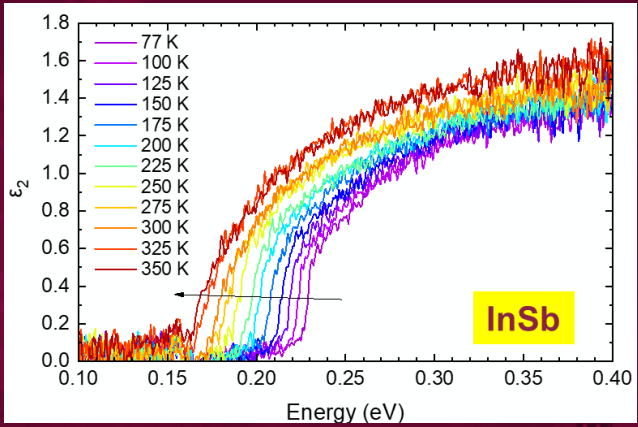
FA9550-20-1-0135 AFOSR
FA9550-24-1-0061 AFOSR
FA9453-23-2-0001 AFRL
DMR-2235447 NSF
DMR-2423992 NSF

Measurements of temperature-dependent optical constants with spectroscopic ellipsometry and comparison with theory



Stefan Zollner

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WWW: http://femto.nmsu.edu
(See lecture series)

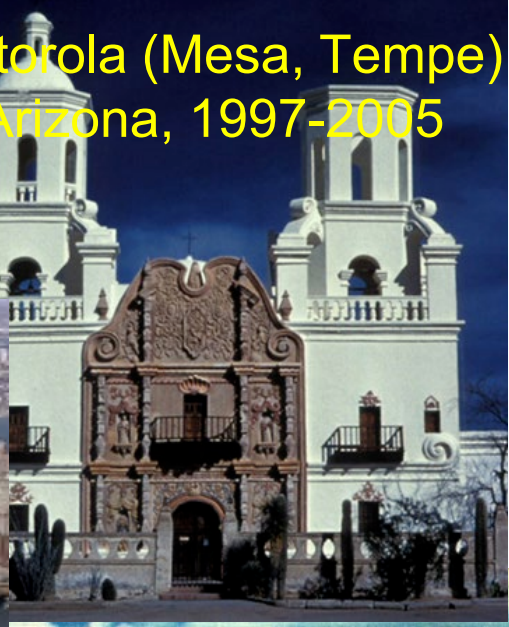
BE BOLD. Shape the Future.

August 25th, 2025, Colloquium

Biography

Regensburg/Stuttgart
Germany

Motorola (Mesa, Tempe)
Arizona, 1997-2005



Freescale, IBM
New York, 91-92; 07-10

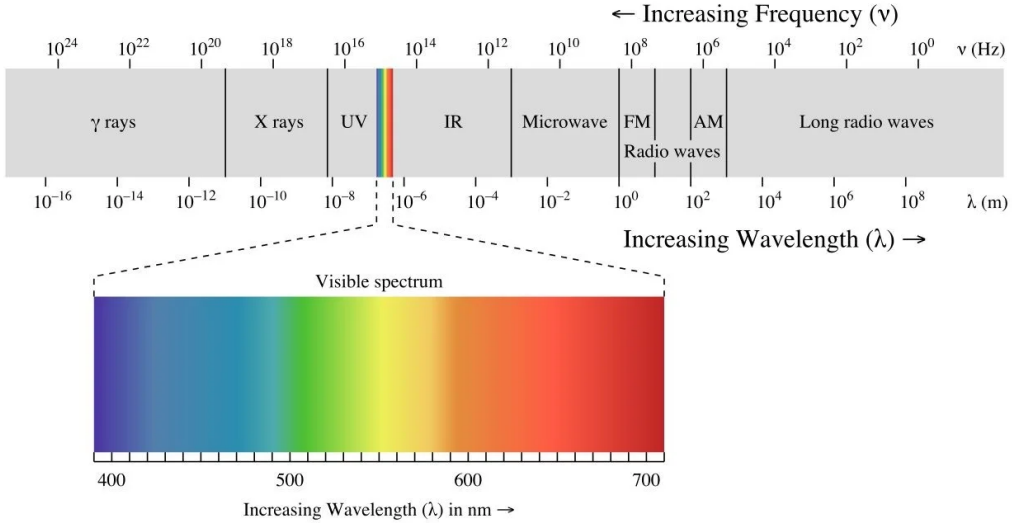
NMSU
Las Cruces, NM
Since 2010

Motorola, Freescale
Texas, 2005-2007

Students and Collaborators (2010-2025)

PhD. students (10): Lina S. Abdallah, Nalin Fernando, Nuwanjula S. Samarasingha, Farzin Abadizaman, Carola Emminger, Rigo A. Carrasco, Carlos A. Armenta, **Yoshitha Hettige, Sonam Yadav**, **Beata Hroncova**.
MS students (5): Travis I. Willett-Gies, Cesar A. Rodriguez, Jaden R. Love, **Haley B. Woolf**, **Aaron Lopez Gonzalez**.
Undergraduate students (22): Amber Medina, Maria Spies, Cayla Nelson, Eric DeLong, Christian Zollner, Khadijih Mitchell, Ayana Ghosh, T. Nathan Nunley, Laura G. Pineda, Luis A. Barrera, Dennis P. Trujillo, Jaime M. Moya, Jacqueline A. Cooke, Alexandra P. Hartmann, Cesy M. Zamarripa, Zachary Yoder, Pablo P. Paradis, Melissa Rivero Arias, Atlantis K. Moses, Danissa P. Ortega, **Gabriel Ruiz**, **Meghan Worrell**.
Ellipsometry collaborators: Jose Menendez (Arizona State), Arnold M. Kiefer (AFRL/RY), Mathias Schubert (Nebraska), Premysl Marsik (Fribourg), Christian Bernhard (Fribourg), Igal Brener (Sandia), Wim Geerts (Texas State), Tom Tiwald (JAW), Preston Webster (AFRL/RV), Martin Veis, **Jan Hrabovsky** (Charles University), Dagmar Chvostova, Alexandr Dejneka, Marina Tyunina (IOP/CAS).
Thin-film epitaxial samples from many different sources: Arizona State, Delaware, Texas, IIT Indore, Texas State, AFRL/RY+RV, Arkansas, Sandia, NREL, NASA, SOITEC, QuantTera, Connecticut, IBM, Global Foundries, UNM, Ohio State, **UCSB**, etc.

Electromagnetic Spectrum



An electromagnetic wave interacts with positive and negative charges through the Coulomb force.

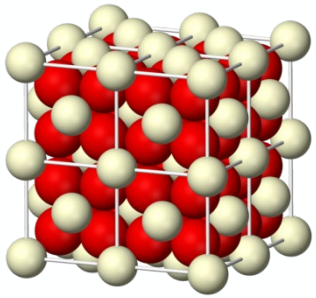
Infrared:

Lattice vibrations (phonons), free carriers (Drude response)

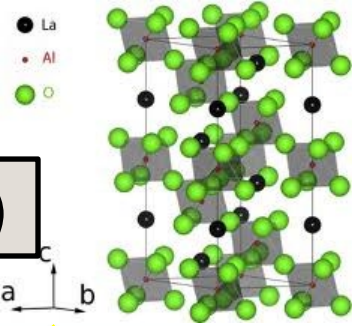
Visible and UV:

Valence electrons, electronic band structure (electrons, holes, interband transitions, critical points)

X-rays: Core electrons; Gamma-rays: Nuclear processes



Solid State Physics (Crystalline)



Crystal Structure (Point & Space Group)

Electrons ⟷ **Phonons**

Defects

0.2-10 eV

10-80 meV

Near-IR, VIS, UV

Far-IR to mid-IR

Ashcroft & Mermin: Solid-State Physics

Magnetism

Superconductivity

Excitons

Plasmons

Surfaces

Topological Insulators

Transport

Polaritons

CMOS

RF

Power

Analog

an Zo

Magnetic Storage

Series 1

Catalysis

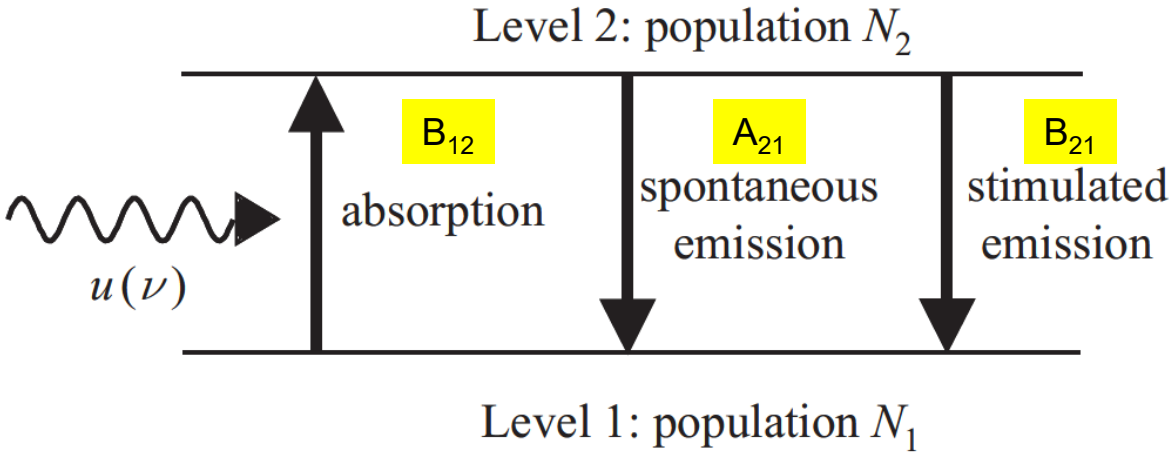
Photovoltaics

Energy Conversion

Lasers

Sensors

Einstein Coefficients for Interaction Processes



One coefficient is sufficient:

$$g_1 B_{12} = g_2 B_{21}$$

$$A_{21} = \frac{2\hbar\omega^3}{\pi c^3} B_{21}$$

In equilibrium: N_1, N_2 constant.
Absorption and emission balance.
Black-body radiation $u(\hbar\omega)$

$$B_{12} N_1 u(\hbar\omega) = A_{21} N_2 + B_{21} N_2 u(\hbar\omega)$$

Use Fermi's Golden Rule to calculate B_{12}

Albert Einstein, *Strahlungs-Emission und Absorption nach der Quantentheorie*, DPG Verh. **18**, 318 (1916); Phys. Z. **18**, 121 (1917).

Microscopic Maxwell's Equations (in Vacuum)

- Electric field strength **E**(**r**)
- Magnetic field strength **H**(**r**)
- Current density **j**(**r**), charge density ρ(**r**)
- Permittivity of free space ε_0, permeability of free space μ_0.

$$\vec{\nabla} \cdot \vec{E} = \frac{\rho}{\varepsilon_0} = 0 \qquad \text{Gauss' Law (Coulomb)}$$

$$\vec{\nabla} \cdot \vec{H} = 0 \qquad \text{Gauss' Law (magnetic field)}$$

$$\vec{\nabla} \times \vec{E} = -\mu_0 \frac{\partial \vec{H}}{\partial t} \qquad \text{Faraday's Law (Lenz)}$$

$$\vec{\nabla} \times \vec{H} = \vec{j} + \varepsilon_0 \frac{\partial \vec{E}}{\partial t} = \varepsilon_0 \frac{\partial \vec{E}}{\partial t} \qquad \text{Ampere's Law}$$

$$\vec{\nabla}^2 \vec{E} - \frac{1}{c^2} \frac{\partial^2 \vec{E}}{\partial t^2} = 0$$

$$\vec{\nabla}^2 \vec{H} - \frac{1}{c^2} \frac{\partial^2 \vec{H}}{\partial t^2} = 0$$

- Homogeneous (in vacuum), linear, first-order, constant coefficients, partial DEQ.
- Vector analysis can be used (Stokes' Theorem) to transform Maxwell's equations into integral form.
- Introduce speed of light
- Units: MKSA (SI).

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}}$$

Jackson, E&M, 1975

Plane-wave solutions to Maxwell's Equations

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

- Select **k** along the z-axis. Then two field components E_x and E_y are sufficient.

$$\vec{E}(\vec{r},t) = \begin{pmatrix} E_{0x} \\ E_{0y} \end{pmatrix} \exp[i(kz - \omega t)]$$

- **An EM wave is described by seven (7) real quantities:**
  - Direction of wave vector (two angles ϕ and θ).
  - Magnitude of wave vector (and angular frequency).
  - Two complex amplitudes E_{0x} and E_{0y} (**Jones vector**).
  - One of these (**absolute phase**) cannot be measured; leaving six parameters.

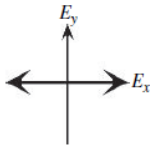
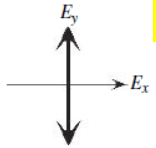
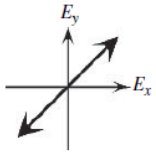
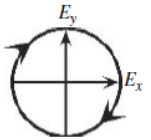
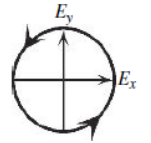
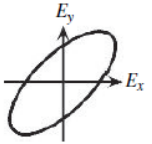
J. Humlicek, in Tompkins & Irene (Handbook of Ellipsometry)

$$\begin{pmatrix} E_{0x} \\ E_{0y} \end{pmatrix} = E_0 \begin{pmatrix} X \exp i\Delta_X \\ Y \exp i\Delta_Y \end{pmatrix} = E_0 \begin{pmatrix} \sin\psi \exp i\Delta \\ \cos\psi \end{pmatrix} \exp i\Delta_y$$

Jones vector

- We don't care about the **light intensity** and the **absolute phase**.
- **ψ and Δ are called the ellipsometric angles; describe polarization of wave.**
- $\psi = \arctan(X/Y)$; $\Delta = \Delta_X - \Delta_Y$; $\rho = \tan\psi \exp(i\Delta)$;

Polarized Light; Jones Vectors

Polarization	Polarization state	Jones vector	Stokes vector
Linear polarization parallel to x axis		p-polarized $\begin{bmatrix}1\\0\end{bmatrix}$	$\begin{bmatrix}1\\1\\0\\0\end{bmatrix}$
Linear polarization parallel to y axis		s-polarized $\begin{bmatrix}0\\1\end{bmatrix}$	$\begin{bmatrix}1\\-1\\0\\0\end{bmatrix}$
Linear polarization oriented at 45°		45° linear $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\1\end{bmatrix}$	$\begin{bmatrix}1\\0\\1\\0\end{bmatrix}$
Right-circular polarization		right-circular $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\i\end{bmatrix}$	$\begin{bmatrix}1\\0\\0\\1\end{bmatrix}$
Left-circular polarization		left-circular $\frac{1}{\sqrt{2}}\begin{bmatrix}1\\-i\end{bmatrix}$	$\begin{bmatrix}1\\0\\0\\-1\end{bmatrix}$
Elliptical polarization		elliptical $\begin{bmatrix}\sin\psi\exp(i\Delta)\\\cos\psi\end{bmatrix}$	$\begin{bmatrix}1\\-\cos 2\psi\\\sin 2\psi\cos\Delta\\-\sin 2\psi\sin\Delta\end{bmatrix}$

$\Delta=0$
$\psi=\pi/2$

$\Delta=0$
$\psi=0$

$\Delta=0$
$\psi=\pi/4$

$\Delta=-\pi/2$
$\psi=\pi/4$

$\Delta=\pi/2$
$\psi=\pi/4$

$-\pi\leq\Delta\leq\pi$
$0\leq\psi\leq\pi/2$

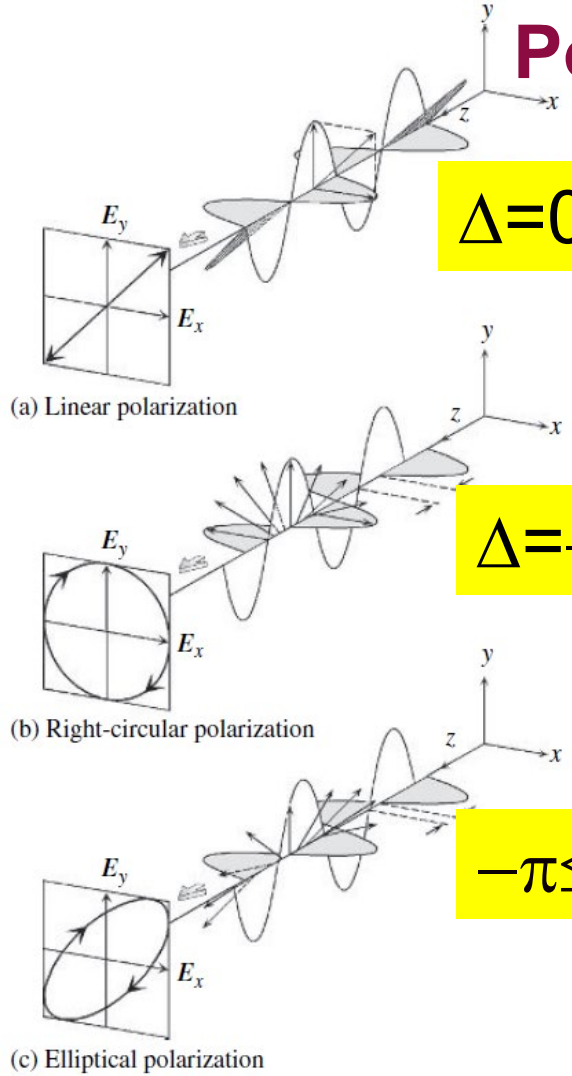
Jones Vector

$$\begin{pmatrix}\sin\psi\exp i\Delta\\\cos\psi\end{pmatrix}$$

The polarization state of polarized light can be described with two parameters **ψ and Δ** called **ellipsometric angles.**

H. Fujiwara

Polarized Light; Jones Vectors



$\Delta=0$

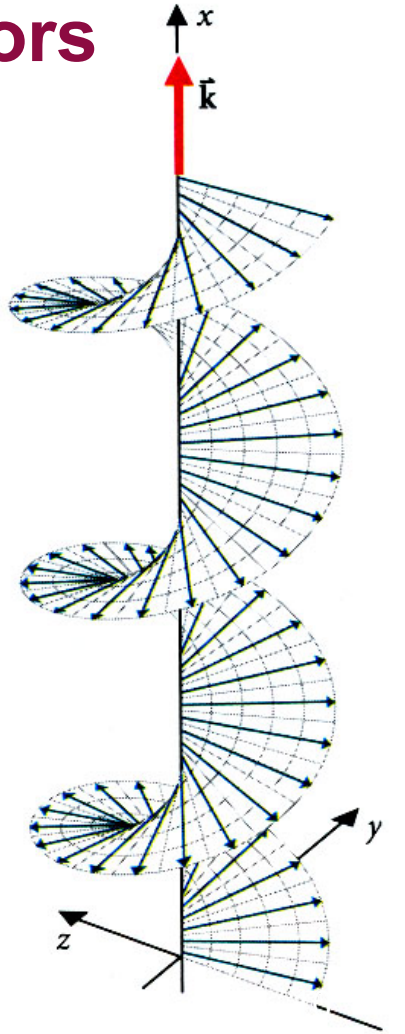
$\Delta=-\pi/2$

$-\pi\leq\Delta\leq\pi$

Jones Vector

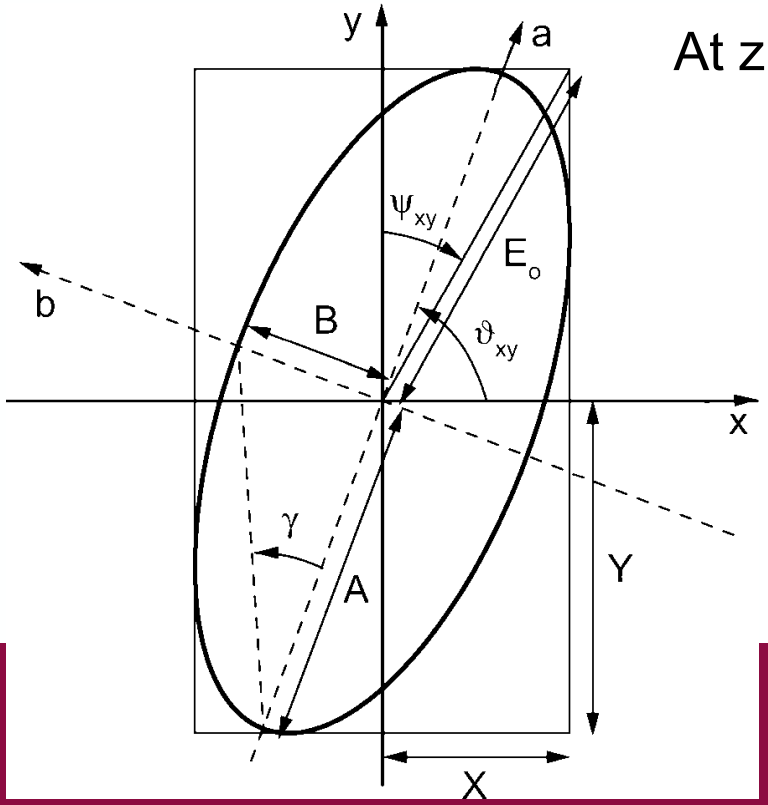
$$\begin{pmatrix} \sin\psi \exp i\Delta \\ \cos\psi \end{pmatrix}$$

Angle ψ:
Direction of linear polarization



Polarization Ellipse

$$\vec{E}(z=0,t) = E_0 \begin{pmatrix} \sin\psi \exp i\Delta \\ \cos\psi \end{pmatrix} \exp[-i\omega(t-\tau)t]$$



At z=0, the electric field vector traces out an ellipse.

