Optical Properties of Solids: Lecture 5

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http://ellipsometry.nmsu.edu

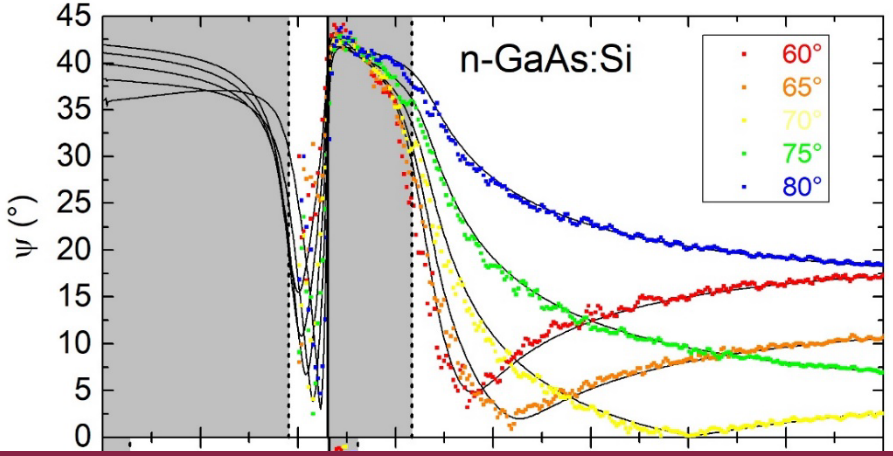
NSF: DMR-1505172

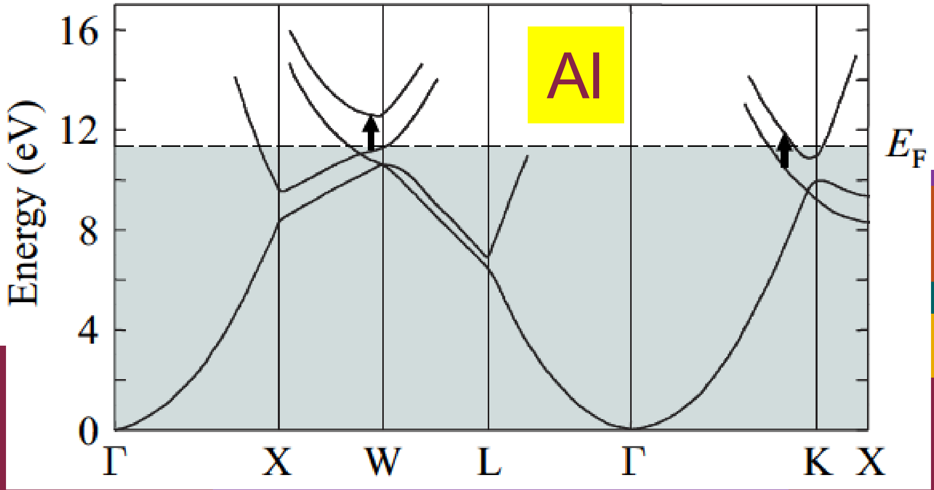
Optical Properties of Solids: Lecture 5+6

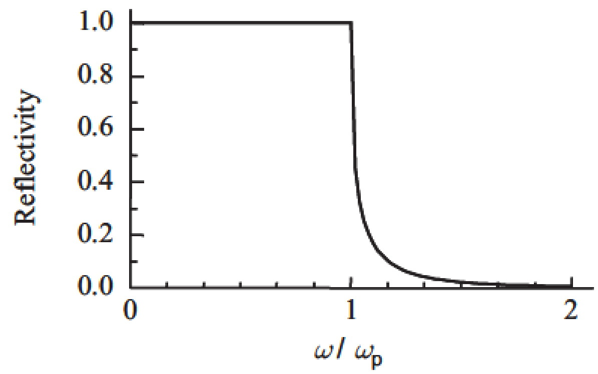
Lorentz and **Drude** model: Applications

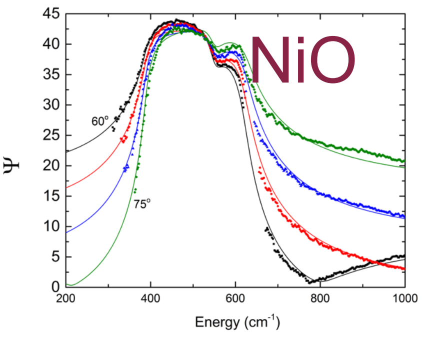
1. Metals, doped semiconductors
2. Insulators

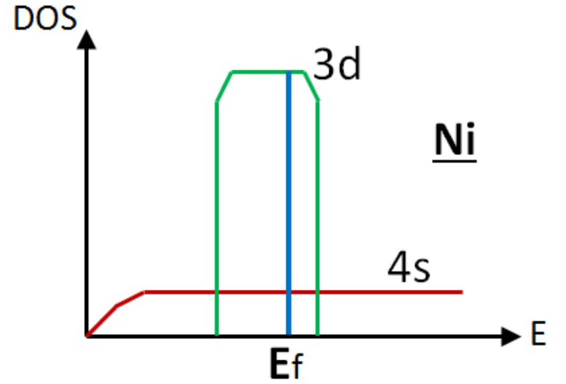
Sellmeier equation, Poles, Cauchy dispersion











References: Dispersion, Analytical Properties

Standard Texts on Electricity and Magnetism:

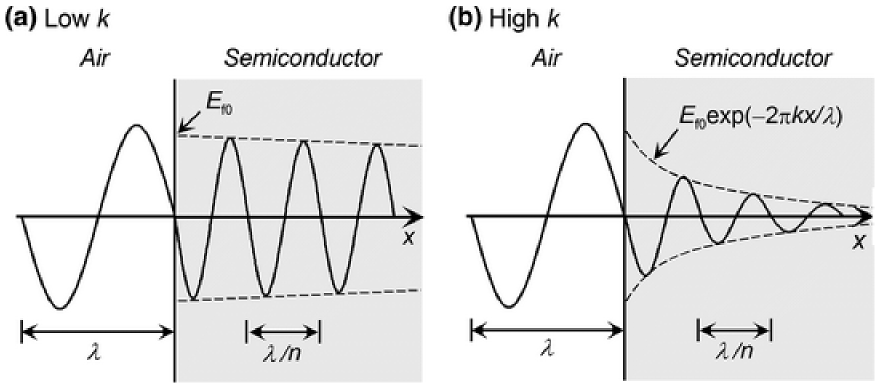
- J.D. Jackson: *Classical Electrodynamics*
- **L.D. Landau & J.M. Lifshitz, Vol. 8: *Electrodynamics of Cont. Media***

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: $$\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_1}{n_2}$$

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

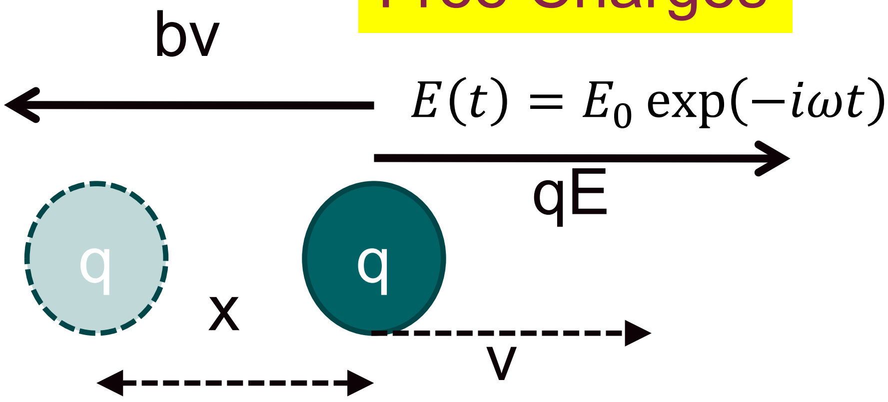
Propagation

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

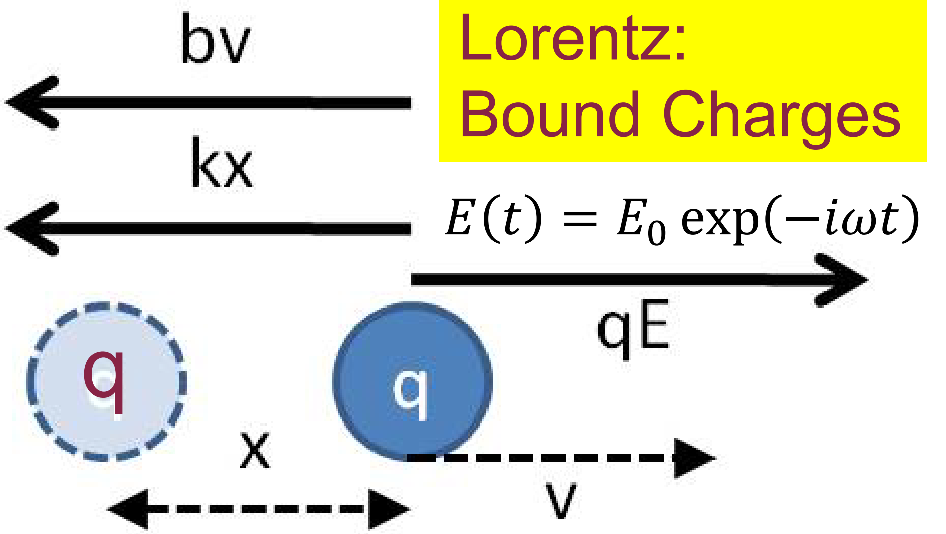
Landau-Lifshitz § 63, Jackson, Clemmow
Dupertuis, Proctor, Acklin, JOSA **11**, 1159 (1994).

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

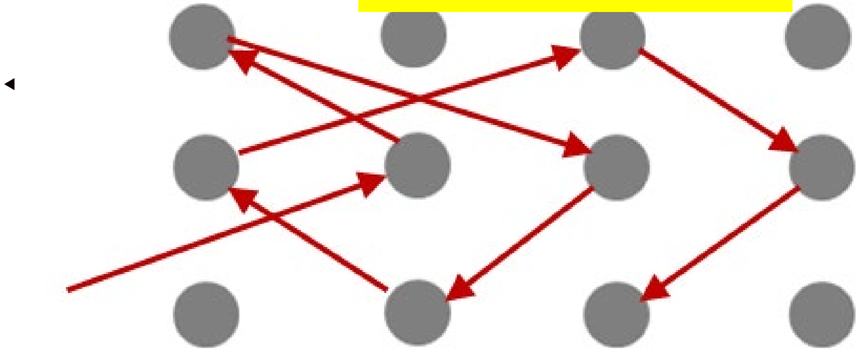
$$\omega_0^2 = \frac{k}{m}$$ resonance frequency

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

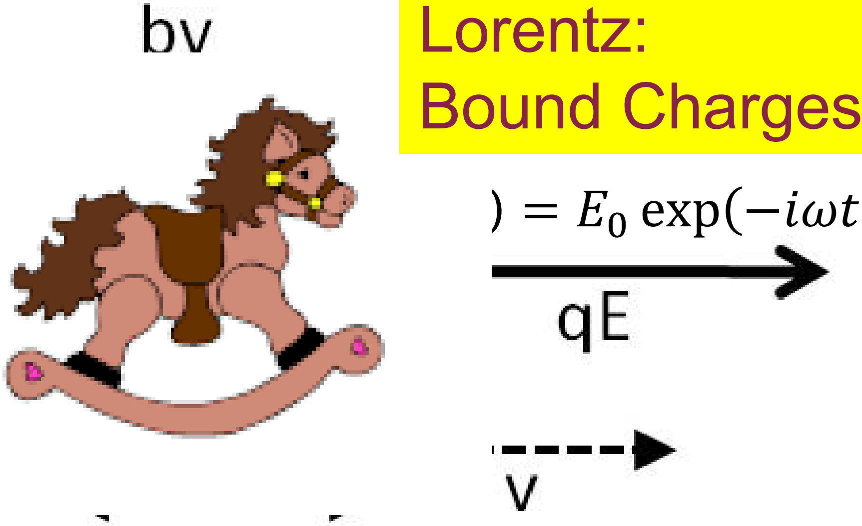
H. Helmholtz, Ann. Phys **230**, 582 (1875)

