Optical Properties of Solids: Lecture 5

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MINISTRY OF EDUCATION, YOUTH AND SPORTS

http://ellipsometry.nmsu.edu

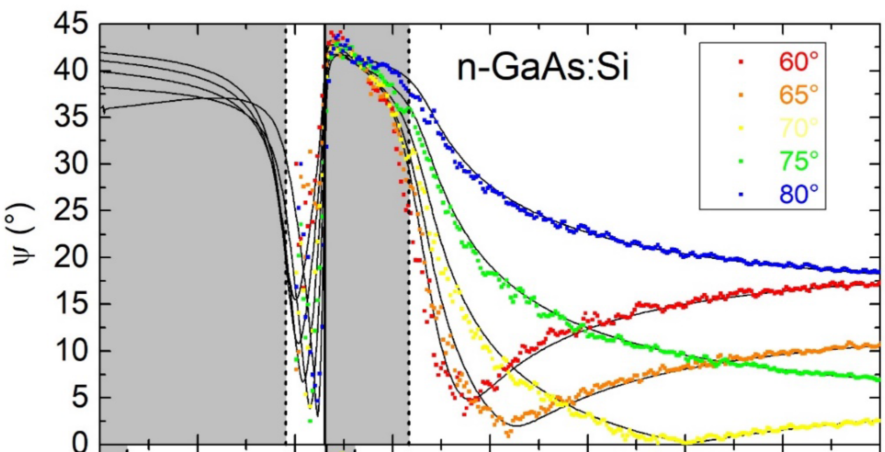
NSF: DMR-1505172

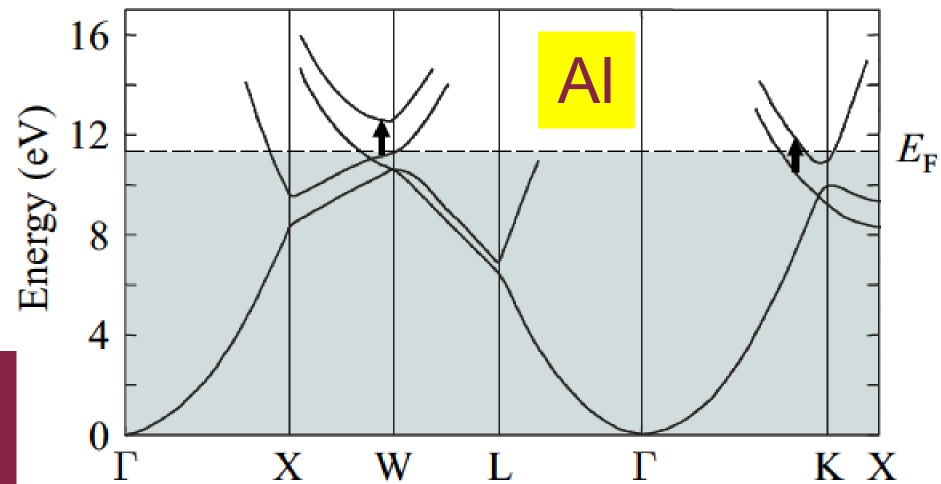
Optical Properties of Solids: Lecture 5+6

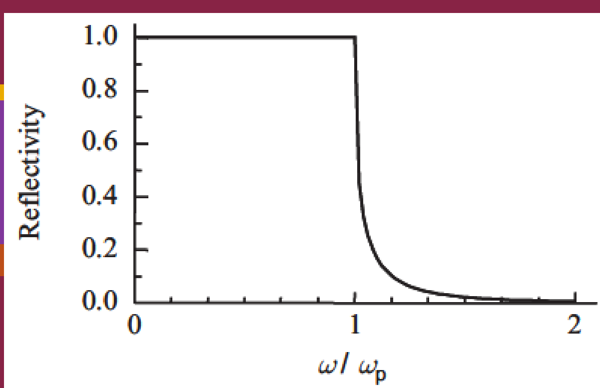
Lorentz and **Drude** model: Applications

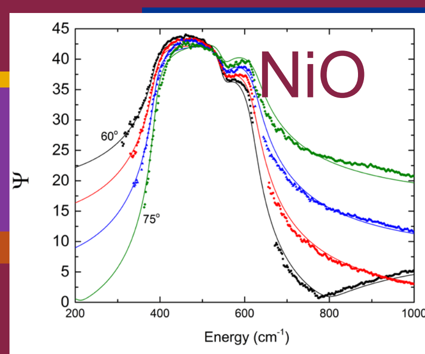
1. Metals, doped semiconductors
2. Insulators

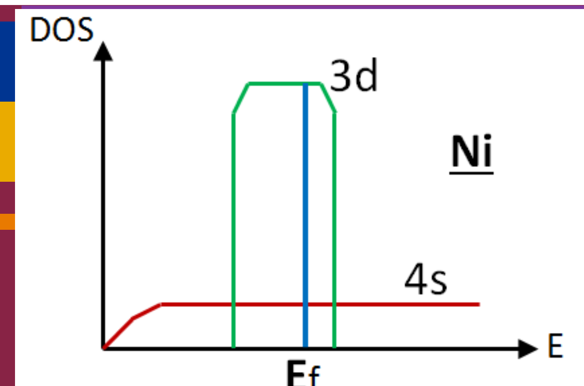
Sellmeier equation, Poles, Cauchy dispersion











References: Dispersion, Analytical Properties

Standard Texts on Electricity and Magnetism:

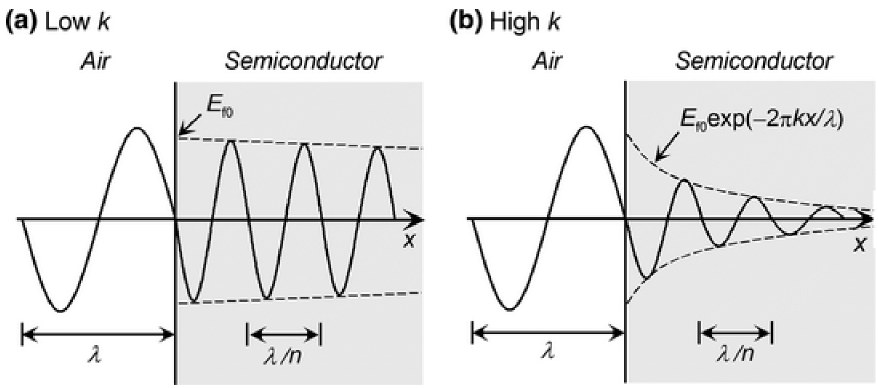
- J.D. Jackson: *Classical Electrodynamics*
- **L.D. Landau & J.M. Lifshitz, Vol. 8: *Electrodynamics of Cont. Media***

Ellipsometry and Polarized Light:

- R.M.A. Azzam and N.M. Bashara: *Ellipsometry and Polarized Light*
- **H.G. Tompkins and E.A. Irene: *Handbook of Ellipsometry* (chapters by Rob Collins and Jay Jellison)**
- **H. Fujiwara, *Spectroscopic Ellipsometry***
- **Mark Fox, *Optical Properties of Solids***
- H. Fujiwara and R.W. Collins: *Spectroscopic Ellipsometry for PV* (Vol 1+2)
- Zollner: *Propagation of EM Waves in Continuous Media* (Lecture Notes)
- Zollner: *Drude and Kukharskii mobility of doped semiconductors extracted from FTIR ellipsometry spectra*, J. Vac. Sci. **37**, 012904 (2019).

Question: Inhomogeneous Plane Waves

Plane waves do not solve Maxwell's equations, if Im(ε)≠0.



The amplitude of the plane wave decays in the medium due to absorption.

Snell: $\dfrac{\sin\theta_1}{\sin\theta_2} = \dfrac{n_1}{n_2}$

Inhomogeneous plane wave (aka generalized plane waves):

$$\vec{E}(\vec{r},t) = \vec{E}_0 \exp\left[i\left(\vec{k}\cdot\vec{r} - \omega t\right)\right]$$

Allow complex wave vector: $\vec{k} = \vec{k}_1 + i\vec{k}_2 = k_1\vec{u} + ik_2\vec{v}$

$$\vec{E}(\vec{r},t) = \vec{E}_0 \exp\left[-\vec{k}_2\cdot\vec{r}\right] \exp\left[i\left(\vec{k}_1\cdot\vec{r} - \omega t\right)\right]$$

Attenuation

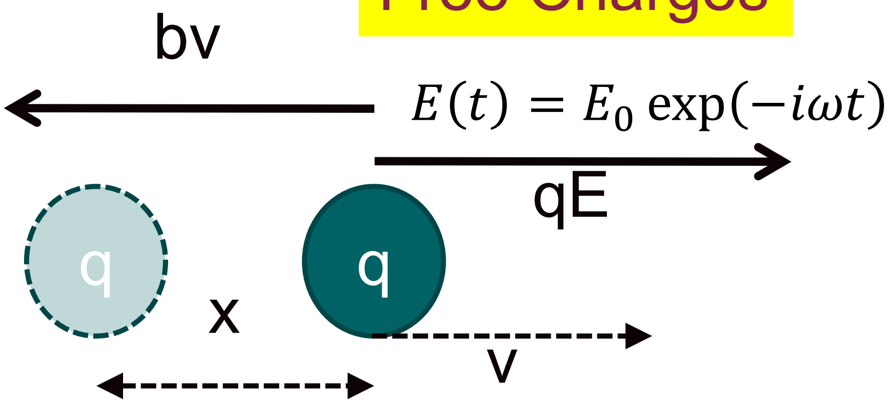
Propagation

Mansuripur, *Magneto-Optical Recording*, 1995
Stratton, *Electromagnetic Theory*, 1941/2007

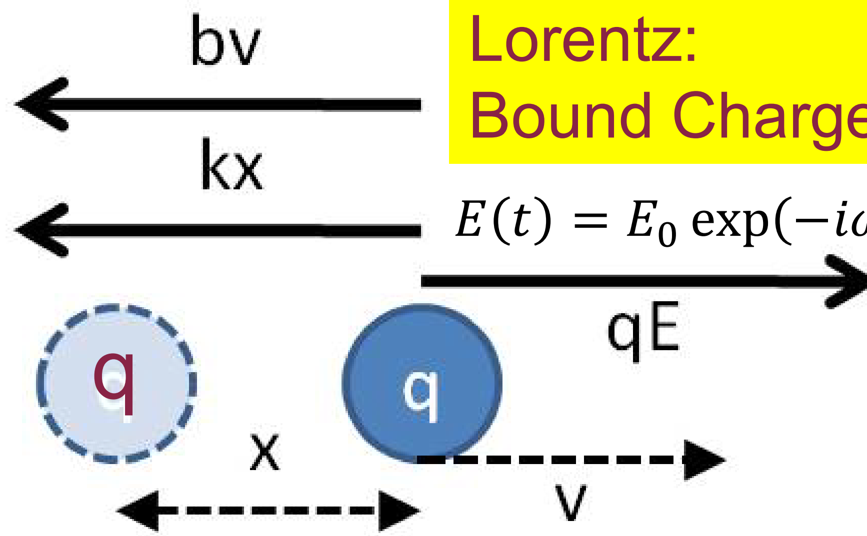
Landau-Lifshitz § 63, Jackson, Clemmow
Dupertuis, Proctor, Acklin, JOSA **11**, 1159 (1994).

Drude and Lorentz Models: Free and Bound Charges

Drude:
Free Charges



Lorentz:
Bound Charges



$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}$$

$$\omega_P^2 = \frac{n_f e^2}{m\varepsilon_0}$$ plasma frequency

$$\omega_0^2 = 0$$ resonance frequency

$$\varepsilon(\omega) = 1 + \frac{\omega_P^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\omega_P^2 = \frac{n_b q^2}{m\varepsilon_0}$$ plasma frequency

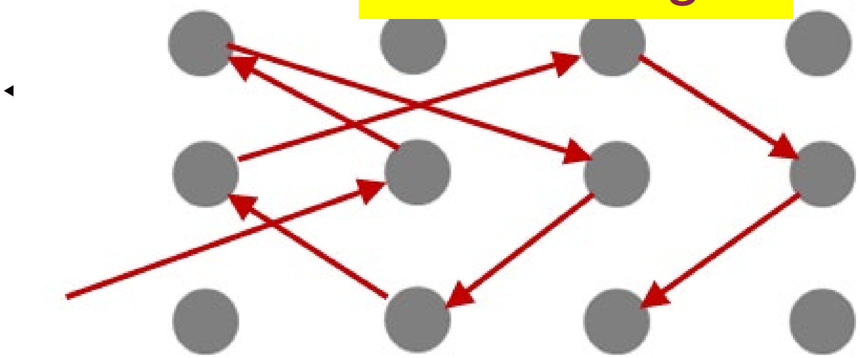
$$\omega_0^2 = \frac{k}{m}$$ resonance frequency

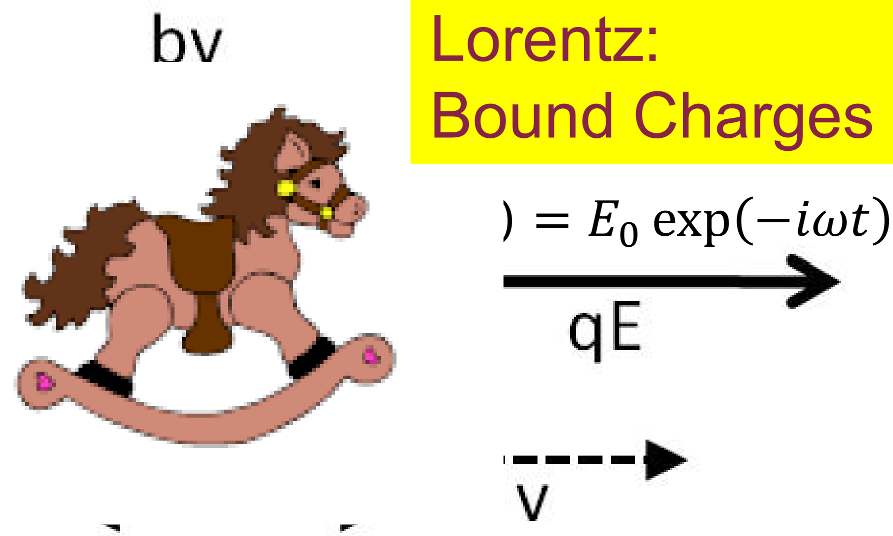
P. Drude, Phys. Z. **1**, 161 (1900).