Parameters of the ellipse:

- **Azimuth** ϑ
- Ratio tanγ major/minor axis
  Ellipticity e=tanγ=B/A

can be calculated from ψ,Δ.

Maxwell's Equations for Continuous Media

$$\vec{\nabla}\cdot\vec{D}=\rho=0$$ Gauss' Law (Coulomb)

$$\vec{\nabla}\cdot\vec{B}=0$$ Gauss' Law (magnetic field)

$$\vec{\nabla}\times\vec{E}=-\frac{\partial\vec{B}}{\partial t}$$ Faraday's Law

$$\vec{\nabla}\times\vec{H}=\vec{j}+\frac{\partial\vec{D}}{\partial t}=\frac{\partial\vec{D}}{\partial t}$$ Ampere's Law

Anisotropic wave equation:

Take curl on both sides in Ampere's Law and Faraday's Law

$$\Delta\vec{E}-\vec{\nabla}\left(\vec{\nabla}\cdot\vec{E}\right)=\mu_0\frac{\partial}{\partial t}\vec{\nabla}\times\mu\vec{H}$$

$$\Delta\vec{H}-\vec{\nabla}\left(\vec{\nabla}\cdot\vec{H}\right)=-\varepsilon_0\frac{\partial}{\partial t}\vec{\nabla}\times\varepsilon\vec{E}$$

The terms in red do not vanish (cannot be simplified) in anisotropic media.

Usually, μ=1 (crystal optics).

Isotropic wave equation:

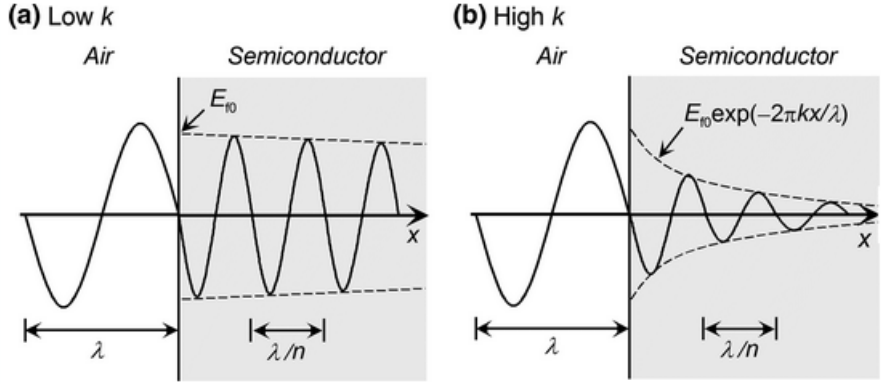
$$\Delta\vec{E}=\frac{\epsilon\mu}{c^2}\frac{\partial^2}{\partial t^2}\vec{E}$$

$$v_{\text{phase}}=\frac{c}{\sqrt{\varepsilon\mu}}=\frac{c}{n\sqrt{\mu}}$$

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

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.

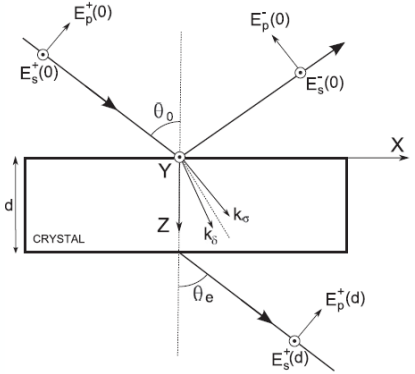
Snell: $\frac{\sin\theta_1}{\sin\theta_2} = \frac{n_1}{n_2}$

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
Orteaga, TSF 571, 701 (2014).

Maxwell's Equations for Plane Waves (μ=1): Crystal Optics

$\vec{k} \cdot \vec{D}_0 = 0$ Gauss' Law (Coulomb)

$\vec{k} \cdot \vec{B}_0 = 0$ Gauss' Law (magnetic field)

$\vec{k} \times \vec{E}_0 = \omega \vec{B}_0$ Faraday's Law

$\vec{k} \times \vec{H}_0 = -\omega \vec{D}_0$ Ampere's Law

$$\vec{D}_0(\vec{k},\omega) = \varepsilon_0 \varepsilon(\vec{k},\omega)\vec{E}_0(\vec{k},\omega)$$
$$\vec{B}_0(\vec{k},\omega) = \mu_0 \mu(\vec{k},\omega)\vec{H}_0(\vec{k},\omega)$$

For μ=1: Algebraic equation for ***E***, from which ***H*** can be calculated.

Anisotropic wave equation:

$$\left|\vec{k}\right|^2 \vec{E}_0 - (\vec{k} \cdot \vec{E}_0)\vec{k} = \frac{\omega^2}{c^2}\varepsilon \vec{E}_0$$
$$\left|\vec{k}\right|^2 \vec{H}_0 = -\varepsilon_0 \omega \vec{k} \times \varepsilon \vec{E}_0$$

Berreman & Yeh 4x4 transfer matrix for (***E***,***H***).

Isotropic wave equation:

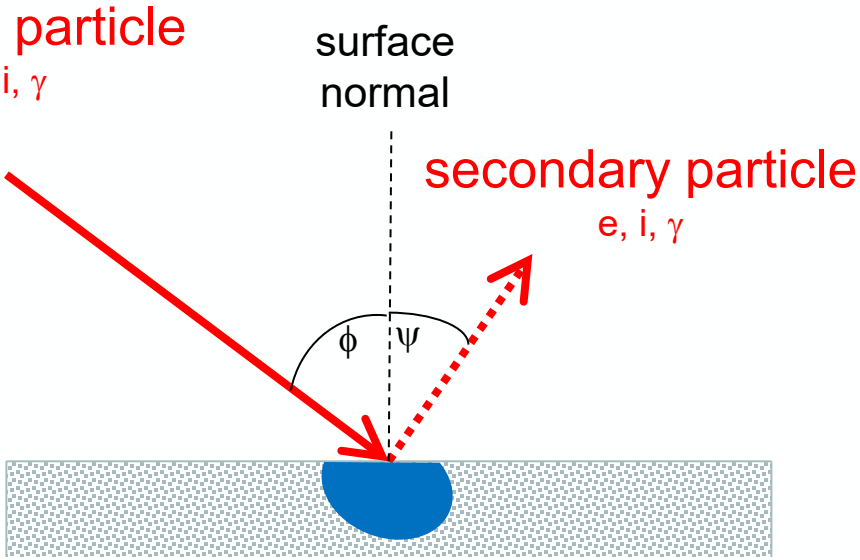
$$\left|\vec{k}\right|^2 = \varepsilon\mu \frac{\omega^2}{c^2}$$

$$v_{\text{phase}} = \frac{c}{\sqrt{\varepsilon\mu}} = \frac{c}{n\sqrt{\mu}}$$

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

Agranovitch & Ginzburg, Crystal Optics

Classification Schemes for Surface Spectroscopy I



Ellipsometry:
Photon in,
Photon out

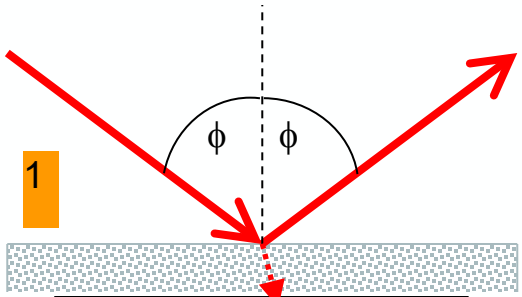
Particles: Electron (e), ion (i), or photon (γ)

The term **spectroscopy** implies that we prepare, vary, or measure the **energy (wavelength)** and/or **momentum** (**direction**) of the primary and/or secondary particle.

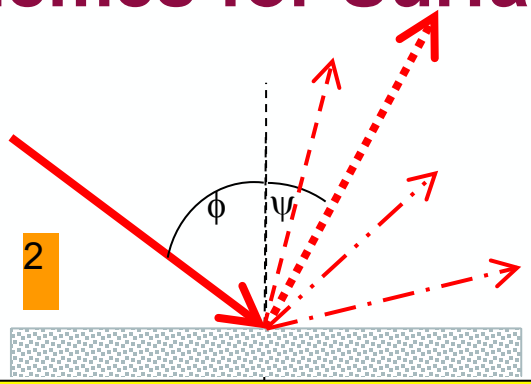
For **photons**, we can also measure the **polarization** of the primary and/or secondary photon.

The **interaction depth** for thin films depends on the **penetration depth** of the primary particle and the **escape depth** of the secondary particle. (This can be nanometers to micrometers, depends on each technique.)

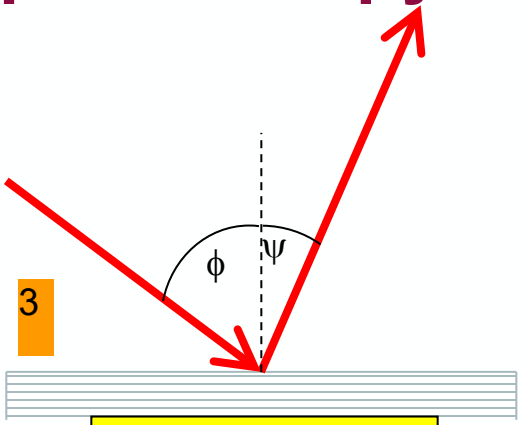
Classification Schemes for Surface Spectroscopy II



Reflection:
Ellipsometry, XRR



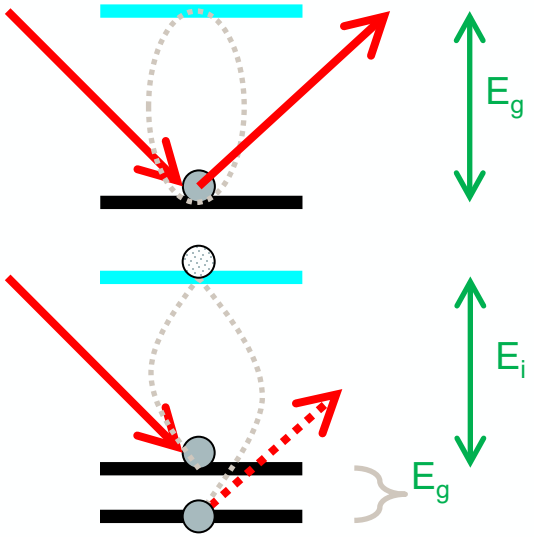
Diffuse reflection/scattering:
PL, Raman, SIMS, Auger, XPS



Diffraction: XRD

1. **Specular reflection:** The angle of reflection is equal to the angle of incidence. For some spectroscopies, the angles are measured relative to the surface (XRR), for others relative to the surface normal (SE).
2. **Diffuse reflection or scattering:** There is no well-defined direction, in which the secondary particle exits. The scattering probability may depend on the angles.
3. **Diffraction:** Requires a periodic (crystalline) layer. There is a well-defined angular relationship between the spacing of the diffraction (Bragg) planes and the momentum of the incident/diffracted beams.

Classification Schemes for Surface Spectroscopy III



Elastic: The intensity of the reflected (relative to the incident) beam depends on the excited states of the system (band gaps).

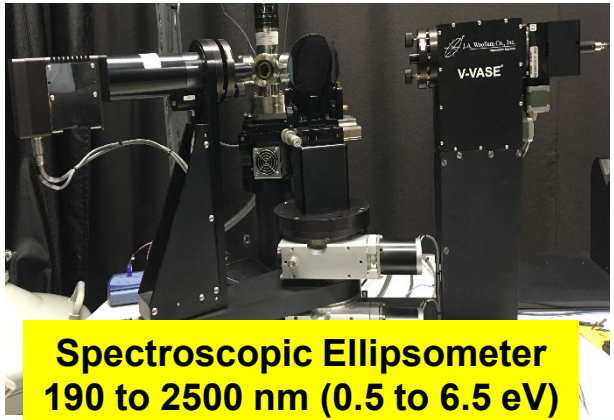
Inelastic: The energy difference (gain or loss) provides information about vibrational (Raman) or electronic (Auger) energy states. The strength of the scattering process depends on the interaction with an intermediate state.

- **Elastic scattering:**
  The energy of the incident particle equals that of the scattered particle.
- **Inelastic scattering:** The two energies are different, depending on the energy gained or lost by the interaction with the thin film.

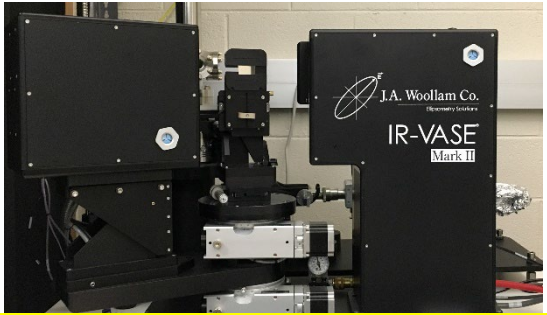
Classification Schemes for Surface Spectroscopy IV

- **Spectroscopic Ellipsometry:** Elastic, specular, $\gamma \rightarrow \gamma$
  Thickness, Energy (band gap), refractive index, composition
- X-ray reflectivity: Elastic, specular, $\gamma \rightarrow \gamma$
  Thickness, density, surface/interface roughness
- X-ray diffraction: Elastic, diffracted, $\gamma \rightarrow \gamma$
  Lattice constant, stress/strain, composition
- UV Raman Spectroscopy: Inelastic, scattered, $\gamma \rightarrow \gamma$
  Vibrational (phonon) energy, composition, stress/strain
- Secondary Ion Mass Spectrometry: Inelastic, scattered, $i \rightarrow i$
  Composition, depth profile (sputtering), doping
- Auger Electron Spectrometry: Inelastic, scattered, $e \rightarrow e$
  Composition, depth profile (sputtering)
- Rutherford backscattering: Inelastic, scattered, $\alpha \rightarrow \alpha$
  Composition, some depth information, primary standard

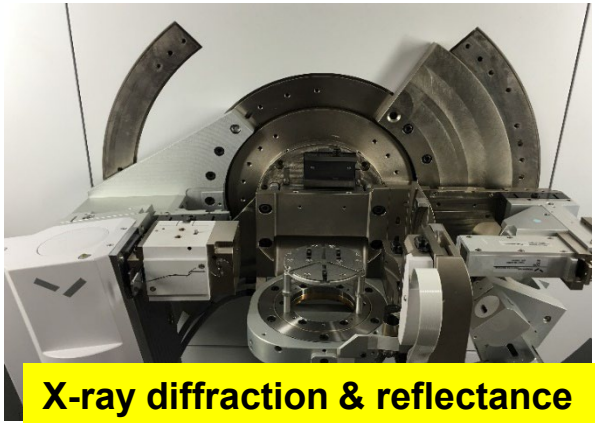
Reflectance Spectroscopy Instrumentation



Spectroscopic Ellipsometer
190 to 2500 nm (0.5 to 6.5 eV)



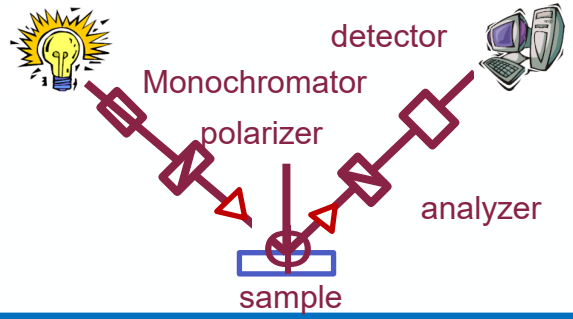
Infrared Ellipsometer
1.25 to 40 μm (250 to 8000 cm^{-1})



X-ray diffraction & reflectance

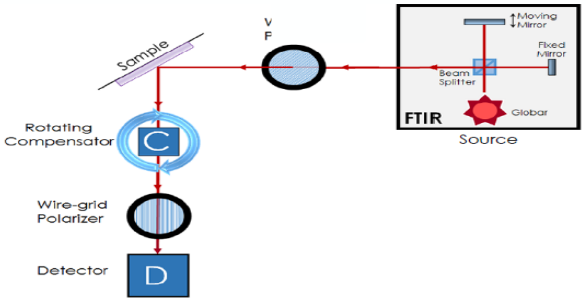
Spectroscopic Ellipsometry:

- Thickness (100 to 10000 Å)
- Absorption, band gap
- Refractive index



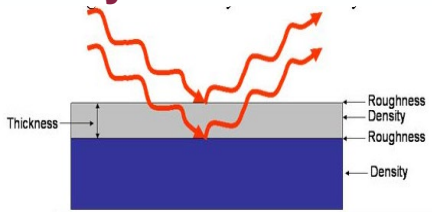
FTIR ellipsometry:

- Very thick films (> 5000 Å)
- Phonon absorption
- Optical Constants



XRD/XRR:

- Crystal structure
- Lattice spacings (strain)
- Thickness (5 Å to 1000 Å)
- Surface, roughness layer
- Density



What happens at an interface?