Drude-Lorentz Model: Free and Bound Charges

Drude:
Free Charges



Lorentz:
Bound Charges



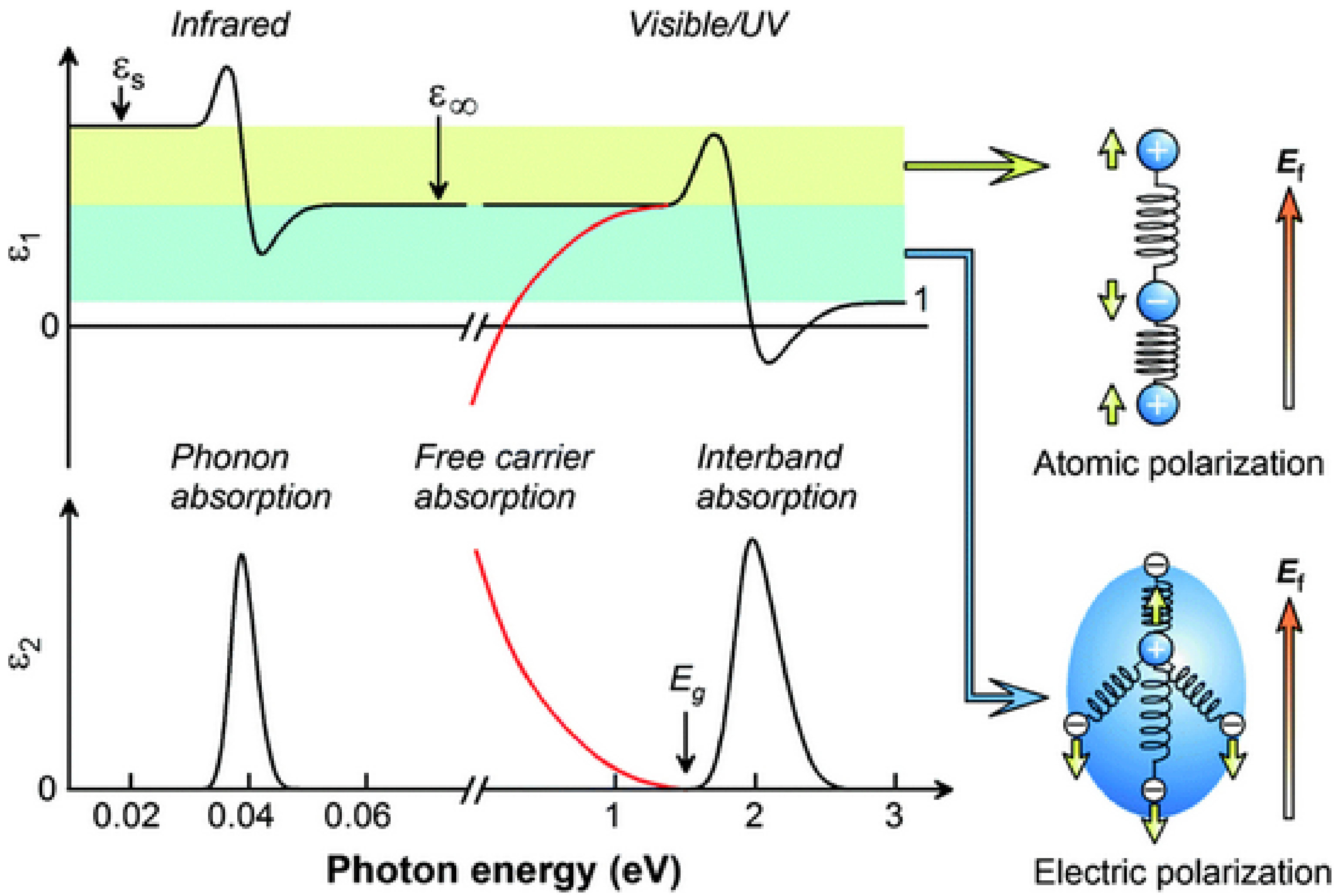
$$\varepsilon(\omega) = 1 - \sum_i \frac{\omega_{P,i}^2}{\omega^2 + i\gamma_{D,i}\omega} + \sum_i \frac{A_i\omega_{0,i}^2}{\omega_{0,i}^2 - \omega^2 - i\gamma_{0,i}\omega}$$

w_P	(unscreened) **plasma frequency** of free charges
w_0	**resonance frequency** of bound charges
g_D, g_0	**broadenings** of free and bound charges
A	**amplitude** of bound charge oscillations (density, strength)

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

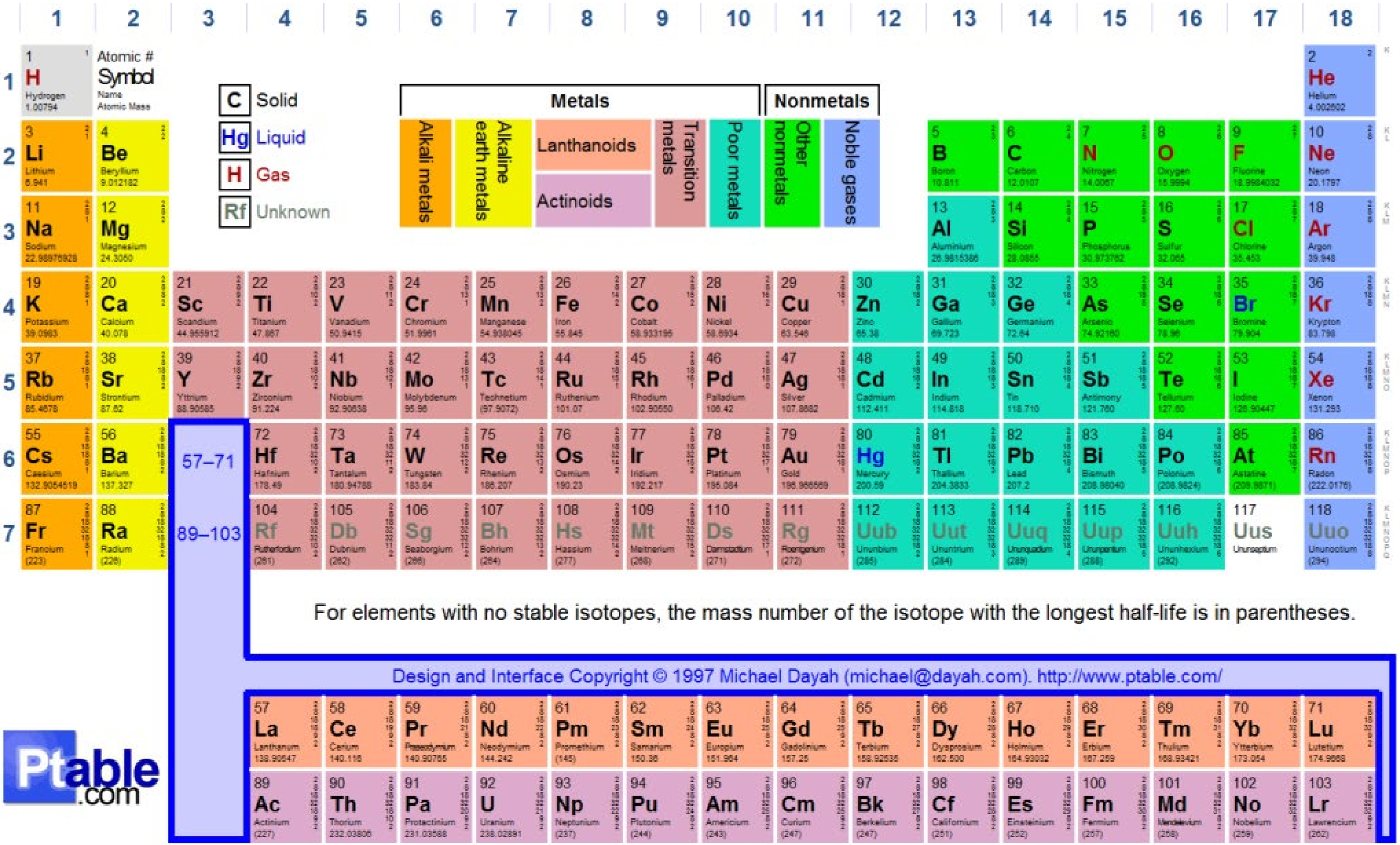
Discuss plasma frequency trends.

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



Atomic #
Symbol
Name
Atomic Mass

C Solid
Hg Liquid
H Gas
Rf Unknown

Metals: Alkali metals, Alkaline earth metals, Lanthanoids, Actinoids, Transition metals, Poor metals

Nonmetals: Other nonmetals, Noble gases

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** Hydrogen 1.00794																	2 **He** Helium 4.002602
2	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
3	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
4	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
5	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
6	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)
7	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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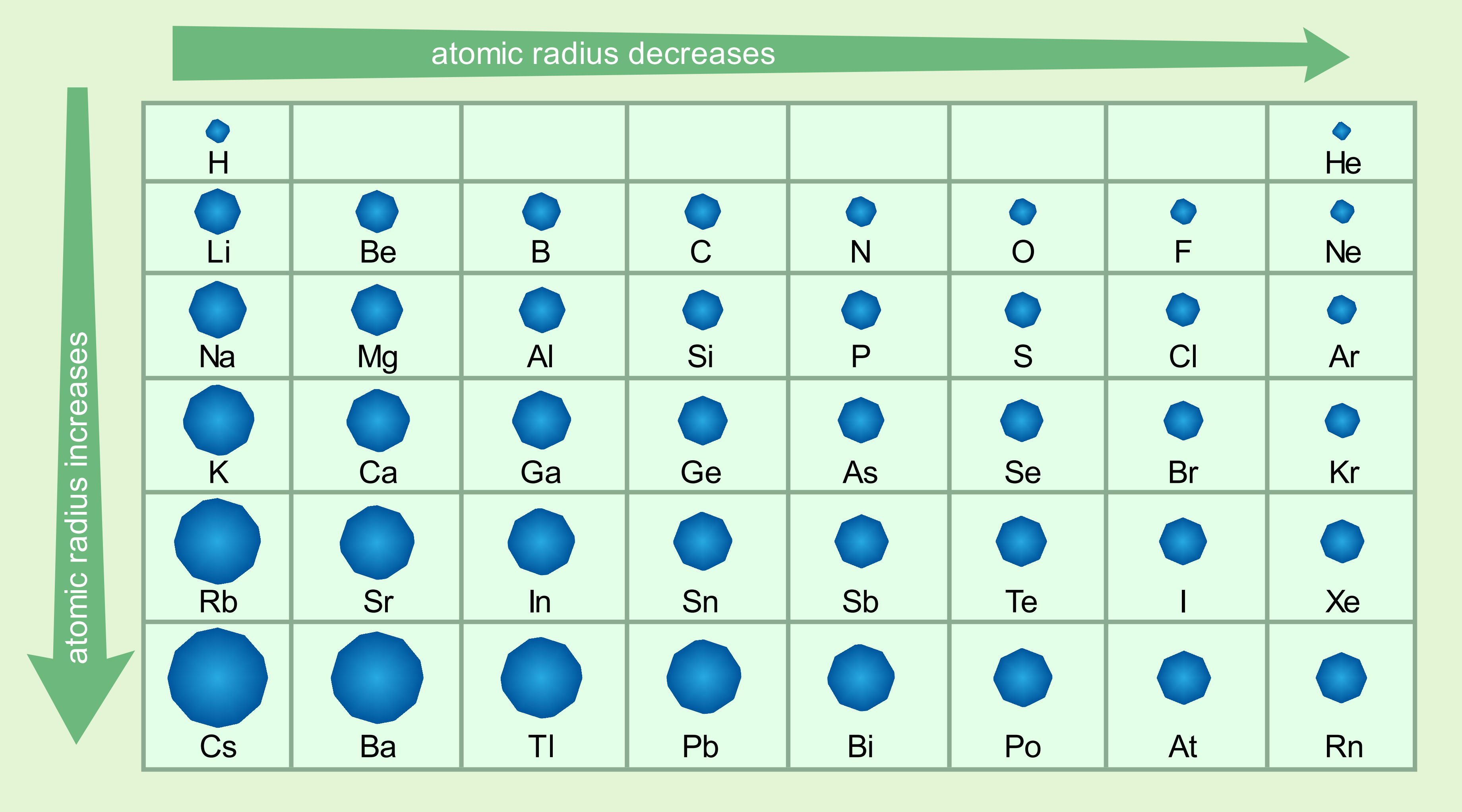
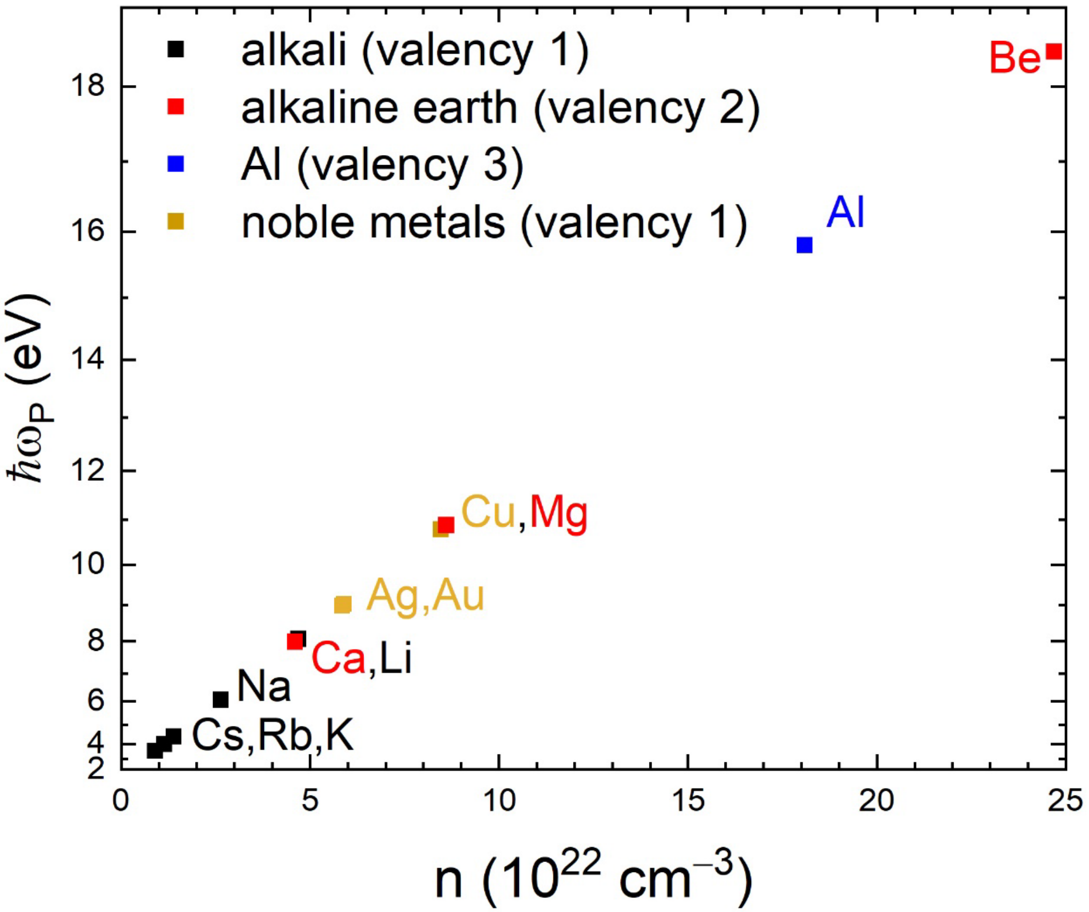
57 **La** Lanthanum 138.90547	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.242	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92535	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.93032	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)