H. Helmholtz, Ann. Phys **230**, 582 (1875)

Drude-Lorentz Model: Free and Bound Charges

Drude:
Free Charges





Lorentz:
Bound Charges

$$\varepsilon(\omega) = 1 - \sum_i \frac{\omega_{P,i}^2}{\omega^2 + i\gamma_{D,i}\omega} + \sum_i \frac{A_i \omega_{0,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_{0,i}\omega}$$

ω_P (unscreened) **plasma frequency** of free charges

ω_0 **resonance frequency** of bound charges

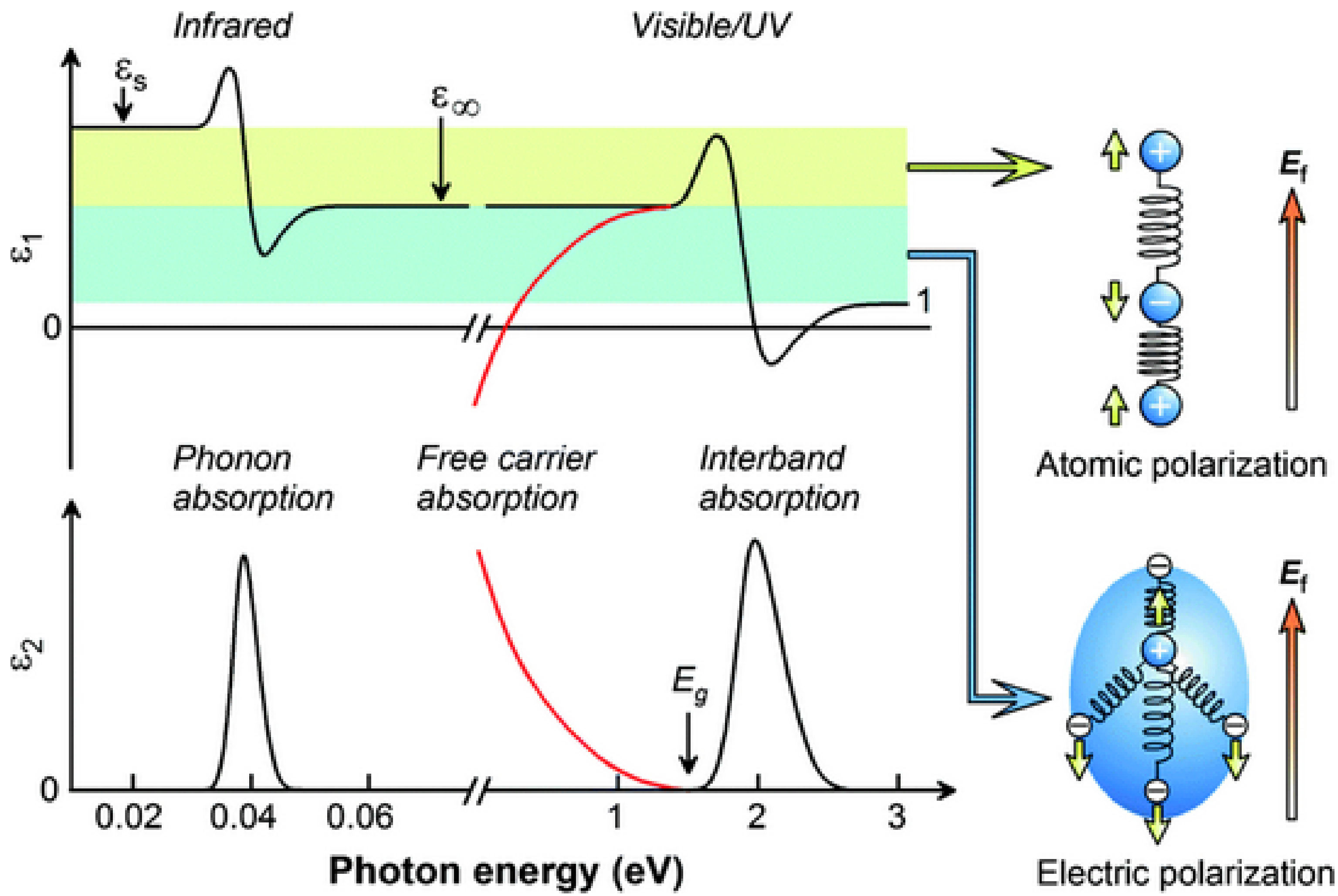
γ_D, γ_0 **broadenings** of free and bound charges

A **amplitude** of bound charge oscillations (density, strength)

$$\omega_P^2 = \frac{n_f e^2}{m\varepsilon_0}$$

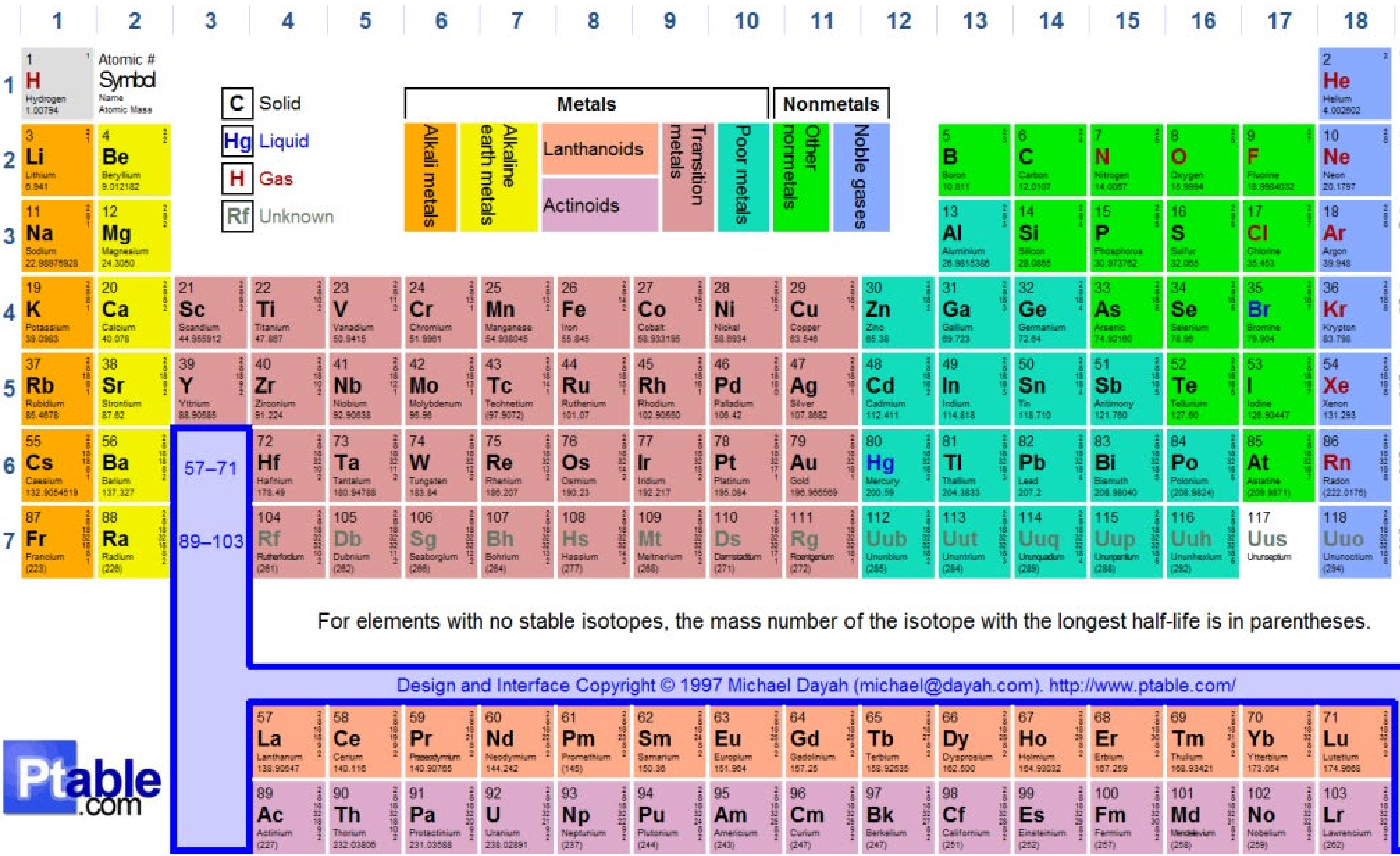
Discuss plasma frequency trends.

Drude-Lorentz Model: Free and Bound Charges



$$\varepsilon(\omega) = 1 - \sum_i \frac{\omega_{P,i}^2}{\omega^2 + i\gamma_{D,i}\omega} + \sum_i \frac{A_i \omega_{0,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_{0,i}\omega}$$

