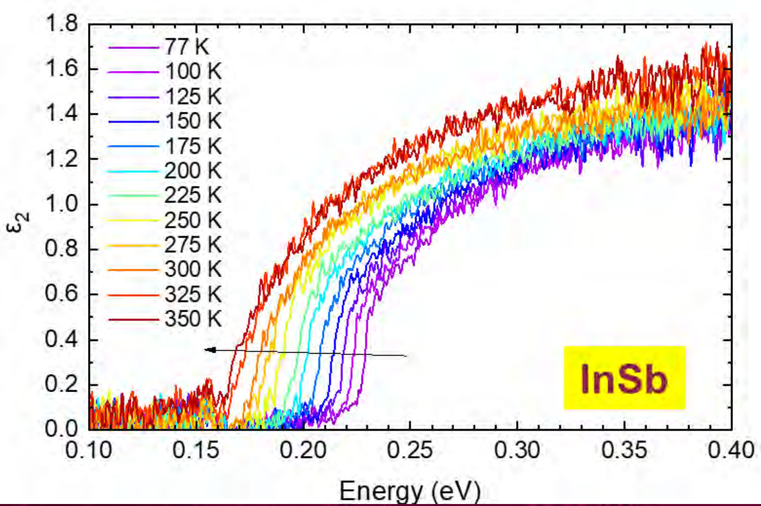
10th International Conference on Spectroscopic Ellipsometry (ICSE-10)
Boulder, CO, USA, 8-13 June 2025

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 and comparison with theory



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NM STATE

BE BOLD. Shape the Future.

Where is Las Cruces, NM ???

White Sands NP

Students and Collaborators (2010-2025)

PhD. students (10): Lina S. Abdallah, Nalin Fernando, Nuwanjula S. Samarasingha, Farzin Abadizaman, Carola Emminger, Rigo A. Carrasco, **Yoshitha Hettige**, **Carlos A. Armenta**, **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 A. Medina, Maria Spies, Cayla M. Nelson, Eric DeLong, Christian J. Zollner, Khadijih N. 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, etc.

ICSE Conference Topics

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

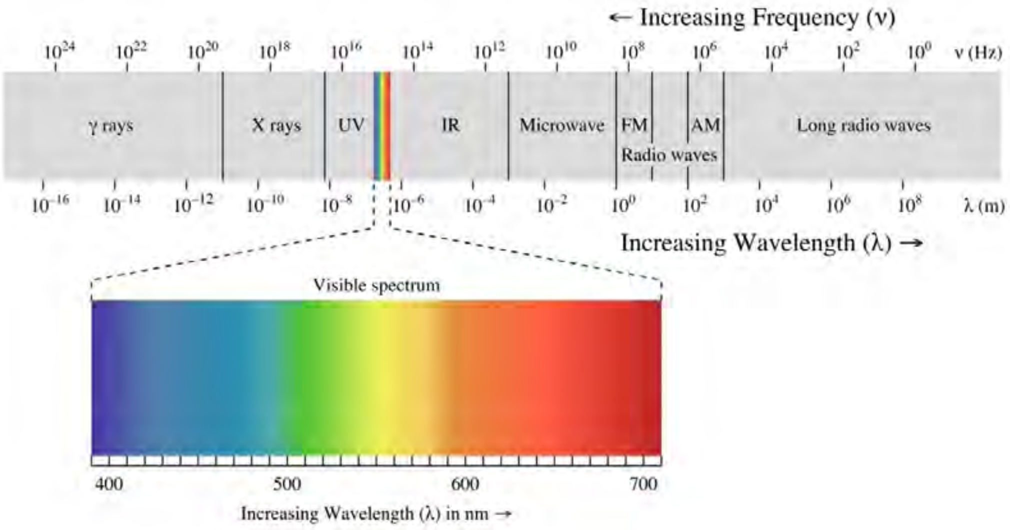
1. **Instrumentation** to acquire ellipsometric angles, Jones matrices, or MM elements.
2. **Analysis** of ellipsometry data to determine (isotropic or anisotropic) **optical constants**.
3. Ellipsometry as a **non-destructive characterization** tool: How thick is my film?

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?

Electromagnetic Spectrum



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

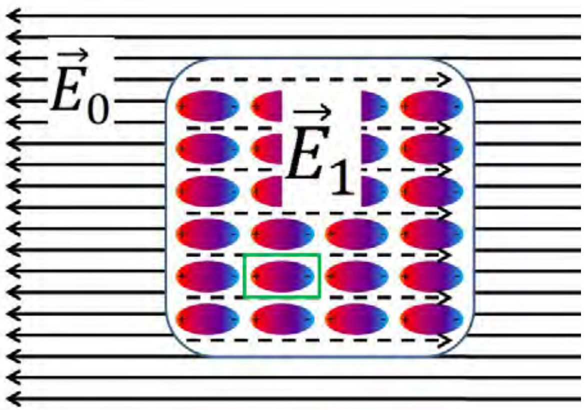
Infrared:
Lattice vibrations (phonons), free carriers (Drude response)
Visible and UV:
Valence electrons, electronic band structure (electrons, holes, interband transitions, critical points)

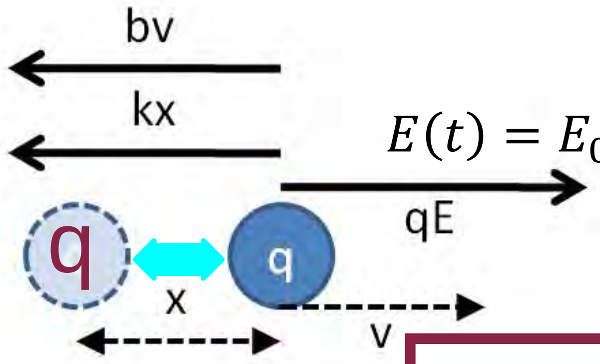
X-rays: Core electrons; Gamma-rays: Nuclear processes

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.

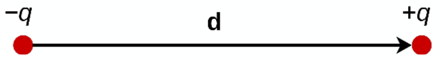
Lorentz Model for Oscillating Charges





$$E(t) = E_0 \exp(-i\omega t)$$

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



$$F = ma$$

$$qE - b\dot{x} - kx = m\ddot{x}$$

Try $x(t) = x_0 \exp(-i\omega t)$

$$x(t) = \frac{-qE_0}{m\omega^2 + ib\omega - k} \exp(-i\omega t)$$

$$P(t) = \chi_e E(t) = \frac{qx(t)}{V}$$

$$\varepsilon = 1 + \chi_e$$

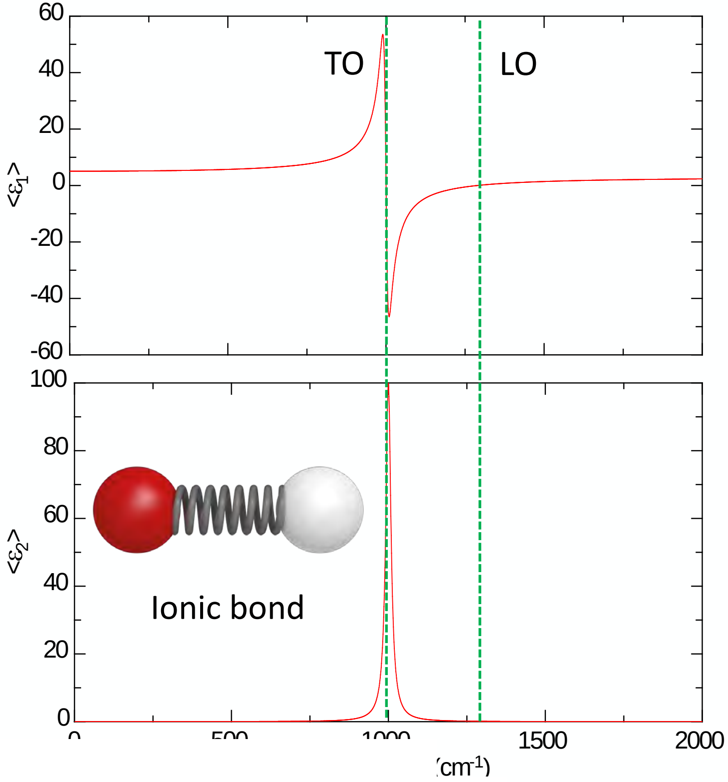
$$\varepsilon(\omega) = 1 + \frac{\omega_P^2}{\omega_0^2 - \omega^2 - i\gamma\omega}$$

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

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

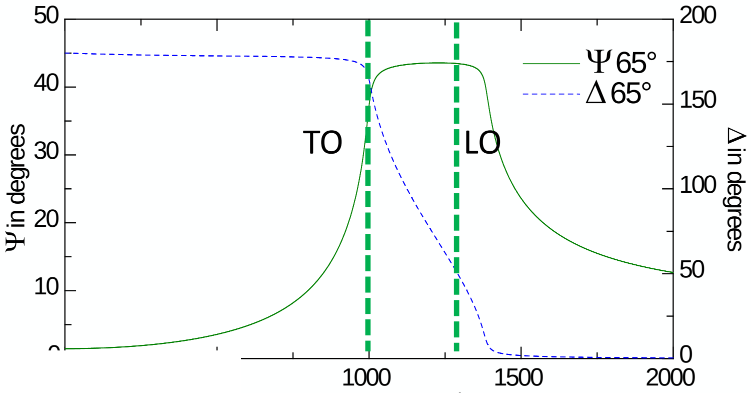
H. Helmholtz, Ann. Phys **230**, 582 (1875)
F. Wooten, *Optical Properties of Solids*, 1972

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.