Atomic Radius

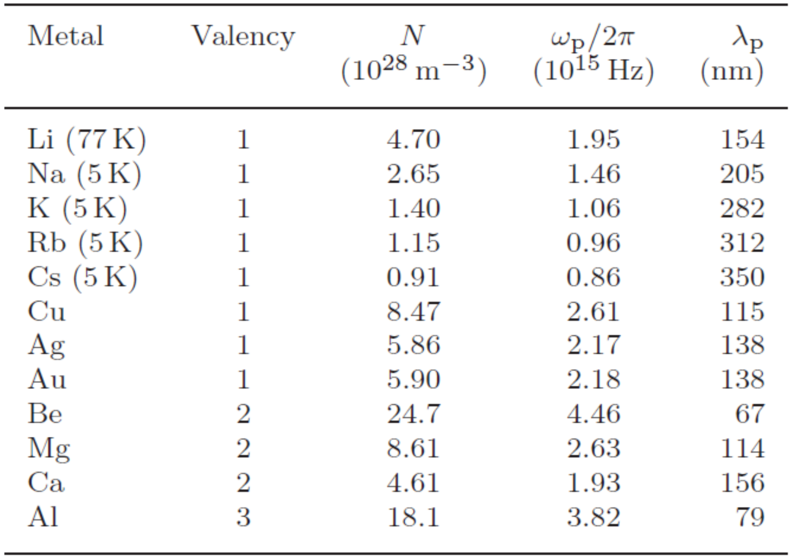


Atomic radius decreases from K to Ca to Cu.

(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

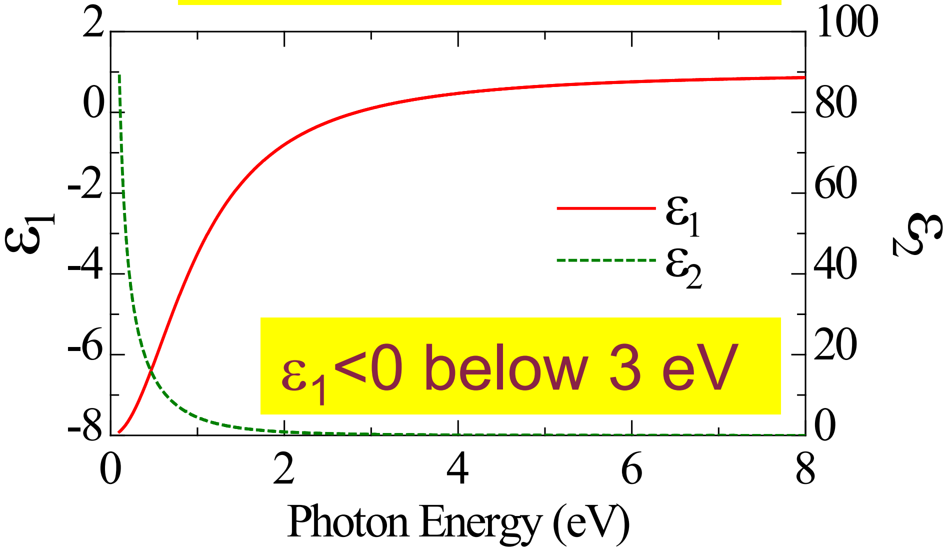
Fox, Table 7.1

Valency determined by row in period table.

Atomic radius decreases from K to Ca to Cu.

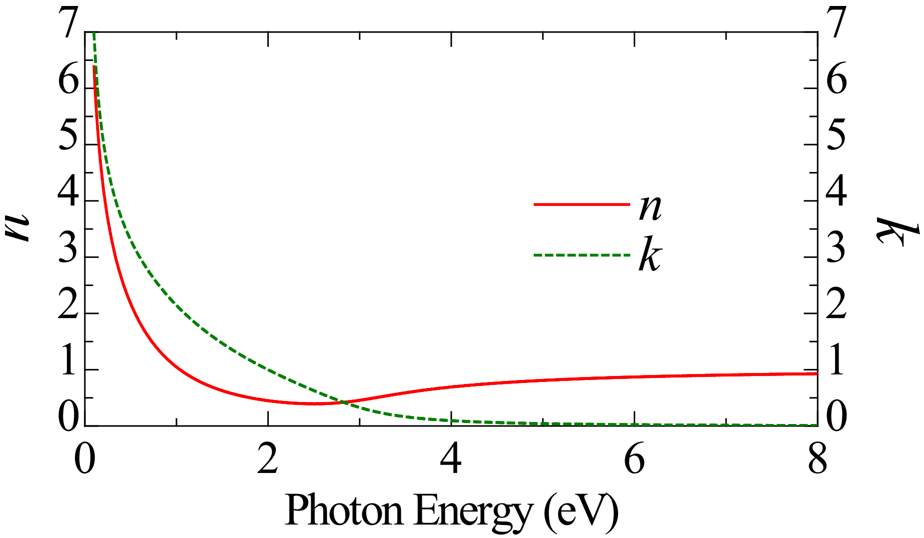
Free-Carrier Reflection/Absorption in Metals

Dielectric function e



$\varepsilon_1<0$ below 3 eV

Refractive index n+ik=√ε

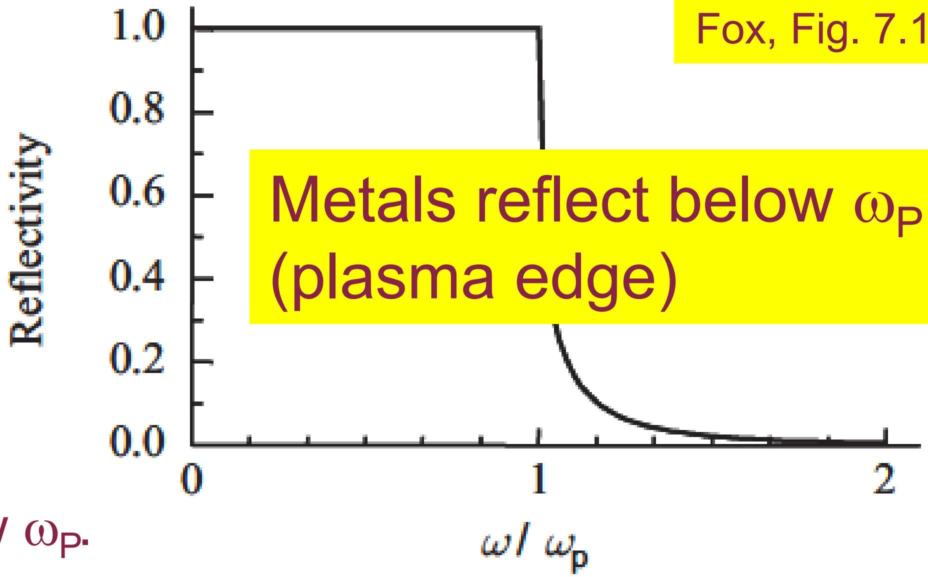


$$\varepsilon(\omega) = 1 - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}$$

ω_p=3 eV, γ=1 eV

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

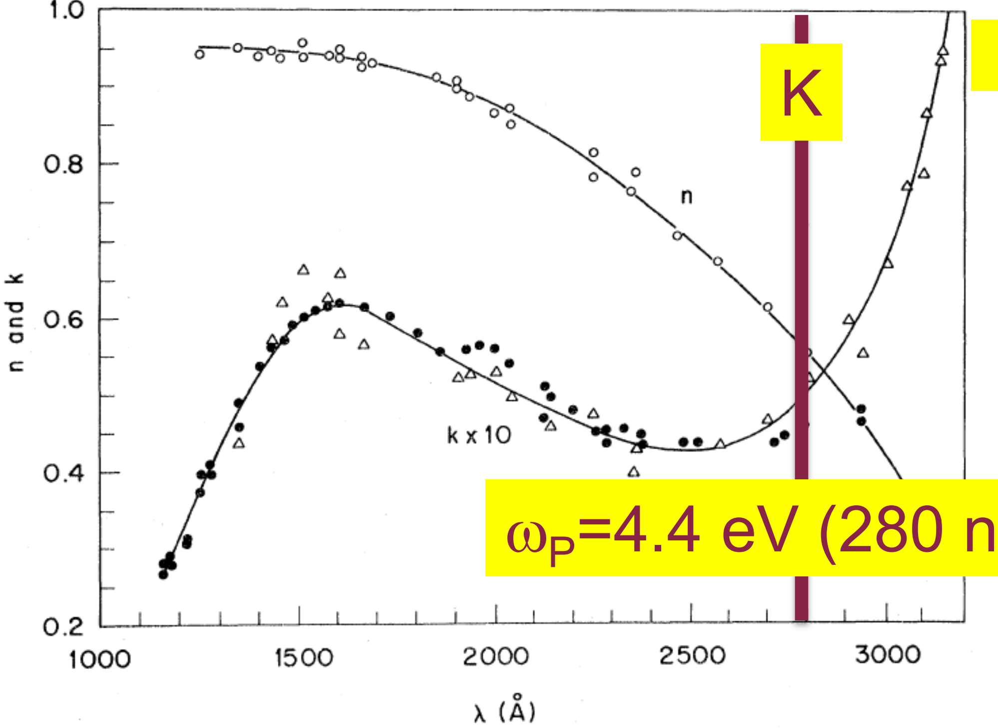
R=1 if n is purely imaginary (γ=0) below ω_P.