Metals



1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
Atomic #
Symbol
Name
Atomic Mass
C Solid
Hg Liquid
H Gas
Rf Unknown
Metals
Nonmetals
Alkali metals
Alkaline earth metals
Lanthanoids
Actinoids
Transition metals
Poor metals
Other nonmetals
Noble gases
1 H Hydrogen 1.00794
2 He Helium 4.002602
3 Li Lithium 6.941
4 Be Beryllium 9.012182
5 B Boron 10.811
6 C Carbon 12.0107
7 N Nitrogen 14.0067
8 O Oxygen 15.9994
9 F Fluorine 18.9984032
10 Ne Neon 20.1797
11 Na Sodium 22.98976928
12 Mg Magnesium 24.3050
13 Al Aluminium 26.9815386
14 Si Silicon 28.0855
15 P Phosphorus 30.973762
16 S Sulfur 32.065
17 Cl Chlorine 35.453
18 Ar Argon 39.948
19 K Potassium 39.0983
20 Ca Calcium 40.078
21 Sc Scandium 44.955912
22 Ti Titanium 47.867
23 V Vanadium 50.9415
24 Cr Chromium 51.9961
25 Mn Manganese 54.938045
26 Fe Iron 55.845
27 Co Cobalt 58.933195
28 Ni Nickel 58.6934
29 Cu Copper 63.546
30 Zn Zinc 65.38
31 Ga Gallium 69.723
32 Ge Germanium 72.64
33 As Arsenic 74.92160
34 Se Selenium 78.96
35 Br Bromine 79.904
36 Kr Krypton 83.798
37 Rb Rubidium 85.4678
38 Sr Strontium 87.62
39 Y Yttrium 88.90585
40 Zr Zirconium 91.224
41 Nb Niobium 92.90638
42 Mo Molybdenum 95.96
43 Tc Technetium (97.9072)
44 Ru Ruthenium 101.07
45 Rh Rhodium 102.90550
46 Pd Palladium 106.42
47 Ag Silver 107.8682
48 Cd Cadmium 112.411
49 In Indium 114.818
50 Sn Tin 118.710
51 Sb Antimony 121.760
52 Te Tellurium 127.60
53 I Iodine 126.90447
54 Xe Xenon 131.293
55 Cs Caesium 132.9054519
56 Ba Barium 137.327
57–71
72 Hf Hafnium 178.49
73 Ta Tantalum 180.94788
74 W Tungsten 183.84
75 Re Rhenium 186.207
76 Os Osmium 190.23
77 Ir Iridium 192.217
78 Pt Platinum 195.084
79 Au Gold 196.966569
80 Hg Mercury 200.59
81 Tl Thallium 204.3833
82 Pb Lead 207.2
83 Bi Bismuth 208.98040
84 Po Polonium (208.9824)
85 At Astatine (209.9871)
86 Rn Radon (222.0176)
87 Fr Francium (223)
88 Ra Radium (226)
89–103
104 Rf Rutherfordium (261)
105 Db Dubnium (262)
106 Sg Seaborgium (266)
107 Bh Bohrium (264)
108 Hs Hassium (277)
109 Mt Meitnerium (268)
110 Ds Darmstadtium (271)
111 Rg Roentgenium (272)
112 Uub Ununbium (285)
113 Uut Ununtrium (284)
114 Uuq Ununquadium (289)
115 Uup Ununpentium (288)
116 Uuh Ununhexium (292)
117 Uus Ununseptium
118 Uuo Ununoctium (294)
For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.
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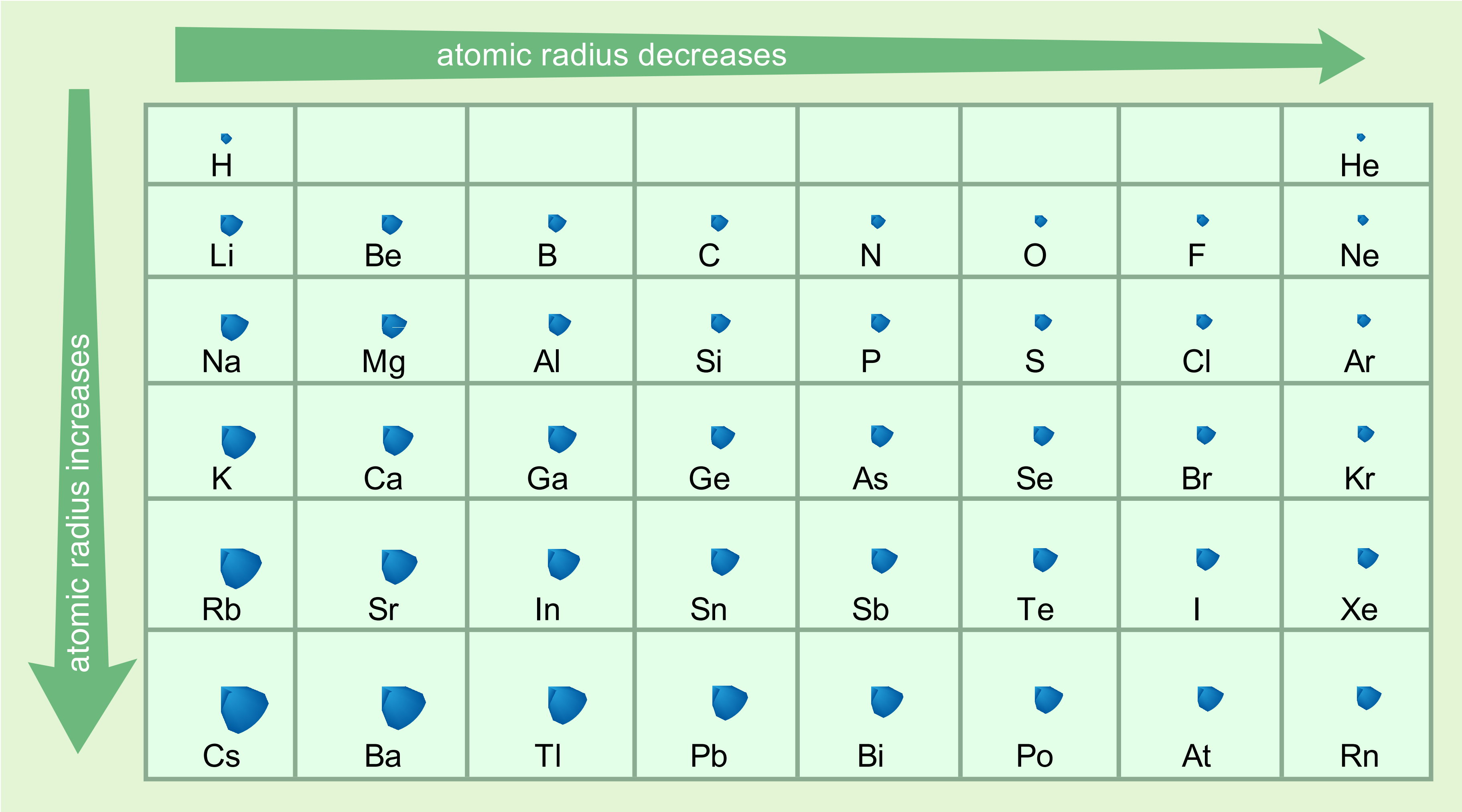
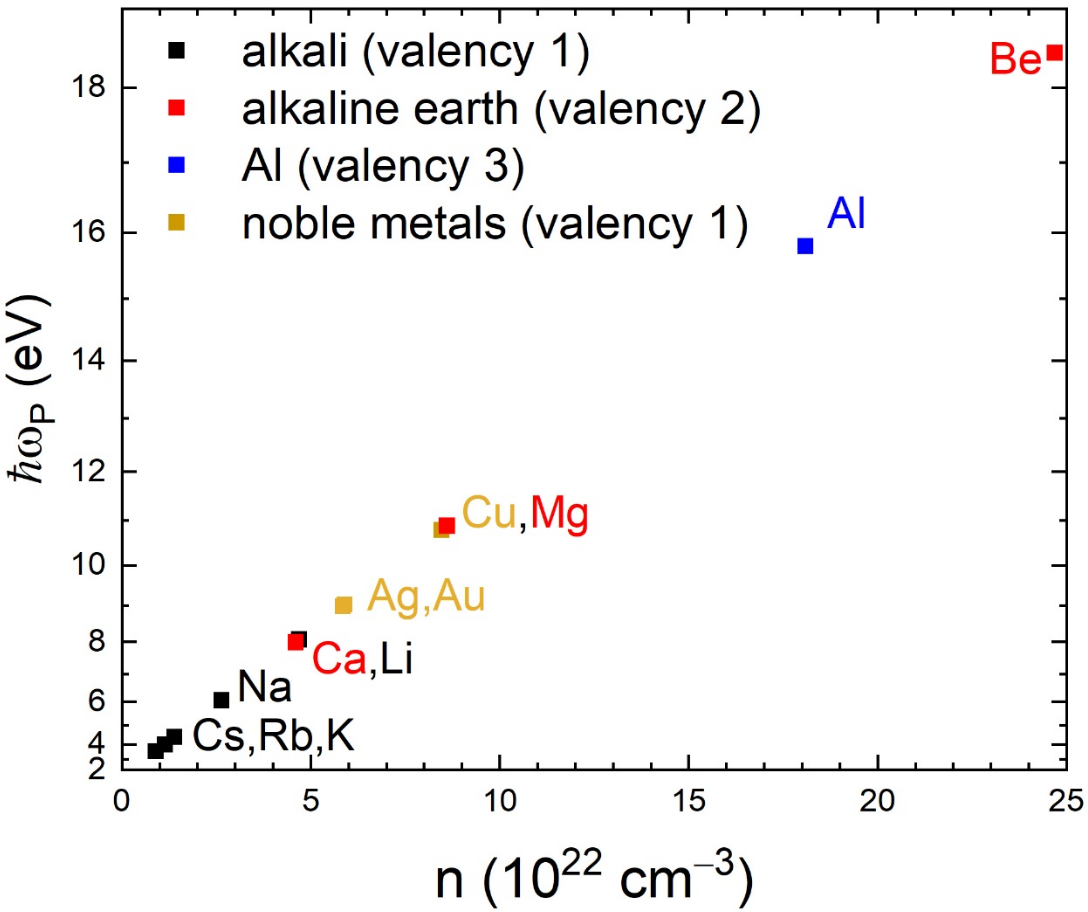
57 La Lanthanum 138.90547
58 Ce Cerium 140.116
59 Pr Praseodymium 140.90765
60 Nd Neodymium 144.242
61 Pm Promethium (145)
62 Sm Samarium 150.36
63 Eu Europium 151.964
64 Gd Gadolinium 157.25
65 Tb Terbium 158.92535
66 Dy Dysprosium 162.500
67 Ho Holmium 164.93032
68 Er Erbium 167.259
69 Tm Thulium 168.93421
70 Yb Ytterbium 173.054
71 Lu Lutetium 174.9668
89 Ac Actinium (227)
90 Th Thorium 232.03806
91 Pa Protactinium 231.03588
92 U Uranium 238.02891
93 Np Neptunium (237)
94 Pu Plutonium (244)
95 Am Americium (243)
96 Cm Curium (247)
97 Bk Berkelium (247)
98 Cf Californium (251)
99 Es Einsteinium (252)
100 Fm Fermium (257)
101 Md Mendelevium (258)
102 No Nobelium (259)
103 Lr Lawrencium (262)
Ptable.com

Atomic Radius



Atomic radius decreases from K to Ca to Cu.

(Unscreened) Plasma Frequency



$$\omega_P^2 = \frac{n_f e^2}{m\varepsilon_0}$$

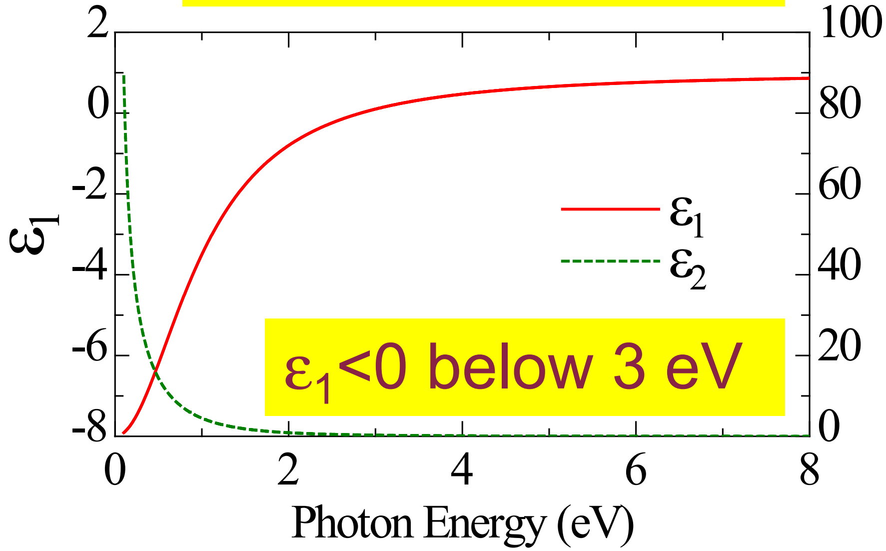
Metal	Valency	N (10^{28} m^{-3})	$\omega_p/2\pi$ (10^{15} Hz)	λ_p (nm)
Li (77 K)	1	4.70	1.95	154
Na (5 K)	1	2.65	1.46	205
K (5 K)	1	1.40	1.06	282
Rb (5 K)	1	1.15	0.96	312
Cs (5 K)	1	0.91	0.86	350
Cu	1	8.47	2.61	115
Ag	1	5.86	2.17	138
Au	1	5.90	2.18	138
Be	2	24.7	4.46	67
Mg	2	8.61	2.63	114
Ca	2	4.61	1.93	156
Al	3	18.1	3.82	79

Fox, Table 7.1

Valency determined by row in period table.
Atomic radius decreases from K to Ca to Cu.

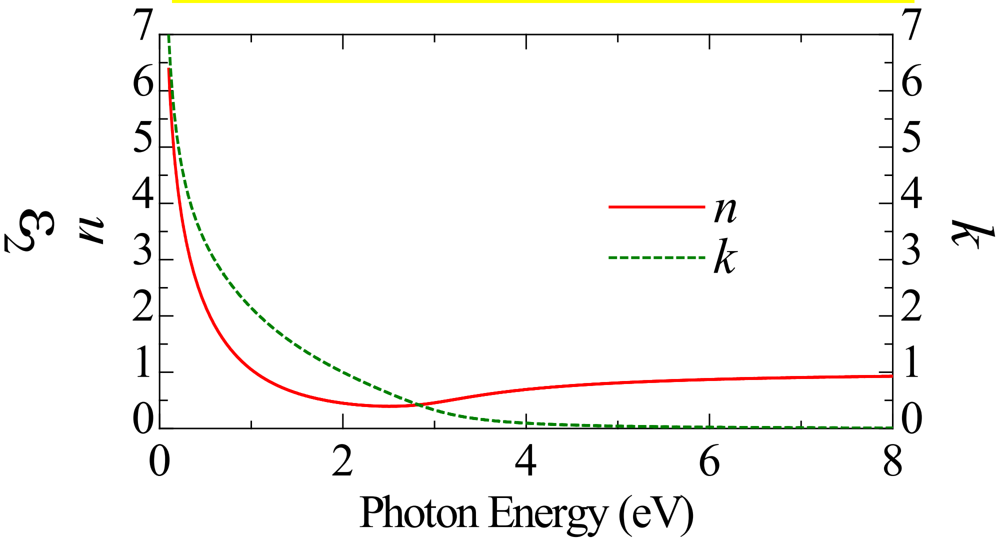
Free-Carrier Reflection/Absorption in Metals