$\varepsilon_\infty = 3$

$A = 2$

$\omega_{TO} = 1000\ \text{cm}^{-1}$

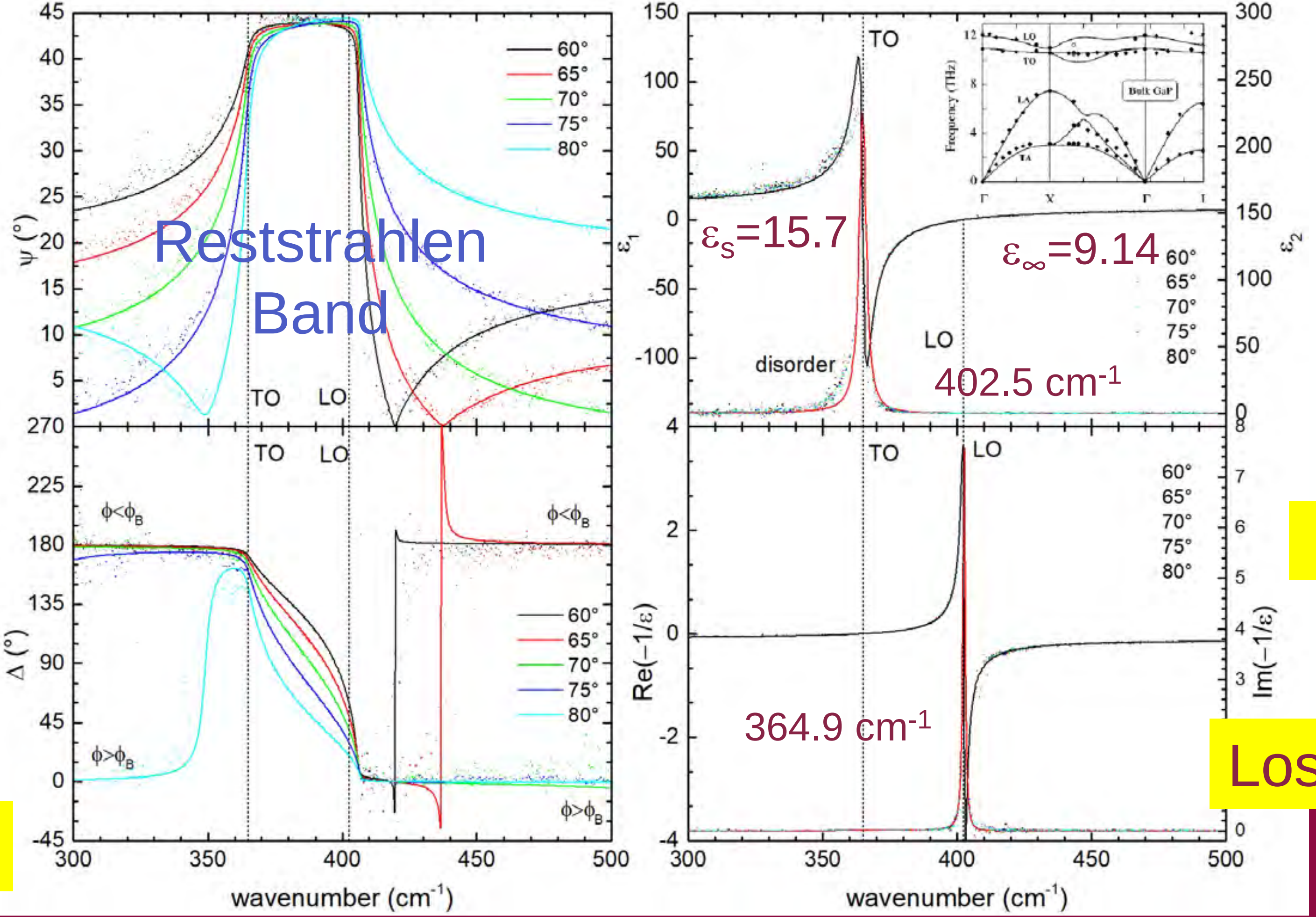
$\gamma = 20\ \text{cm}^{-1}$

$\omega_{LO} = 1290\ \text{cm}^{-1}$

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

GaP shows nearly perfect Lorentz oscillator

psi



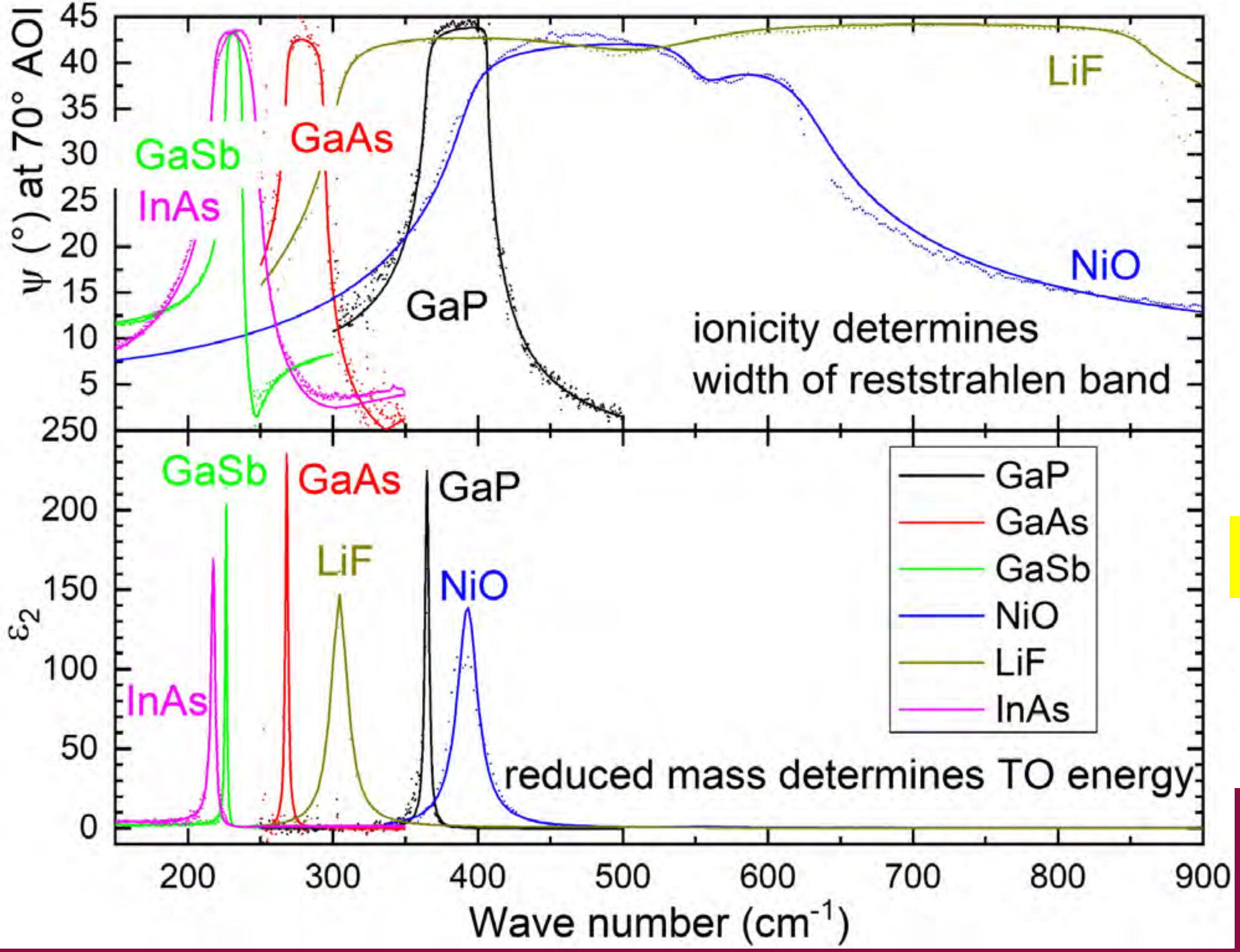
Delta

epsilon

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

Loss function

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).

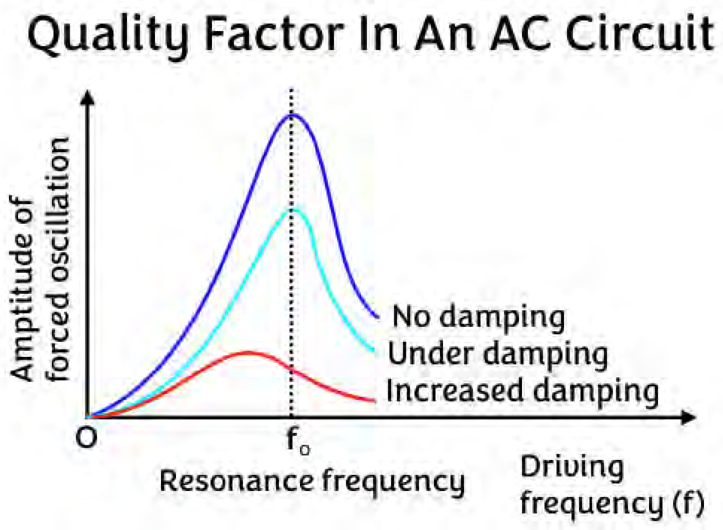
- Finite lifetime: Quality factor decreases (**broadening increases**).
- Temperature decreases the lifetime.

- 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).

SZ, *Spectroscopic ellipsometry from 10 to 700 K*, Adv. Opt. Techn. **11**, 117 (2022).

Tools for Temperature-Dependent Ellipsometry

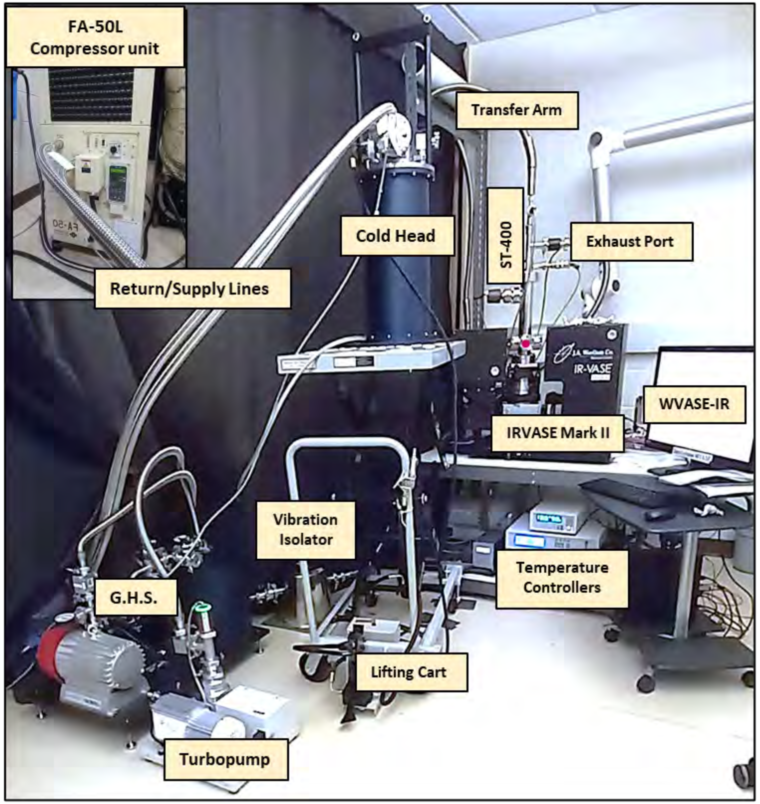
Combined System for Temperature Dependent SE	
FA-50L Helium Compressor Unit	Sumitomo Heavy Industries, Ltd.
RGC4 Cryogen Free Recirculating Gas Cooler	Lake Shore Cryotronics, Inc.
ST-400 Cryostat	Lake Shore Cryotronics, Inc.
IR-VASE Mark II	J.A. Woollam Co.

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.

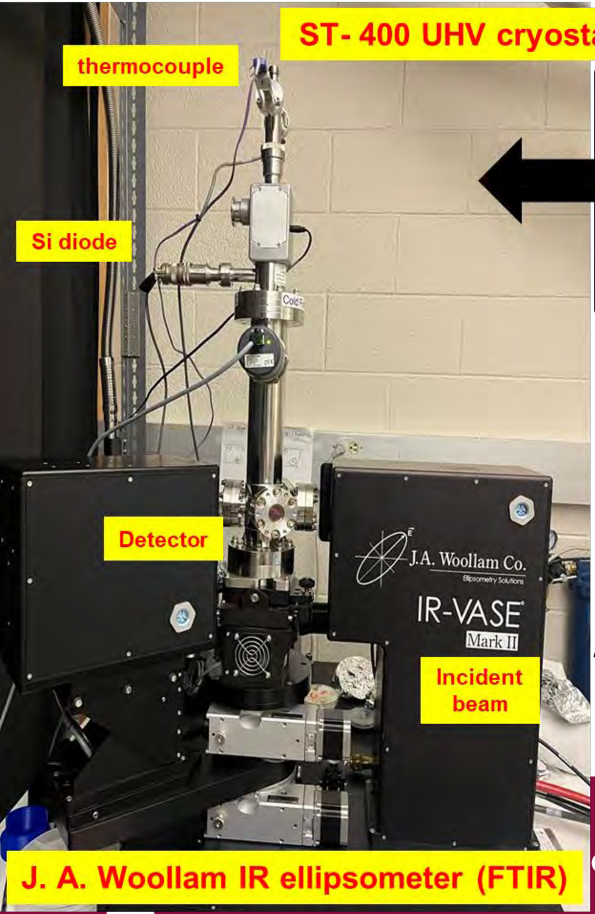
Custom feature:
Diamond windows for cryostat.