Electrostatic boundary conditions:

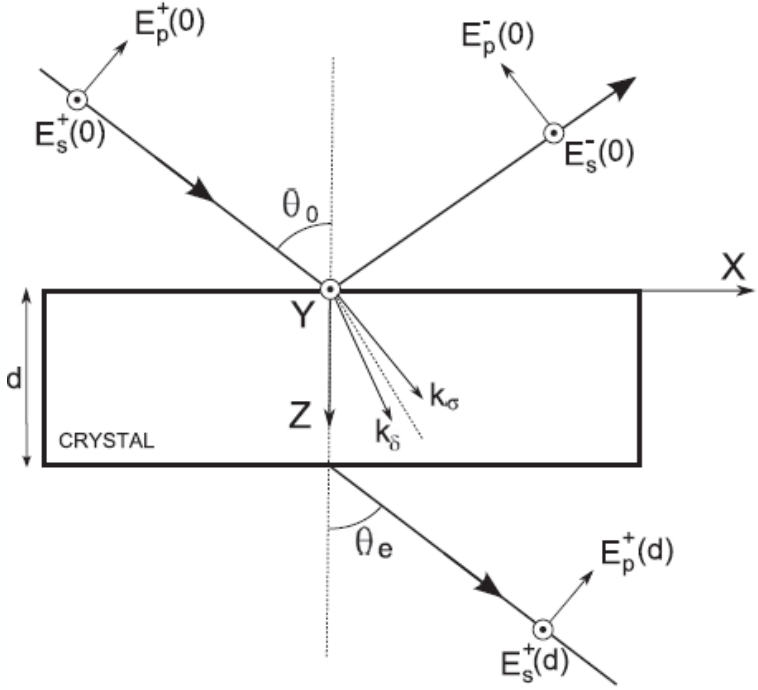
- Normal components of **D** and **B** continuous.
- In-plane components of **E** and **H** continuous.
- Law of Reflection, Snell's Law.
- **Fresnel equations (isotropic):**

$$r_s = \frac{n_1 \cos\theta_i - n_2 \cos\theta_t}{n_1 \cos\theta_i + n_2 \cos\theta_t},$$

$$t_s = \frac{2n_1 \cos\theta_i}{n_1 \cos\theta_i + n_2 \cos\theta_t},$$

$$r_p = \frac{n_2 \cos\theta_i - n_1 \cos\theta_t}{n_2 \cos\theta_i + n_1 \cos\theta_t},$$

$$t_p = \frac{2n_1 \cos\theta_i}{n_2 \cos\theta_i + n_1 \cos\theta_t}.$$



Ellipsometry Measurement

Polarization State
Jones Vector

$$J = \begin{pmatrix} E_{0x} \\ E_{0y} \end{pmatrix}$$

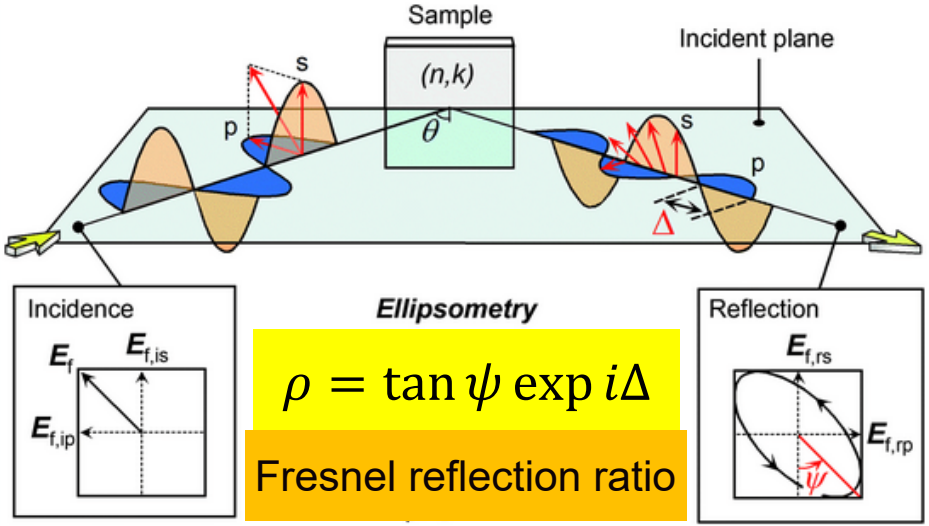
Ellipsometry Experiment

$$J_{\text{out}} = \begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} J_{\text{in}}$$

Fresnel reflection coefficients

$$\begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} = r_{ss} \begin{pmatrix} \rho & \rho_{ps} \\ \rho_{sp} & 1 \end{pmatrix}$$

Isotropic surface:
Off-diagonal elements vanish.



$$\rho = \tan\psi \exp i\Delta$$

Fresnel reflection ratio

Anisotropy or depolarization (not both)

$$\begin{pmatrix} r_{pp} & r_{ps} \\ r_{sp} & r_{ss} \end{pmatrix} = r_{ss} \begin{pmatrix} \rho & 0 \\ 0 & 1 \end{pmatrix}$$

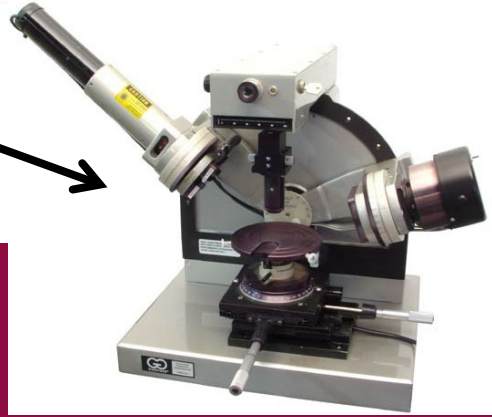
Ellipsometry Instrumentation

VASE: One wavelength at a time:
Calculate derivatives.
Resolve narrow line shapes.

Dual rotating compensator (**RC2**):
Full 4 by 4 Mueller matrix

Fourier-Transform Infrared (**FTIR**)

Single-wavelength ellipsometer



Far-infrared ellipsometer (not shown)
Terahertz ellipsometer (not shown)
VUV ellipsometer (not shown)
Inline (fab) metrology tools
Imaging ellipsometer (Accurion)
What's next ???

Spectroscopic Ellipsometry Research Topics

International Conferences:
1993 (Paris), 1997 (Charleston, SC, USA), 2003 (Vienna), ~~2007 (Stockholm)~~, 2010 (Albany), 2013 (Kyoto), 2016 (Berlin), 2019 (Barcelona), ~~2022 (Beijing)~~, 2025 (Boulder, CO, USA)

1. **Instrumentation** to acquire ellipsometric angles, Jones matrices, or MM elements.
2. **Analysis** of ellipsometry data to determine (isotropic or anisotropic) **optical constants**.
3. Ellipsometry as a **non-destructive characterization** tool: How thick is my film?

S. Zollner in *Ellipsometry at the Nanoscale* ed. by M. Losurdo and K. Hingerl (Springer, Heidelberg, 2013), p. 607-627.

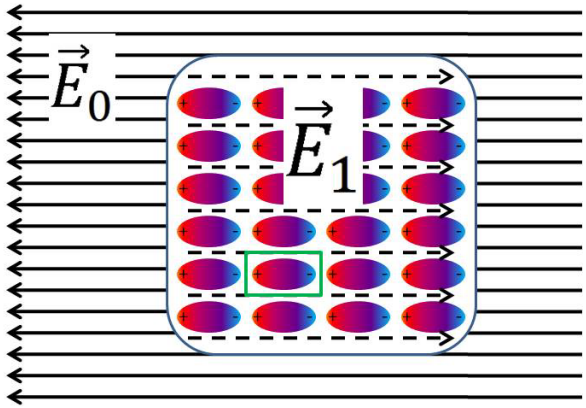
4. **Fundamental mechanisms of light-matter interactions.**

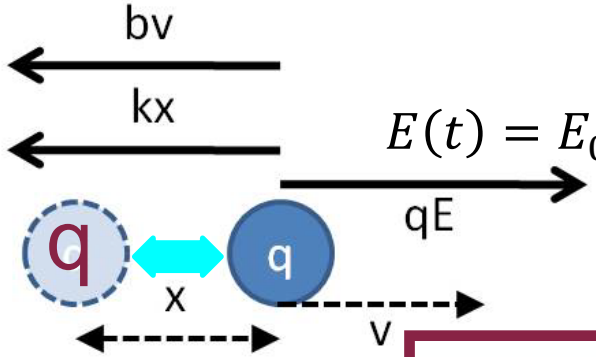
What can the dielectric function tell us about a material?

Outline: Infrared Response of Crystalline Solids

- Lorentz model for absorption by optical phonons in polar crystals.
  - Trends with mass and ionicity.
- Temperature dependence of optical phonon energies:
  - Anharmonic decay of optical phonons.
  - Two-phonon absorption in LiF and NiO.
- Beyond the Lorentz model: Frequency-dependent decay rate
  - Lowndes model (TO/LO oscillator).
- Splitting of optical phonons in uniaxial crystals: ZnO, SiC, NiO
- Multimode behavior in $GaAs_{1-x}P_x$ alloys
- Berreman effect at LO energy: Insulator on metal (LiF on Ag)
- Drude model for free carrier absorption: Ni and Au
- Plasmon-phonon coupling.

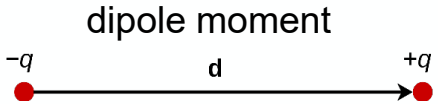
Lorentz Model for Oscillating Charges





Static screening.
Friction proportional to velocity.
Small displacement (harmonic).

$$F = ma$$
$$qE - b\dot{x} - kx = m\ddot{x}$$
$$\text{Try } x(t) = x_0 \exp(-i\omega t)$$
$$x(t) = \frac{-qE_0}{m\omega^2 + ib\omega - k} \exp(-i\omega t)$$
$$P(t) = \chi_e E(t) = \frac{qx(t)}{V}$$
$$\varepsilon = 1 + \chi_e$$



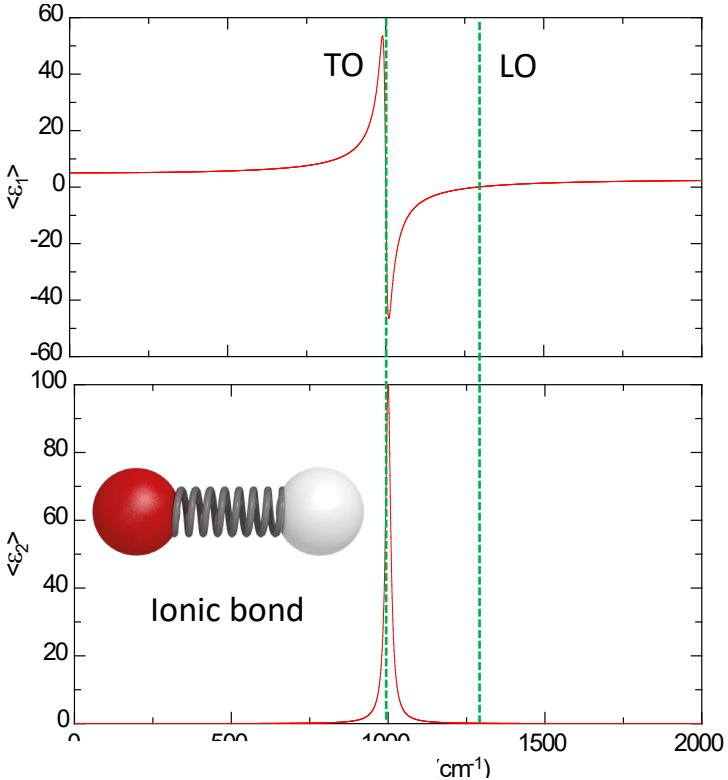
$$\varepsilon(\omega) = 1 + \frac{\omega_P^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

$$\omega_P^2 = \frac{nq^2}{m\varepsilon_0}$$ Charge density

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

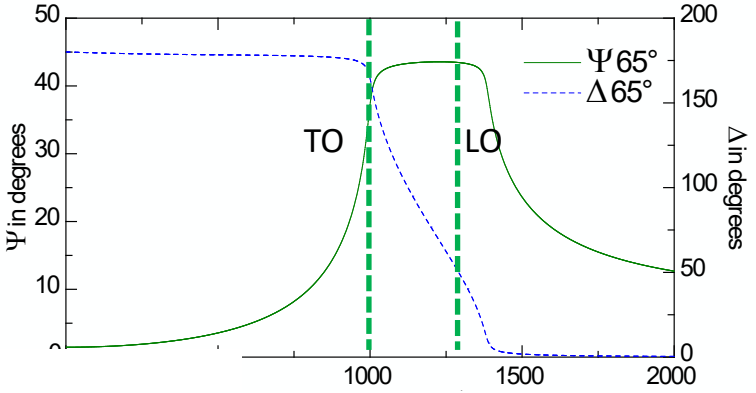
H. Helmholtz, Ann. Phys **230**, 582 (1875)
F. Wooten, *Optical Properties of Solids*, 1972

Lorentz Model for Oscillating Charges



$$\varepsilon(\omega) = \varepsilon_\infty + \frac{A\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma\omega}$$

ε(ω) shows symmetric TO resonance peak.
Loss function Im(–1/ε) peaks at LO frequency.



$$\varepsilon_\infty = 3$$
$$A = 2$$
$$\omega_{TO} = 1000\ \text{cm}^{-1}$$
$$\gamma = 20\ \text{cm}^{-1}$$
$$\omega_{LO} = 1290\ \text{cm}^{-1}$$

F. Wooten, *Optical Properties of Solids*, 1972
M. Schubert, *Infrared Ellipsometry*, 2004

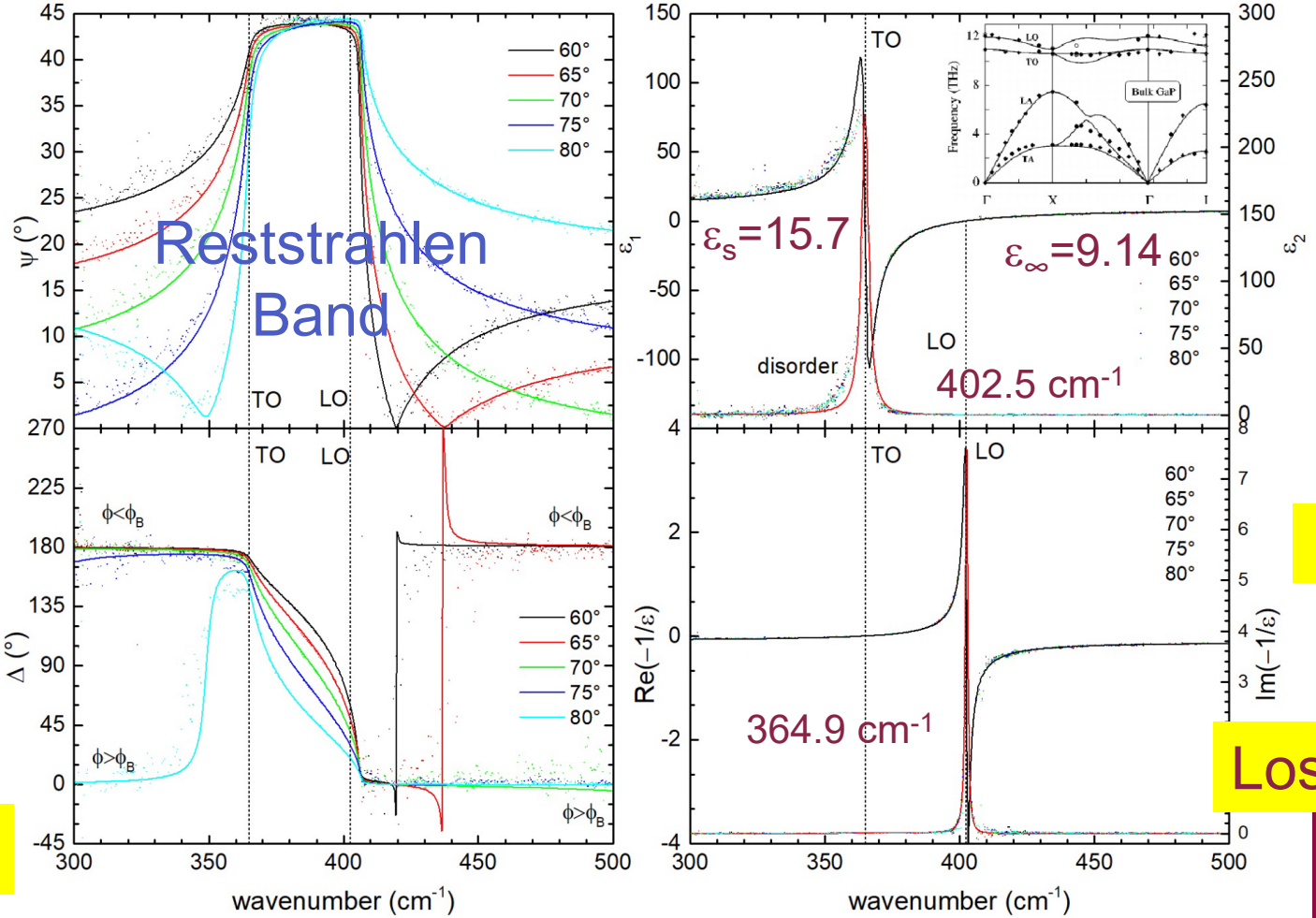
GaP shows nearly perfect Lorentz oscillator