Dielectric function ε



$\varepsilon_1<0$ below 3 eV

Refractive index $n+ik=\sqrt{\varepsilon}$

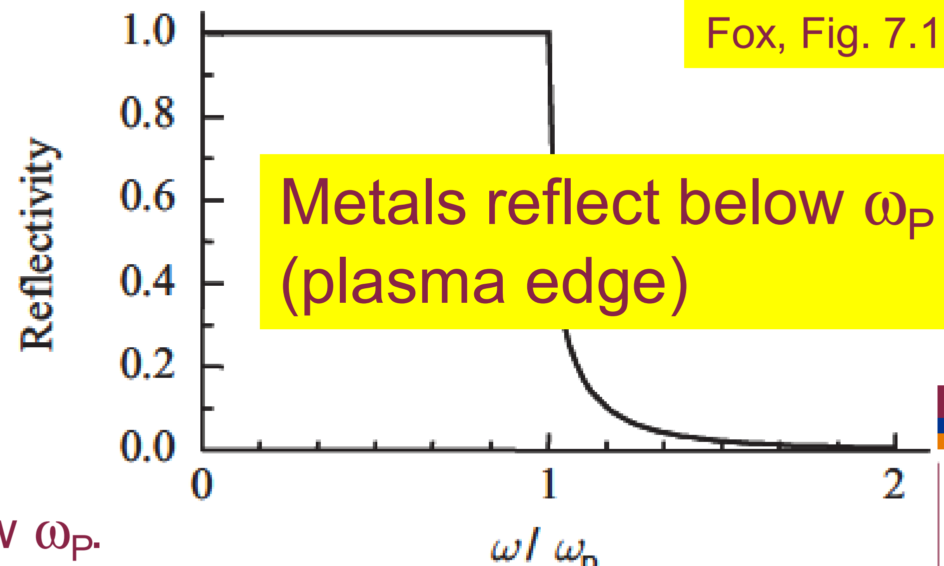


$$\varepsilon(\omega)=1-\frac{\omega_P^2}{\omega^2+i\gamma\omega}$$

ω_p=3 eV, γ=1 eV

$$R_{90}(\omega)=\left|\frac{n+ik-1}{n+ik+1}\right|^2$$

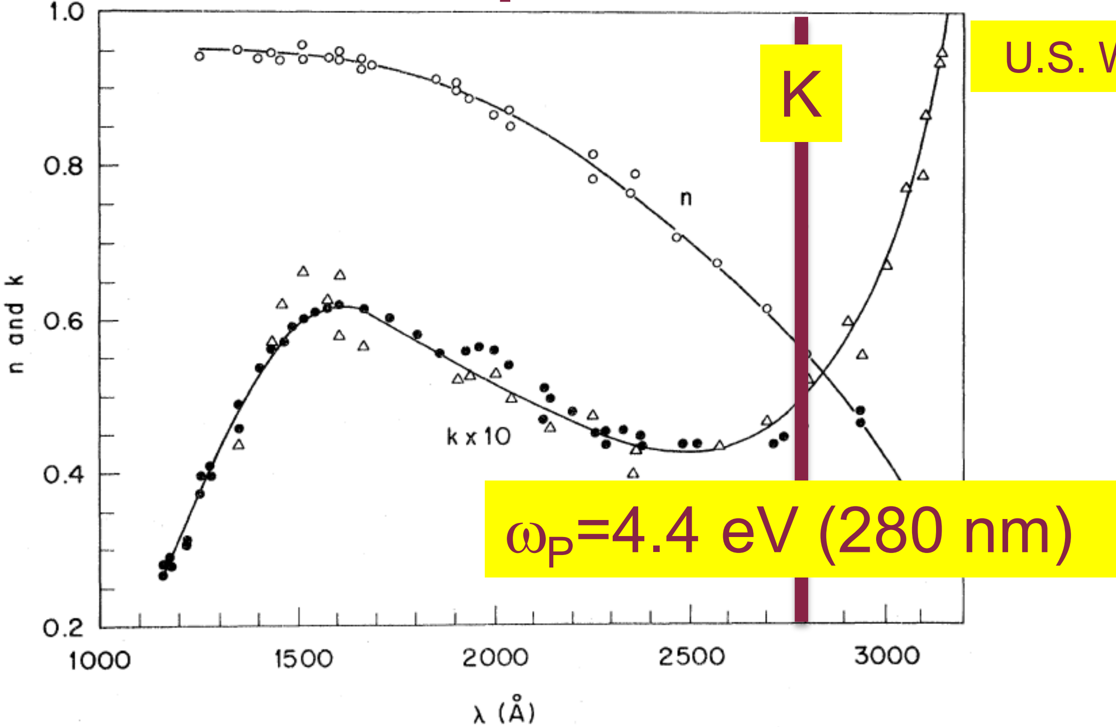
Fox, Fig. 7.1



Metals reflect below ω_P (plasma edge)

R=1 if n is purely imaginary (γ=0) below ω_P.

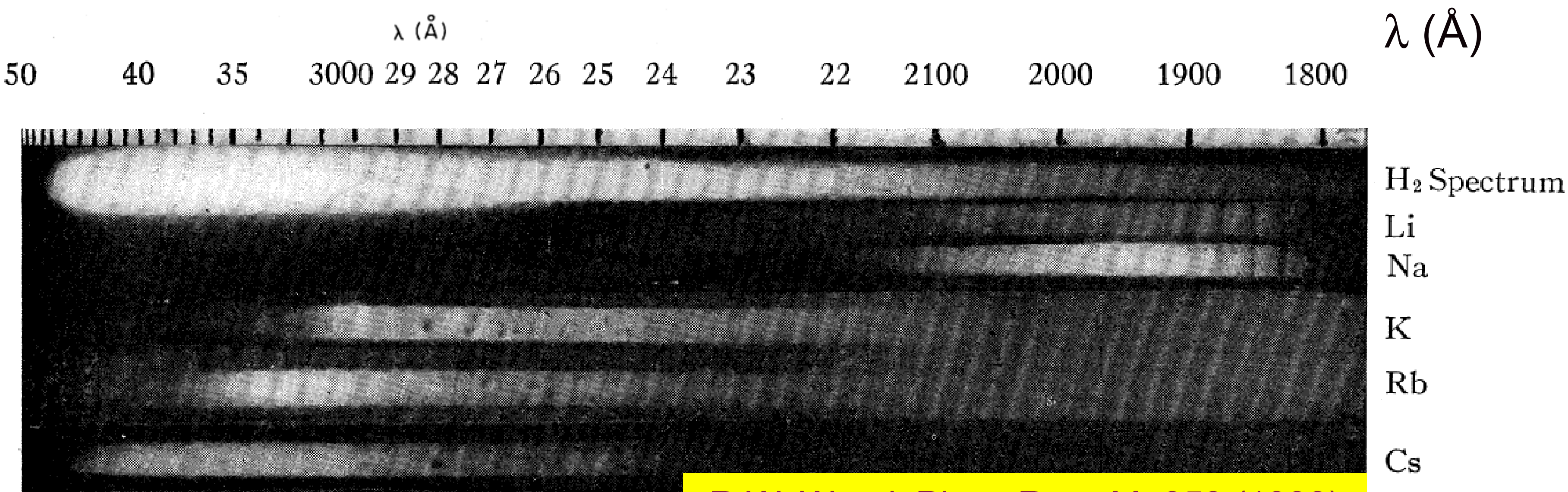
Transparent Alkali Metals above ω_P



U.S. Whang *et al.*, PRB **6**, 2109 (1972)

Metal	λ_{UV} (nm)
Li	205
Na	210
K	315
Rb	360
Cs	440

Fox, Table 7.2



R.W. Wood, Phys. Rev. **44**, 353 (1933)

Bands of Total Reflection

Occur below plasma frequency and between TO/LO energies.
Increased sensitivity to weak absorption processes.

Drude model:

$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}$$

Small damping (γ ` ω_P):

$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega^2}$$ (real, negative)

Small frequency ($\omega<\omega_P$):

$$\varepsilon(\omega) < 0$$

Refractive index ($\omega<\omega_P$):

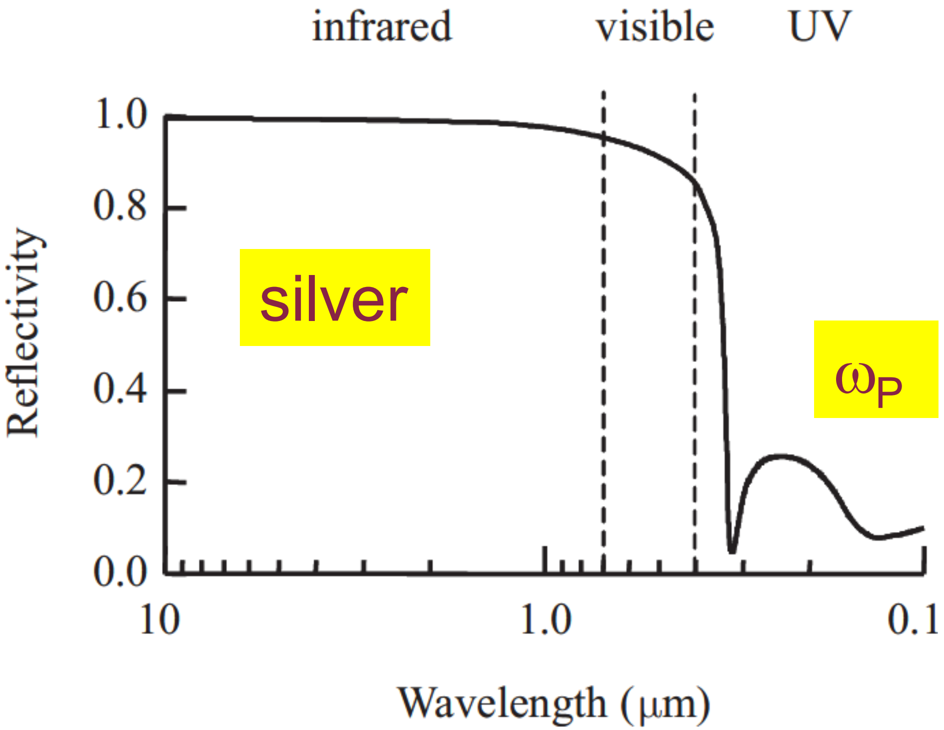
$$\tilde{n}(\omega) = \sqrt{\varepsilon(\omega)} = ik$$

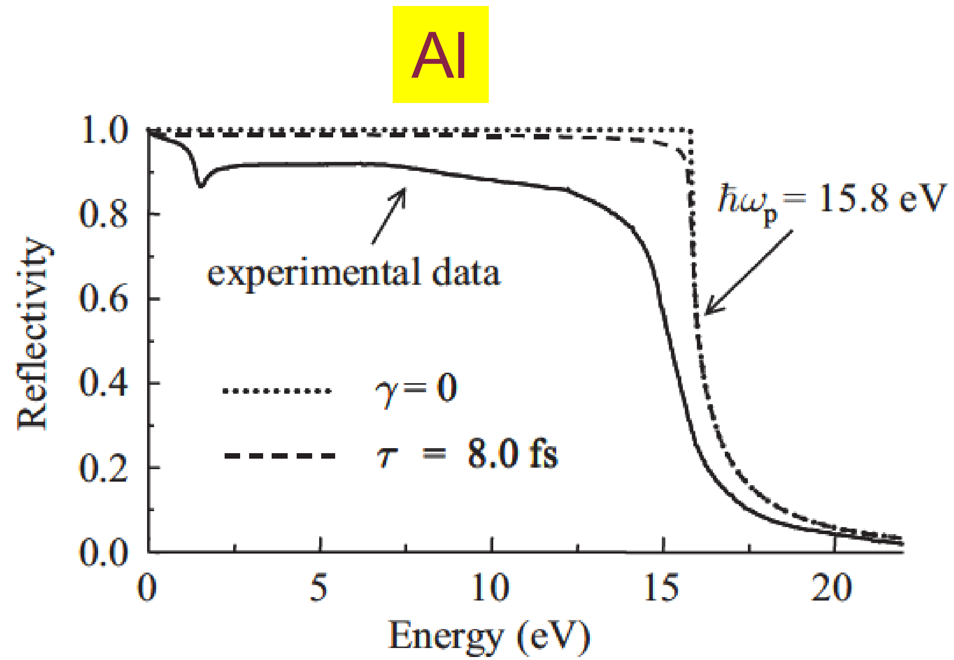
(purely imaginary)

Reflectance at 90Ø ($\omega<\omega_P$):

$$R_{90}(\omega) = \left|\frac{n + ik - 1}{n + ik + 1}\right|^2 = \left|\frac{ik - 1}{ik + 1}\right|^2 = \frac{(ik-1)(-ik-1)}{(ik+1)(-ik+1)} = 1$$

Free-Carrier Reflection in Ag and Al



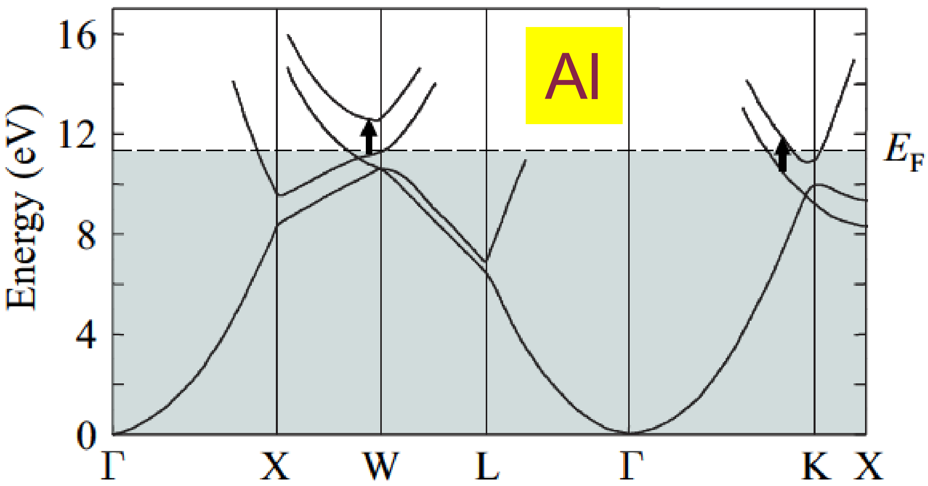


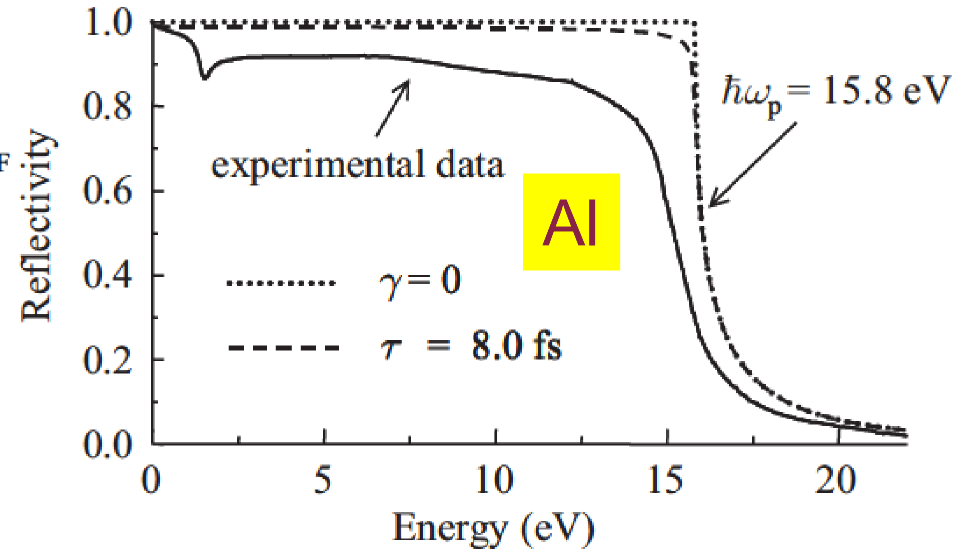
Ag is a noble metal.
Filled 4d-shell, $5s^1$
High reflectance
below ω_P=9 eV (138 nm)
Sharp drop above ω_P. Damping.

