi(\mathbf{k})| = \pm t \cdot \left| 1 + e^{\mathbf{k} \cdot (\delta_1 - \delta_3)} + e^{\mathbf{k} \cdot (\delta_2 - \delta_3)} \right|, \quad (26)$$

the real part of the conductivity can be calculated to

$$\begin{aligned} \Re \sigma_{xx}(\omega) &= \frac{t^2 e^2 a^2}{8 \hbar^3 \omega N_c A_c} \sum_{\mathbf{k}} f[\phi(\mathbf{k})] [F(-t|\phi(\mathbf{k})| - \mu) - F(t|\phi(\mathbf{k})| - \mu)] \\ &\times \left[\pi \delta \left(\omega - \frac{2t|\phi(\mathbf{k})|}{\hbar} \right) - \pi \delta \left(\omega + \frac{2t|\phi(\mathbf{k})|}{\hbar} \right) \right], \end{aligned} \quad (27)$$

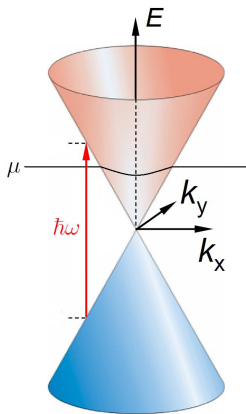
where $f[\phi(\mathbf{k})]$ can be written in the Dirac-cone approximation as

$$f[\phi(\mathbf{k})] \simeq 18 - 4 \cdot |\phi(\mathbf{k})|^2, \quad (28)$$

with the Fermi distribution $F(x)$ and the chemical potential μ .

The density of states per spin and per unit cell $\rho(E)$:

$$\rho(E) = \frac{1}{N_c} \sum_{\mathbf{k}} \delta(E - t \cdot |\phi(\mathbf{k})|) \quad (29)$$



By interaction with a photon of the energy $\hbar\omega$:

- Electrons can be excited from valence to conduction band, but
- Conservation of momentum requires

$$E = \frac{\hbar\omega}{2} \quad (30)$$

- Presence of a chemical potential leads in the case of $T = 0\text{K}$ to a threshold

$$\hbar\omega > 2\mu \quad (31)$$

With equation (25), the density of states is given by

$$\rho\left(\frac{\hbar\omega}{2}\right) = \frac{1}{N_c} \sum_{\mathbf{k}} \delta\left(\frac{\hbar\omega}{2} - t \cdot |\phi(\mathbf{k})|\right) = \frac{1}{N_c} \sum_{\mathbf{k}} \frac{\hbar}{2} \cdot \delta\left(\omega - \frac{2t \cdot |\phi(\mathbf{k})|}{\hbar}\right). \quad (32)$$

With equation (21), (23) and (27) the real part of the conductivity can be calculated to

$$\begin{aligned} \Re\sigma_{xx}(\omega) &= \sigma_0 \cdot \frac{\pi t^2 a^2}{8A_c \hbar \omega} \cdot \rho\left(\frac{\hbar\omega}{2}\right) \left[18 - \frac{(\hbar\omega)^2}{t^2}\right] \\ &\quad \times \left[\tanh\frac{\hbar\omega + 2\mu}{4k_B T} + \tanh\frac{\hbar\omega - 2\mu}{4k_B T}\right], \end{aligned} \quad (33)$$

where $\sigma_0 = (e^2/4\hbar)$ and k_B is the Boltzmann constant. Additionally one can see that

$$\lim_{T \rightarrow 0} \Re\sigma_{xx}(\hbar\omega < 2\mu) = 0. \quad (34)$$

$$\Re\sigma_{xx}(\omega) = \sigma_0 \frac{\pi t^2 a^2}{8A_c \hbar \omega} \rho\left(\frac{\hbar\omega}{2}\right) \left[18 - \frac{(\hbar\omega)^2}{t^2}\right] \left[\tanh\frac{\hbar\omega + 2\mu}{4k_B T} + \tanh\frac{\hbar\omega - 2\mu}{4k_B T}\right]$$

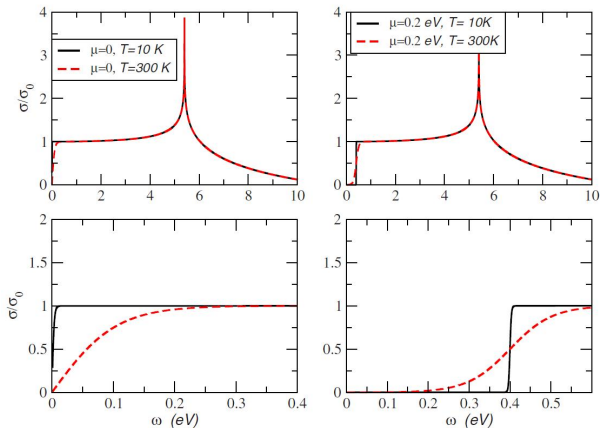


Figure: Real part of the optical conductivity for different chemical potentials and temperatures.