ARO (W911NF-22-2-0130)

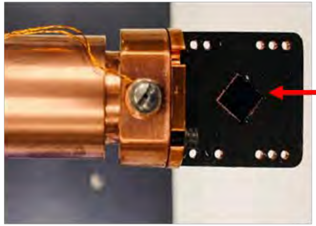
Jaden Love
Atlantis Moses

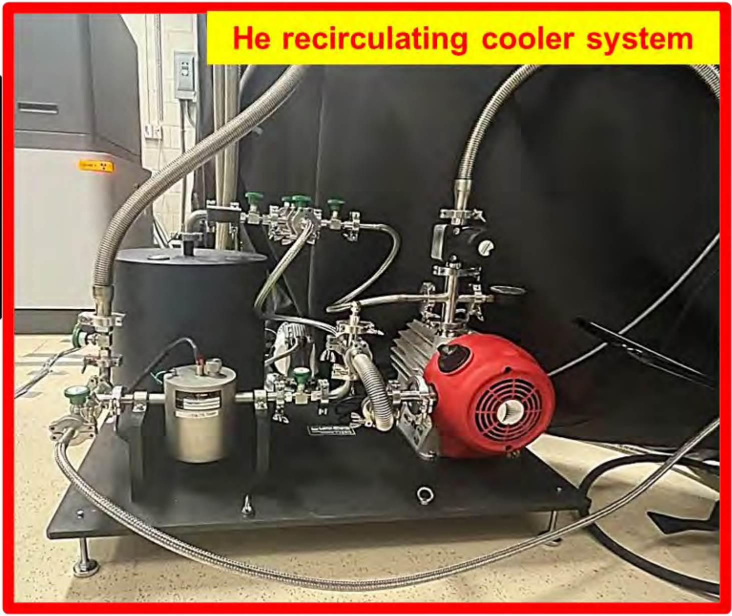
Tools for Temperature-Dependent Ellipsometry

Lake Shore model RGC 4 cryogen free closed cycle refrigerated system

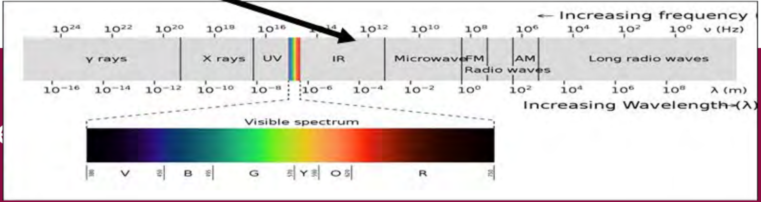


- Temperature range : **25 K to 500 K** (He recirculating cooler).
- Pressure : **10^{-8} Torr**.
- Resolution : **8 cm^{-1}**



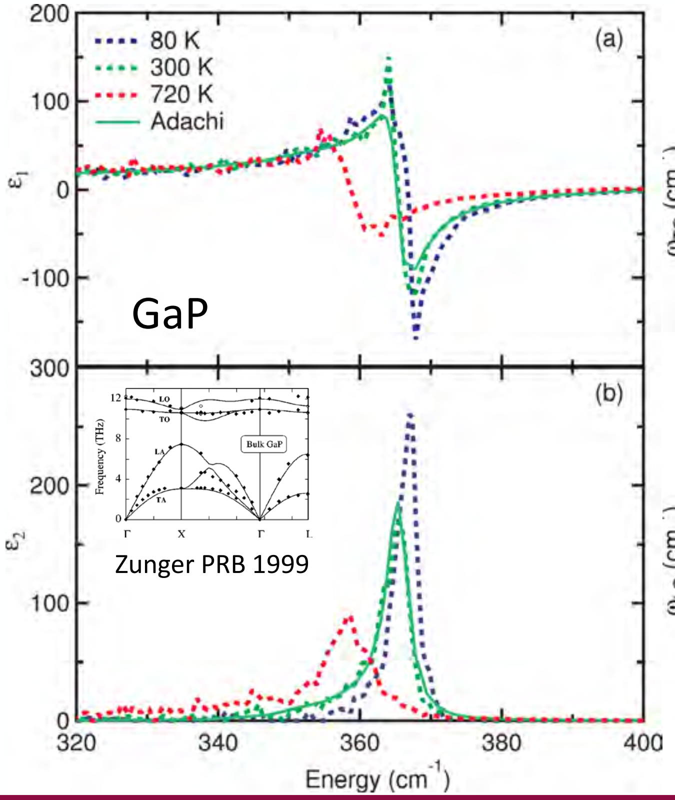


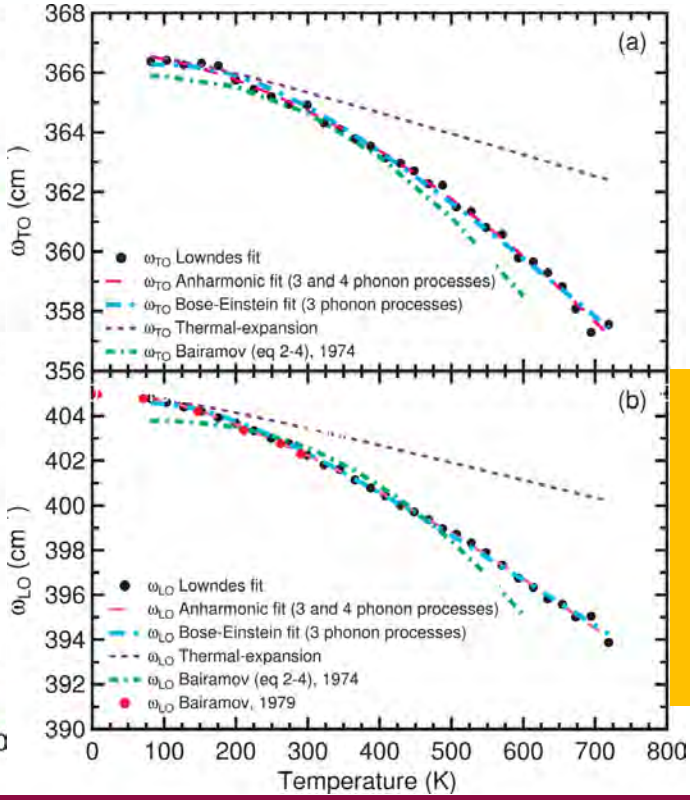
Measured the ellipsometric angles Ψ and Δ of NiO from 250-8000 cm^{-1} at 8 cm^{-1} resolution from 25 to 500 K.

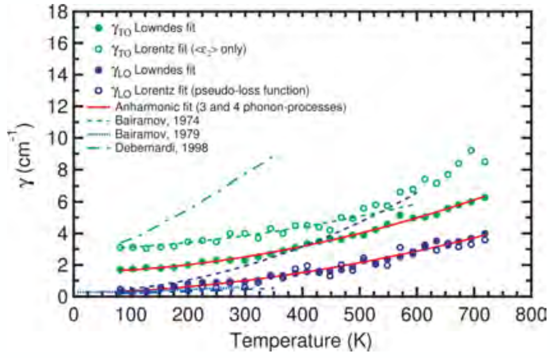


Jaden Love
Atlantis Moses

Temperature dependence of GaP phonon energies





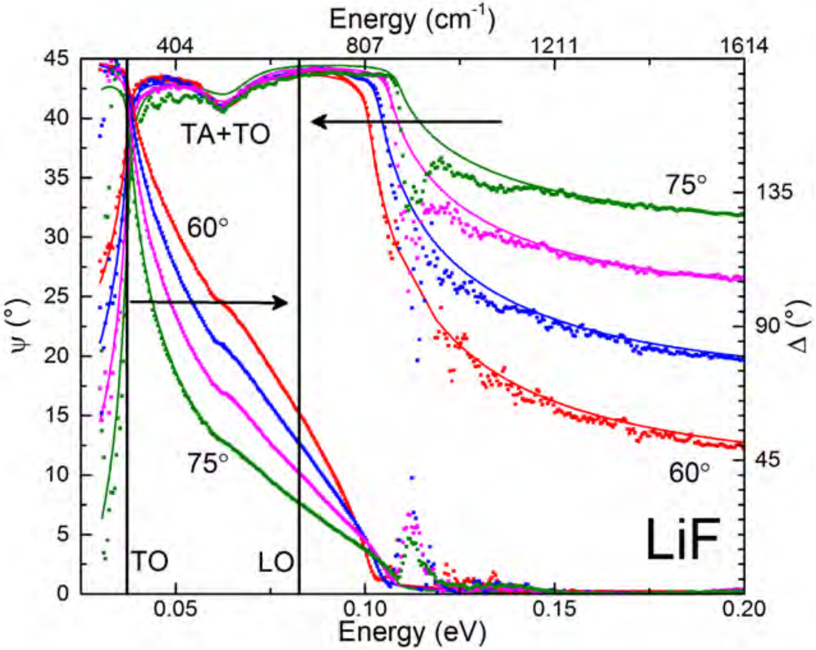


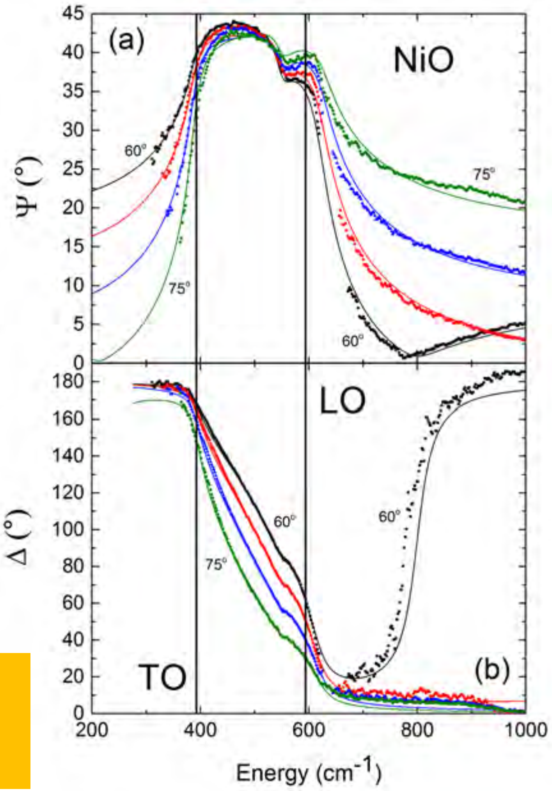
Anharmonic phonon decay:
TO, LO -> TA + LA
Broadenings increase.
TO and LO energies decrease.
Born effective charge: constant.
ε_s, ε_∞ increase (Penn gap)

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

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

Two-phonon absorption in LiF and NiO





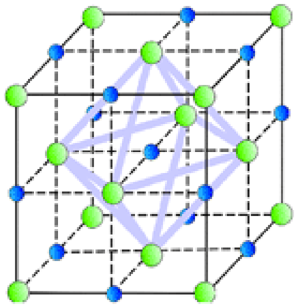
Small absorption in the reststrahlen band causes a dip or terrace.
Compare also with Al, Cu, Au (Fox, *Optical Properties of Metals*).

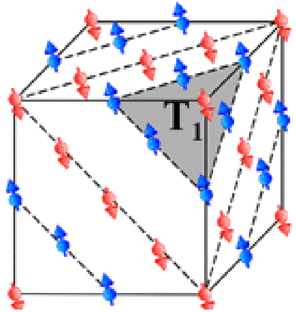
Willett-Gies & Nelson, JVST A **33**, 061202 (2015).
Also Humlicek TSF **313-314**, 687 (1998).

Two-Phonon Absorption in NiO

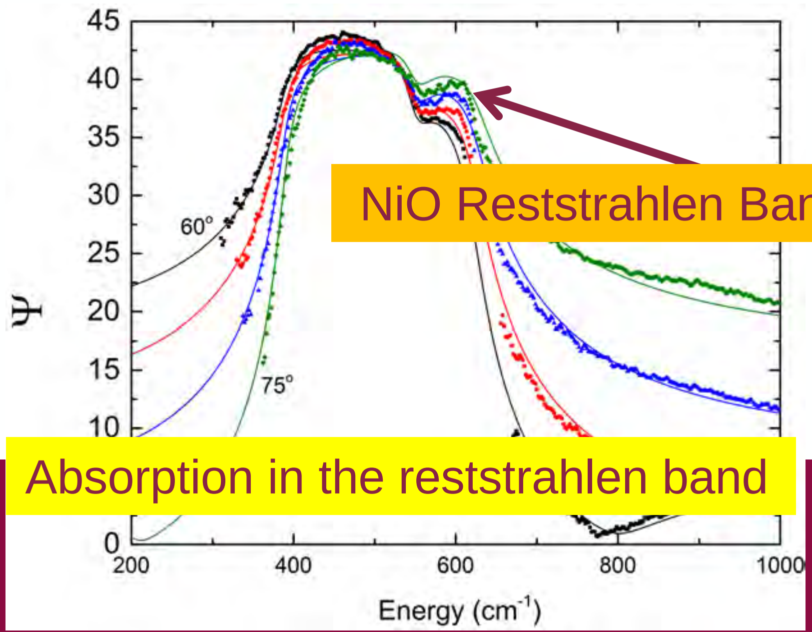
- Rocksalt crystal structure (FCC), Space group 225 (Fm-3m).
- Single TO/LO phonon pair: Γ_{15}
- Antiferromagnetic ordering along (111), causes phonon splitting (8-30 cm^{-1}).
- **Second-order phonon absorption.**