psi

Delta

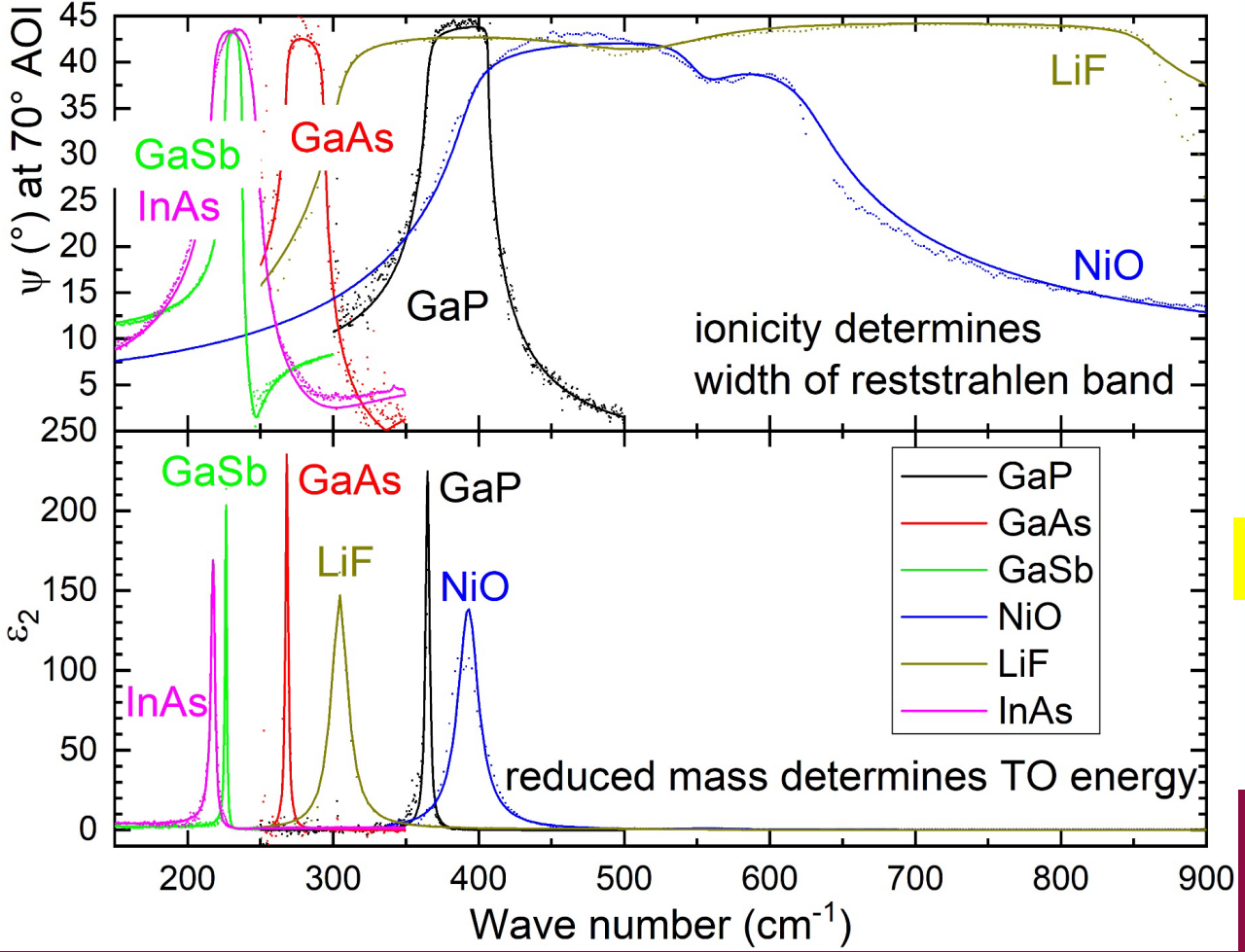
epsilon

Loss function



N. Samarasingha,
JVSTB **39**, 052201 (2021)

Infrared Lattice Vibrations (Lorentz model)



$$\omega_{TO} = \sqrt{\frac{k}{\mu}}$$

N. Samarasingha,
JVSTB **39**, 052201 (2021)

Why Temperature-Dependent Ellipsometry ???

- **Practical applications**: Optical devices at low or high T.
- Peaks get **sharper** at low temperature (easier to detect).
- **Thermal expansion** is trivial (usually small contribution).

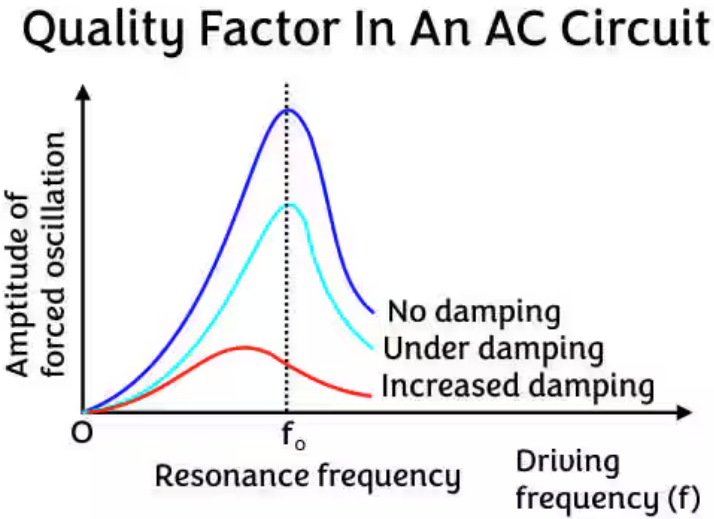
- Finite lifetime: Quality factor decreases (**broadening increases**).
- Temperature decreases the lifetime.

- Damped oscillator is broader and has **lower energy** then undamped oscillator.

- Temperature dependence yields energy of decay product and strength of interaction (**complex self energy**).

- Distinguish intrinsic lifetime (**homogeneous**) broadening from **inhomogenous** broadening (disorder, defects, alloy, etc).
- Inhomogeneous broadening does not change with temperature.

- Phase transitions (Ni Curie temperature, phase change materials).



$$E(T) = E_a - E_b\left[1 + \frac{2}{e^{\frac{\Omega}{kT}} - 1}\right]$$

$$\Delta E \propto 2N + 1$$

L. Viña *et al.*, PRB 30, 1979 (1984).

Tools for Temperature-Dependent Ellipsometry

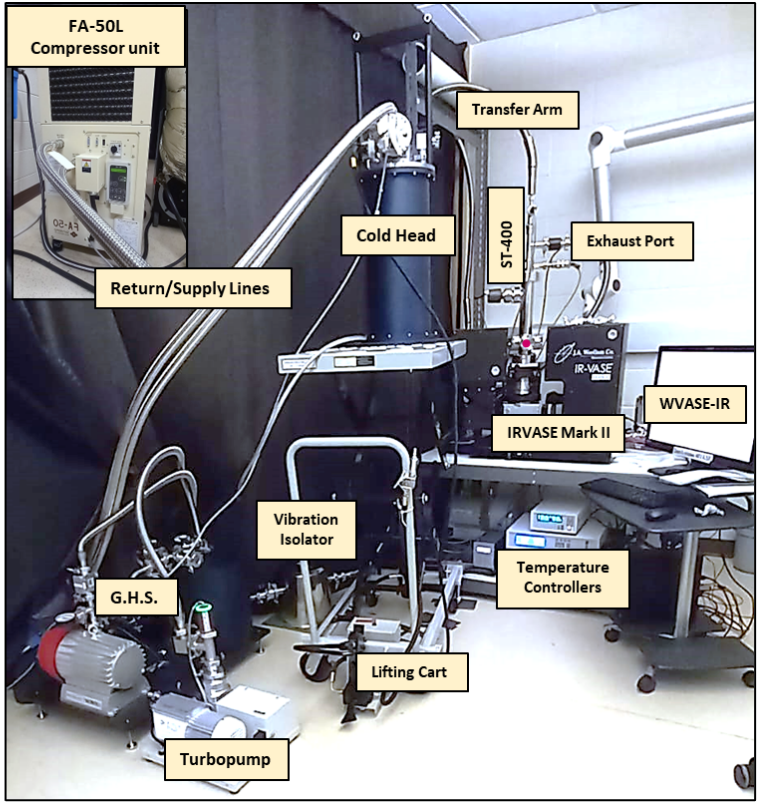
Combined System for Temperature Dependent SE	
FA-50L Helium Compressor Unit	Sumitomo Heavy Industries, Ltd.
RGC4 Cryogen Free Recirculating Gas Cooler	Lake Shore Cryotronics, Inc.
ST-400 Cryostat	Lake Shore Cryotronics, Inc.
IR-VASE Mark II	J.A. Woollam Co.

Sample preparation:

- Samples were mounted using Ag conductive paint.
- Light pressure was applied to maximize contact with the cryostat sample stage.
- The Ag paint cured overnight at room temperature.

Measurement procedure:

- 300 K scans were taken outside of the cryostat.
- The sample was then aligned inside the cryostat.
- Programed an automated temperature series in WVASE-IR.
- Collected data from 300 K to 10 K in 25 K steps with 64 cm^{-1} resolution.



Closed-cycle system works well.

Vibrations do not seem to be a problem.

Ongoing issue: Thin ice layer forms on sample (even in UHV).

Window calibration is important.

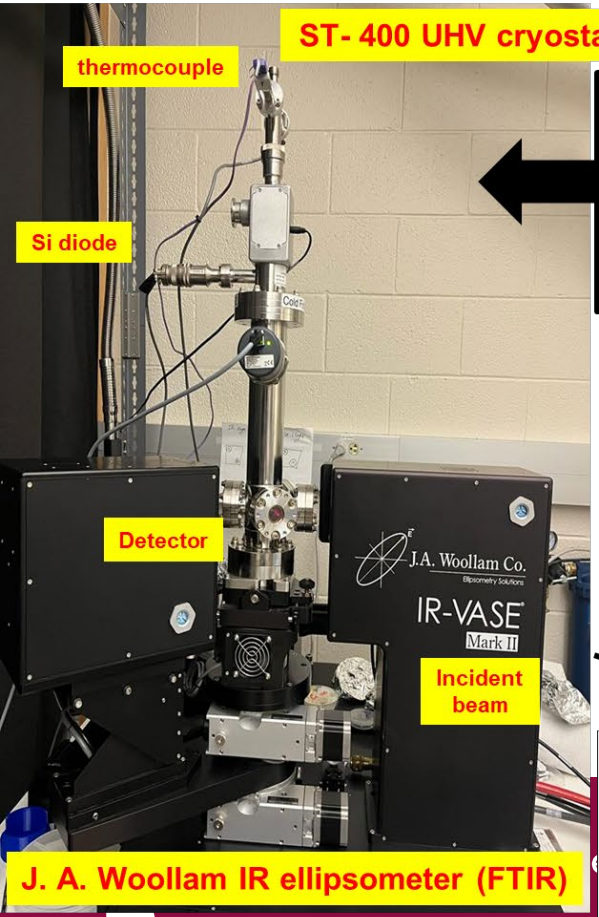
Custom feature: **Diamond windows** for cryostat.

ARO (W911NF-22-2-0130)

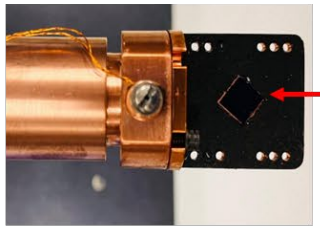
Jaden Love
Atlantis Moses

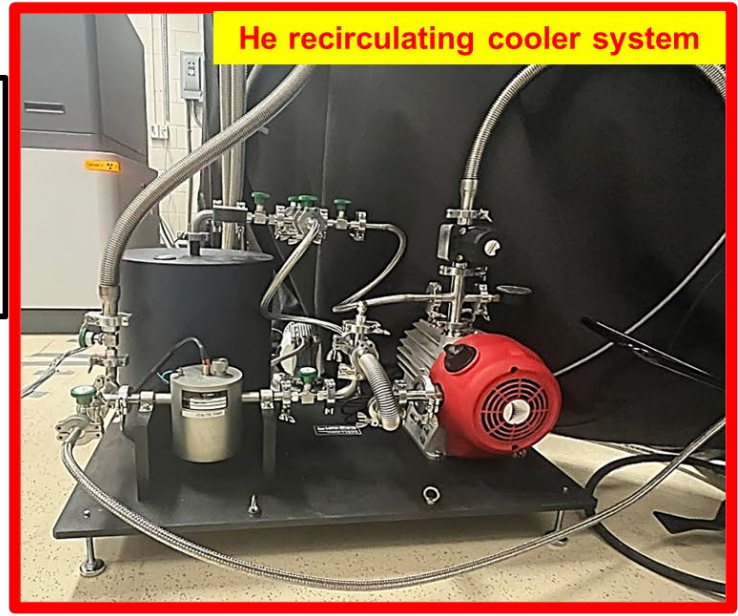
Tools for Temperature-Dependent Ellipsometry

Lake Shore model RGC 4 cryogen free closed cycle refrigerated system

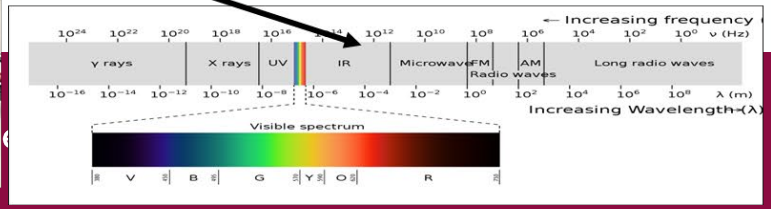


- Temperature range : **25 K to 500 K** (He recirculating cooler).
- Pressure : **10^{-8} Torr**.
- Resolution : **8 cm^{-1}**



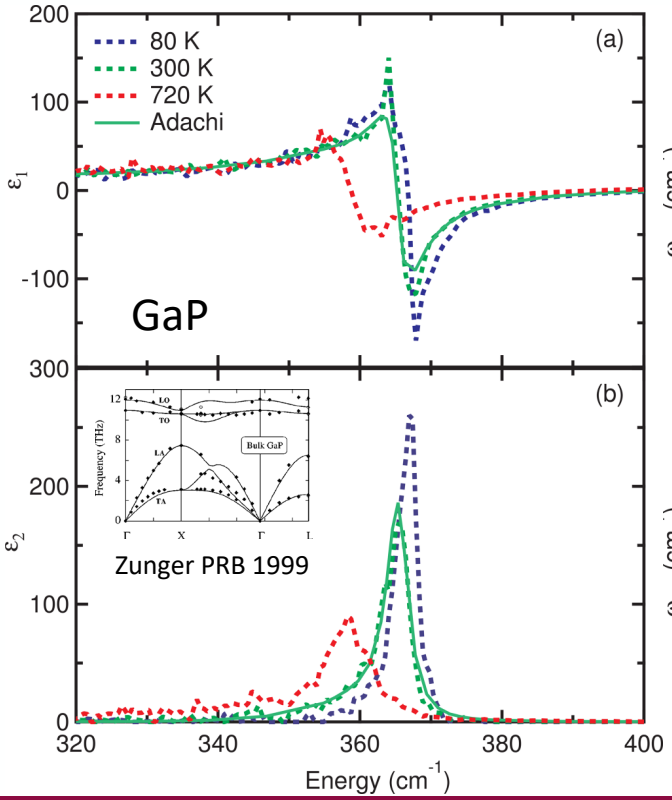


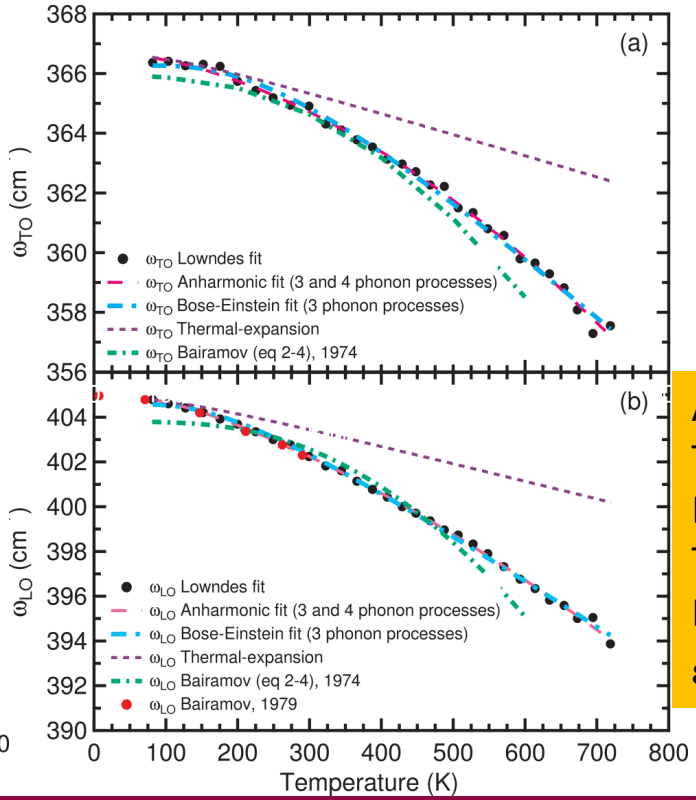
Measured the ellipsometric angles Ψ and Δ of NiO from 250-8000 cm^{-1} at 8 cm^{-1} resolution from 25 to 500 K.

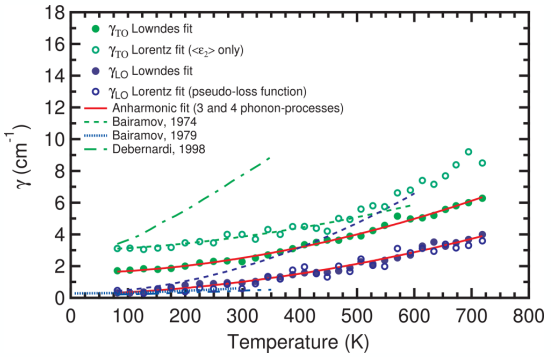


Jaden Love
Atlantis Moses

Temperature dependence of GaP phonon energies





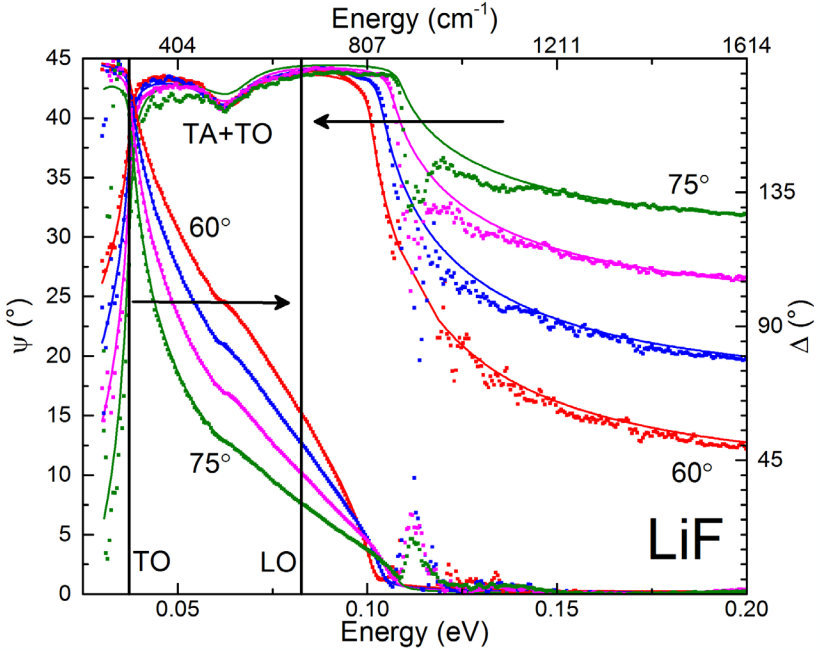


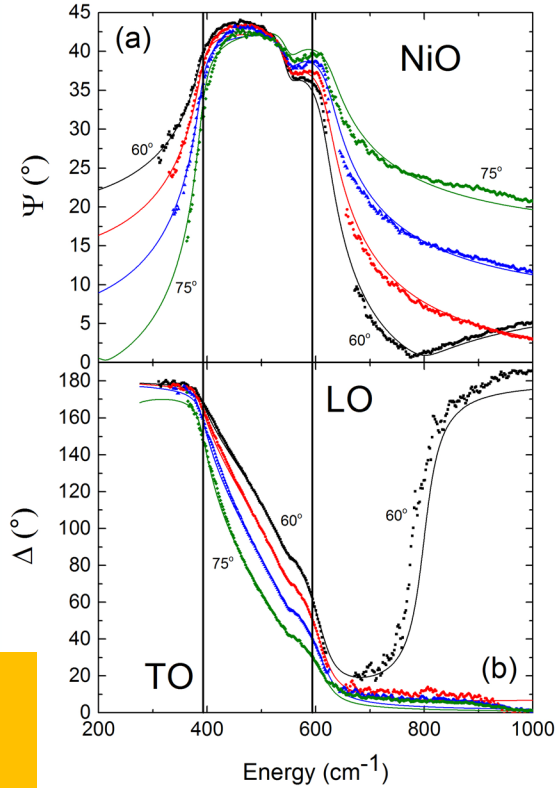
Anharmonic phonon decay:
TO, LO -> TA + LA
Broadenings increase.
TO and LO energies decrease.
Born effective charge: constant.
ε_s, ε_∞ increase (Penn gap)

$$E(T) = E_a - E_b\left[1 + \frac{2}{e^{\frac{\Omega}{kT}} - 1}\right]$$

N. Samarasingha *et al.*, JVSTB **39**, 052201 (2021)

Two-phonon absorption in LiF and NiO





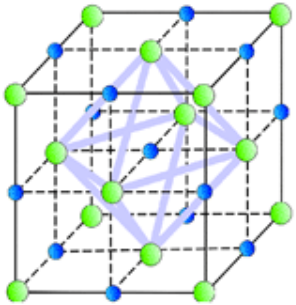
Small absorption in the reststrahlen band causes a dip or terrace.
Compare also with Al, Cu, Au (Fox, *Optical Properties of Metals*).