Performing an asymptotic expansion of the density of states around $E = 0$, one gets the useful result:

$$\Re\sigma_{xx}(\omega) = \sigma_0 \left[\frac{1}{2} + \frac{(\hbar\omega)^2}{72t^2} \right] \left(\tanh \frac{\hbar\omega + 2\mu}{4k_B T} + \tanh \frac{\hbar\omega - 2\mu}{4k_B T} \right) \quad (35)$$

The imaginary part of the optical conductivity $\Im\sigma_{xx}(\omega)$ can be calculated in a similar way giving

$$\begin{aligned} \Im\sigma_{xx}(\omega) &= \sigma_0 \cdot \frac{4}{\pi\hbar\omega} \left(\mu - \frac{2\mu^3}{9t^2} \right) - \frac{\sigma_0}{\pi} \log \frac{|\hbar\omega + 2\mu|}{|\hbar\omega - 2\mu|} \\ &\quad - \frac{\sigma_0}{26\pi} \left(\frac{\hbar\omega}{t} \right)^2 \log \frac{|\hbar\omega + 2\mu|}{|\hbar\omega - 2\mu|}, \end{aligned} \quad (36)$$

where one can see that

$$\Im\sigma_{xx}(\mu = 0) = 0. \quad (37)$$

and

$$\Im\sigma_{xx}(\omega) \rightarrow \infty \quad \text{for} \quad \hbar\omega \rightarrow 2\mu. \quad (38)$$

Optical absorption

$$T(\theta_1 = 0) = \sqrt{\frac{\epsilon_2}{\epsilon_1}} \cdot \frac{4(\epsilon_1 \epsilon_0)^2}{\left| (\sqrt{\epsilon_1 \epsilon_2} + \epsilon_1) \epsilon_0 + \frac{\sqrt{\epsilon_1} \sigma_{xx}(\omega)}{c} \right|^2}, \quad (39)$$

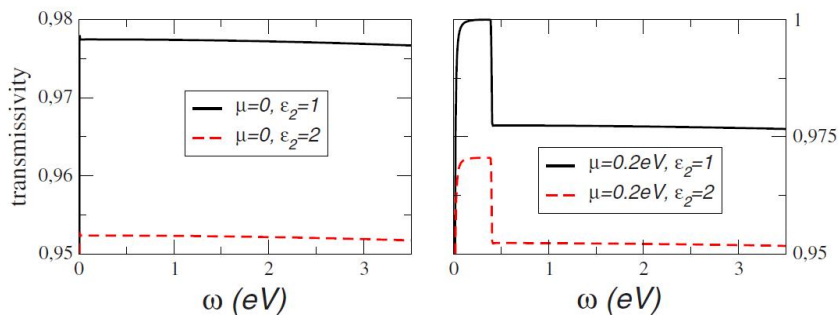


Figure: Transmissivity for normal incidence and $T = 10$ K, for the first medium vacuum ($\epsilon_1 = 1$) and the second is either vacuum ($\epsilon_2 = 1$) or a SiO₂ substrate ($\epsilon_2 = 2$).

$$R(\theta_1 = 0) = \frac{\left| (\sqrt{\epsilon_1 \epsilon_2} - \epsilon_1) \epsilon_0 + \sqrt{\epsilon_1} \frac{\sigma_{xx}(\omega)}{c} \right|^2}{\left| (\sqrt{\epsilon_1 \epsilon_2} + \epsilon_1) \epsilon_0 + \sqrt{\epsilon_1} \frac{\sigma_{xx}(\omega)}{c} \right|^2}. \quad (40)$$