NiO cell





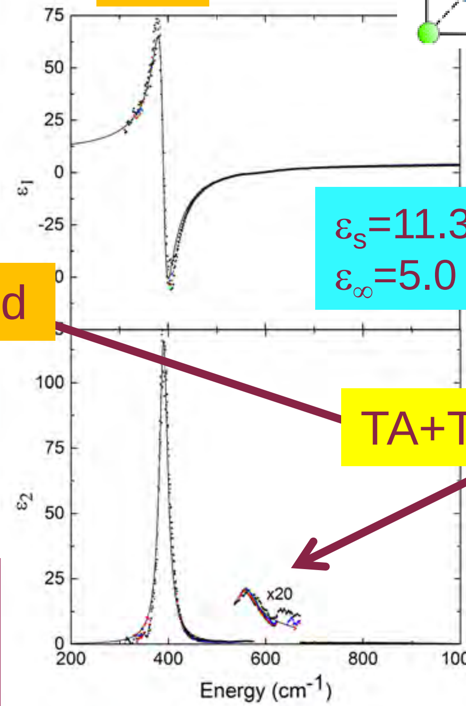
Rooksby, Nature, 1943



NiO Reststrahlen Band

Absorption in the reststrahlen band

TO

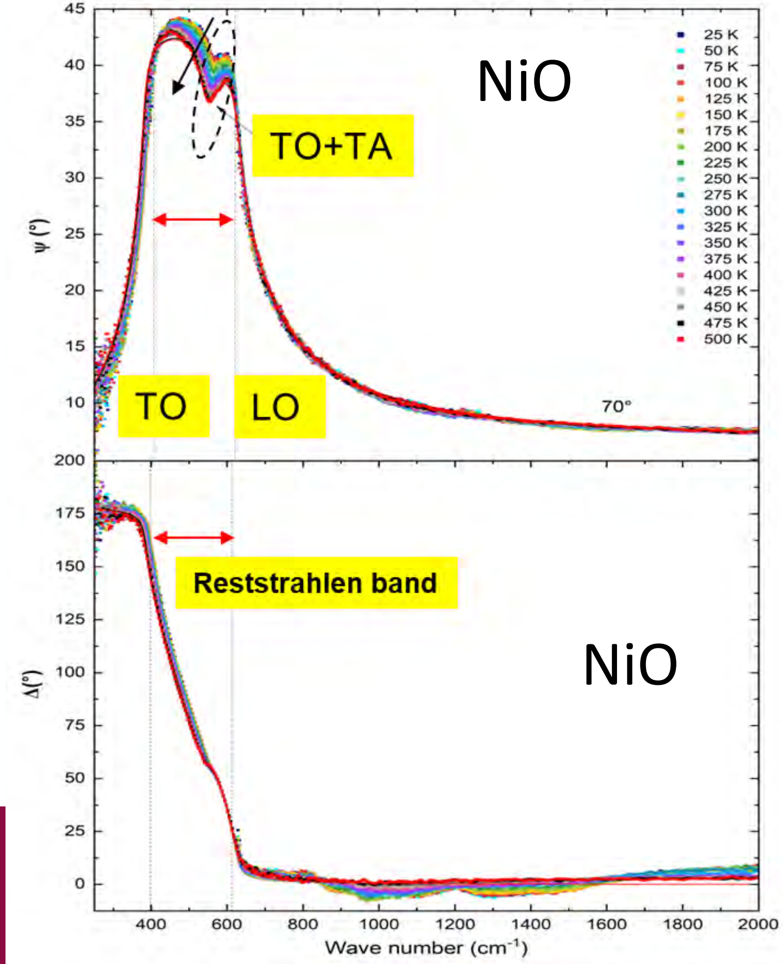


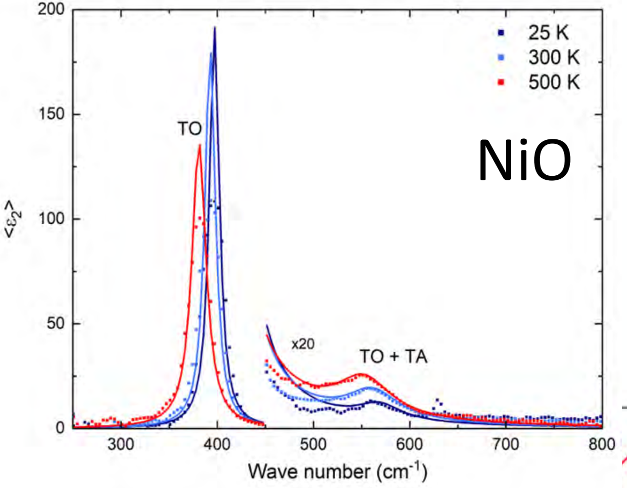
ε_s=11.3
ε_∞=5.0

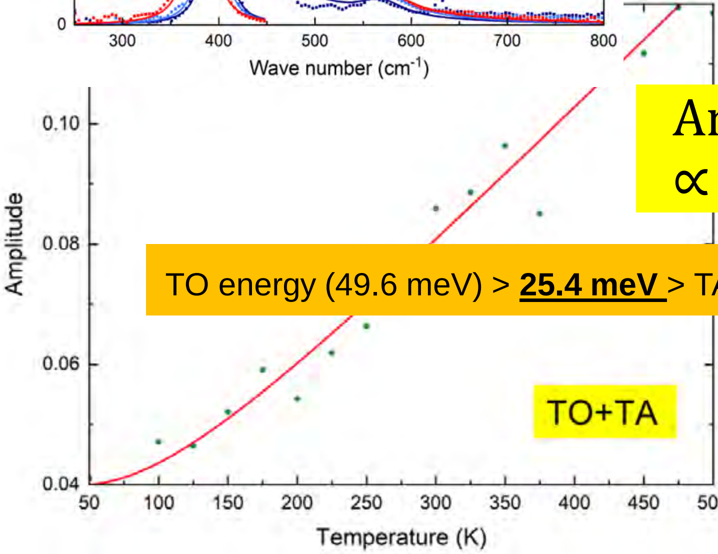
TA+TO phonon

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

Temperature Dependence of Two-Phonon Absorption







Amplitude $\propto 2N(\Omega) + 1$

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

Yoshitha Hettige
(ICSE-10)

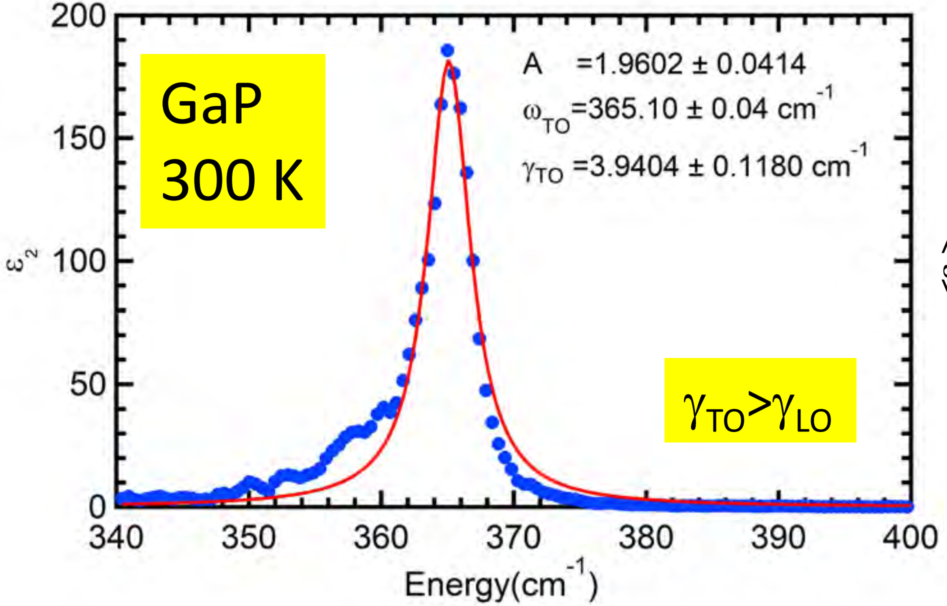
Frequency-Dependent Decay Rate

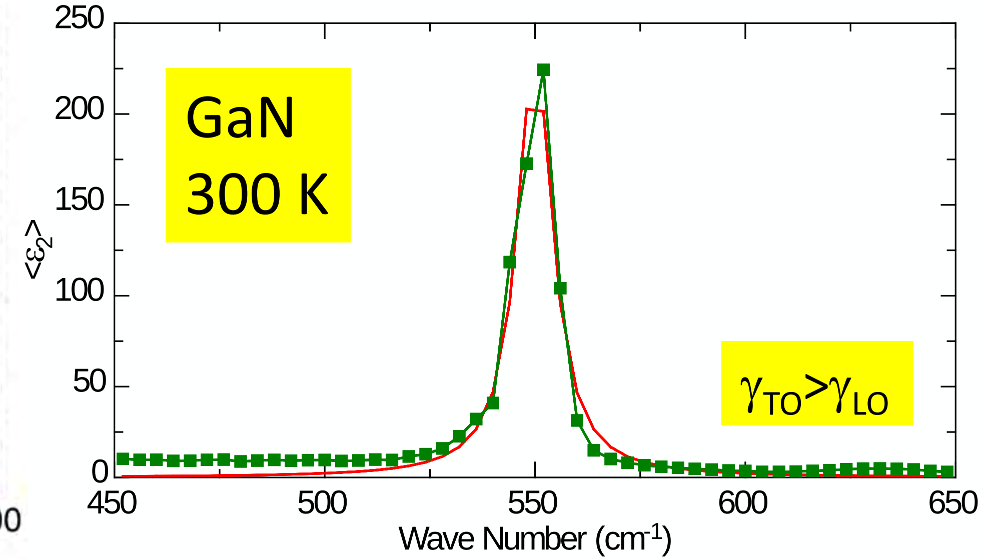
Lorentz oscillator: constant γ

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

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

Difficult to evaluate because of noise.





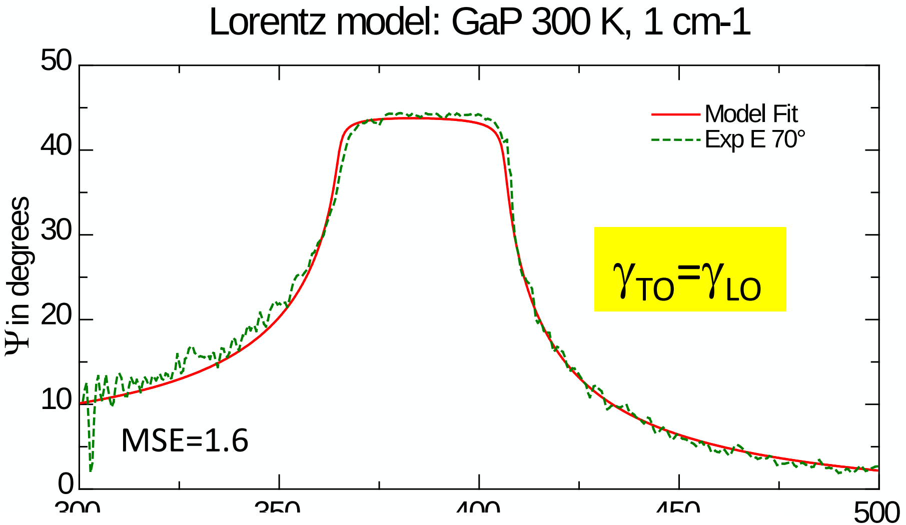
N. Samarasingha *et al.*, JVSTB **39**, 052201 (2021).
E. Baron et al., Phys. Rev. Mater. **3**, 104603 (2019).