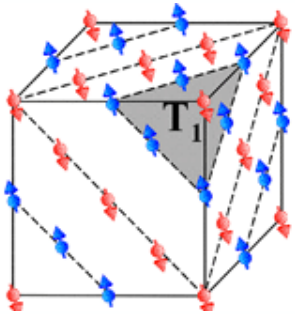
Willett-Gies & Nelson, JVST A **33**, 061202 (2015).
Also Humlicek TSF **313-314**, 687 (1998).

Two-Phonon Absorption in NiO

- Rocksalt crystal structure (FCC), Space group 225 (Fm-3m).
- Single TO/LO phonon pair: Γ_{15}
- Antiferromagnetic ordering along (111), causes phonon splitting (8-30 cm^{-1}).
- **Second-order phonon absorption.**

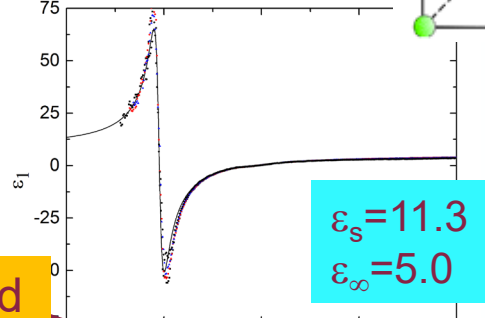
NiO cell



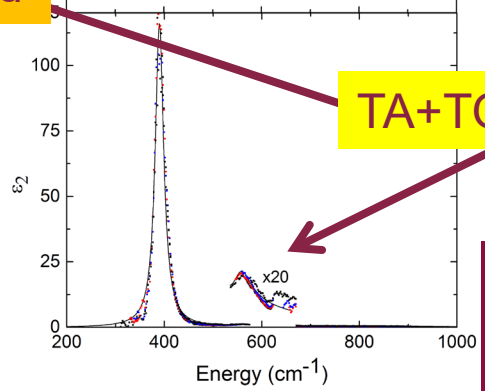


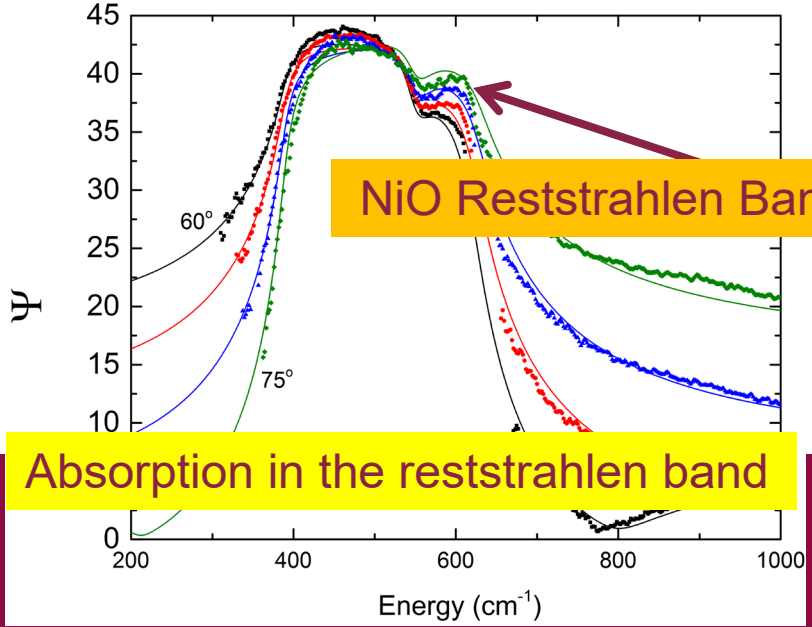
Rooksby, Nature, 1943

TO



ε_s=11.3
ε_∞=5.0





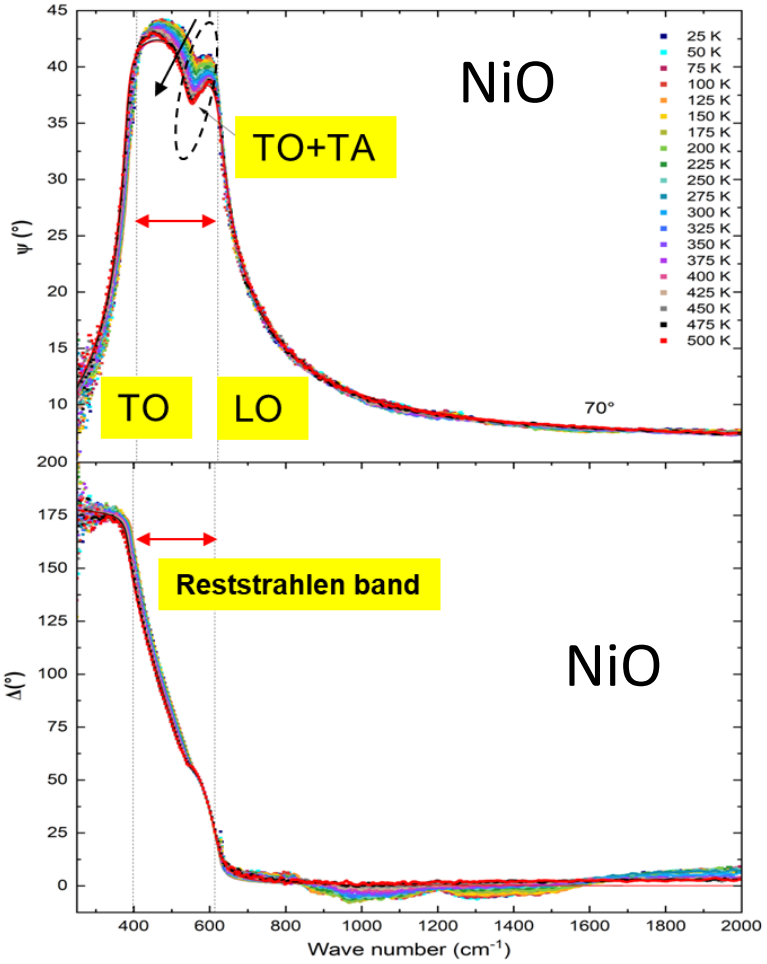
NiO Reststrahlen Band

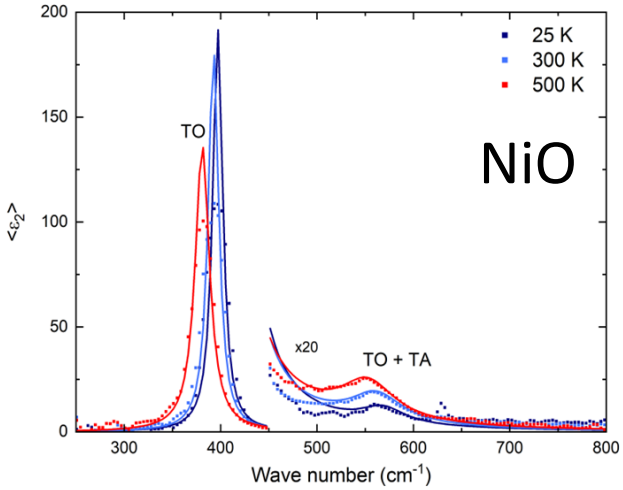
TA+TO phonon

Absorption in the reststrahlen band

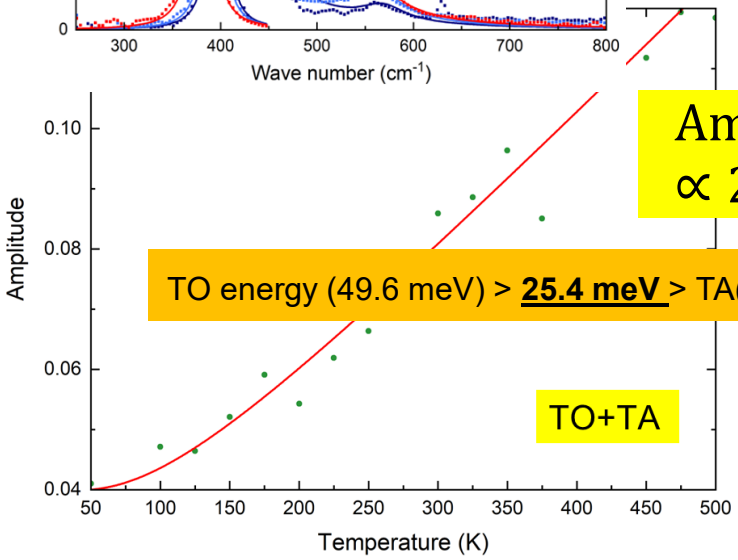
Willett-Gies & Nelson, JVST A **33**, 061202 (2015)

Temperature Dependence of Two-Phonon Absorption





Yoshitha Hettige
(ICSE-10)



$$\text{Amplitude} \propto 2N(\Omega) + 1$$

TO energy (49.6 meV) > **25.4 meV** > TA(X) energy (16.5 meV)

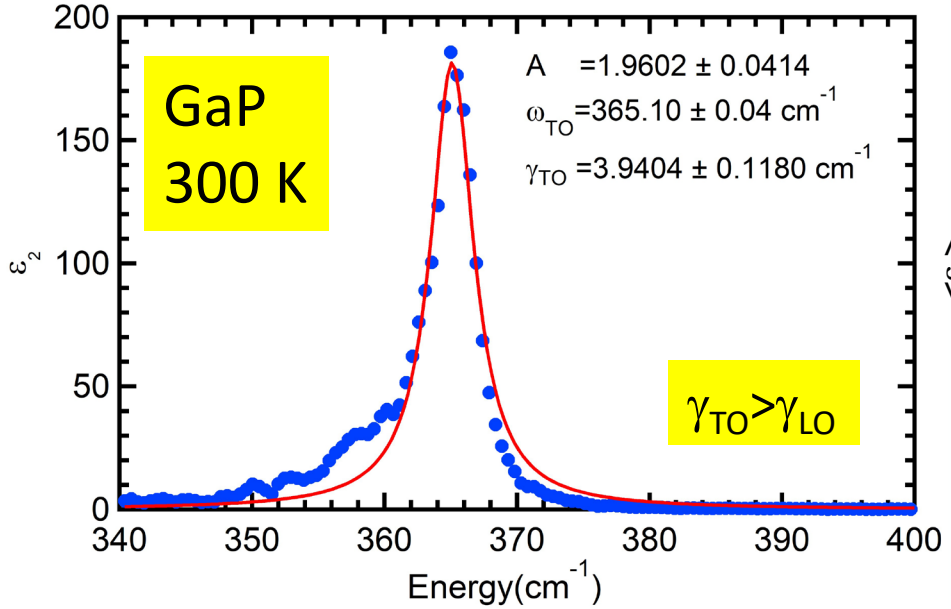
Frequency-Dependent Decay Rate

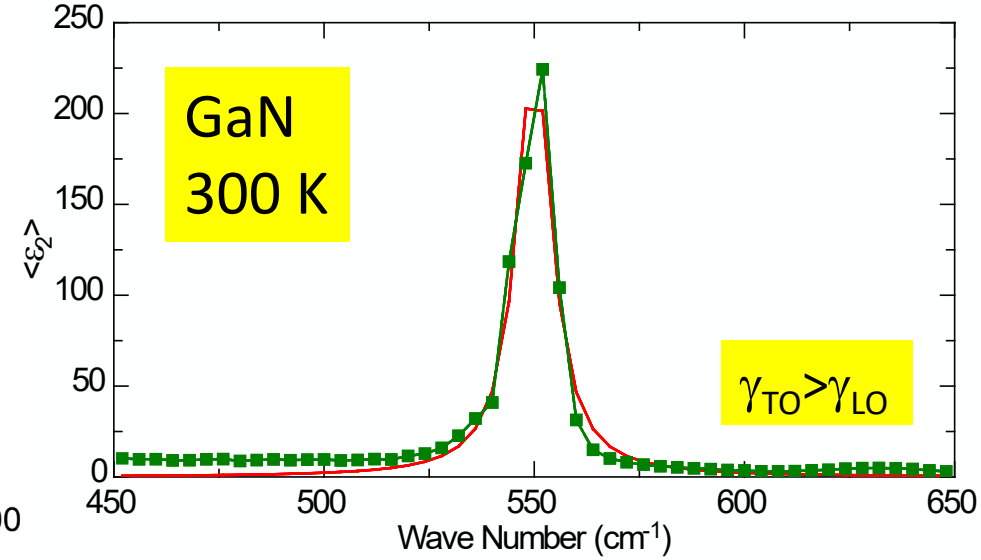
Lorentz oscillator: constant γ

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

$$i\gamma\omega = \omega_{TO}^2 \frac{\varepsilon - \varepsilon_S}{\varepsilon - \varepsilon_\infty} - \omega^2$$

Difficult to evaluate because of noise.





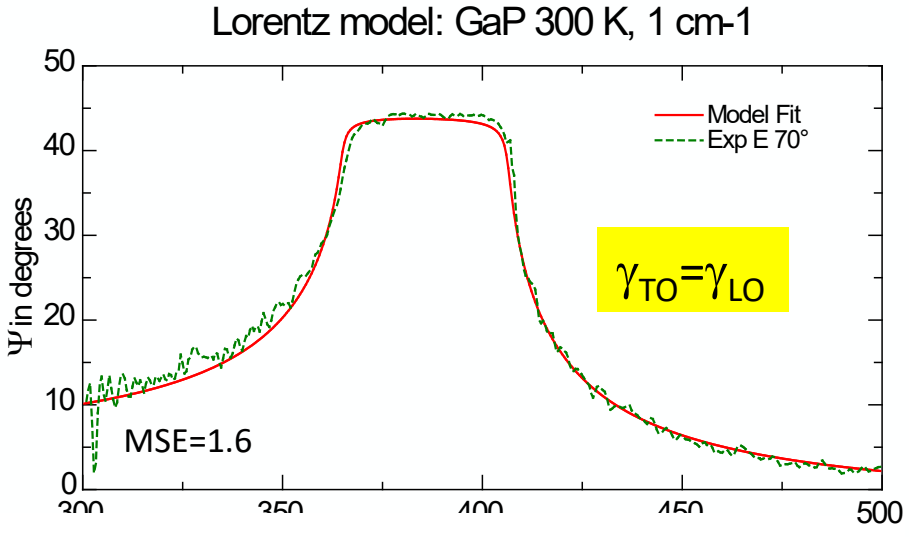
N. Samarasingha *et al.*, JVSTB **39**, 052201 (2021).
E. Baron et al., Phys. Rev. Mater. **3**, 104603 (2019).

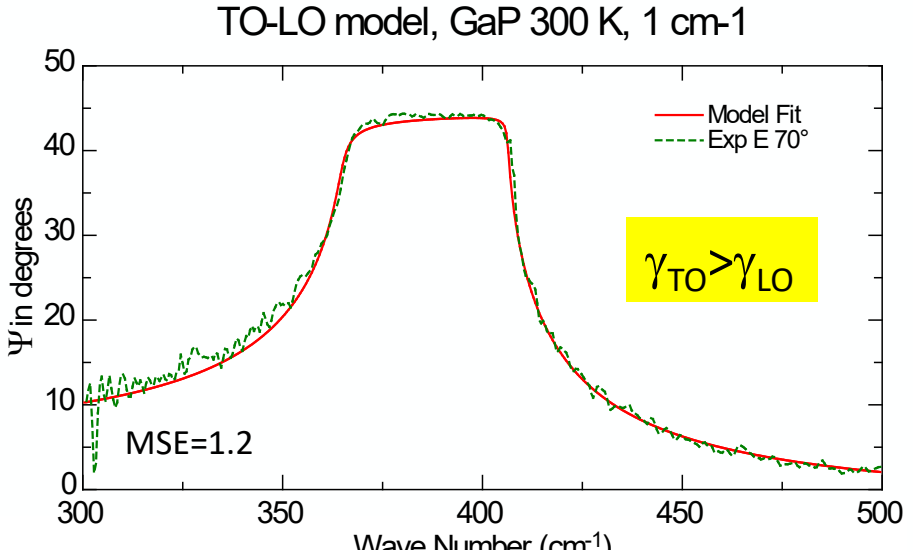
Frequency-Dependent Decay Rate: TO-LO

Simplest case: Two different broadening parameters for TO and LO phonons.

$$\varepsilon(\omega) = \varepsilon_\infty \frac{\omega_{LO}^2 - \omega^2 - i\gamma_{LO}\omega}{\omega_{TO}^2 - \omega^2 - i\gamma_{TO}\omega} = \varepsilon_\infty + \frac{(A - iB\omega)\omega_{TO}^2}{\omega_{TO}^2 - \omega^2 - i\gamma_{TO}\omega}$$

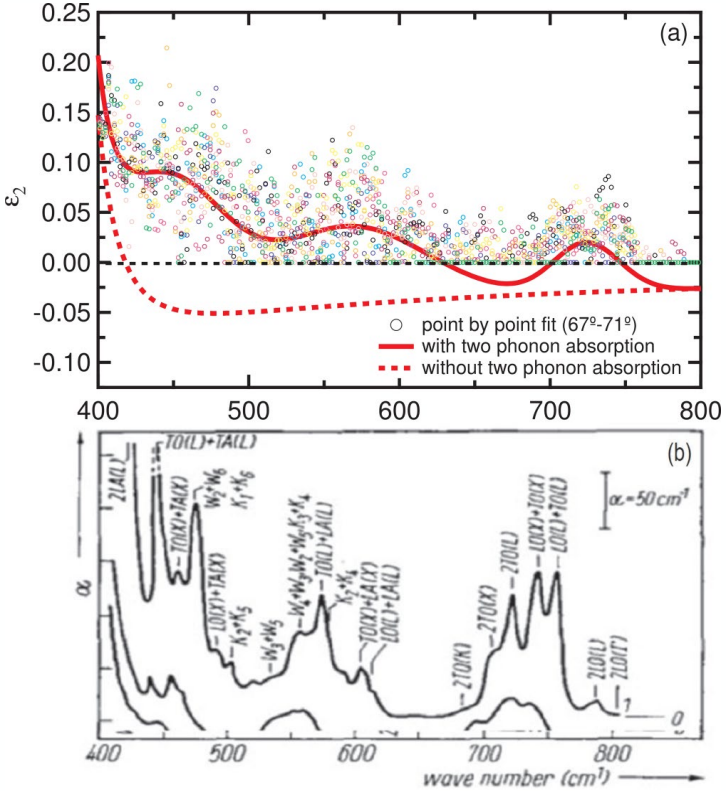
Or a complex Lorentzian amplitude.