Al has three electrons ($3s^2$, $3p^1$)
High reflectance
below ω_P=16 eV (78 nm)
Sharp drop above ω_P.
Damping, interband absorption.

Fox, *Optical Properties of Solids*

Free-Carrier Reflection in Al





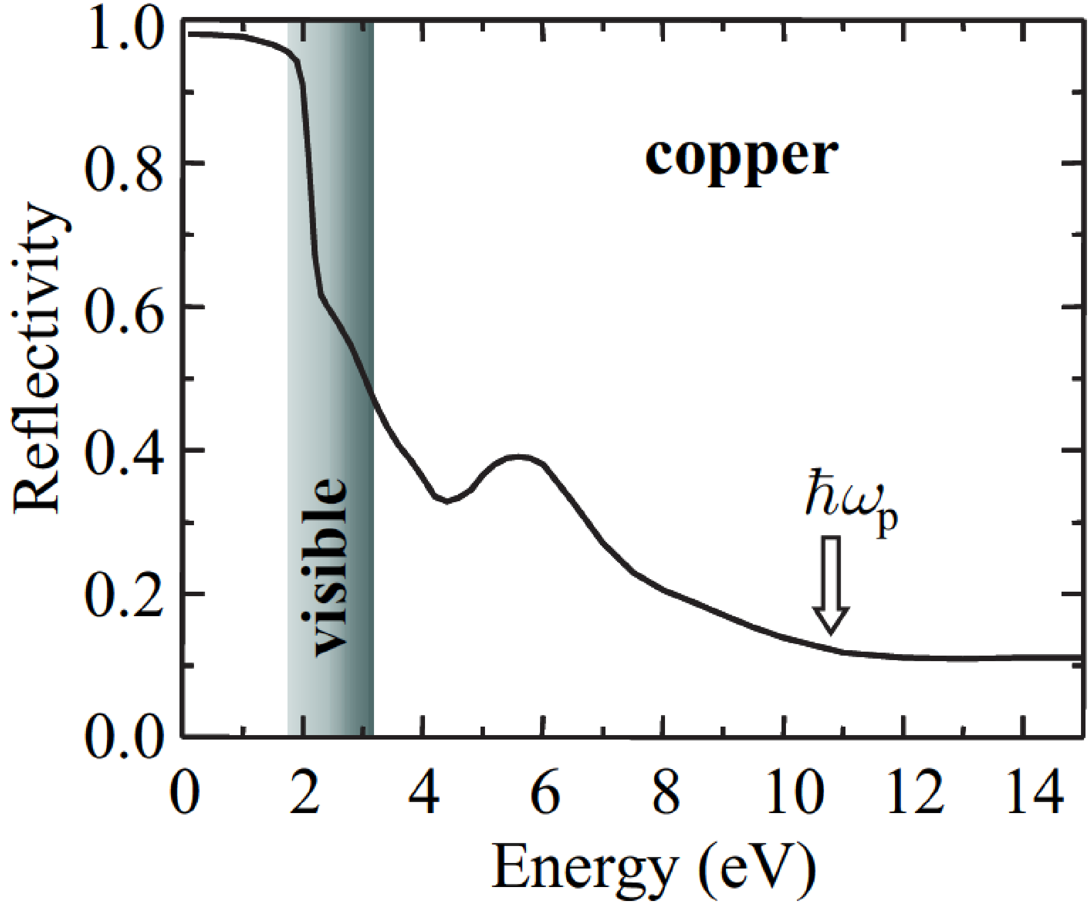
Interband transitions at W cause absorption band at 1.5 eV, lowers reflectivity.

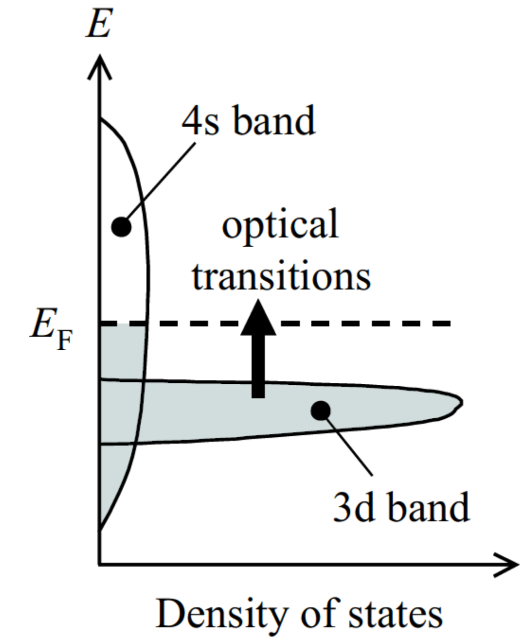
Al has three electrons ($3s^2$, $3p^1$)
High reflectance
below ω_P=16 eV (78 nm)
Sharp drop above ω_P.
Damping, interband absorption.

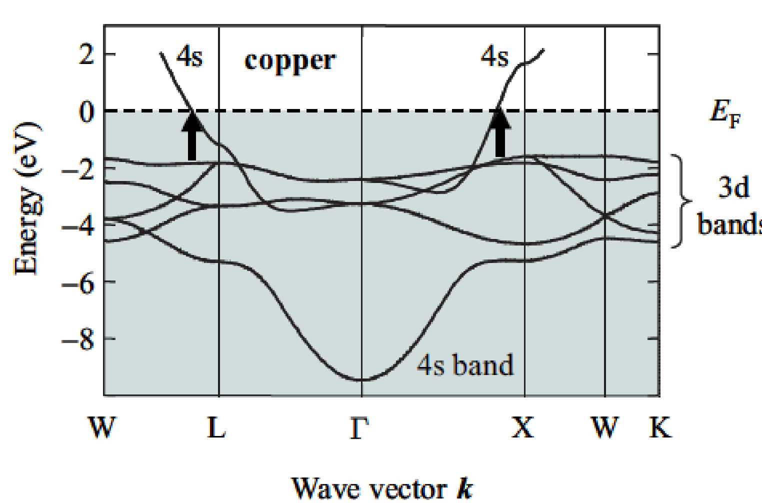
See also: G. Jungk, Thin Solid Films **234**, 428 (1993).

Fox, *Optical Properties of Solids*

Free-Carrier Reflection in Cu



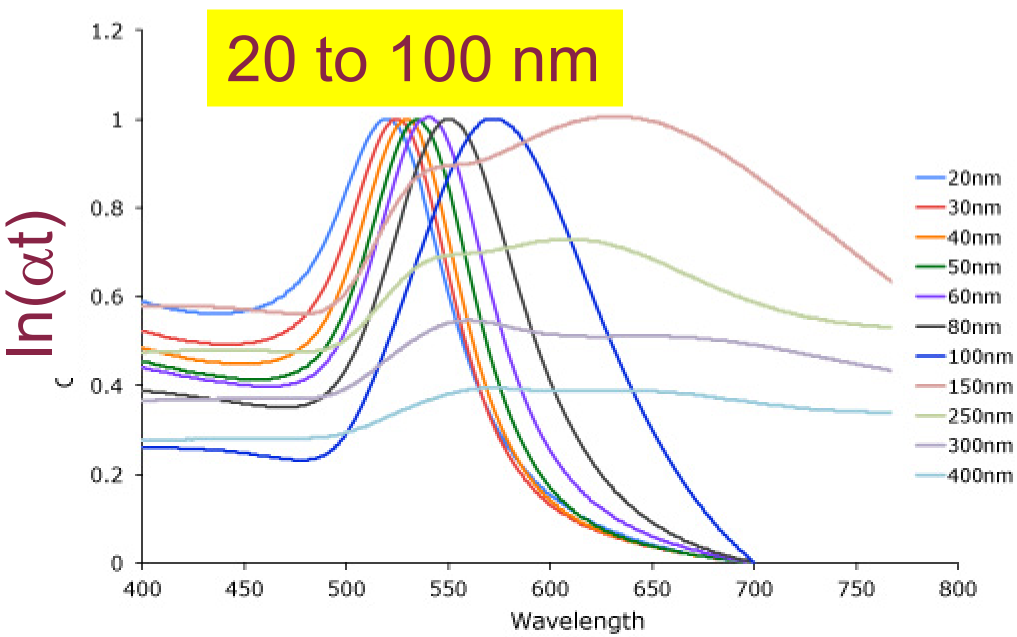


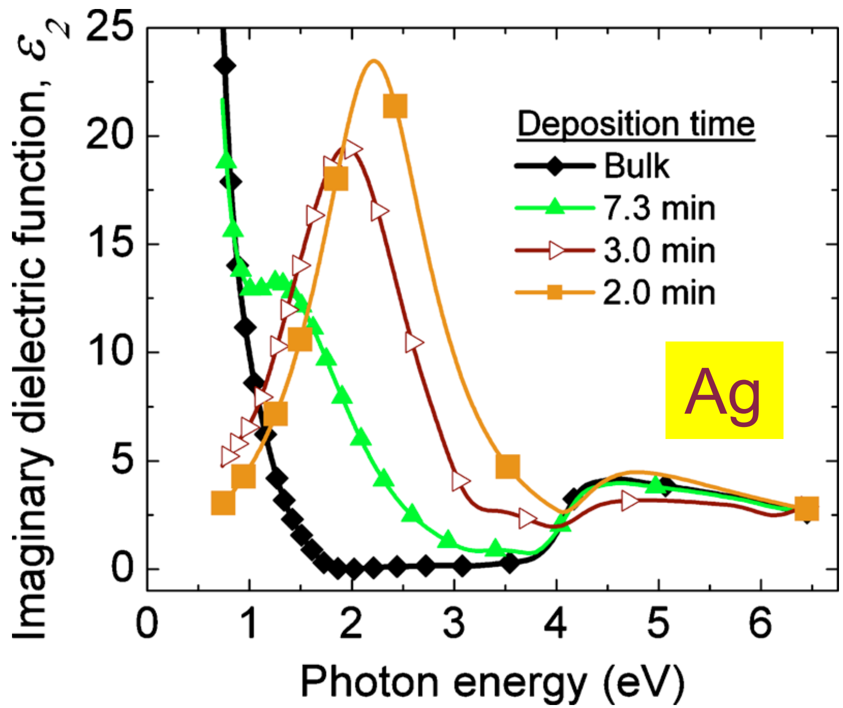


Noble metal, $4s^1$, ω_P=10.8 eV
Transitions from 3d to 4s at 2 eV (near L and X). Similar for Ag, Au.

Fox, *Optical Properties of Solids*

Plasmon resonance in gold nanoparticles





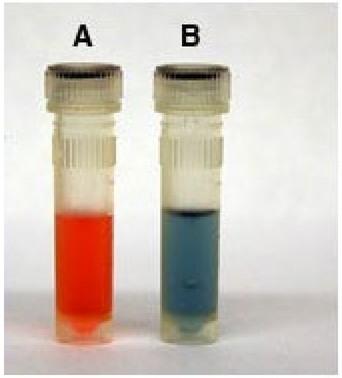
Gold is not always yellow.

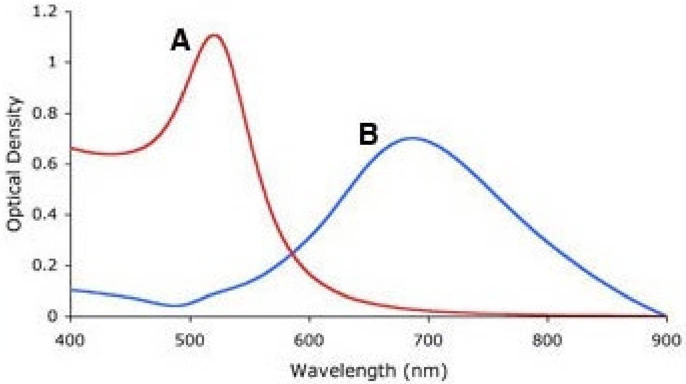
Nanoparticle radius a<λ

$$\alpha = 4\pi a^3 \frac{\varepsilon_m - \varepsilon_d}{\varepsilon_m + \epsilon_d}$$

m: metal, d: dielectric

Enhance molecular absorption.