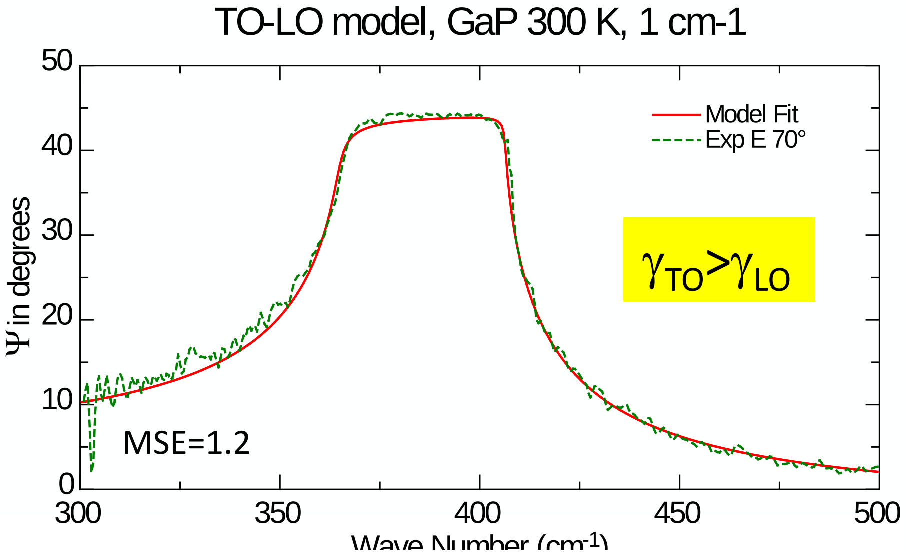
Frequency-Dependent Decay Rate: TO-LO

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

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

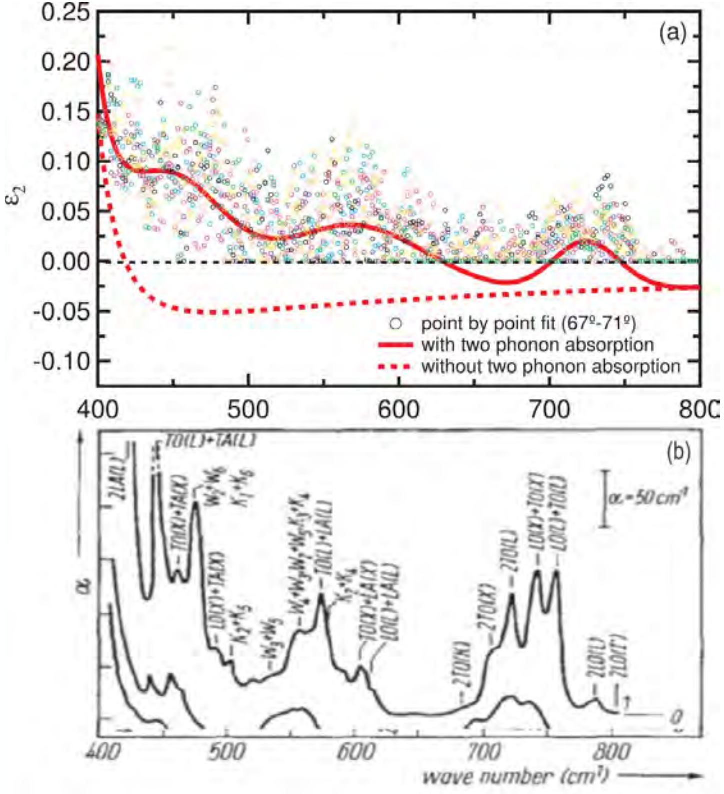
Or a complex Lorentzian amplitude.





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).**

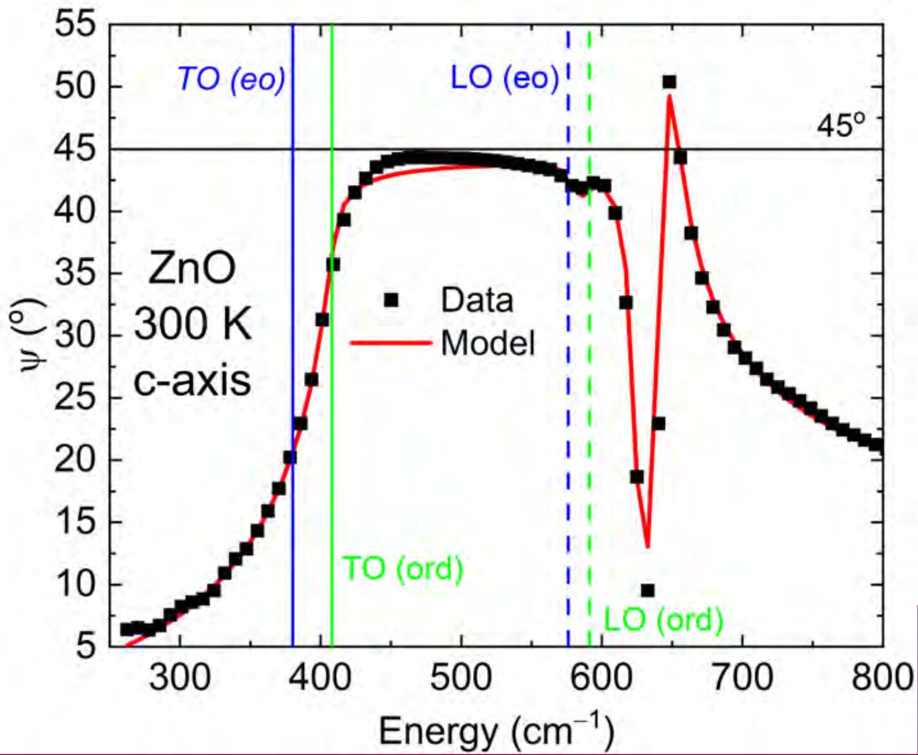
- **How do we fix this?**
  The two-phonon absorption also contributes to the absorption, keeping the total absorption coefficient positive.

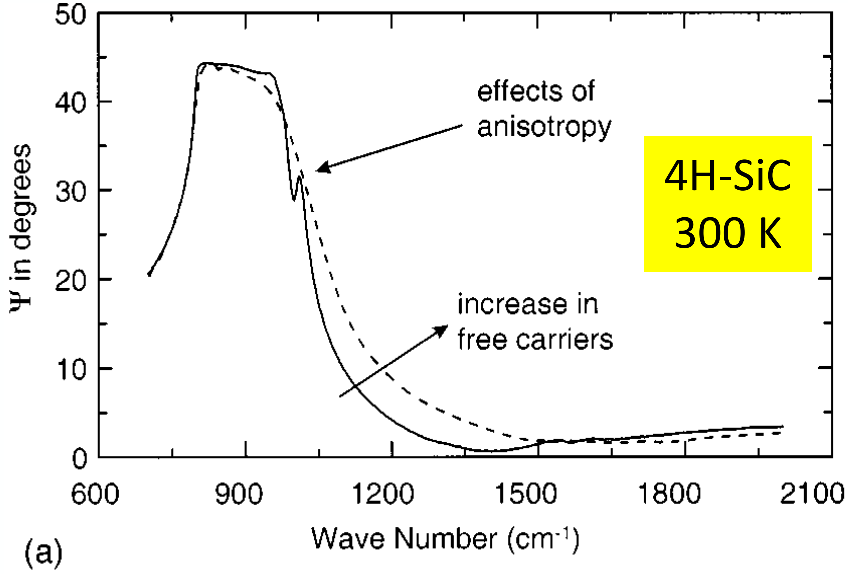
Reststrahlen Band in Uniaxial Crystal ZnO

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.



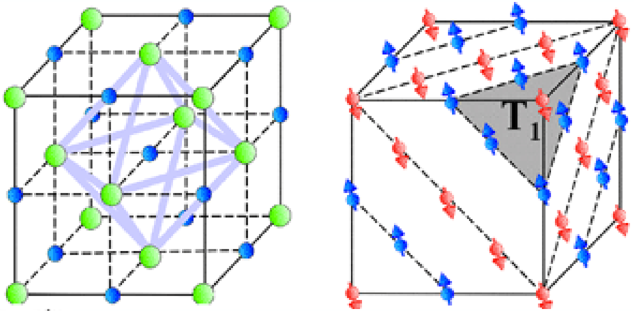


T. E. Tiwald *et al.*, PRB **60**, 11464 (1999).
N. Samarasingha *et al.*, JVSTB **39**, 052201 (2021).
Also: E. Franke *et al.*, APL **70**, 1668 (1997).

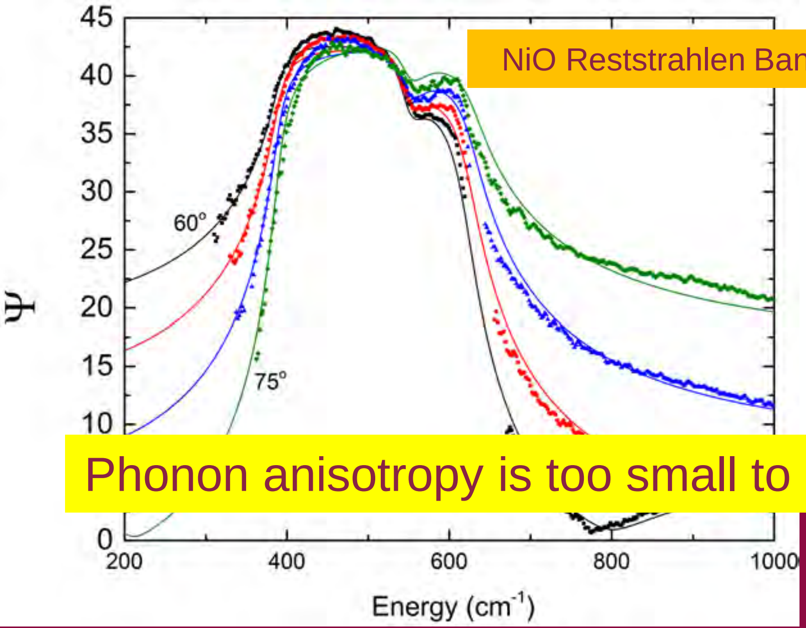
No Phonon Anisotropy in c-axis NiO $(111)_{cubic}$

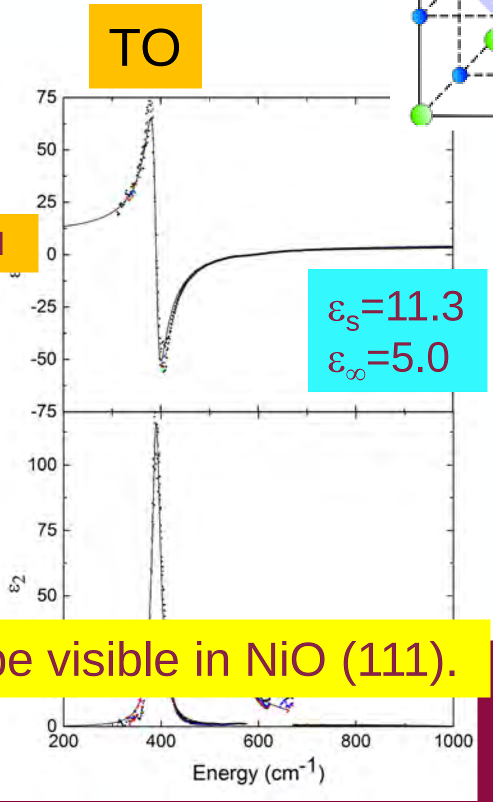
- Rocksalt Crystal Structure (FCC), Space Group 225 (Fm-3m).
- Single TO/LO phonon pair.
- Antiferromagnetic ordering along (111), should cause phonon splitting (8-30 cm^{-1}).
- **Anisotropy not visible in NiO (111).**