Berreman and Unterwald, Phys. Rev. **174**, 791 (1968)
Lowndes, Phys. Rev. B **1**, 2754 (1970)
Gervais and Piriou, J. Phys. C Solid State Phys. **7**, 2374 (1974).
N. Samarasingha *et al.*, JVSTB **39**, 052201 (2021).

Frequency-Dependent Scattering Rate



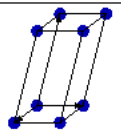
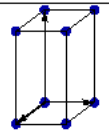
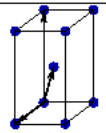
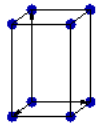
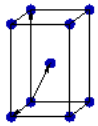
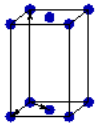
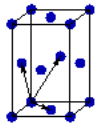
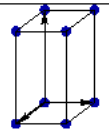
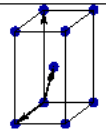
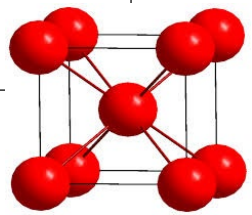
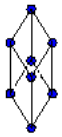
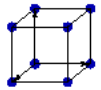
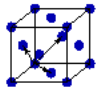
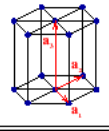
$\gamma_{TO} > \gamma_{LO}$

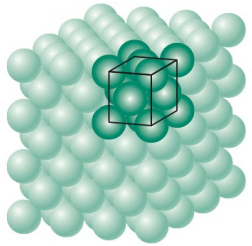
- Anharmonic decay of optical phonons into acoustic phonons (TO, LO -> LA +TA phonon).
- Frequency dependent decay rate: $\gamma_{TO} > \gamma_{LO}$.
- **TO phonon absorption coefficient becomes negative above LO energy (dotted line).**

- **How do we fix this?**
  The two-phonon absorption also contributes to the absorption, keeping the total absorption coefficient positive.

N. Samarasingha *et al*., JVSTB **39**, 052201 (2021).

Crystallography: Fourteen Bravais Lattices

Bravais lattice	Parameters	Simple (P)	Volume centered (I)	Base centered (C)	Face centered (F)
Triclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} \neq \alpha_{23} \neq \alpha_{31}$				
Monoclinic	$a_1 \neq a_2 \neq a_3$ $\alpha_{23} = \alpha_{31} = 90°$ $\alpha_{12} \neq 90°$				
Orthorhombic	$a_1 \neq a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Tetragonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Trigonal	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} < 120°$				
Cubic	$a_1 = a_2 = a_3$ $\alpha_{12} = \alpha_{23} = \alpha_{31} = 90°$				
Hexagonal	$a_1 = a_2 \neq a_3$ $\alpha_{12} = 120°$ $\alpha_{23} = \alpha_{31} = 90°$				



P	simple
I	body-centered
F	face-centered
C	base-centered

Seven crystal systems become
14 Bravais lattices with centering.

Crystal = Lattice + Basis
(Wyckoff positions)
32 point groups
230 space groups (Intl. Tables)
Group Theory, Symmetry

Rohrer: Structure and Bonding in Crystalline Materials

Nye: Physical Properties of Crystals

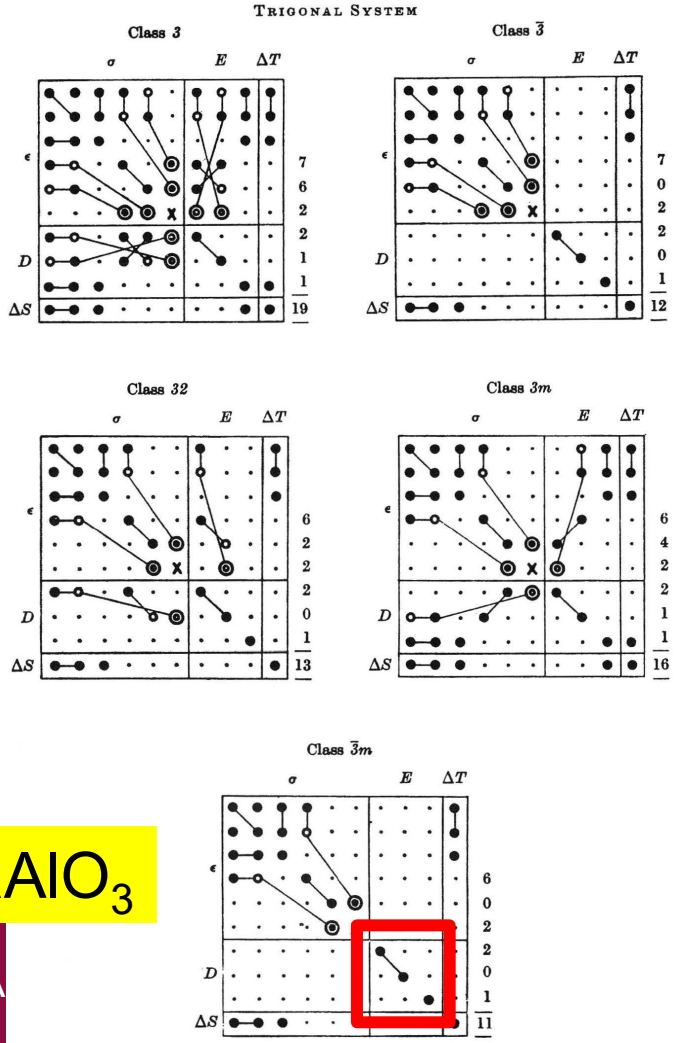
D	Dielectric displacement
E	electric field
ε	**dielectric tensor**

$$\vec{D} = \varepsilon \vec{E}$$

For crystal class -3m,
the dielectric tensor

- has **two independent diagonal** components.
- **off-diagonal components are zero**.

Also: Stress/strain, magnetic, piezo, …
Many different tensor properties.



$LaAlO_3$

Matrix Elements: Selection Rules

Problem Statement:

- Initial state <i|: symmetry Γ_i
- Final state <f|: symmetry Γ_f
- Interaction Hamiltonian: symmetry Γ_H

Symmetry produces selection rules.
H-atom: $\Delta l = \pm 1$

Question:

Is the transition from <i| to <f| allowed?
Is the matrix element <f|H|i> zero (i.e., transition forbidden).

Answer: The transition is forbidden, unless the final state symmetry Γ_f is contained in the product of Γ_i and Γ_H.
This calculation uses character tables (or similar tools).

Example:

Optical transition from Γ_7^+ to Γ_7^- ($E_0'+\Delta_0$) forbidden in Ge.

Note: Selection rules are relaxed, if symmetry is lowered.
(If we lose the inversion symmetry, parity rules go away.)

For O_h complexes

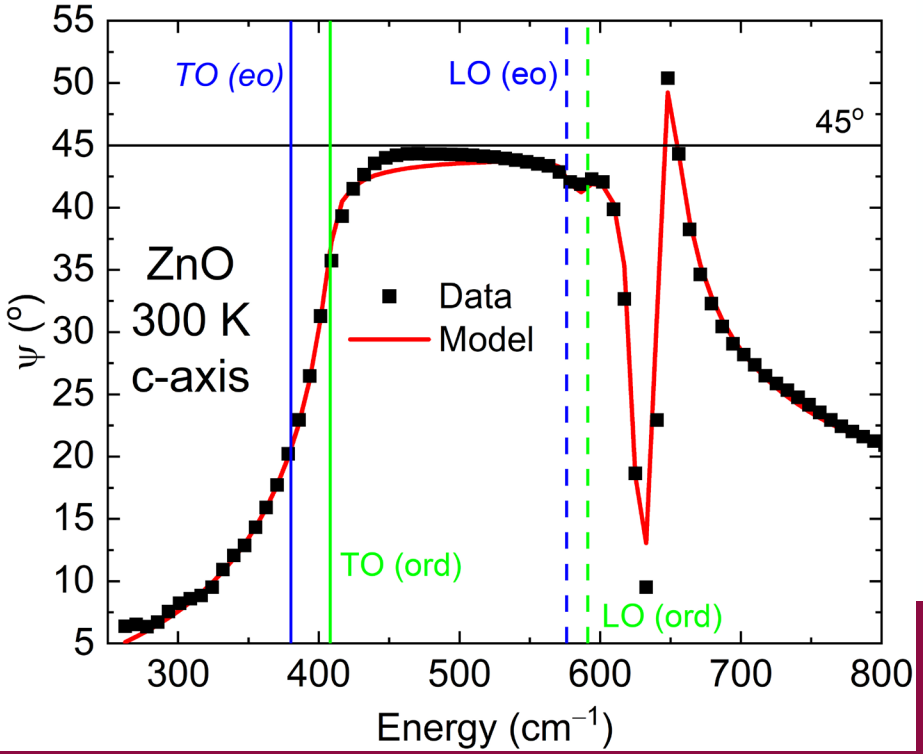
$d \rightarrow d$	Forbidden
$t_{2g} \rightarrow e_g$	
$d \rightarrow p$	Allowed
$t_{2g} \rightarrow t_{1u}$	
$p \rightarrow p$	Forbidden
$t_{1u} \rightarrow t_{1u}$	

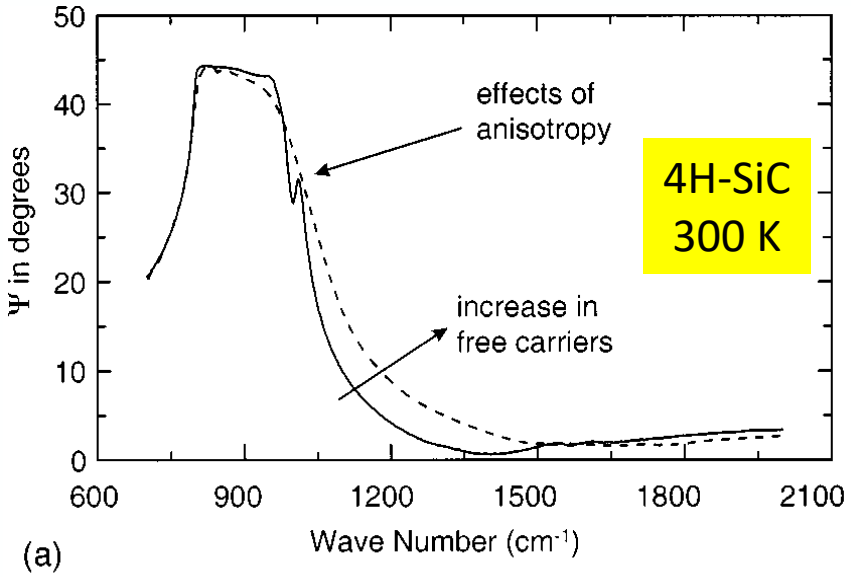
Reststrahlen Band in Uniaxial Crystal ZnO

Uniaxial crystal: Ordinary and extraordinary dielectric function.

Aspnes 1980: For c-axis oriented crystal, we measure the ordinary dielectric function (ε>>1).

Assumption breaks down near the LO frequency where ε is near zero.





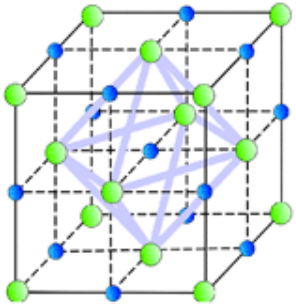
T. E. Tiwald *et al.*, PRB **60**, 11464 (1999).

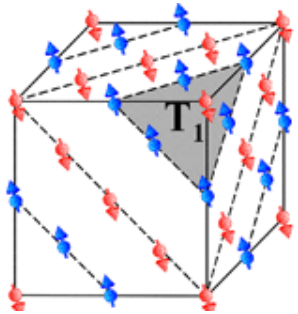
N. Samarasingha *et al.*, JVSTB **39**, 052201 (2021).

No Phonon Anisotropy in c-axis NiO (111)$_{cubic}$

- Rocksalt Crystal Structure (FCC), Space Group 225 (Fm-3m).
- Single TO/LO phonon pair.
- Antiferromagnetic ordering along (111), should cause phonon splitting (8-30 cm^{-1}).
- **Anisotropy not visible in NiO (111).**

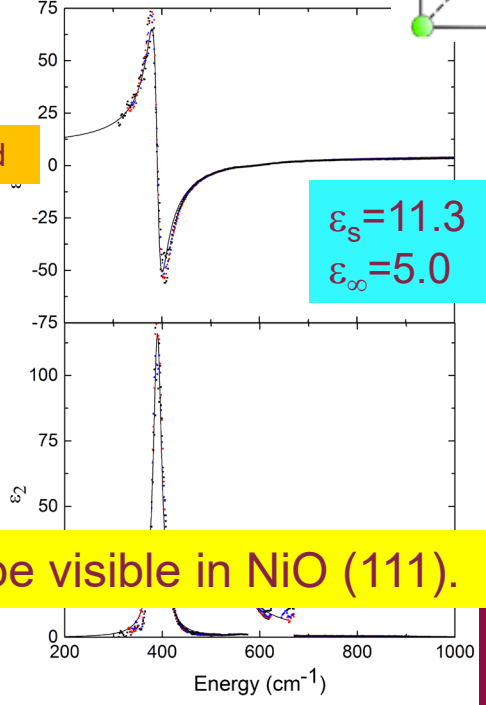
NiO cell





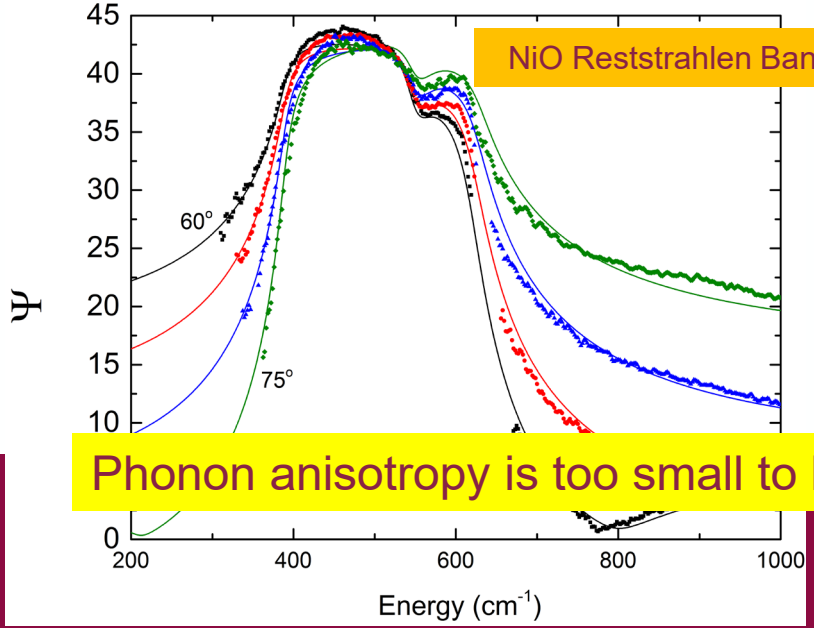
Rooksby, Nature, 1943

TO



ε_s=11.3
ε_∞=5.0

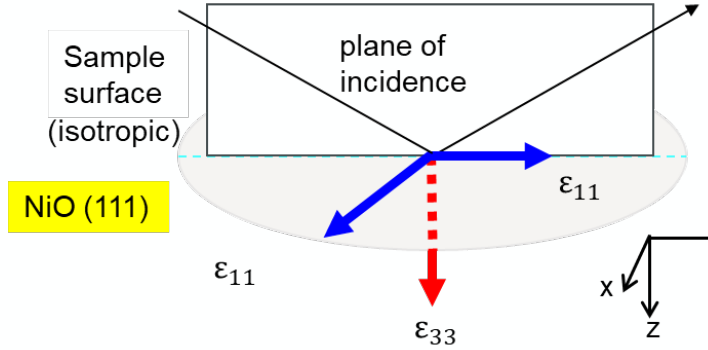
NiO Reststrahlen Band

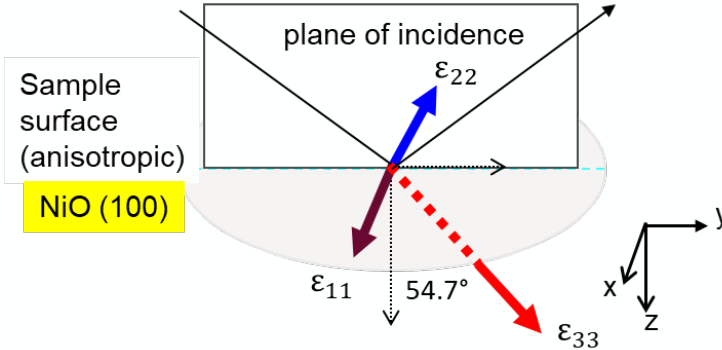


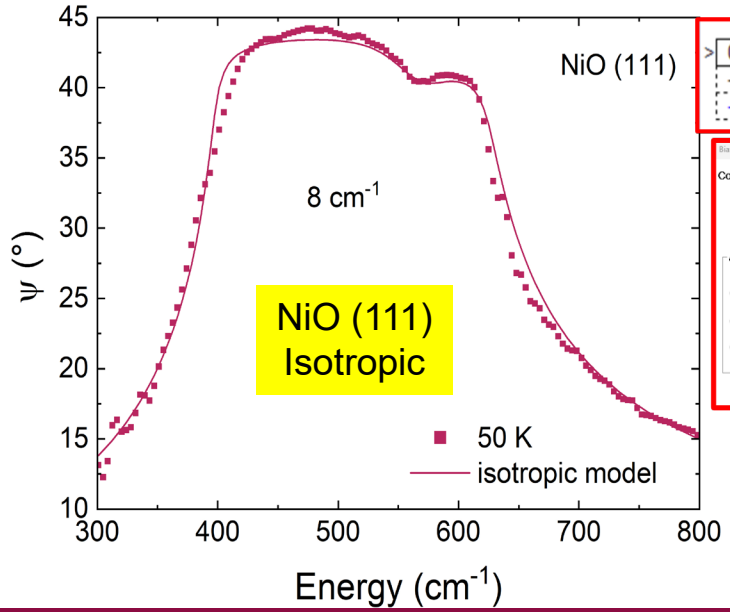
Phonon anisotropy is too small to be visible in NiO (111).