Fox, Fig. 7.1

Metals reflect below ω_P (plasma edge)

Transparent Alkali Metals above ω_P



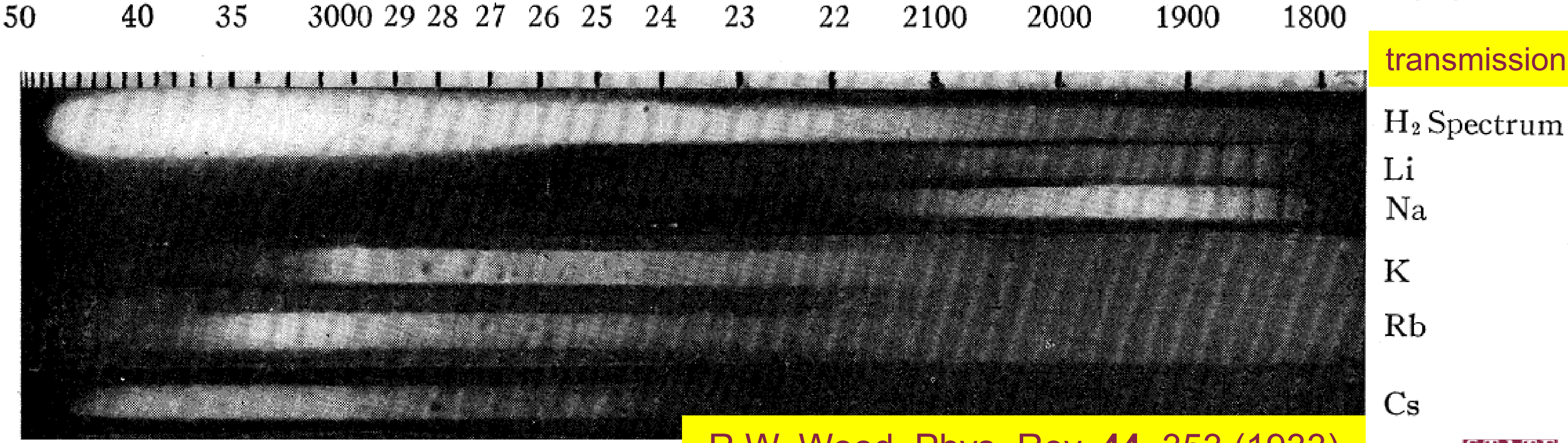
K

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

ω_P=4.4 eV (280 nm)

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

Fox, Table 7.2



transmission

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 ($\gamma \ll \omega_P$):

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

(real, negative)

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

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

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

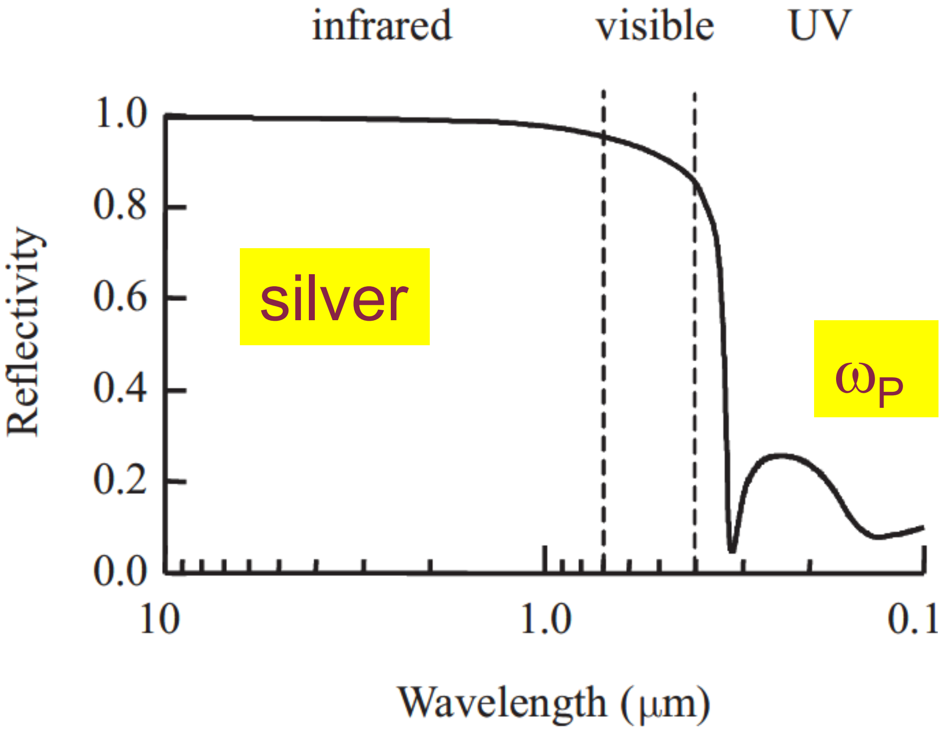
$$\tilde{n}(\omega) = \sqrt{\varepsilon(\omega)} = ik$$

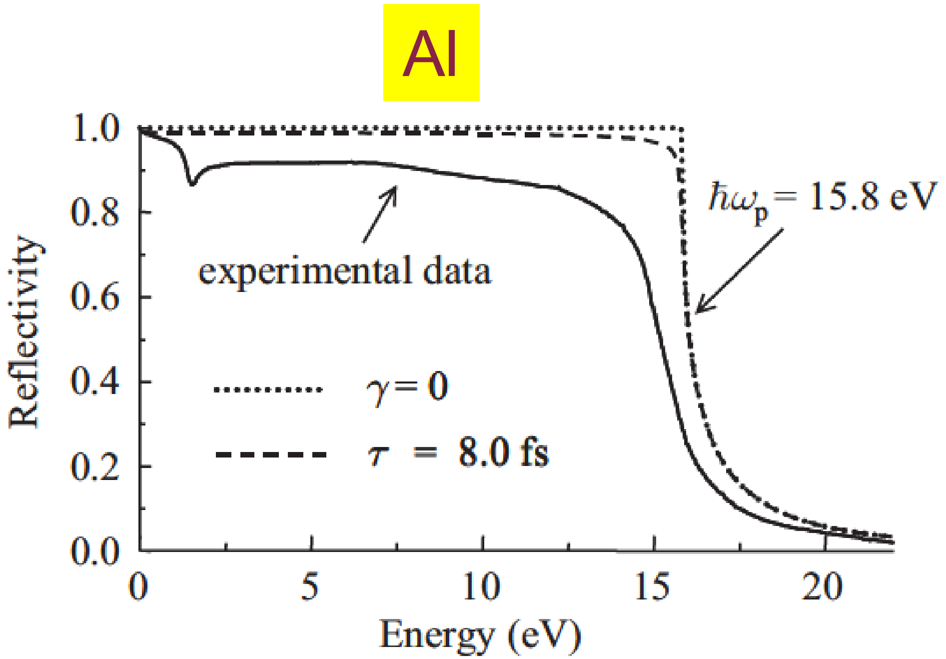
(purely imaginary)

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

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

Free-Carrier Reflection in Ag and Al



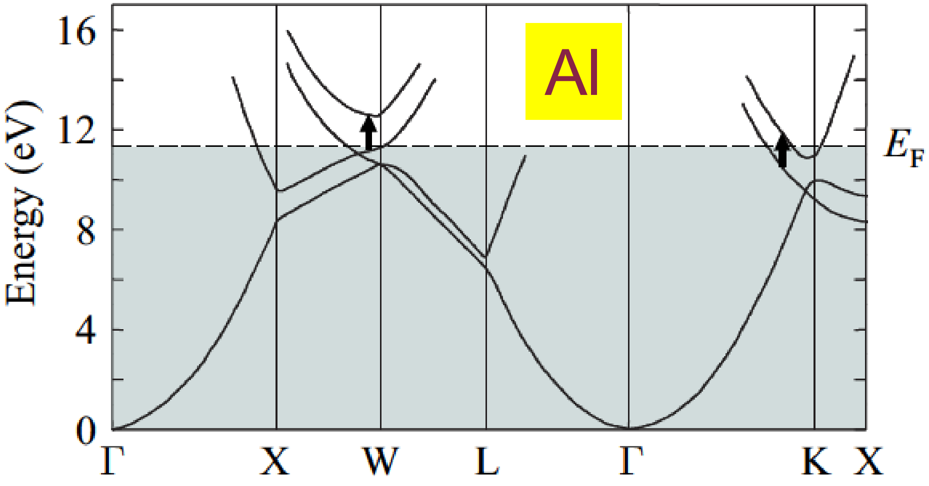


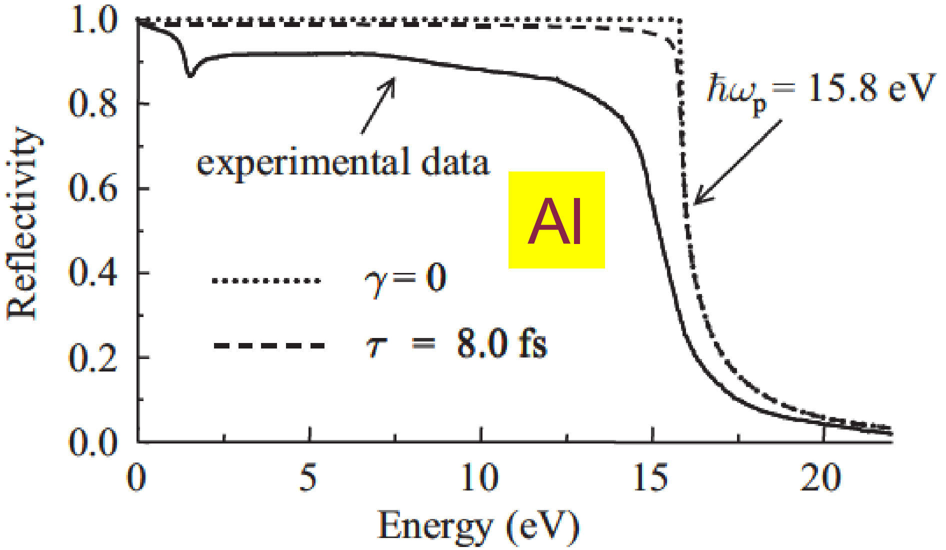
Ag is a noble metal.
Filled 4d-shell, $5s^1$
High reflectance
below ω_P=9 eV (above 138 nm)
Sharp drop above ω_P. Damping.

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

Fox, *Optical Properties of Solids*

Free-Carrier Reflection in Al





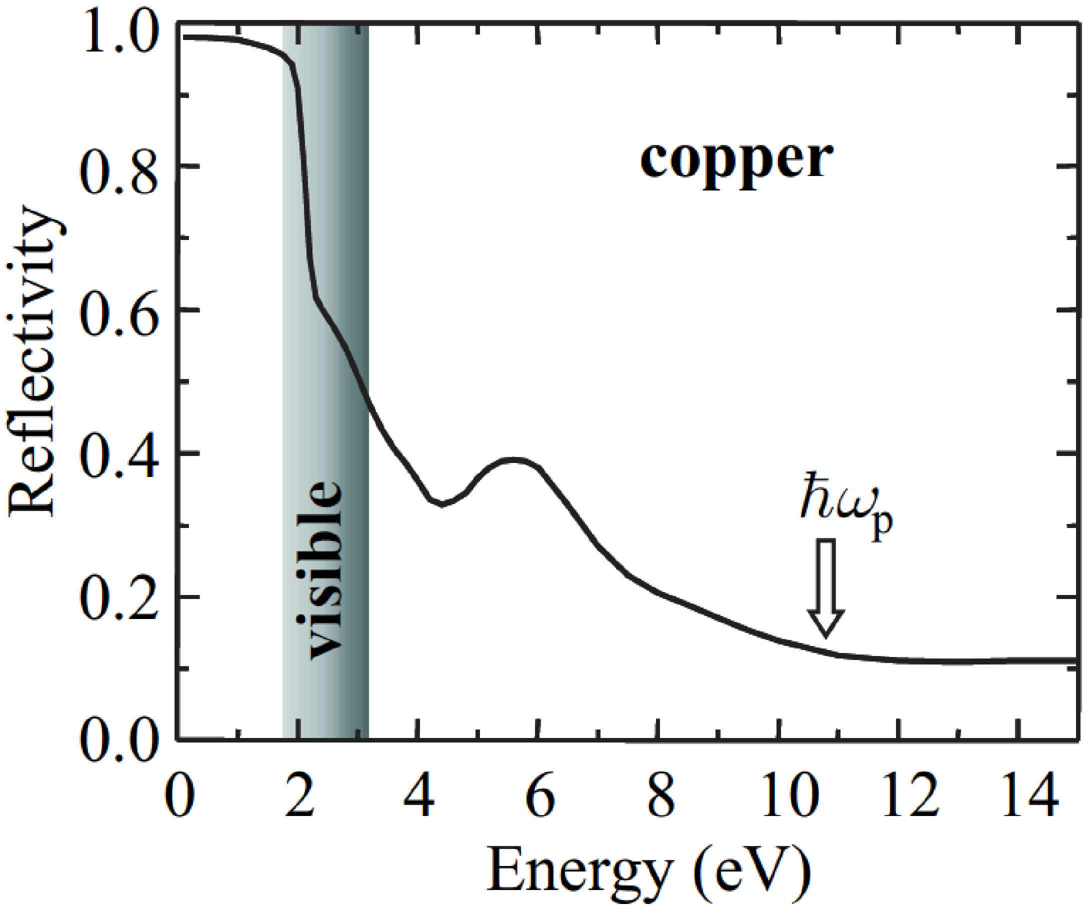
Interband transitions at W cause absorption band at 1.5 eV, lowers reflectivity.