NiO cell



Rooksby, Nature, 1943

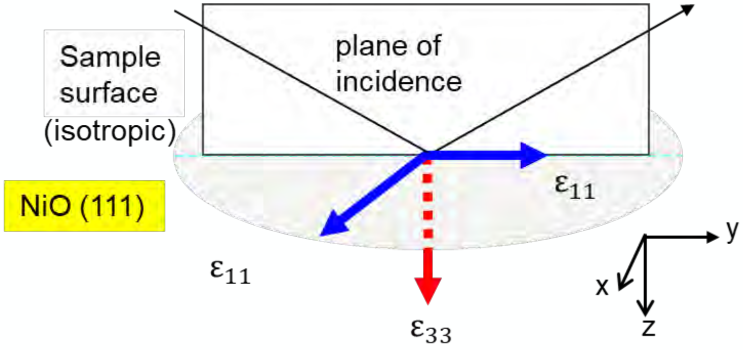


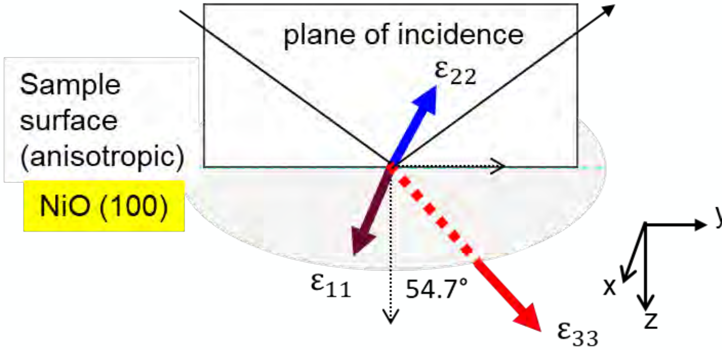


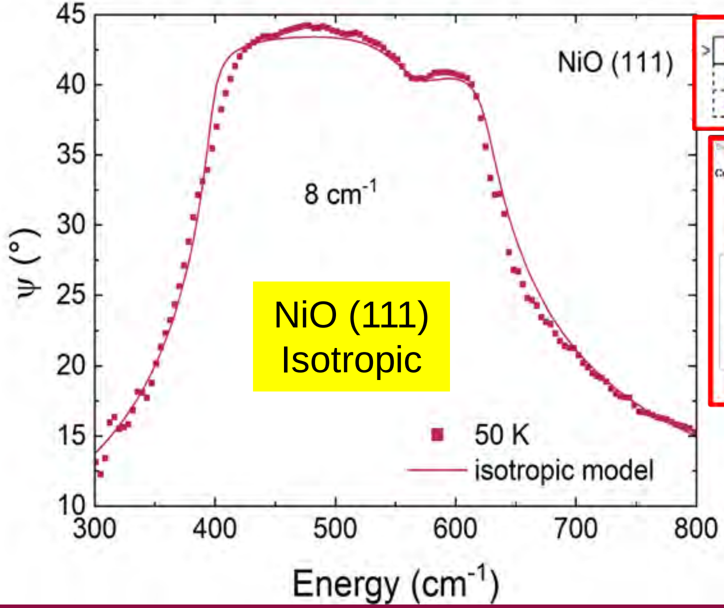
Phonon anisotropy is too small to be visible in NiO (111).

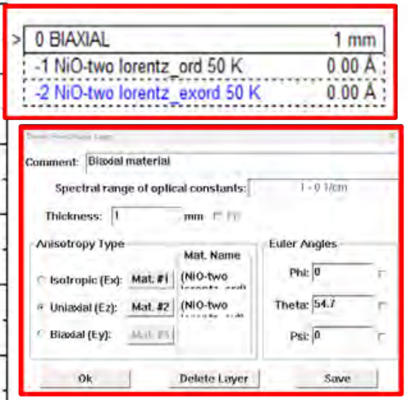
Willett-Gies & Nelson, JVST A **33**, 061202 (2015)

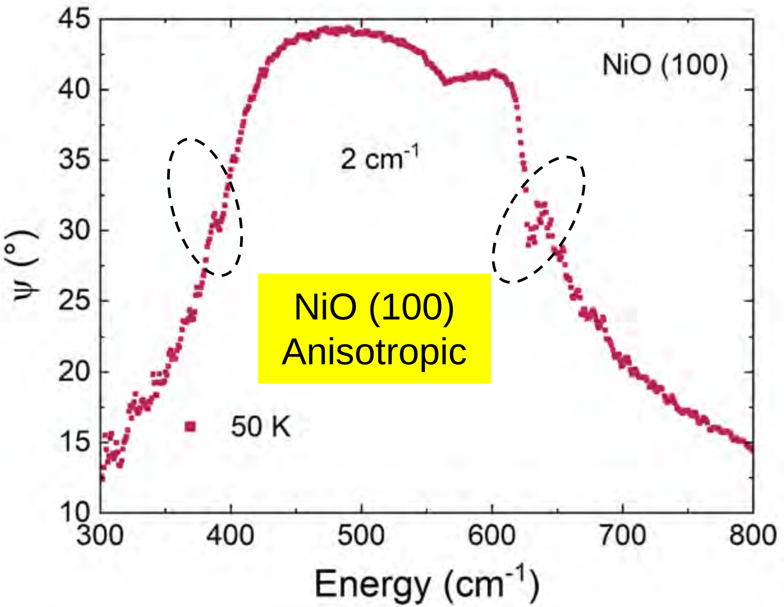
Compare NiO (111) and (100)



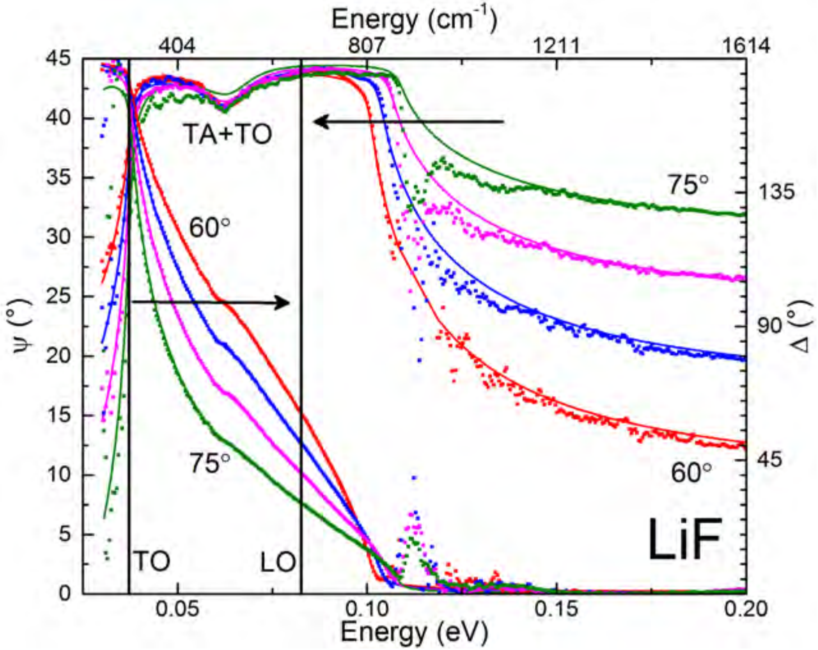








Two-phonon absorption in LiF



Phonon energies in LiF:

TO: 304 cm^{-1}

LO: 669 cm^{-1}

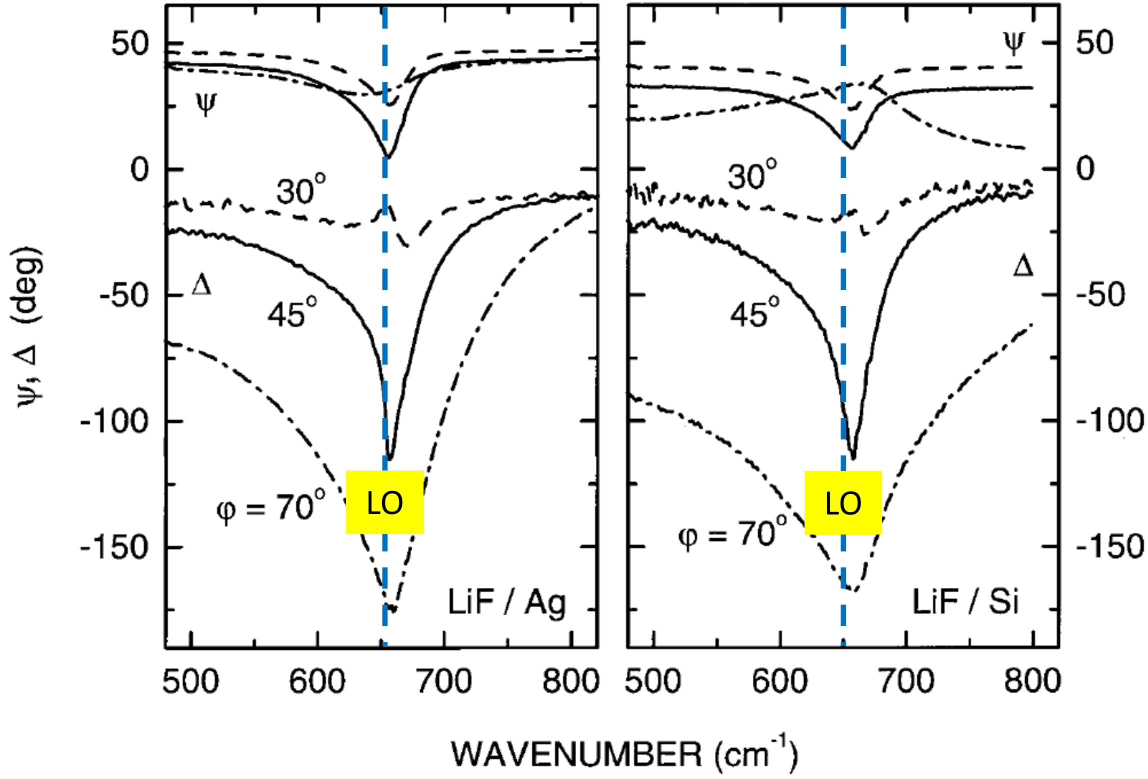
LO phonon not seen in ε_2.

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).

Berreman Effect: LiF on Ag



Light is a transverse wave:

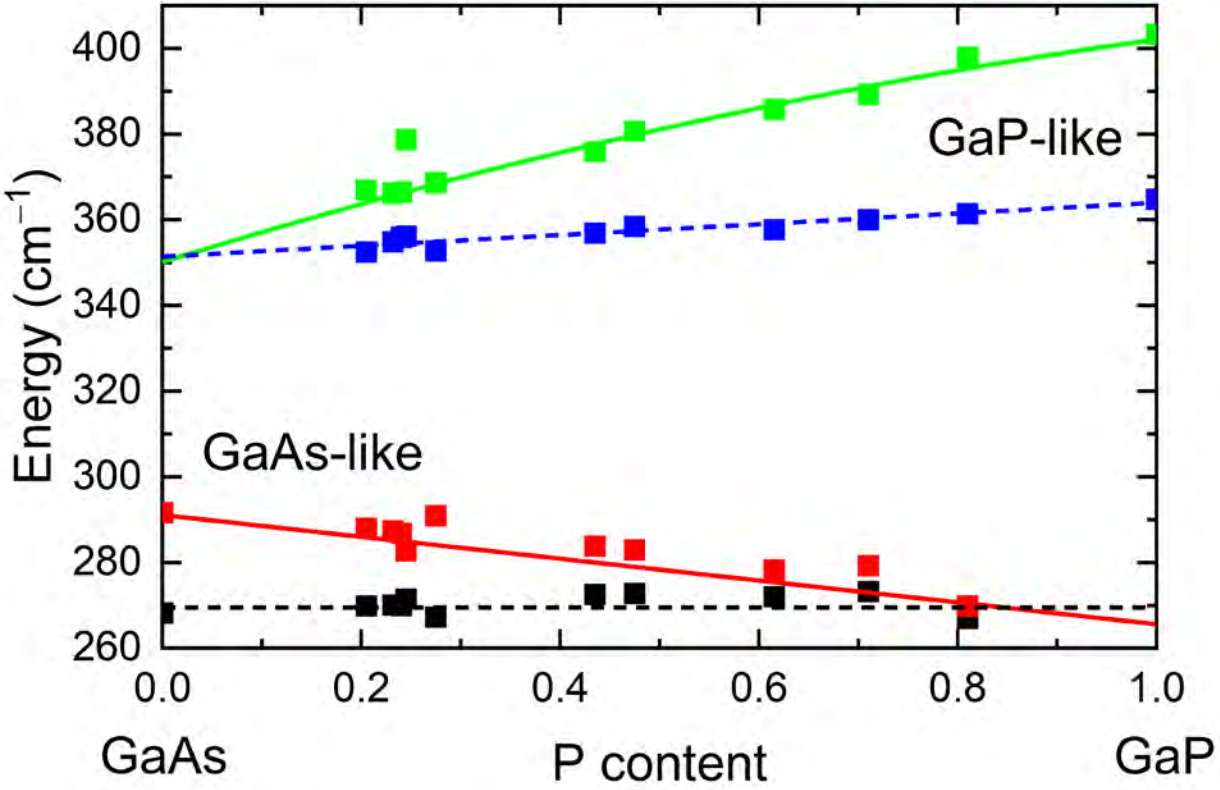
- only couples to TO phonons.
- cannot excite LO phonons.