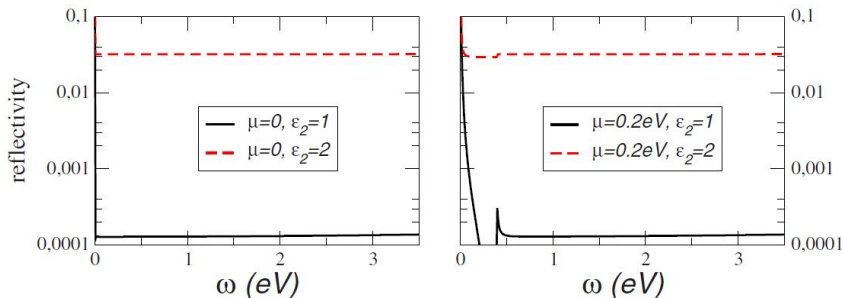


Figure: Reflectivity for normal incidence and $T = 10\text{K}$, for the first medium vacuum ($\epsilon_1 = 1$) and the second is either vacuum ($\epsilon_2 = 1$) or a SiO_2 substrate ($\epsilon_2 = 2$).

\Rightarrow Transmissivity and reflectivity remain nearly constant up to the end of the visible part of the spectrum (3.1eV)!

In the case of the media being vacuum ($\epsilon_1 = \epsilon_2 = 1$) and no chemical potential [$\sigma(\omega) \simeq \sigma_0$] one obtains

$$T = \frac{1}{\left(1 + \frac{\pi\alpha}{2}\right)^2} \simeq 1 - \pi\alpha \approx 0.977, \quad (41)$$

and

$$R = \frac{\pi^2\alpha^2}{4} T \approx 0.00013, \quad (42)$$

with the fine structure-constant

$$\alpha = \frac{e^2}{4\pi\epsilon_0 c \hbar}. \quad (43)$$

Due to a non vanishing optical conductivity there is an absorbed intensity A with

$$A = 1 - T - R = \frac{\pi\alpha}{\left(1 + \frac{\pi\alpha}{2}\right)^2} \approx 0.022. \quad (44)$$

For a bilayer graphene the transmissivity is in the limit $\hbar\omega \gg t_{\perp}$, with t_{\perp} being the hopping parameter between the layers, given by

$$T \simeq 1 - 2\pi\alpha. \quad (45)$$

It is again only dependent on the fine-structure constant α and reduced by twice the value of a single layer.

⇒ The stepwise reduction of the transmitted intensity due to reflection and absorption of a single layer or bilayer graphene is only dependent on universal constants

⇒ The optical absorption due to a "universal current" is caused by interband transitions of massless electrons

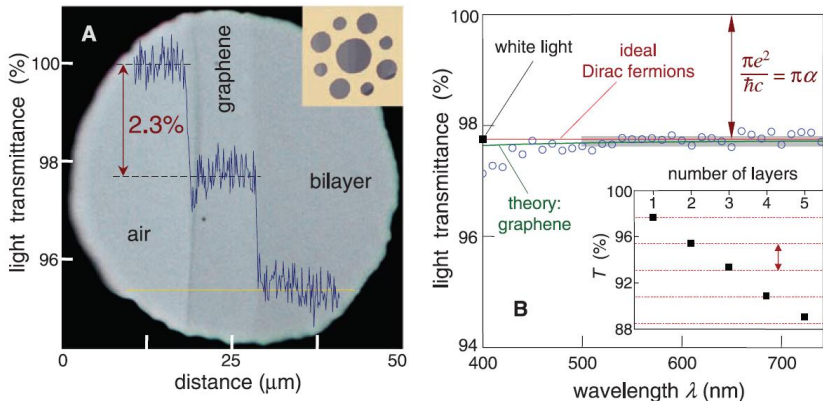


Fig. 1. Looking through one-atom-thick crystals. **(A)** Photograph of a 50- μm aperture partially covered by graphene and its bilayer. The line scan profile shows the intensity of transmitted white light along the yellow line. (Inset) Our sample design: A 20- μm -thick metal support structure has several apertures of 20, 30, and 50 μm in diameter with graphene crystallites placed over them. **(B)** Transmittance spectrum of single-layer graphene (open circles). Slightly lower transmittance for $\lambda < 500$ nm is probably due to hydrocarbon contamination (5). The red line is the transmittance $T = (1 + 0.5\pi\alpha)^{-2}$ expected for two-dimensional Dirac fermions, whereas the green curve takes into account a nonlinearity and triangular warping of graphene's electronic spectrum. The gray area indicates the standard error for our measurements (5). (Inset) Transmittance of white light as a function of the number of graphene layers (squares). The dashed lines correspond to an intensity reduction by $\pi\alpha$ with each added layer.

Figure: Nair et al., Science, Vol. 320, p.1308 (2008).

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