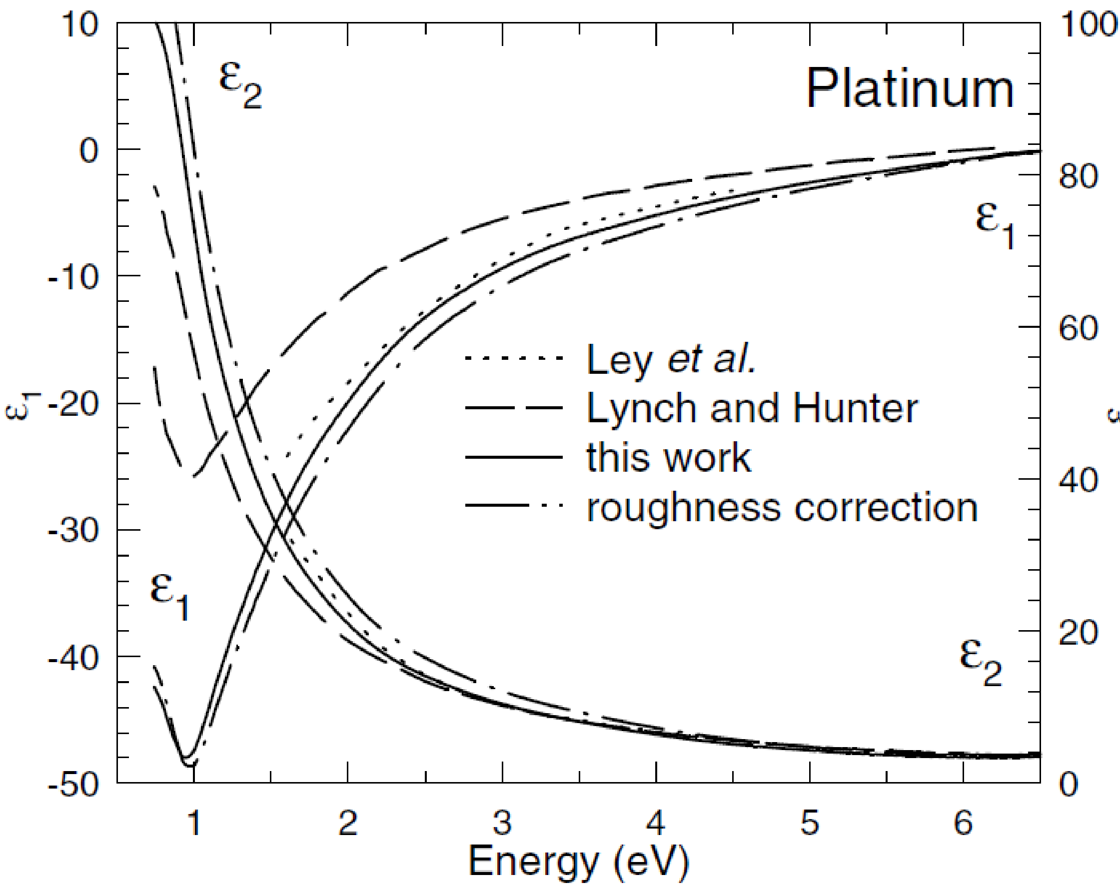




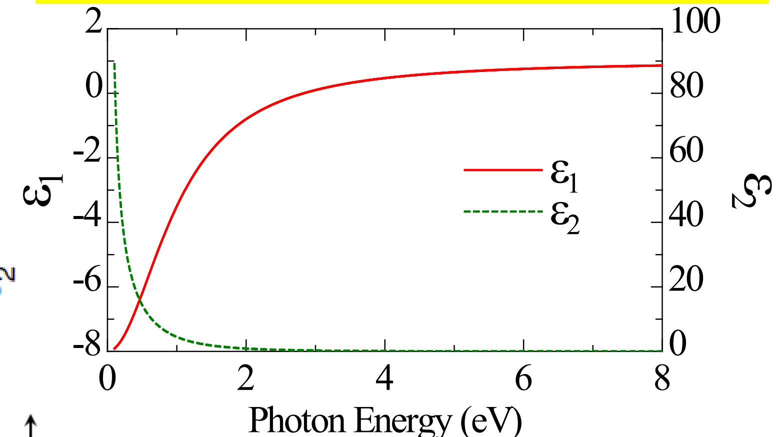
Fox, *Optical Properties of Solids*

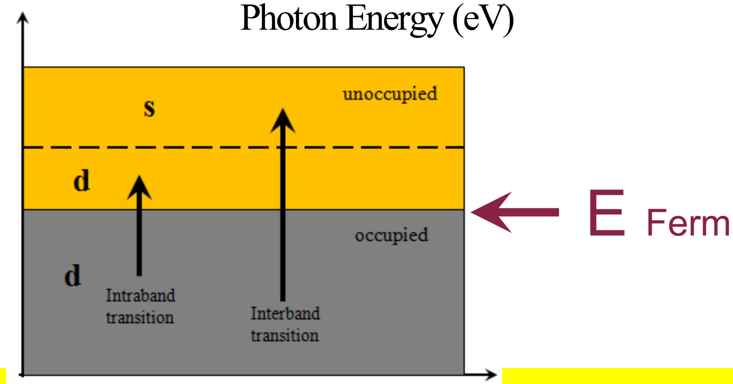
Little, *APL* **98**, 101910 (2011)

Dielectric function of transition metals (Pt)



Drude-like ε above 1 eV



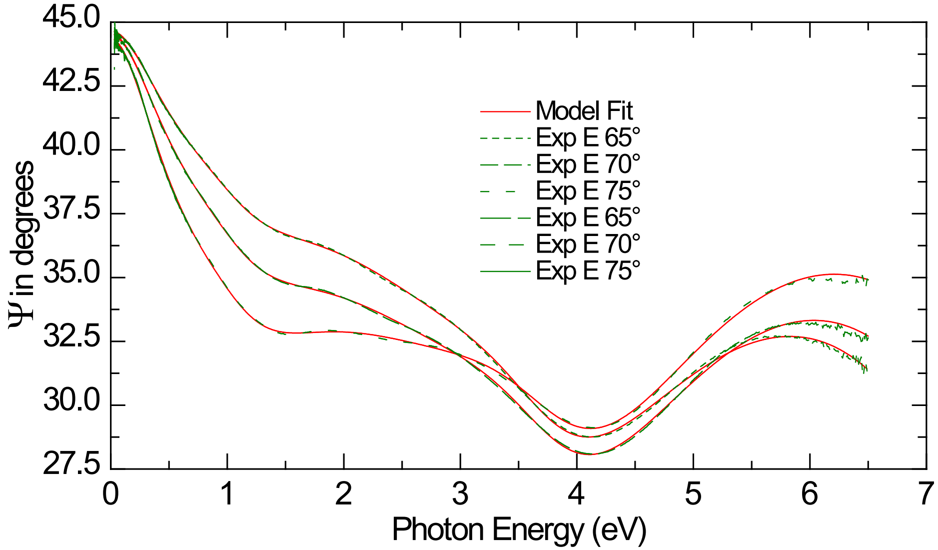


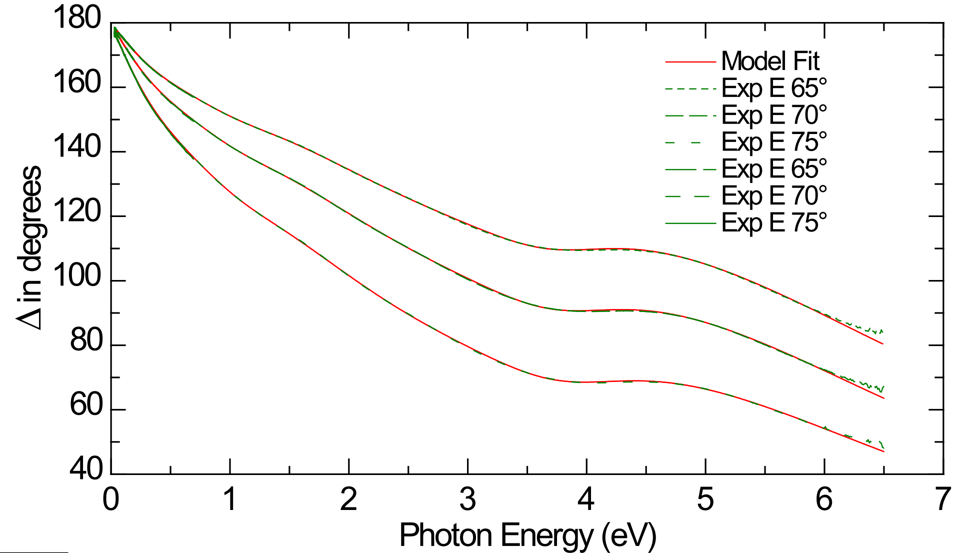
The dielectric function of Pt deviates from the Drude model below 1 eV due to d-interband transitions.
Pt is **not a noble metal**, partially filled d-shell.

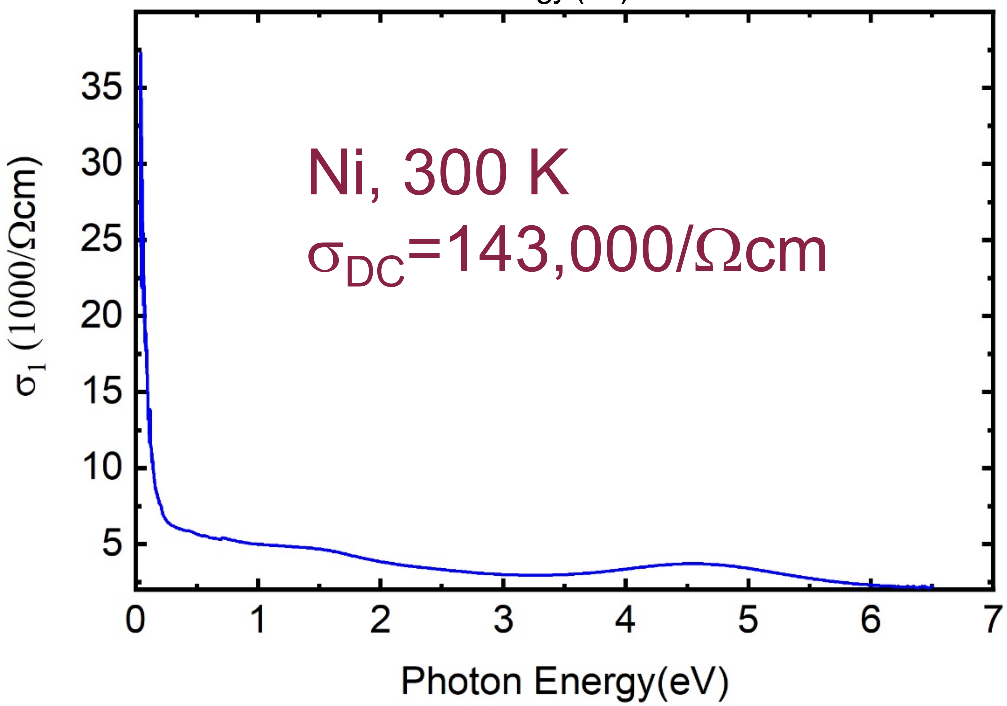
S. Zollner, phys. stat. solidi (a) **177**, R7 (2000)

NM STATE

Dielectric function of transition metals (Ni)





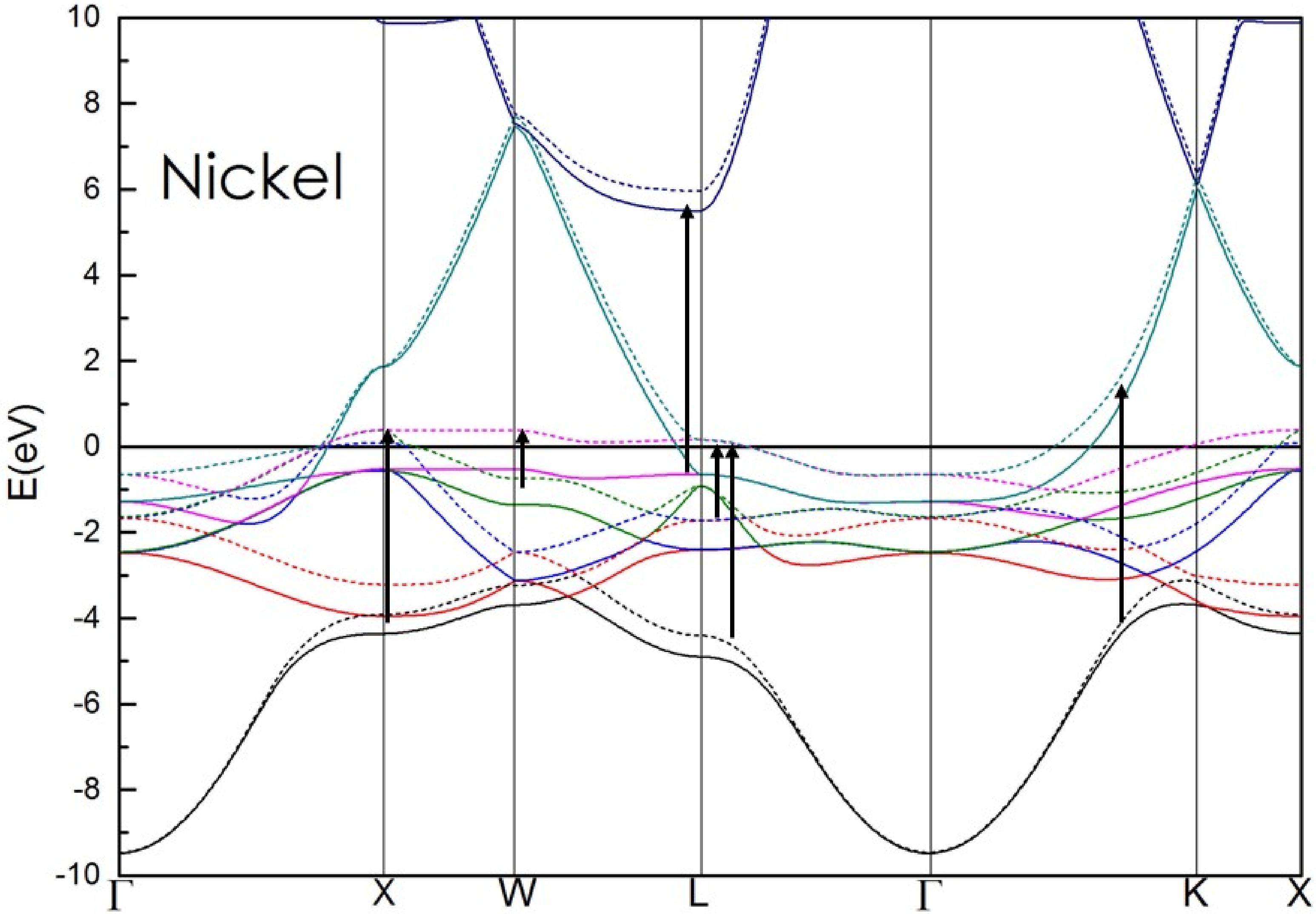


Low frequency:
$\psi \to 0$, $\Delta \to 180°$

Even at 30 meV, the optical σ is still much smaller than σ_{DC}.