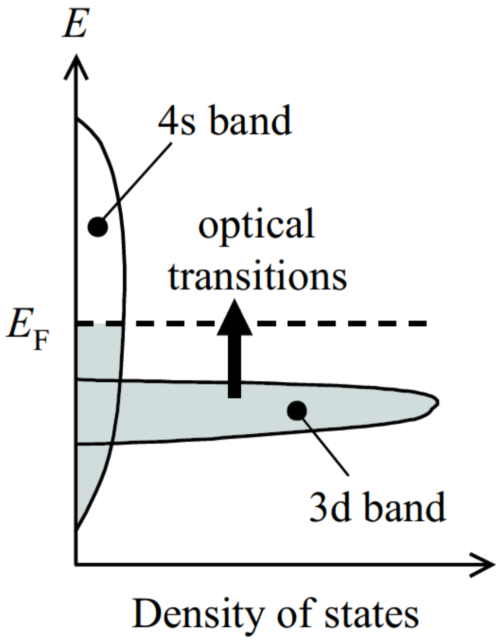
Al has three electrons ($3s^2$, $3p^1$)
High reflectance
below ω_P=16 eV (above 78 nm)
Sharp drop above ω_P.
Damping, interband absorption.

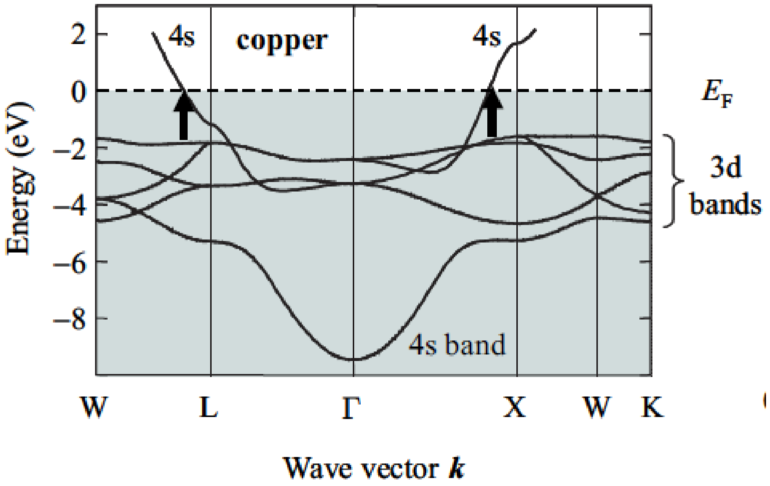
See also: G. Jungk, Thin Solid Films **234**, 428 (1993).

Fox, *Optical Properties of Solids*

Free-Carrier Reflection in Cu



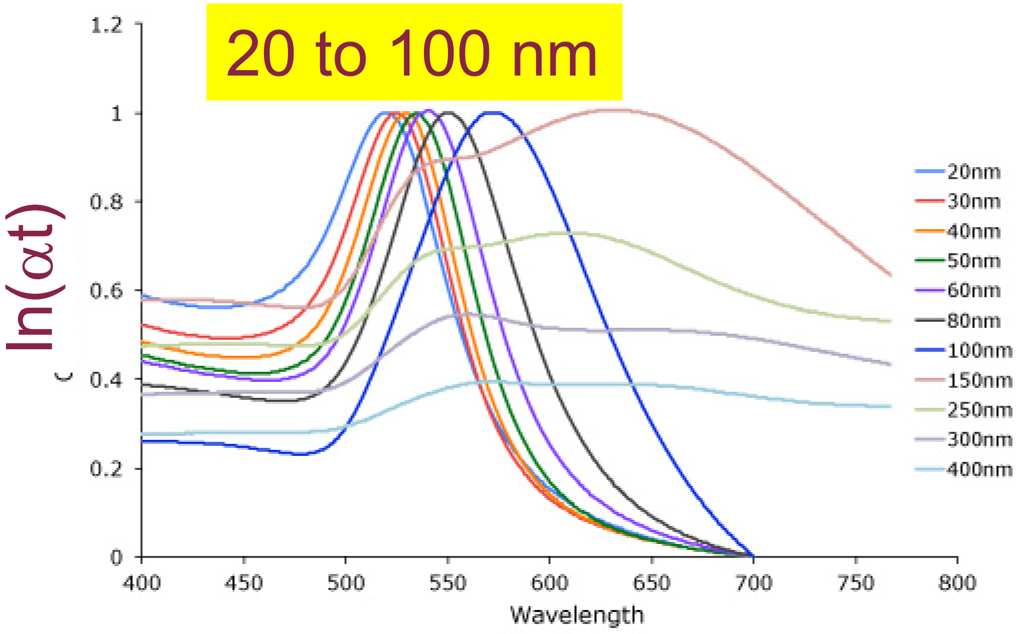




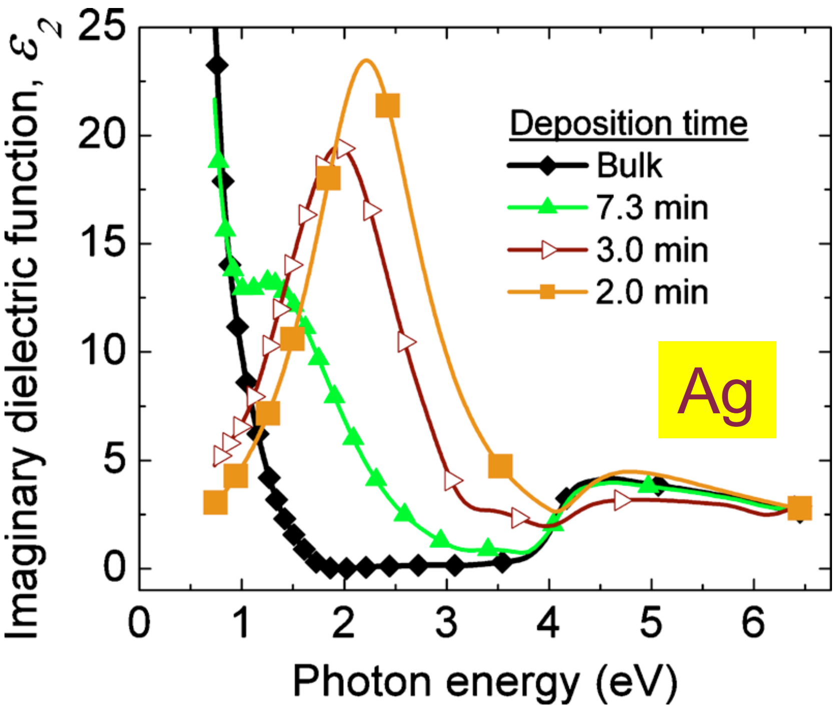
Noble metal, $4s^1$, ω_P=10.8 eV
Transitions from 3d to 4s at 2 eV
(near L and X). Similar for Ag, Au.

Fox, *Optical Properties of Solids*

Plasmon resonance in gold nanoparticles



20 to 100 nm



Ag

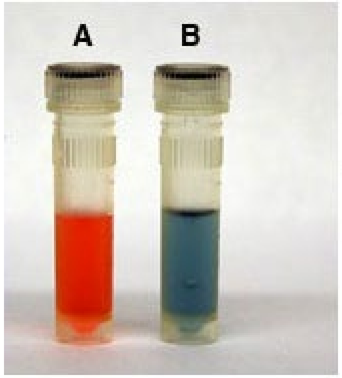
Gold is not always yellow.

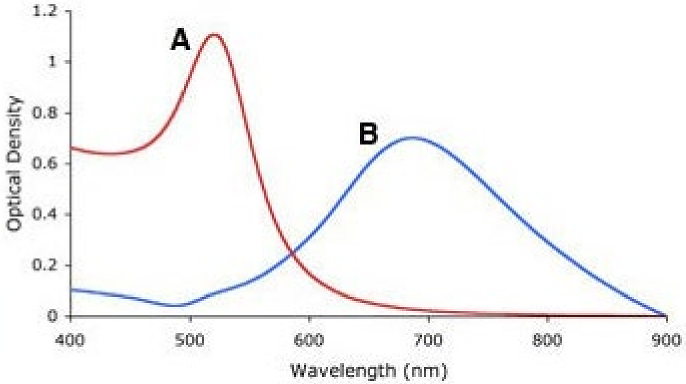
Nanoparticle radius a<λ

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

m: metal, d: dielectric

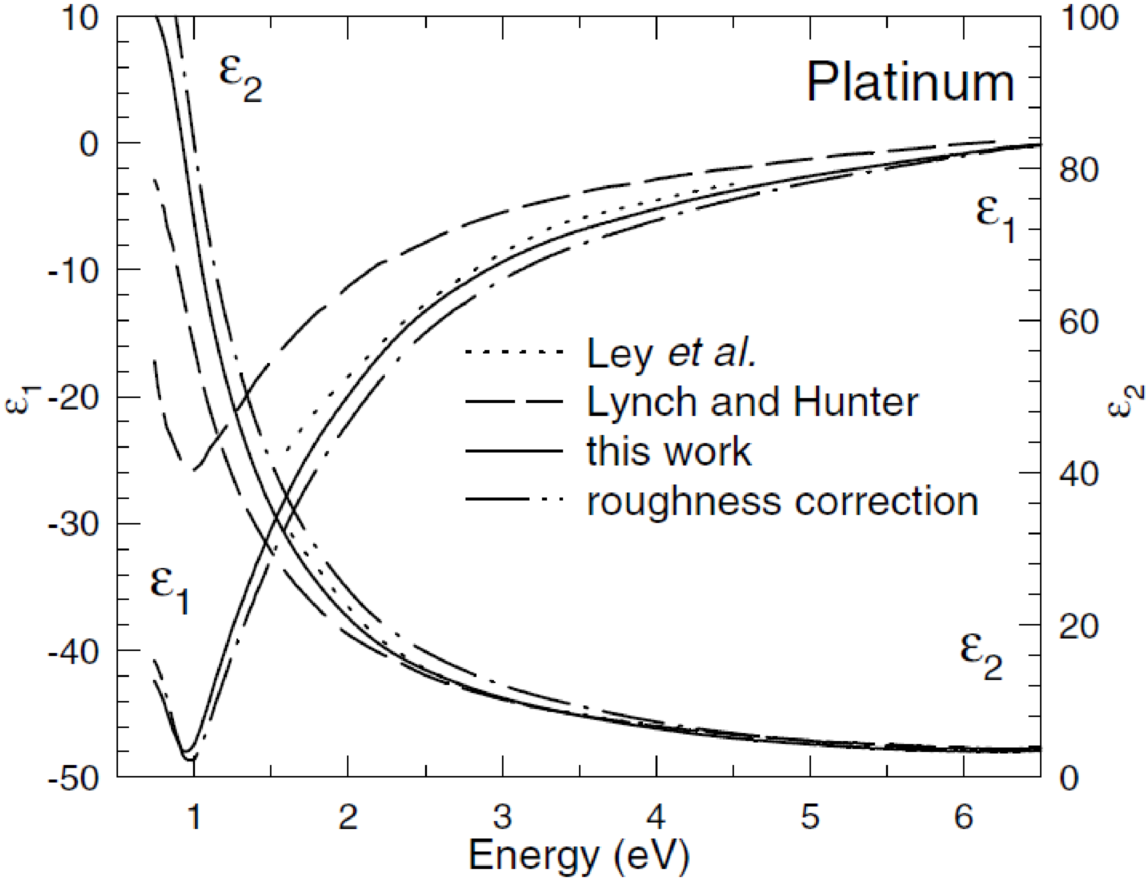
Enhance molecular absorption.