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**.

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.

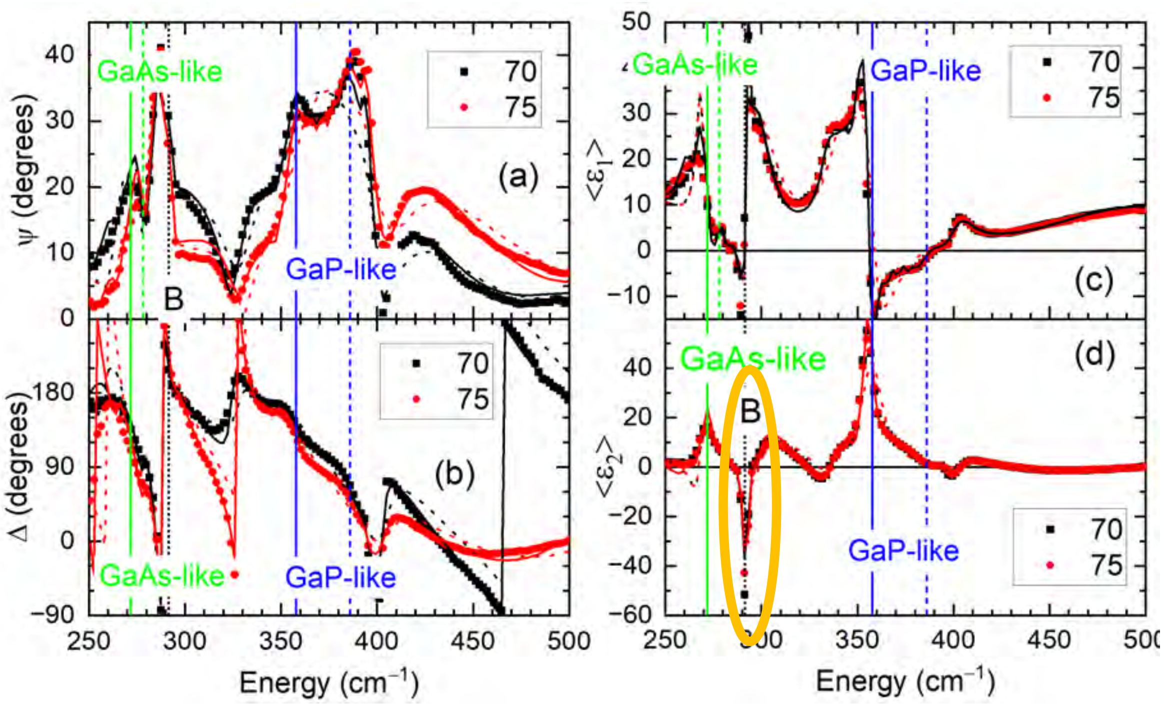
Some dependence of phonon energies on composition.

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:

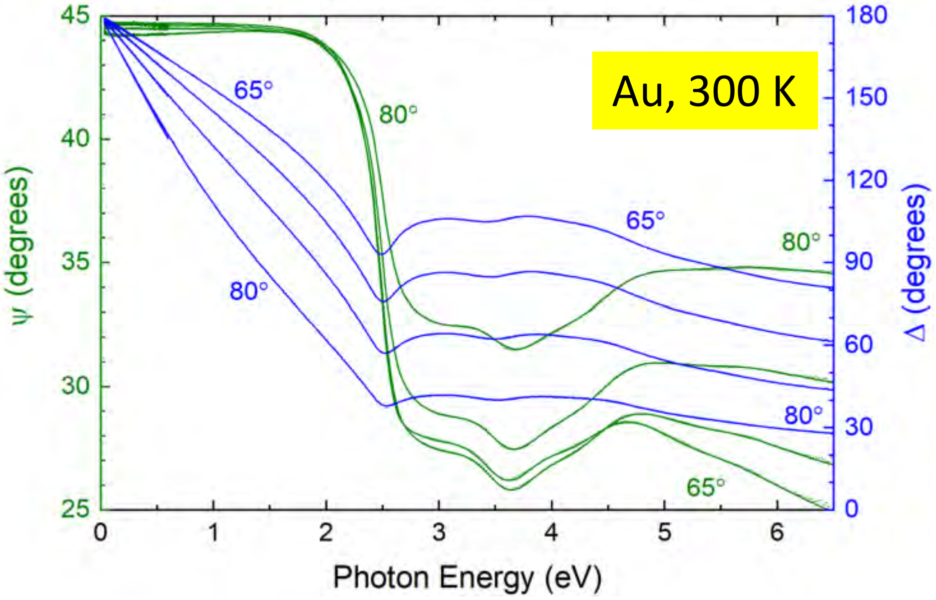
- GaAs-like (TO, LO)
- GaP-like (TO, LO)

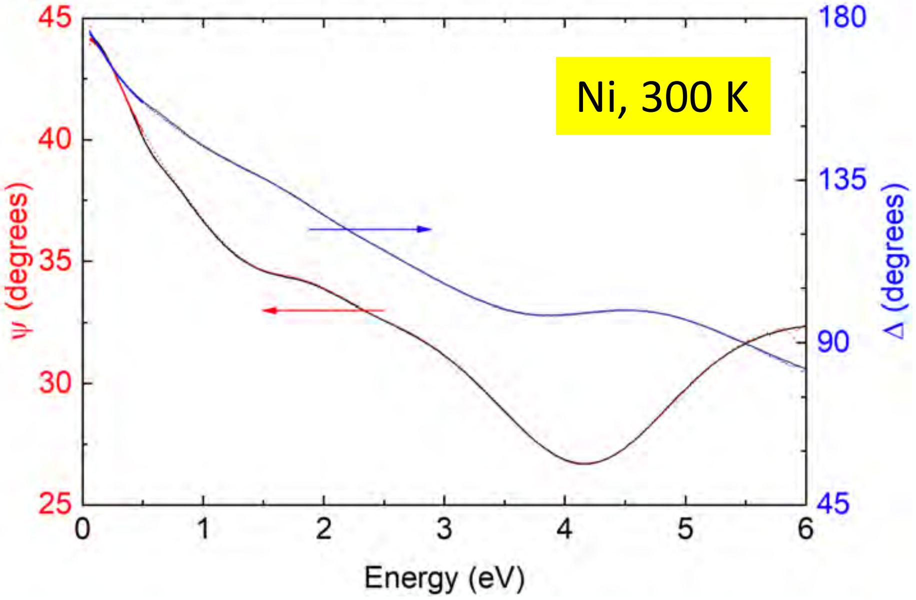
Berreman mode:
LO phonon of GaAs substrate shows up in ellipsometry spectra

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.

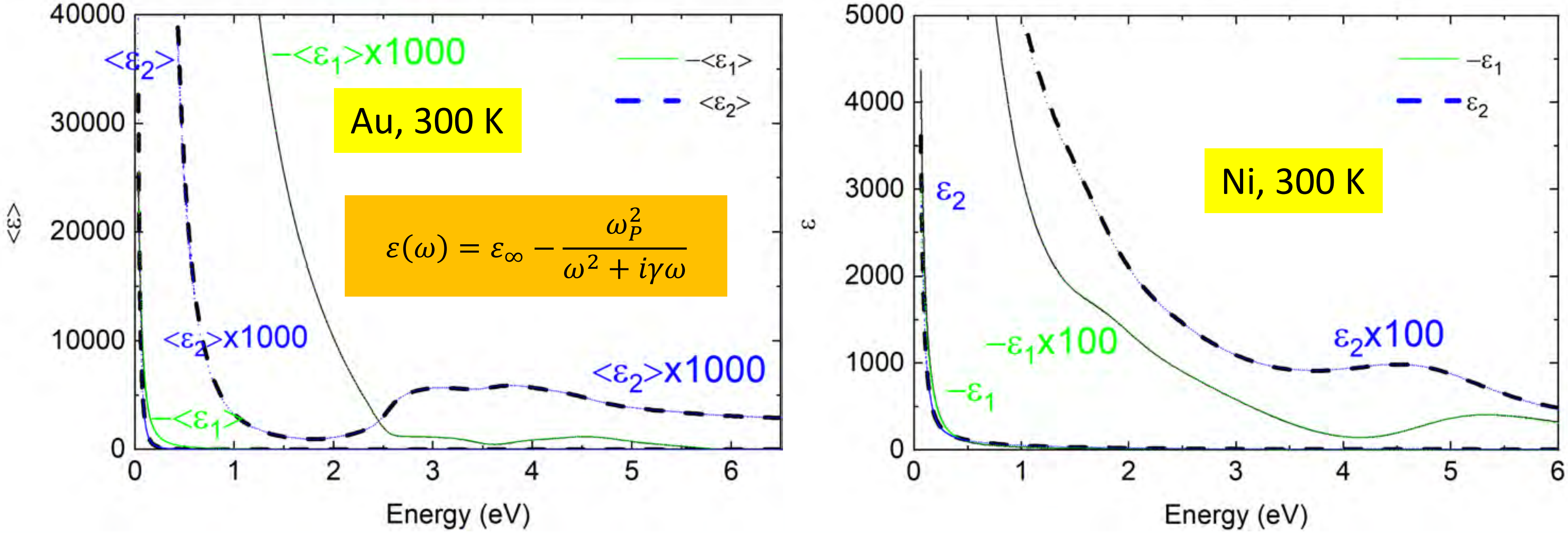
For a metal, psi should be 45 degrees up to VUV region.

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)



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

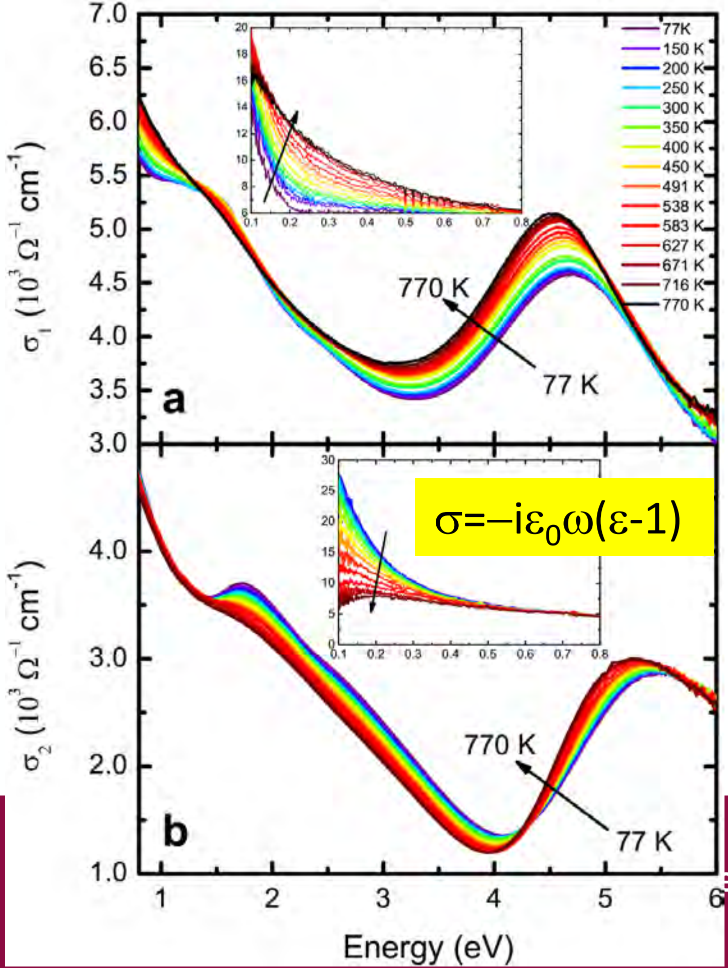
$-\varepsilon_1$, ε_2 very large in IR.

Interband transitions in UV range.