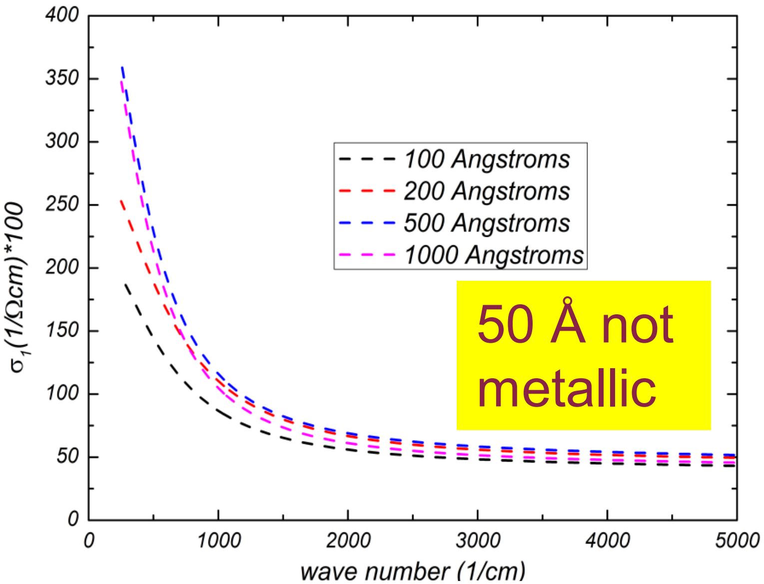
Farzin Abadizaman (unpublished)

Band structure of Ni; Interband transitions

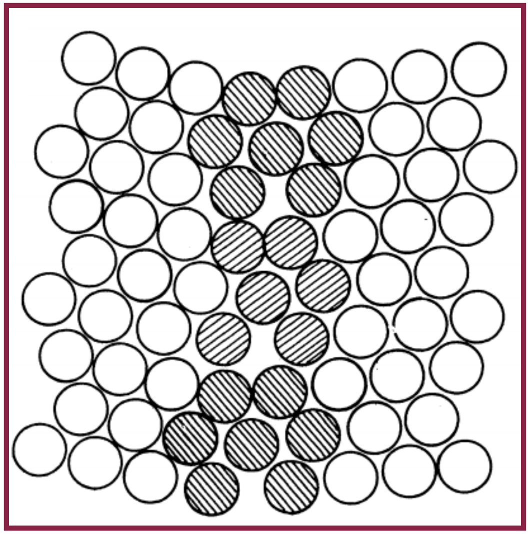


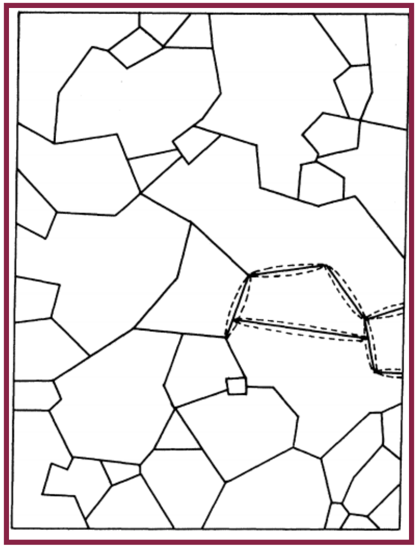
Lina Abdallah, Ph.D. thesis (2014)

Thickness dependence of dielectric function (Ni)

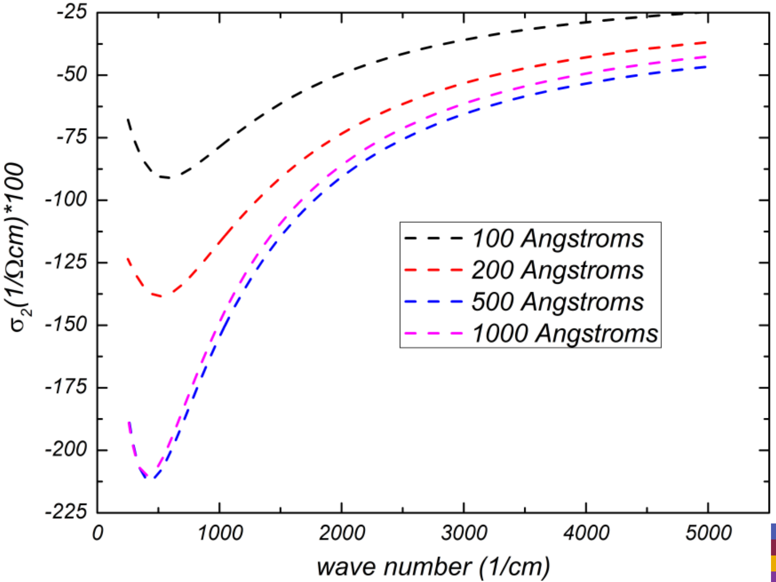


50 Å not metallic





Ola Hunderi, PRB, 1973



$\sigma_1\uparrow$ with $t\uparrow$
reduced grain boundary scattering in thicker films

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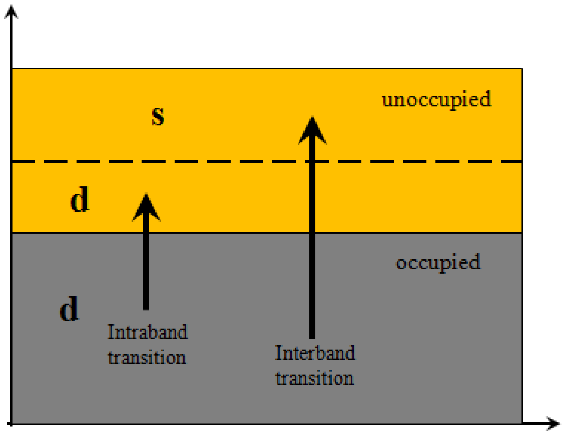
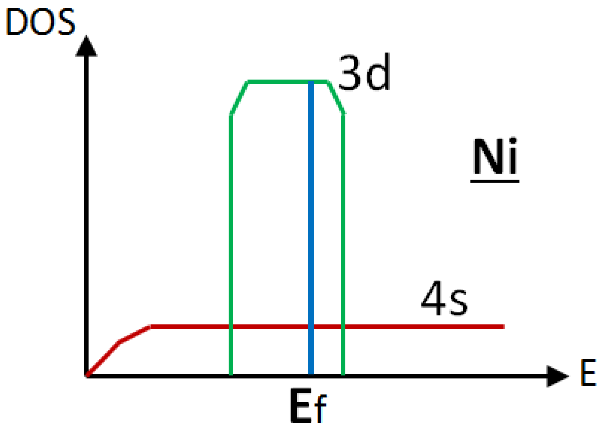
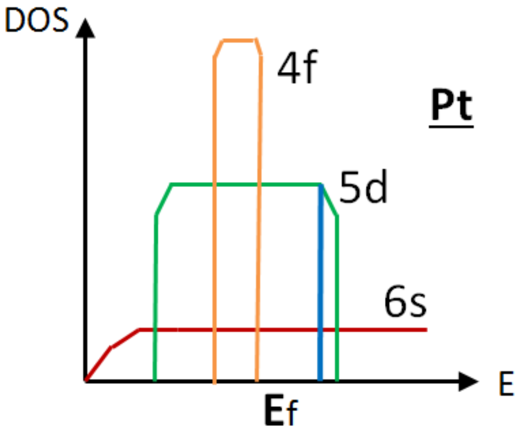
Difference between Ni and Pt







Ni 3d states are more localized.
Pt 5d states are broader, more dispersive.

Ni-Pt alloys have broader transitions than pure Ni.

- Alloy broadening: Potential fluctuations
- Initial Pt 5d states broader than Ni 3d states.

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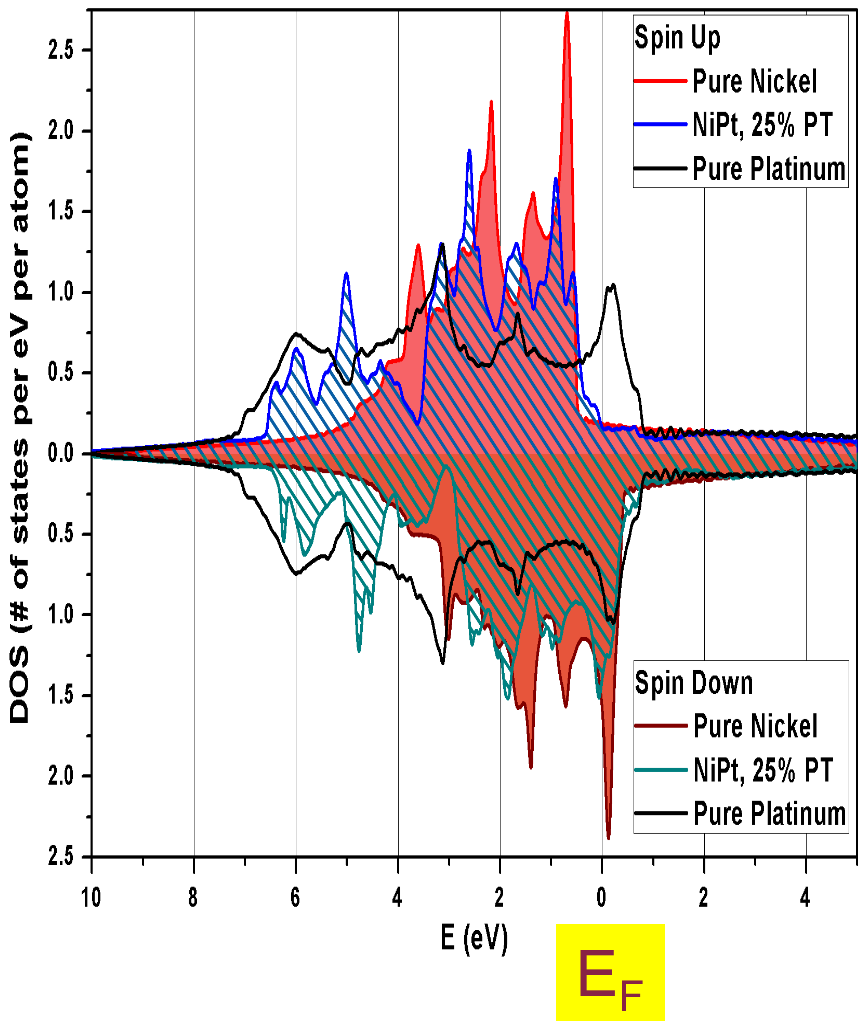
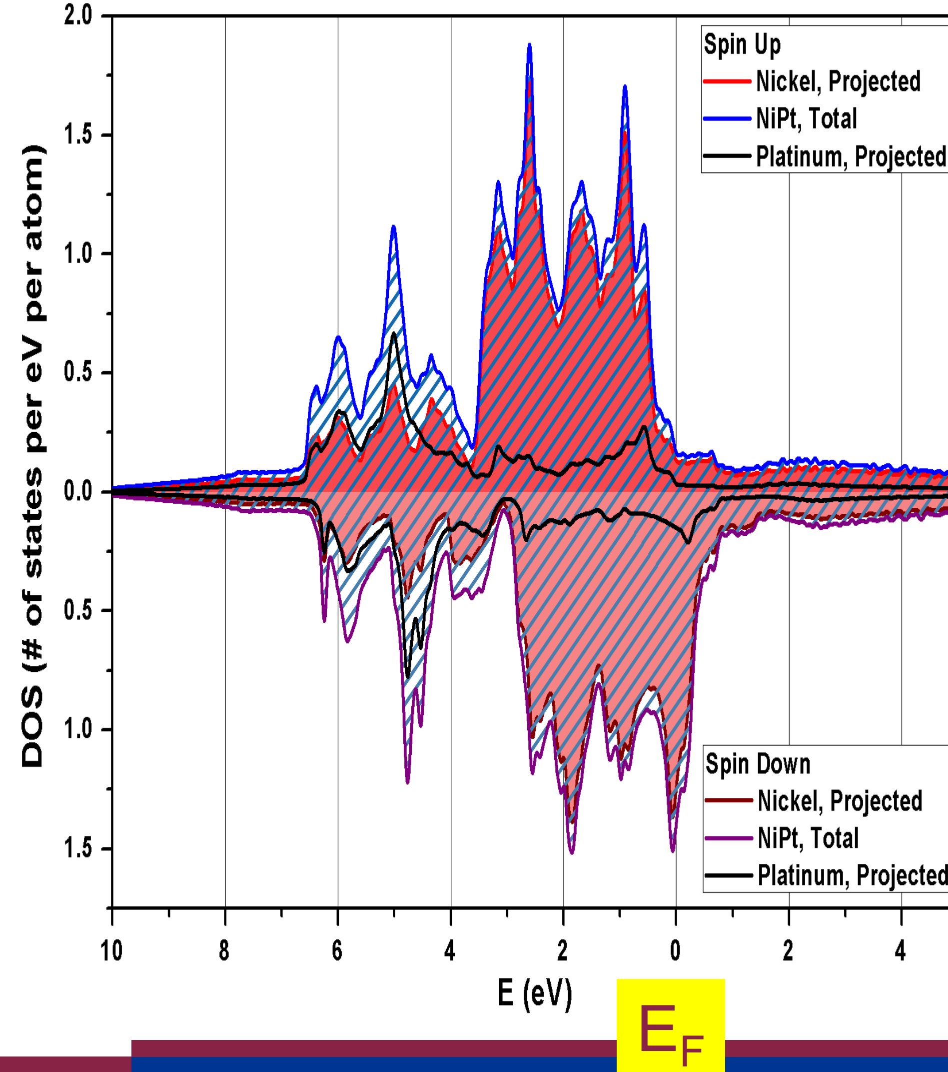
Total DOS