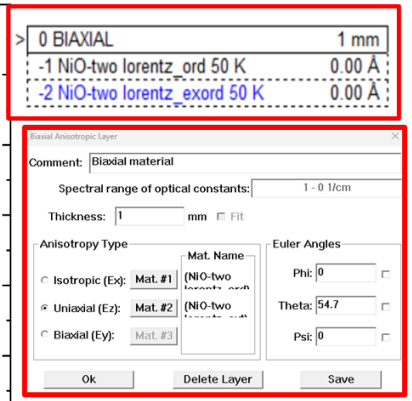
Willett-Gies & Nelson, JVST A **33**, 061202 (2015)

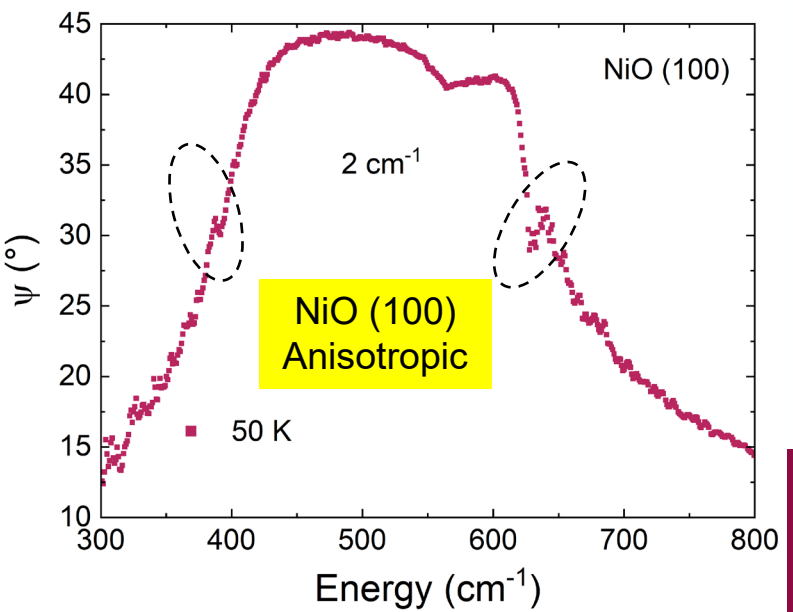
Compare NiO (111) and (100)



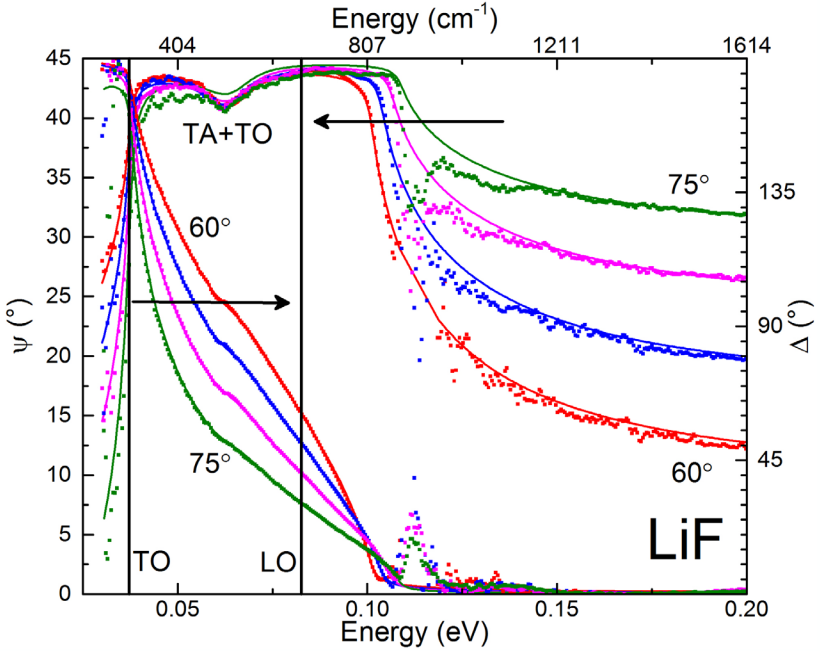








Two-phonon absorption in LiF



Phonon energies in LiF:

TO: 304 cm^{-1}

LO: 669 cm^{-1}

LO phonon not seen in ε_2.

Ellipsometry only sees the TO phonon in bulk crystals.

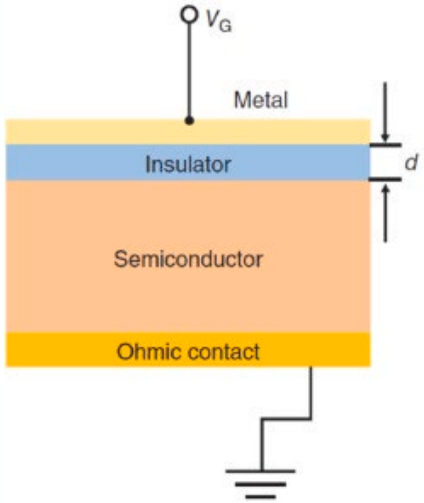
Small absorption in the reststrahlen band causes a dip or terrace.
Compare also with Al, Cu, Au (Fox, *Optical Properties of Metals*).

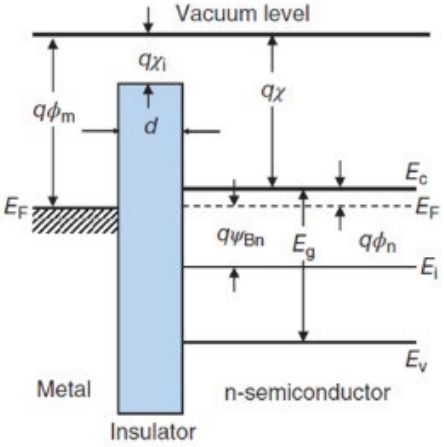
Willett-Gies & Nelson, JVST A **33**, 061202 (2015).
Also Humlicek TSF **313-314**, 687 (1998).

What happens at interfaces?

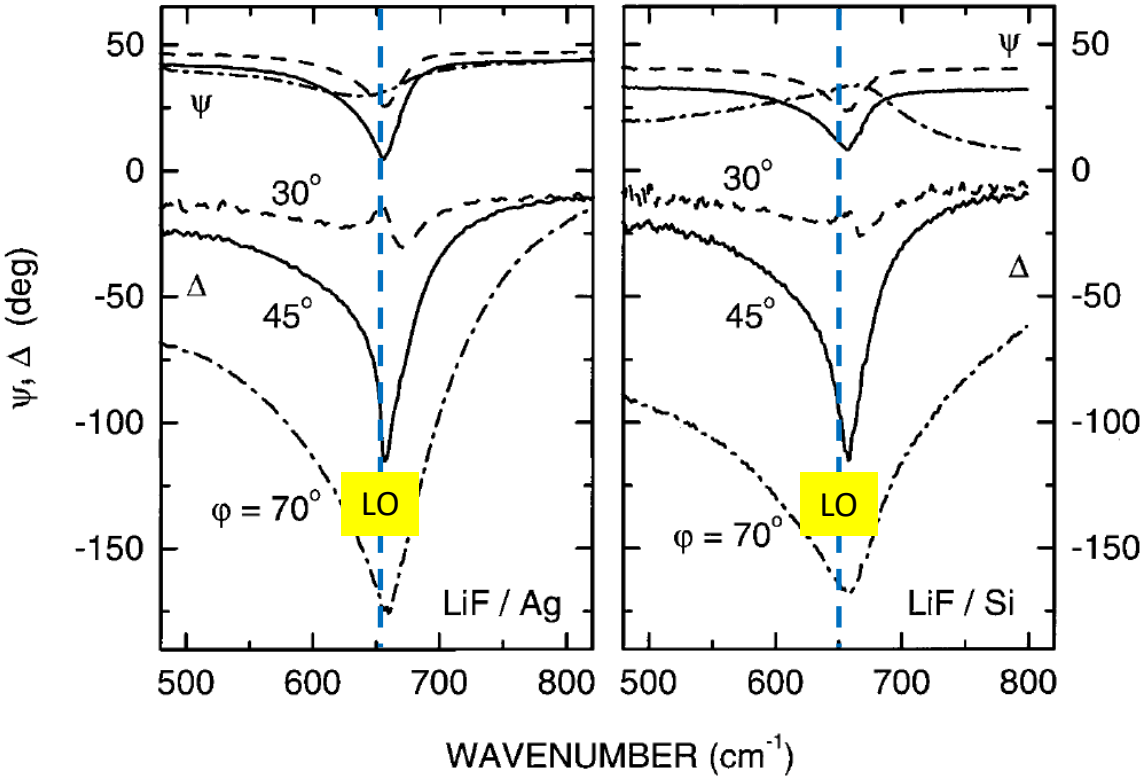
What happens at an interface between two dissimilar materials?
For example at a metal/insulator interface.

Example: LiF/Ag
LiF is an insulator.
Ag is a metal.





Berreman Effect: LiF on Ag



Light is a transverse wave:

- only couples to TO phonons.
- cannot excite LO phonons.

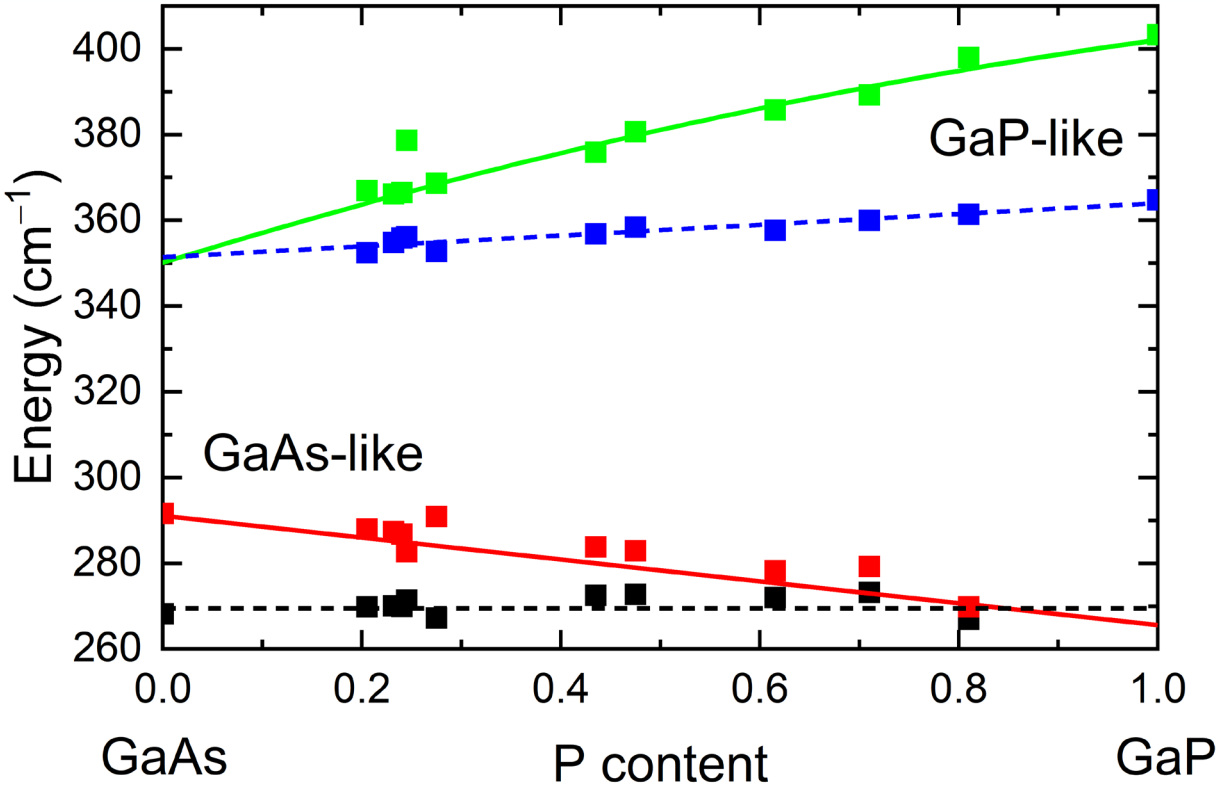
TO: peak in ε_2.
LO: peak in loss function.

However: Interference effects cause structures at the LO phonon energy in thin films.

That's called the **Berreman effect**.

J. Humlicek, PSSB **215**, 155 (1999).

Multimode Behavior in Semiconductor Alloys



$GaAs_{1-x}P_x$ alloys have four phonons: 2 TO, 2 LO.

Phonons cannot mix.
Energy pap between
GaAs and GaP modes.

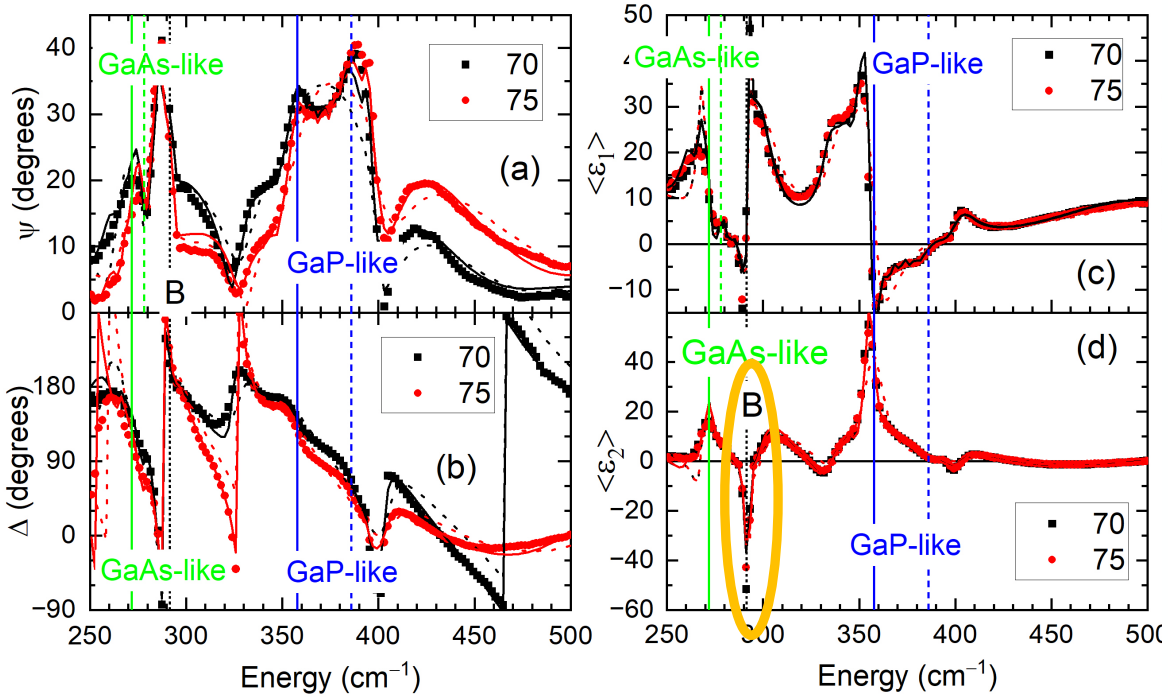
Some dependence of phonon energies on composition.

Vegard's Law does not hold.

Two-mode behavior.

SZ *et al*., Appl. Phys. Lett. **123**, 172102 (2023).

Berreman Effect in Semiconductor Alloys



$GaAs_{1-x}P_x$ alloys (on GaAs substrate) have four phonons:
2 TO, 2 LO.

Two reststrahlen bands:

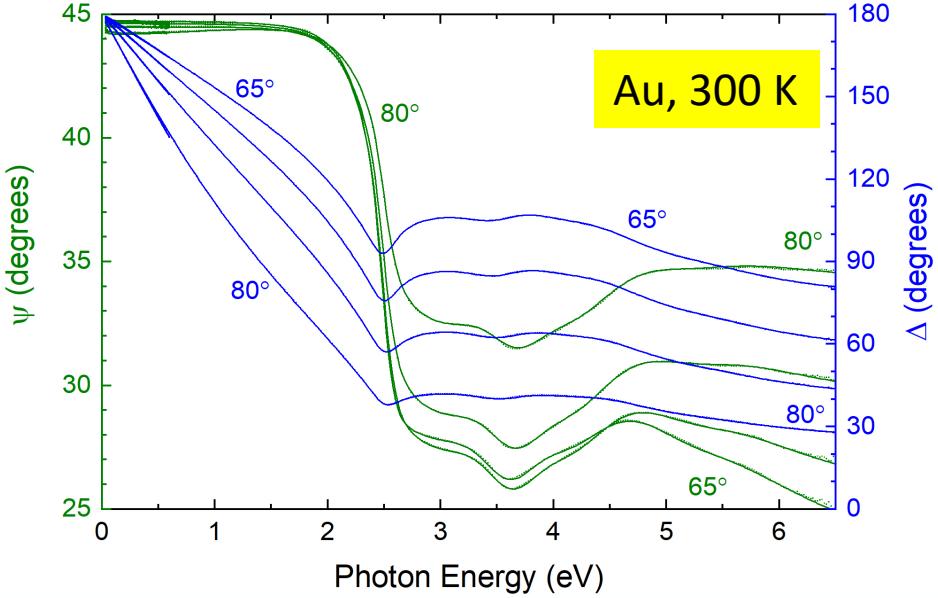
- GaAs-like (TO, LO)
- GaP-like (TO, LO)

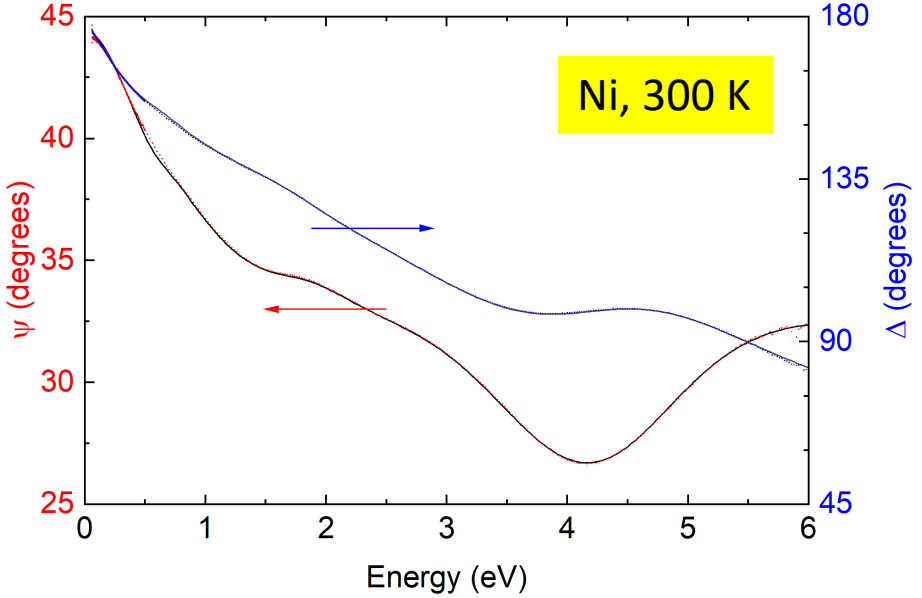
Berreman mode:
LO phonon of GaAs substrate shows up in ellipsometry spectra

LO phonons (of substrate or layer) are seen in many ellipsometry spectra of thin films.