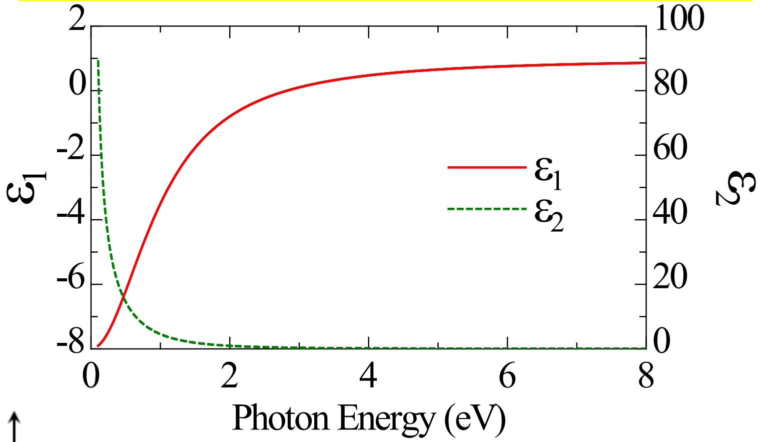


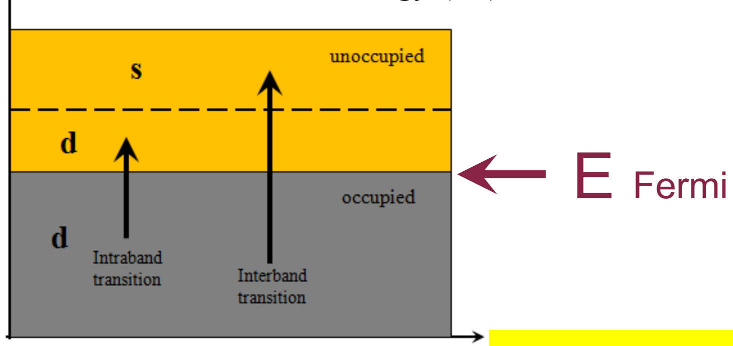
Fox, *Optical Properties of Solids*
Little, *APL* **98**, 101910 (2011)

Dielectric function of transition metals (Pt)



Drude-like ε above 1 eV



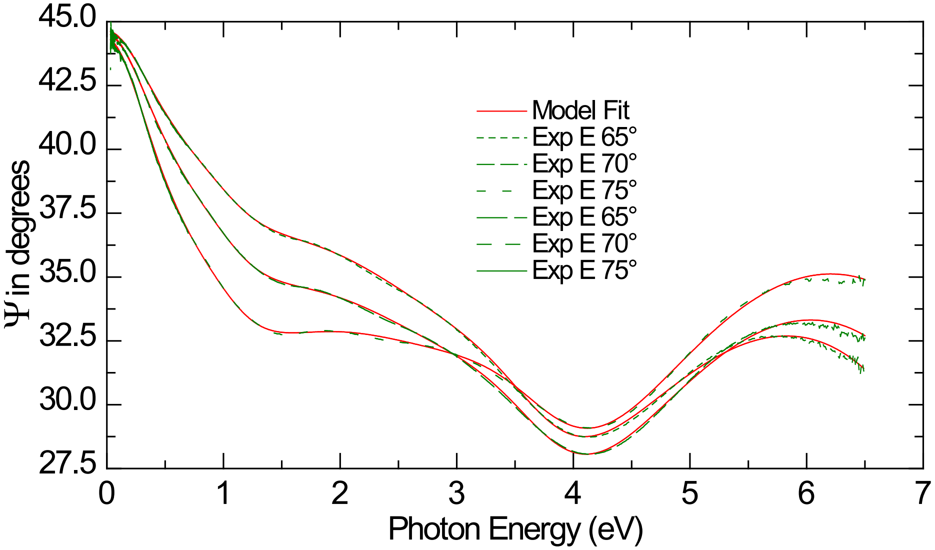


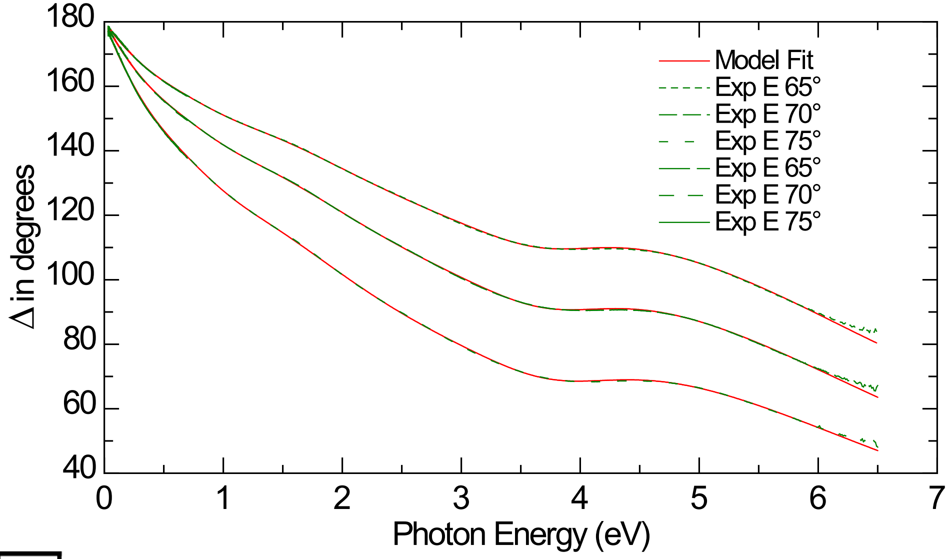
The dielectric function of Pt deviates from the Drude model below 1 eV due to d-interband transitions.

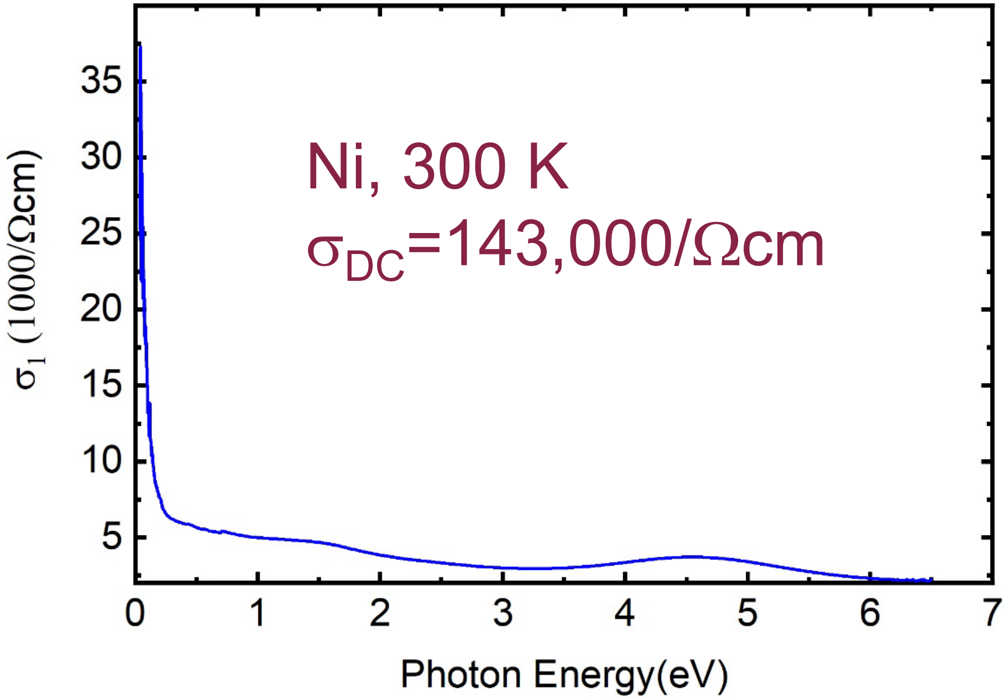
Pt is **not a noble metal**, partially filled d-shell.

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

Dielectric function of transition metals (Ni)







Ni, 300 K

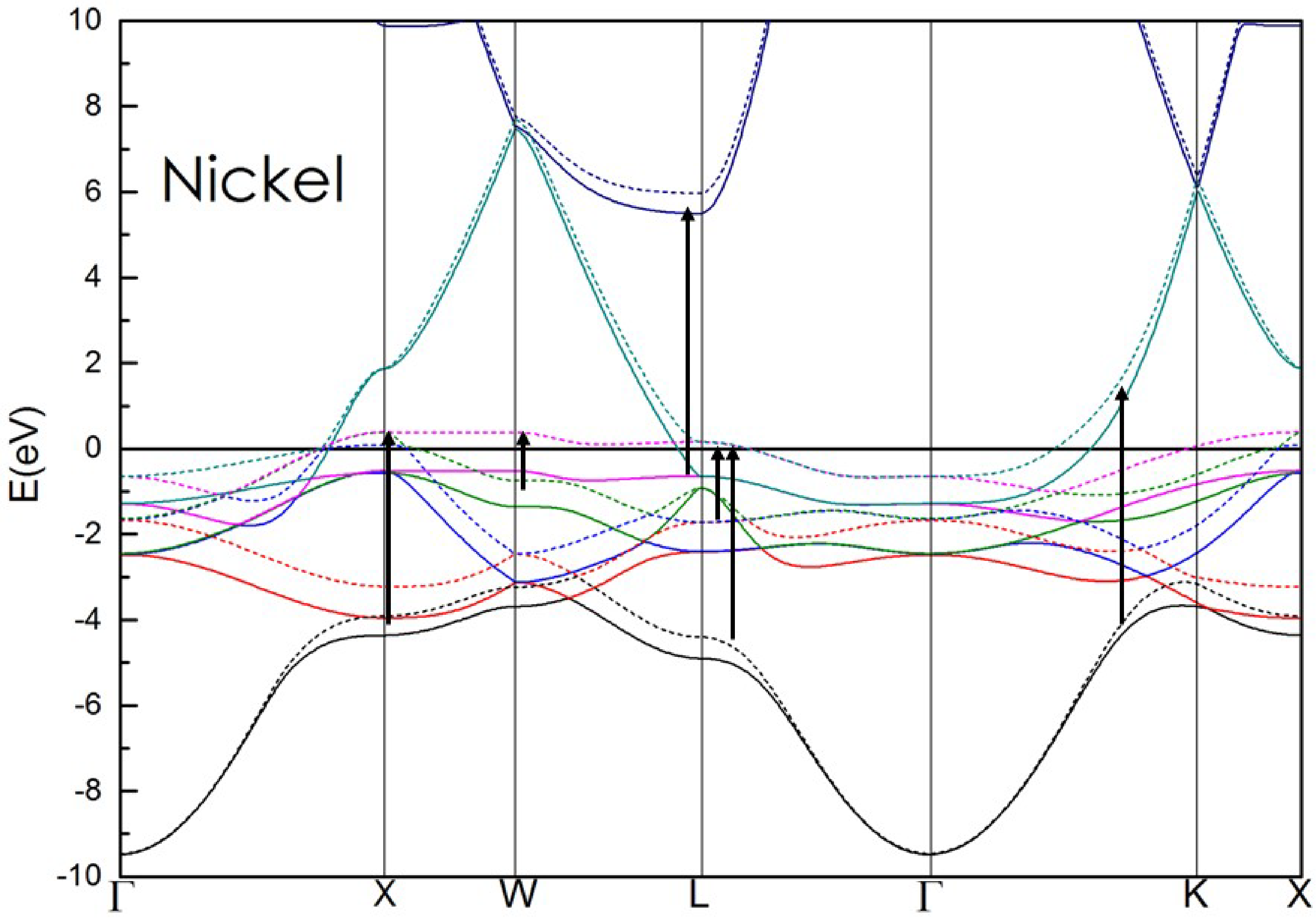
σ_{DC}=143,000/Ωcm

Low frequency:
$\psi \to 0$, $\Delta \to 180^\circ$

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

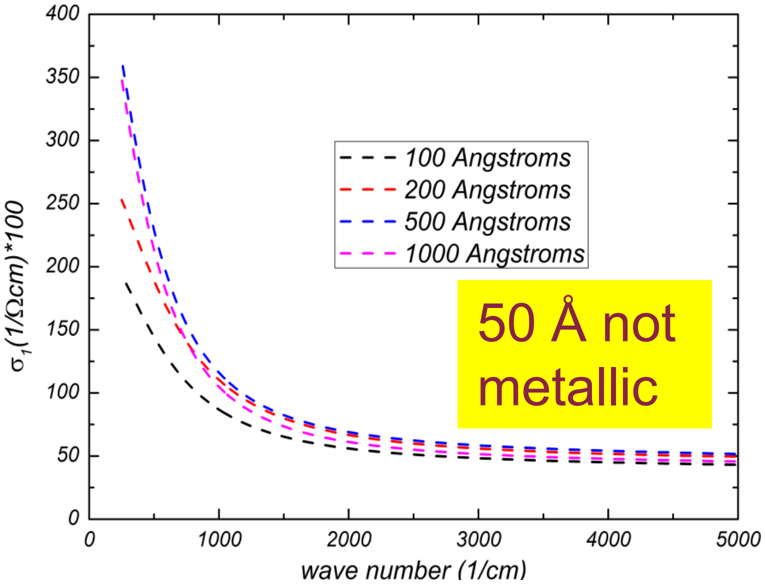
Farzin Abadizaman, JVST B **37**, 062920 (2019); JVST A **40**, 033202 (2022).