Ni_3Pt Projected DOS



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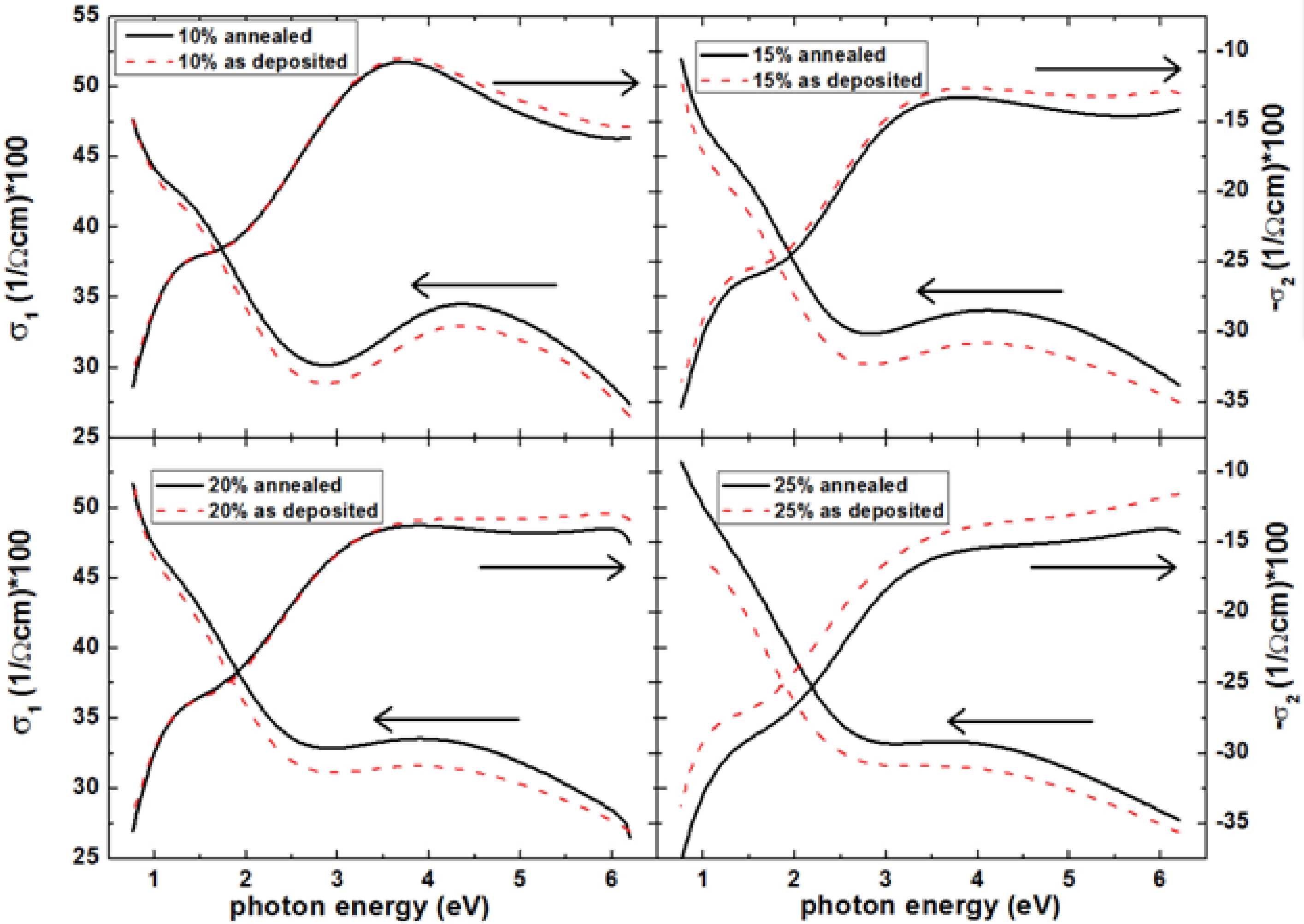
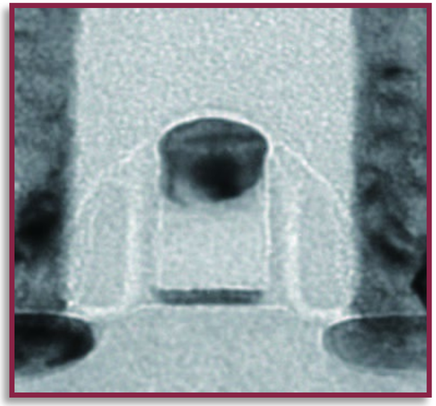
NM STATE

Optical conductivity of Ni-Pt alloys





Si CMOS
32 nm
(~10% Pt)

Interband transitions broader in Ni-Pt alloys than in pure Ni.

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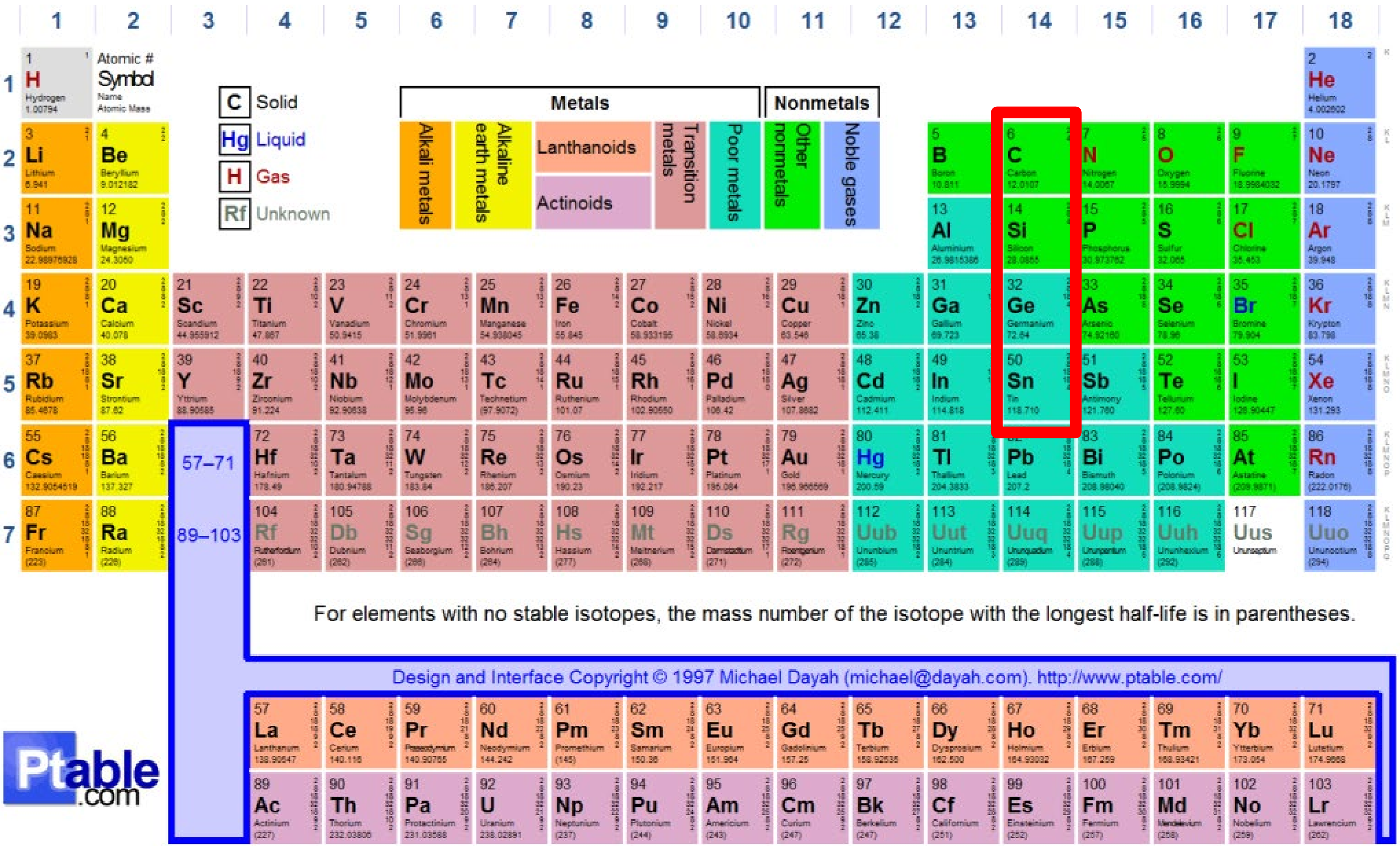
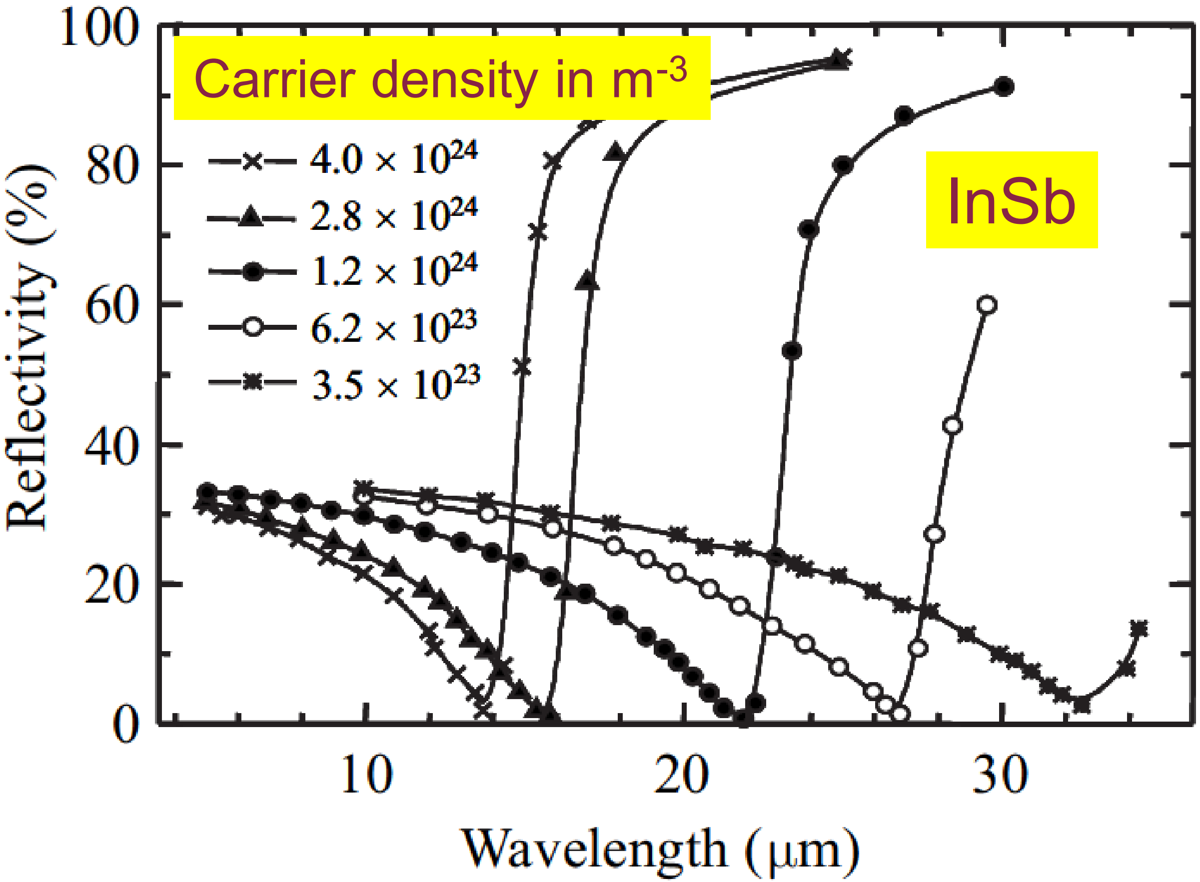
Semiconductors



Free-Carrier Reflection in doped semiconductors



Reflectance minimum near plasma frequency

Doped semiconductors behave just like a metal, except for the lower carrier density; **plasma frequency in infrared region.**

Fox, *Optical Properties of Solids*

Why infrared ellipsometry ?

Advantages:

- Measures amplitude ψ and phase Δ.
- Direct access to complex ε (no Kramers-Kronig transform).
- Modeling may contain depth information.
- No need to subtract substrate reference data.
- Anisotropy information (off-diagonal Jones and MM data)
- Possible measurements in a magnetic field (optical Hall effect)
- Obtain plasma frequency and scattering rate (B=0)
- Obtain *carrier density*, scattering rate, *effective mass* ($B\neq0$).

Disadvantages:

- Time-consuming (15 FTIR reflectance spectra)
- Requires polarizing elements (polarizer, compensator)
- Requires **large samples** (no focusing), at least 5 by 10 mm^2
- Requires modeling for thin layer on substrate.
- Commercial instruments **only down to 30 meV (250 cm^{-1})**

NM STATE

Summary

- **Drude model** explains optical response of metals.
- High reflectance below the plasma frequency.
- Interband transitions overlap with Drude absorption.

- Doped semiconductors have infrared plasma frequencies.

- **Lorentz model** explains infrared lattice absorption.
- TO/LO modes result in reststrahlen band.
- Multiple modes for complex crystal structures.