SZ *et al*., Appl. Phys. Lett. **123**, 172102 (2023).

Drude Response of Metals





Cleaning of surface (heating in UHV) is very important to obtain accurate results.

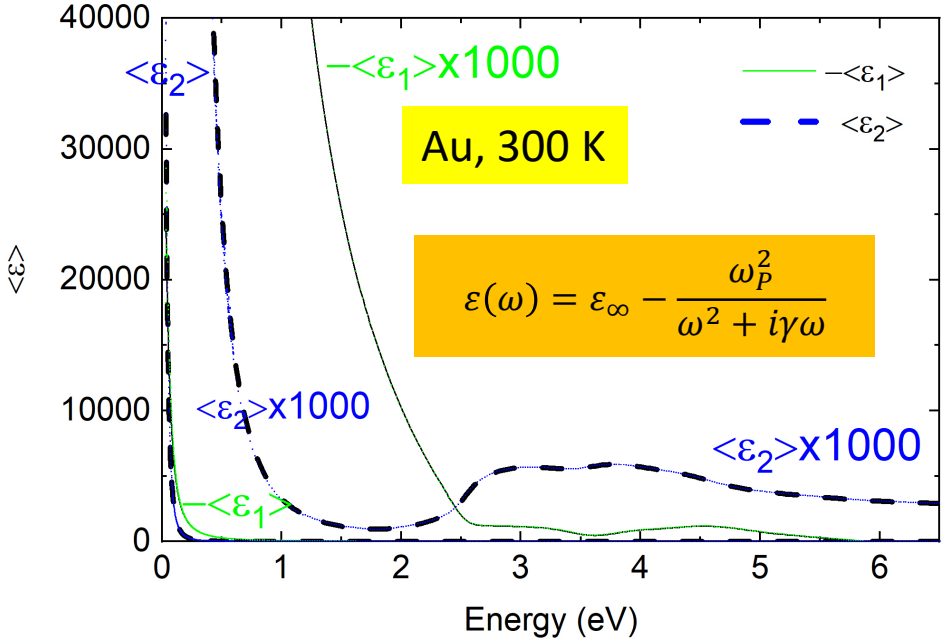
For a metal, psi should be 45 degrees up to VUV region.

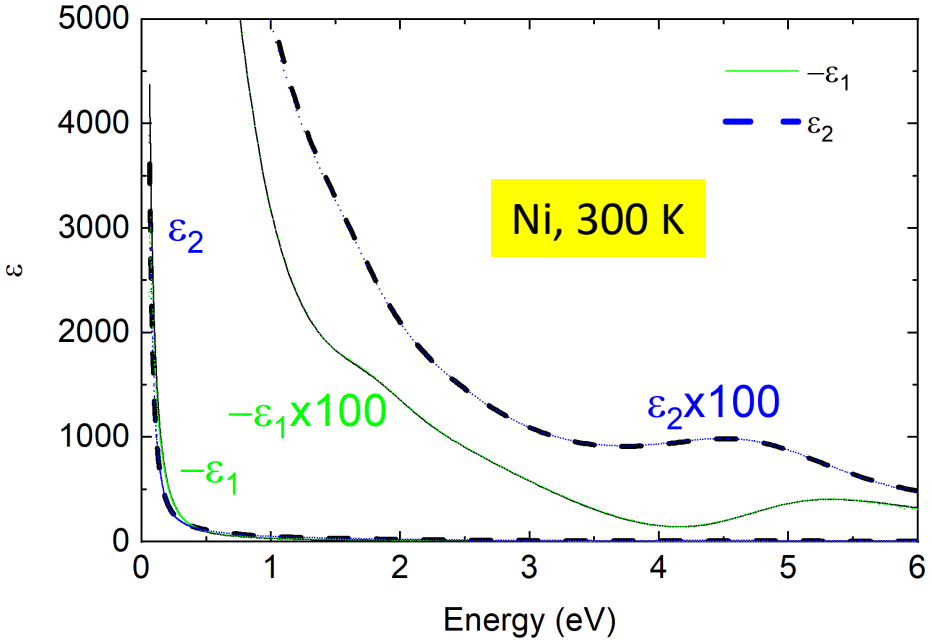
Lowered because of interband transitions (more important for Ni because of partially filled d bands).

Why does psi never reach 45 degrees at low energies? Needs to be investigated. Anomalous skin effect?

F. Abadizaman and SZ, JVSTB **37**, 062920 (2019).

Dielectric Function of Metals (Drude Response)

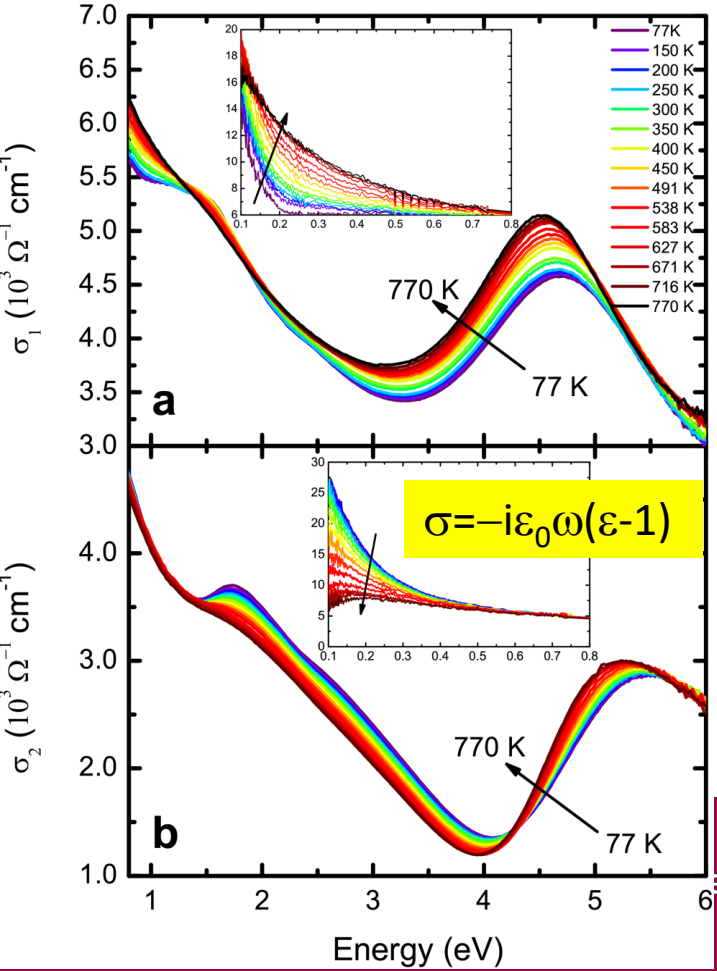




$-\varepsilon_1$, ε_2 very large in IR.
Interband transitions in UV range.
Better representation of data with optical conductivity: $\sigma = -i\varepsilon_0\omega(\varepsilon-1)$

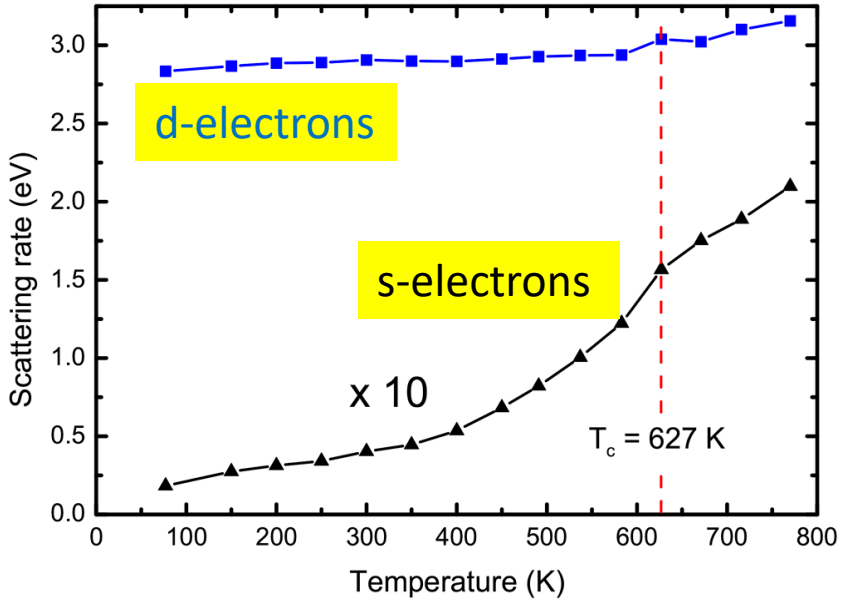
F. Abadizaman and SZ, JVSTB **37**, 062920 (2019).

Drude Response of Ni (Temperature-dependent)



Fitting the dielectric function of Ni:

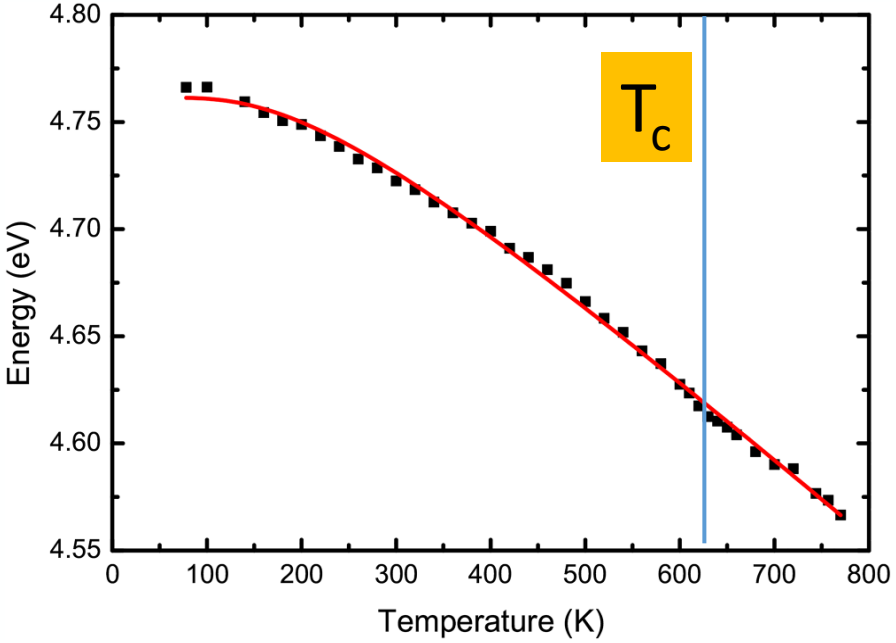
- Two Drude terms (s-, d-electrons)
- Four Lorentz oscillators for interband transitions.

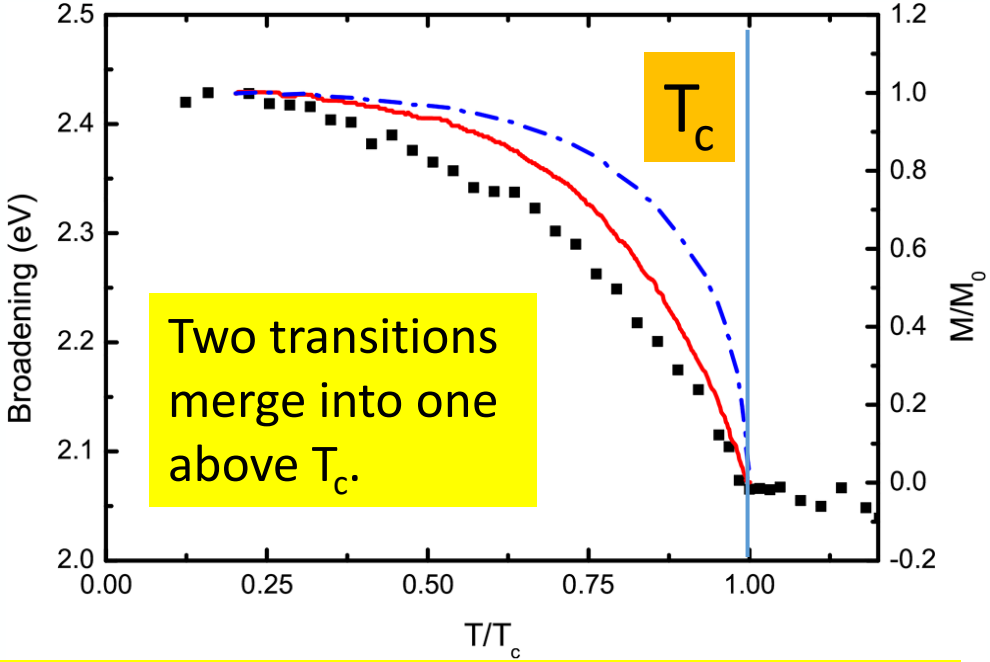


$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}$$

F. Abadizaman, Jaden Love, and SZ, JVSTA **40**, 033202 (2022).

Singularity at the Curie Temperature of Ni

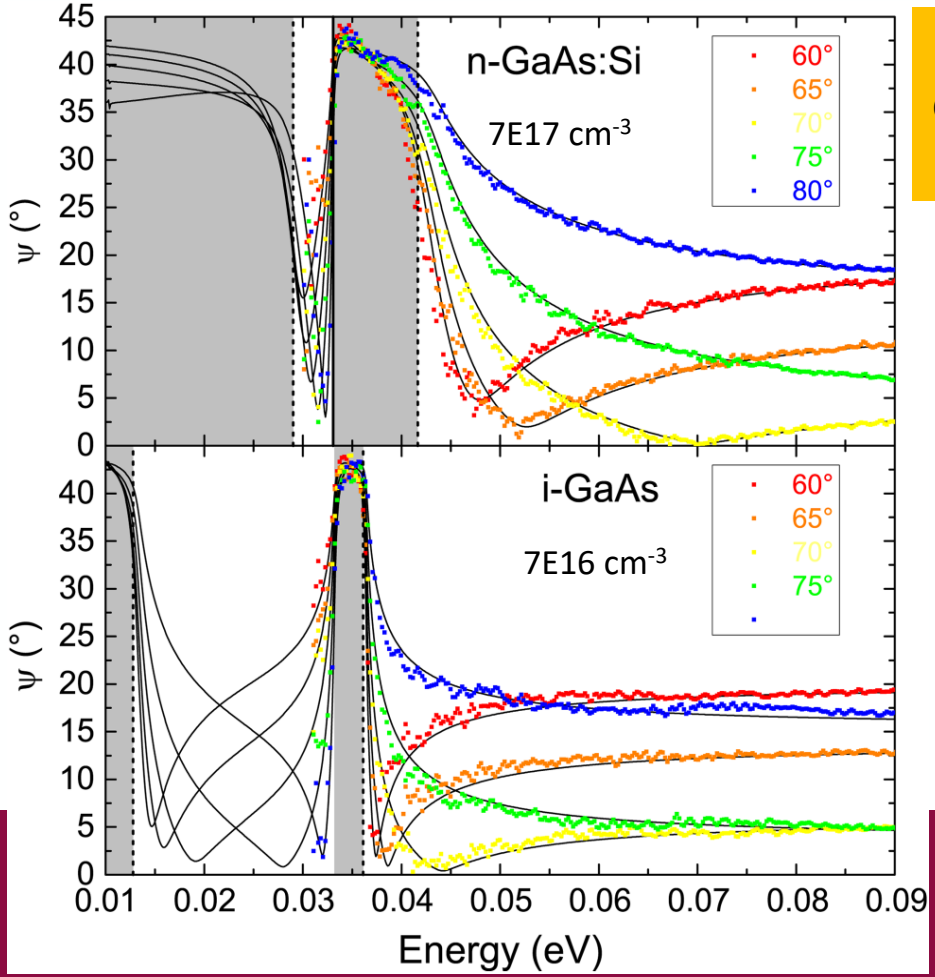




Energy of interband transition at 4.8 eV shows typical redshift with increasing temperature.
Broadening <u>decreases</u> and shows singular behavior at the Curie temperature (similar to magnetization).

F. Abadizaman, Jaden Love, and SZ, JVSTA **40**, 033202 (2022).

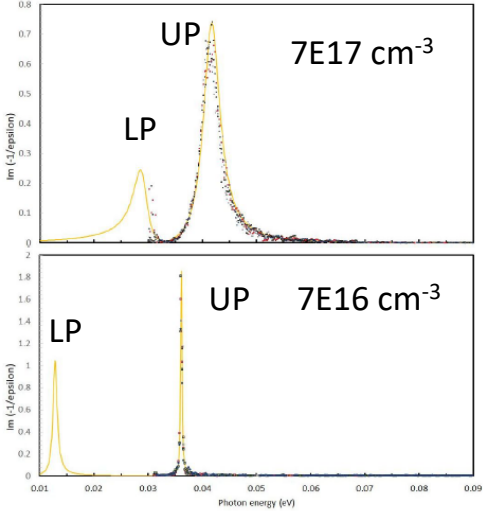
Plasmon-Phonon Coupling



Free carriers are longitudinal excitations, cannot mix with TO phonons.
Look at the **loss function**! Also, **broadening**.

$$\omega_P^2 + \omega_{LO}^2 = \omega_{LP}^2 + \omega_{UP}^2$$

$$\omega_P \omega_{TO} = \omega_{LP} \omega_{UP}$$



LO mode couples with free carrier plasmon to form **lower** and **upper** plasmon-phonon **polaritons**.

A. A. Kukharskii, Solid-State Commun. **13**, 1761 (1973).
SZ, JVSTB **37**, 012904 (2019).

Also see posters by Daniel Franta.

Summary and Outlook

- **Lorentz model** for absorption by optical phonons in polar crystals.
  - Trends with mass and ionicity.
- Temperature dependence of optical phonon energies:
  - **Anharmonic** decay of optical phonons.
  - **Two-phonon absorption** in LiF and NiO.
- Beyond the Lorentz model: **Frequency-dependent decay rate**
  - Lowndes model (TO/LO oscillator).
- Splitting of optical phonons in **uniaxial** crystals: ZnO, SiC, NiO
- **Multimode** behavior in $GaAs_{1-x}P_x$ alloys
- **Berreman** effect at LO energy: Insulator on metal (LiF on Ag)
- Drude model for **free carrier absorption**: Ni and Au
- **Plasmon-phonon coupling**

Thank you! Questions?

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