Band structure of Ni; Interband transitions

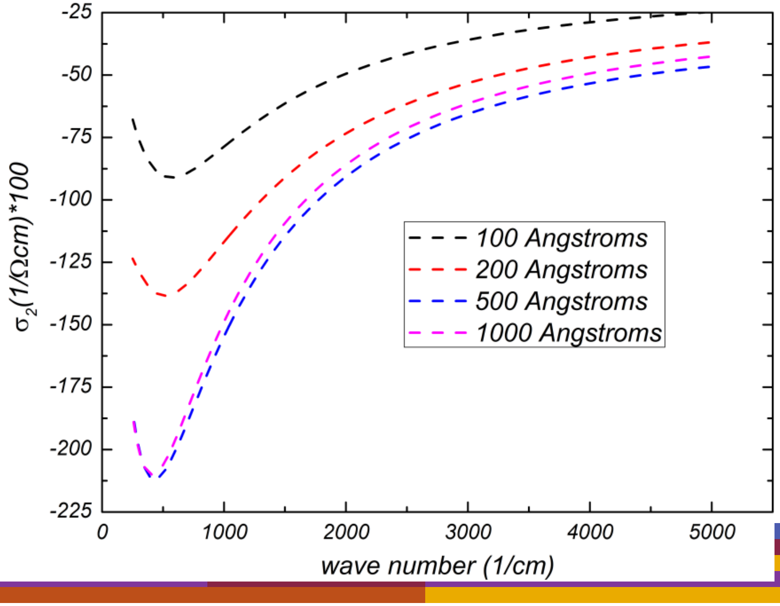


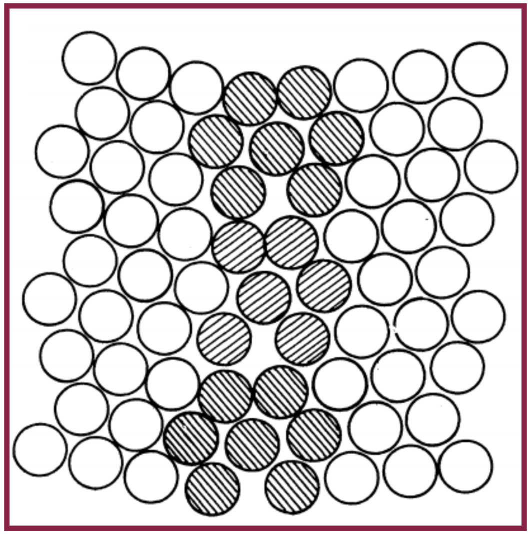
Lina Abdallah, Ph.D. thesis (2014)

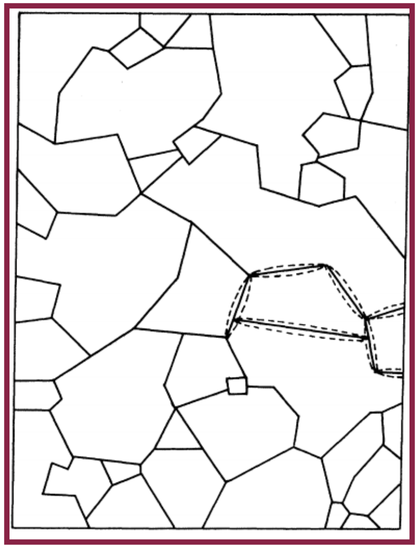
Thickness dependence of dielectric function (Ni)



50 Å not metallic







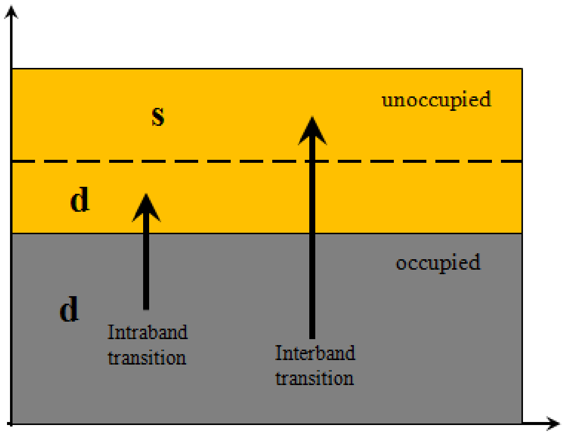
Ola Hunderi, PRB, 1973

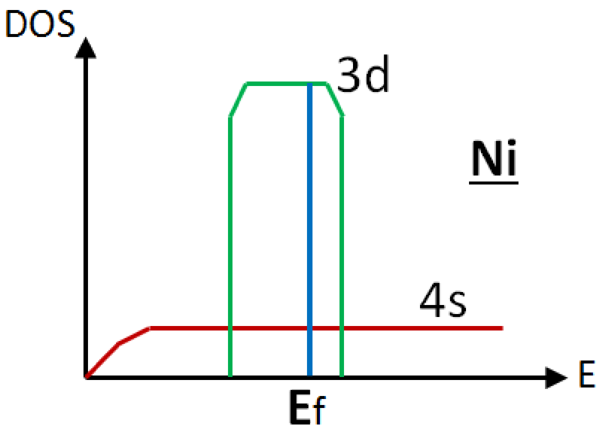
σ_1↑ with t↑

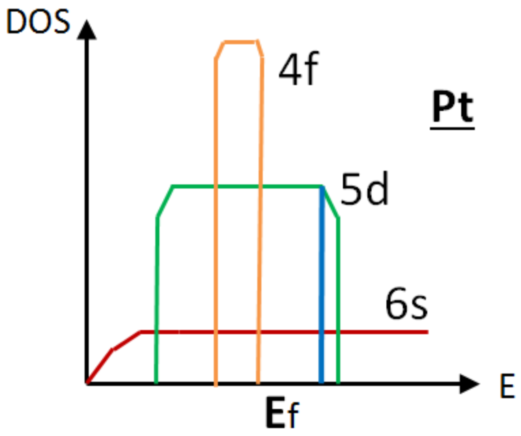
reduced grain boundary scattering in thicker films

Lina Abdallah, Ph.D. thesis (2014)

Difference between Ni and Pt







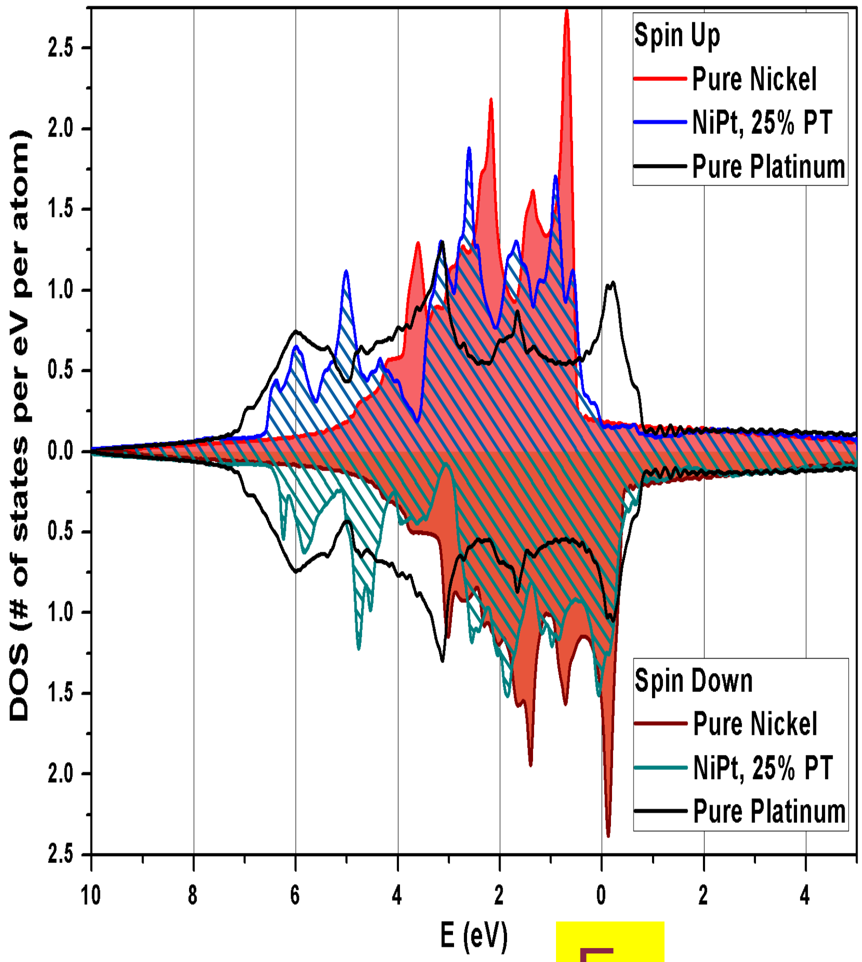
Ni 3d states are more localized.
Pt 5d states are broader, more dispersive.

Ni-Pt alloys have broader transitions than pure Ni.

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

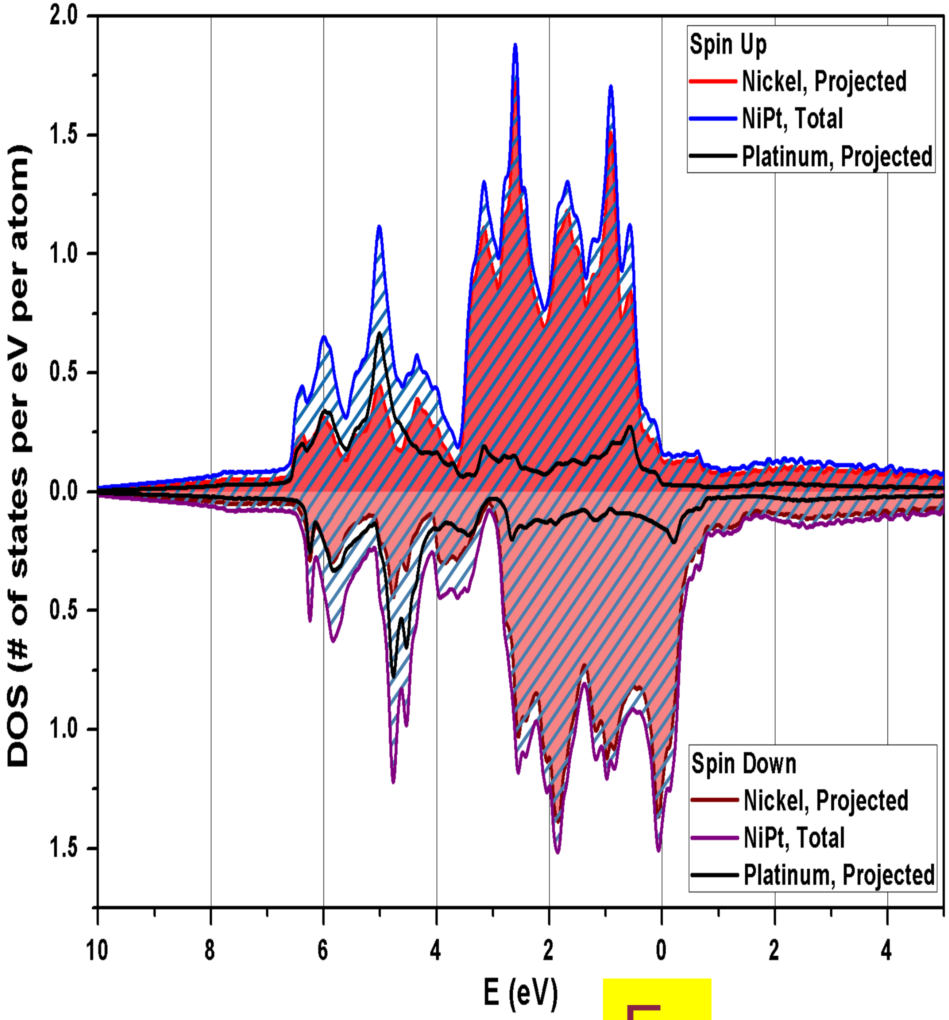
Lina Abdallah, Ph.D. thesis (2014)