Better representation of data with optical conductivity: $\sigma = -i\varepsilon_0\omega(\varepsilon - 1)$

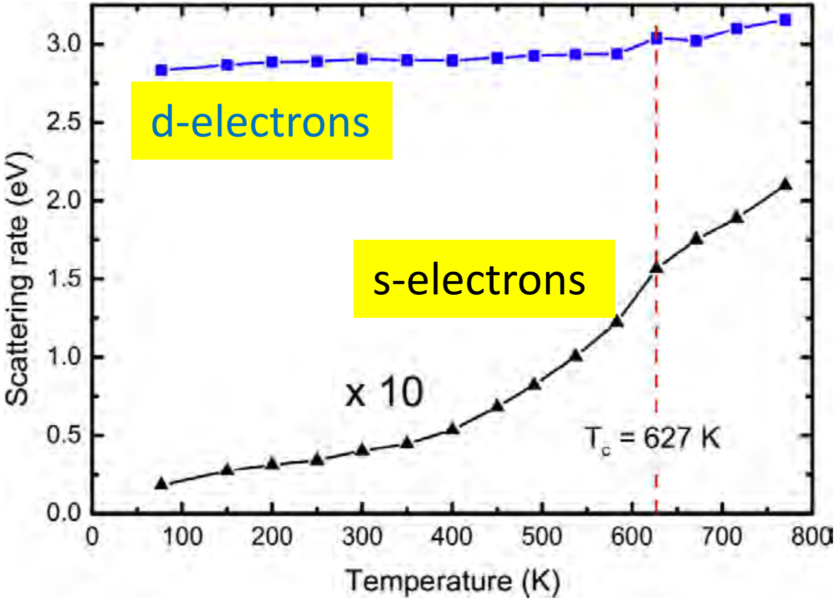
F. Abadizaman and SZ, JVSTB **37**, 062920 (2019).

Drude Response of Ni (Temperature-dependent)



Fitting the dielectric function of Ni:

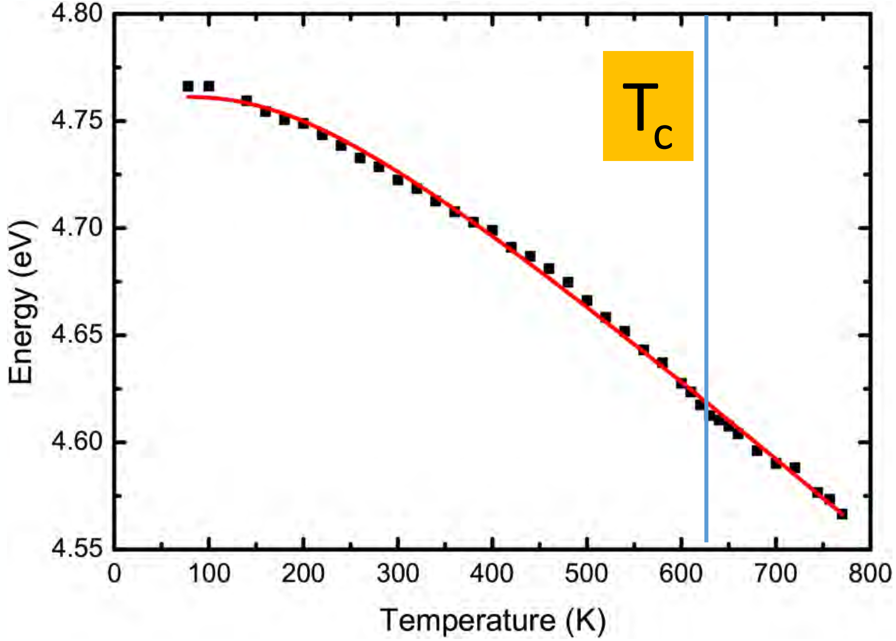
- Two Drude terms (s-, d-electrons)
- Four Lorentz oscillators for interband transitions.

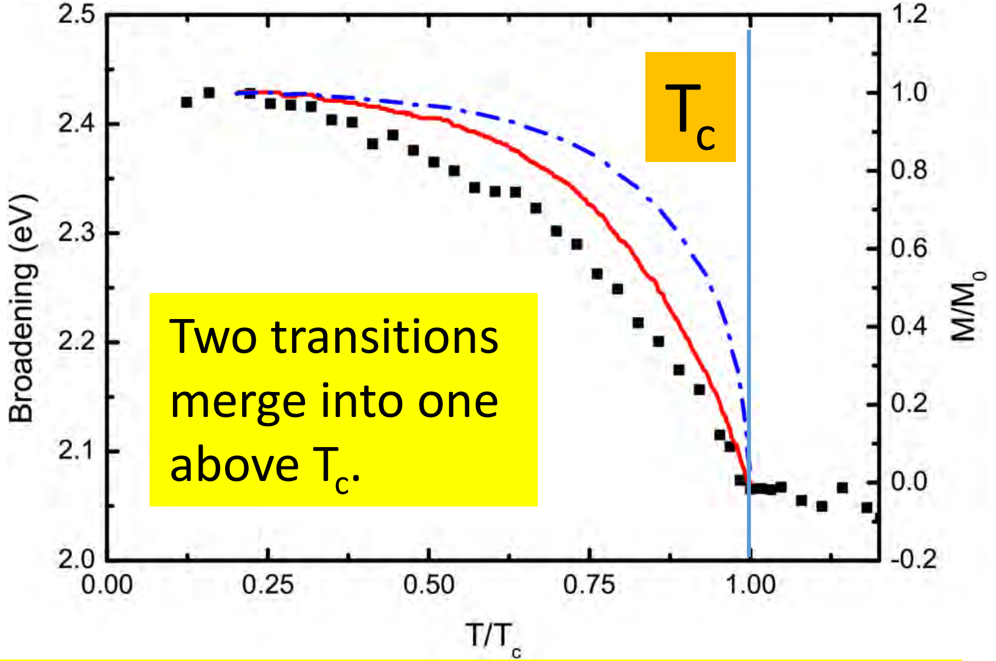


$$\varepsilon(\omega) = \varepsilon_\infty - \frac{\omega_P^2}{\omega^2 + i\gamma\omega}$$

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

Singularity at the Curie Temperature of Ni

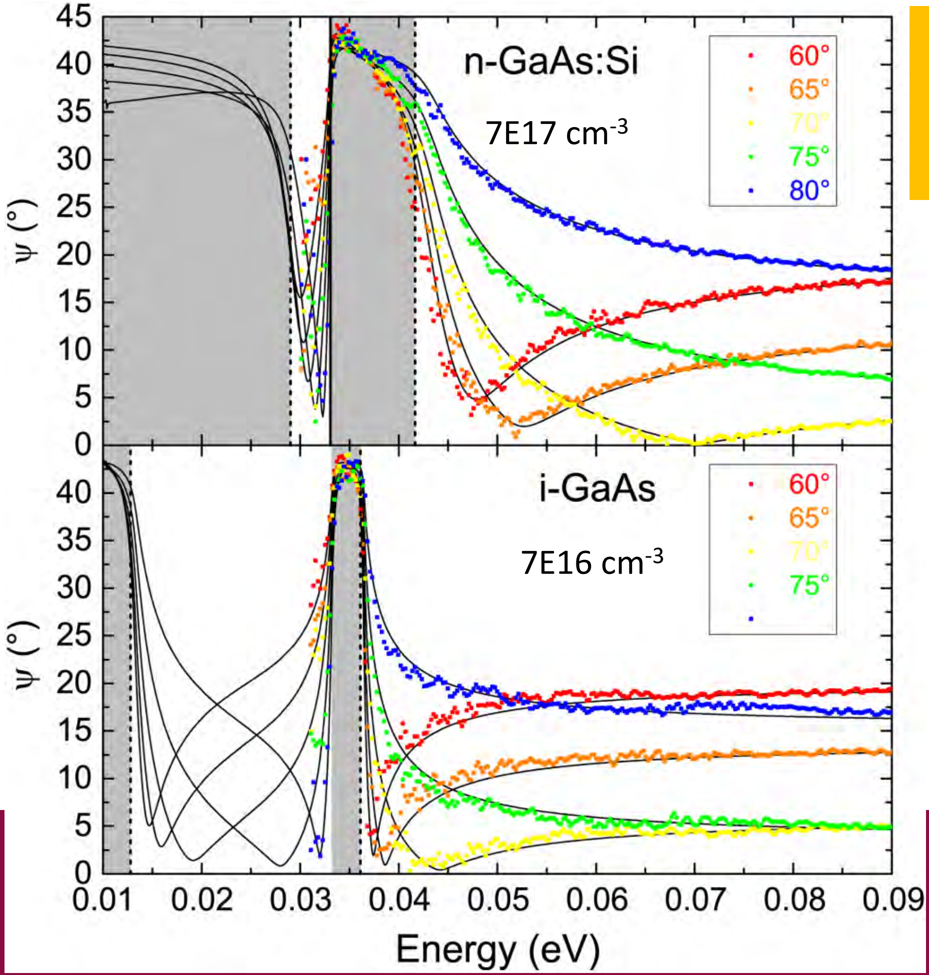




Energy of interband transition at 4.8 eV shows typical redshift with increasing temperature.
Broadening decreases and shows singular behavior at the Curie temperature (similar to magnetization).

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

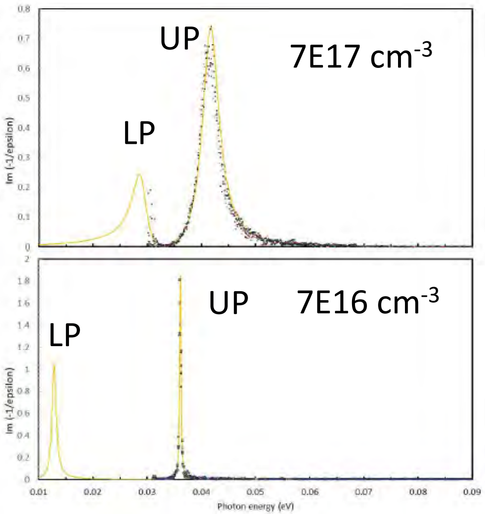
Plasmon-Phonon Coupling



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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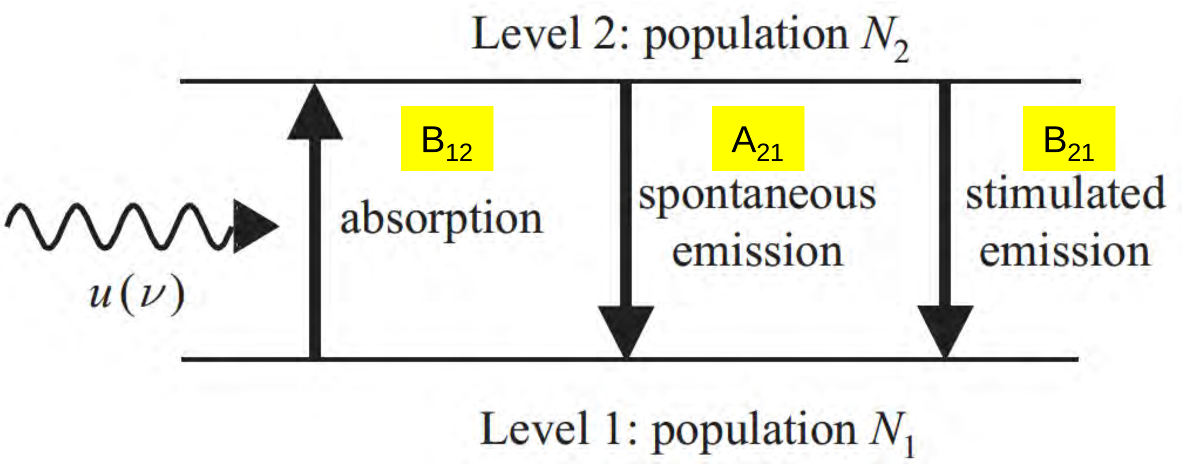
Thin-film epitaxial samples from many different sources: Arizona State, Delaware, Texas, IIT Indore, Texas State, AFRL/RY+RV, Arkansas, Sandia, NREL, NASA, SOITEC, QuantTera, Connecticut, IBM, Global Foundries, UNM, Ohio State, etc.

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).