Total DOS



E_F

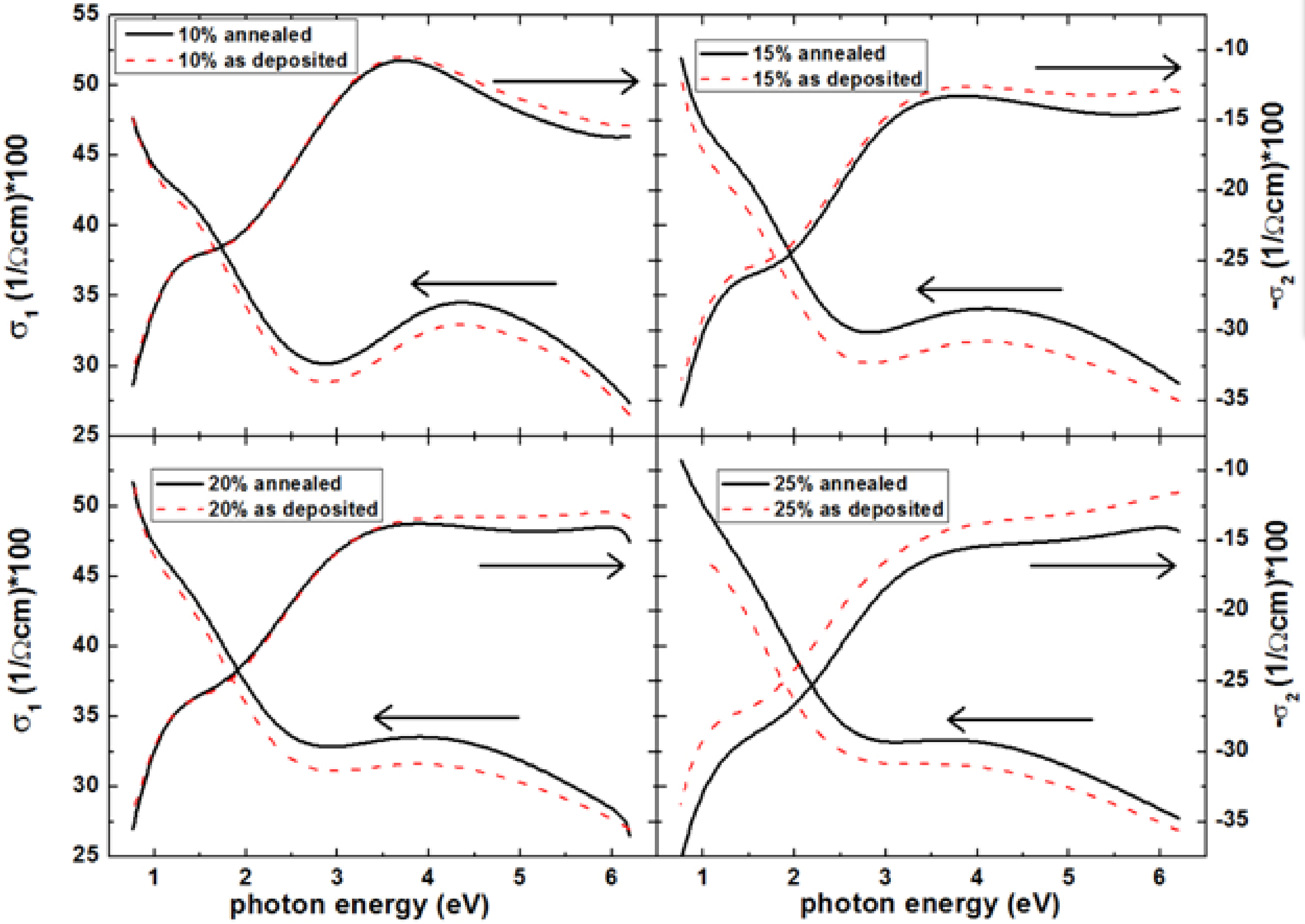
Ni$_3$Pt Projected DOS

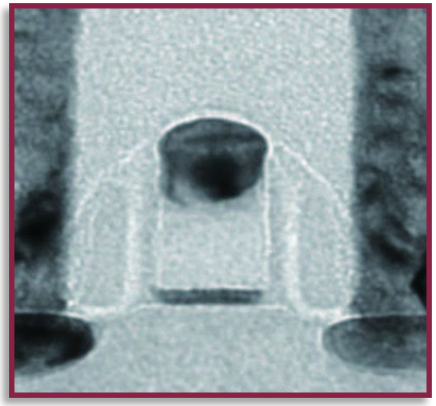


E_F

Lina Abdallah, Ph.D. thesis (2014)

Optical conductivity of Ni-Pt alloys



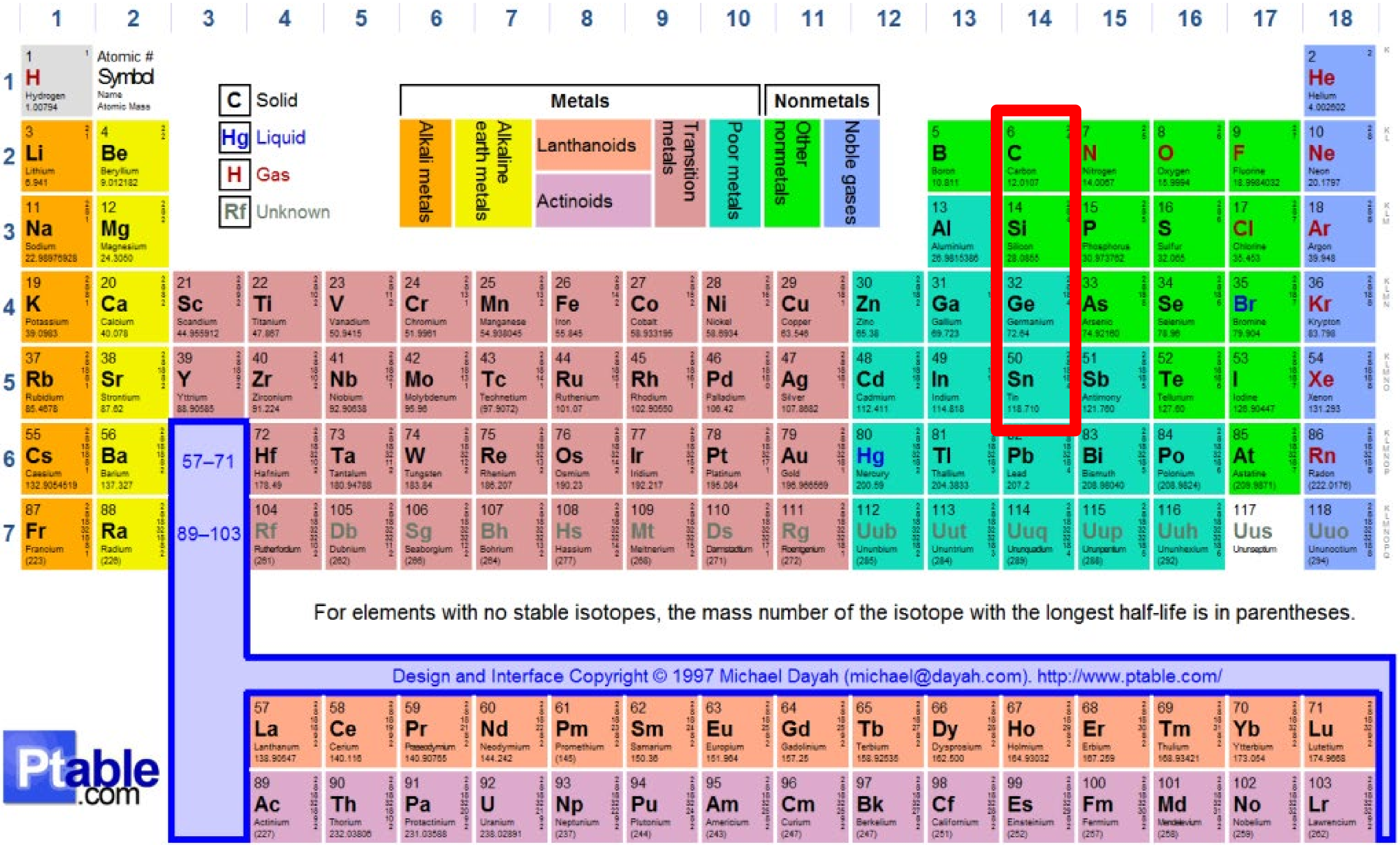


Si CMOS
32 nm
(~10% Pt)

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

Lina Abdallah, Ph.D. thesis (2014)

Semiconductors



C Solid
Hg Liquid
H Gas
Rf Unknown

Metals: Alkali metals, Alkaline earth metals, Lanthanoids, Actinoids, Transition metals, Poor metals
Nonmetals: Other nonmetals, Noble gases

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 **H** Hydrogen 1.00794	Atomic # Symbol Name Atomic Mass																2 **He** Helium 4.002602
2	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
3	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
4	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
5	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
6	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)
7	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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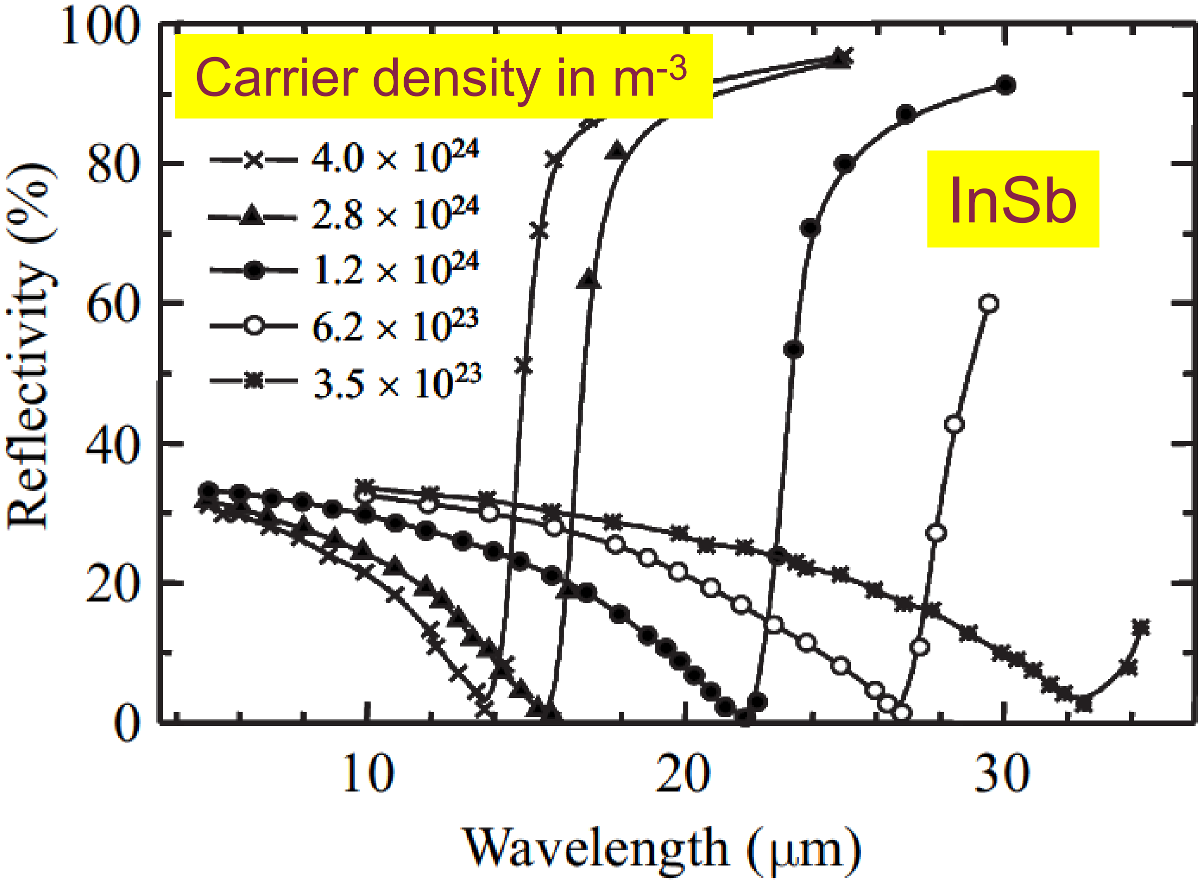
57 **La** Lanthanum 138.90547	58 **Ce** Cerium 140.116	59 **Pr** Praseodymium 140.90765	60 **Nd** Neodymium 144.242	61 **Pm** Promethium (145)	62 **Sm** Samarium 150.36	63 **Eu** Europium 151.964	64 **Gd** Gadolinium 157.25	65 **Tb** Terbium 158.92535	66 **Dy** Dysprosium 162.500	67 **Ho** Holmium 164.93032	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

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* ($B\neq 0$).

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})**

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.