

Solid-state spectroscopy

E.V. Lavrov*

Institut für Angewandte Physik, Halbleiterphysik

Contents

| | | |
|----------|--|-----------|
| 1 | Electromagnetic waves in media | 4 |
| 1.1 | Electromagnetic spectrum | 4 |
| 1.2 | Maxwell equations | 4 |
| 1.3 | Optical constants | 5 |
| 2 | Dielectric function | 7 |
| 2.1 | Free carriers (metals) | 7 |
| 2.2 | Damped oscillator | 8 |
| 2.3 | Damped oscillator and free carriers | 11 |
| 3 | Experimental equipment | 12 |
| 3.1 | Light sources | 12 |
| 3.1.1 | Broad band sources | 12 |
| 3.1.2 | Lasers | 12 |
| 3.2 | Detectors | 12 |
| 3.2.1 | Photomultiplier | 12 |
| 3.2.2 | Photodiodes | 12 |
| 3.2.3 | Bolometer | 12 |
| 3.3 | Spectral analysis of light | 12 |
| 3.3.1 | Monochromators | 12 |
| 3.3.2 | Fabry-Perot interferometer | 12 |
| 3.3.3 | Fourier spectroscopy | 12 |
| 4 | Spectral line shapes | 12 |
| 4.1 | Lorentzian | 12 |
| 4.2 | Gaussian | 12 |
| 4.3 | Fano-resonance | 12 |
| 4.4 | Apparatus function & convolution | 12 |
| 5 | Symmetry and selection rules | 12 |
| 5.1 | Representation of groups and selection rules | 12 |
| 5.2 | Influence of perturbation: magnetic & electric field, stress | 12 |

*Tel: (0351) 463 33637, Physikgebäude C305, e-mail: edward.lavrov@physik.tu-dresden.de, <http://www.physik.tu-dresden.de/~lavrov>

| | | |
|-----------|--|-----------|
| 6 | IR spectroscopy | 12 |
| 6.1 | Absorption | 12 |
| 6.2 | Reflection | 12 |
| 6.3 | Photoconductivity | 12 |
| 7 | Scattering of light | 12 |
| 7.1 | Raman scattering: CARS, SERS, micro-Raman | 12 |
| 7.2 | Scattering by: phonons/plasmons, defects, free carriers, Brillouin scattering | 12 |
| 8 | Luminescence | 12 |
| 8.1 | Types of recombination: band-band, band-impurity, impurity-impurity, ex- citons | 12 |
| 8.2 | Photo-, cathodo-, electro-, etc. luminescence, excitation spectroscopy . . . | 12 |
| 9 | Magnetic resonance spectroscopy | 12 |
| 9.1 | EPR, NMR | 12 |
| 9.2 | ODMR | 12 |
| 10 | Deep level transient spectroscopy | 12 |
| 11 | Spectroscopy with electrons, positrons, muons | 12 |
| A | Tables | 13 |
| B | Solutions to the problems | 14 |
| B.1 | Electromagnetic waves in media | 14 |
| B.2 | Dielectric function | 14 |

Literature

- N. W. Ashcroft & N. D. Mermin: **Festkörperphysik**
Oldenbourg
- C. Kittel: **Einführung in die Festkörperphysik**
Oldenbourg
- O. Madelung: **Grundlagen der Halbleiterphysik**
Springer
- P.Y. Yu & M. Cardona: **Fundamentals of Semiconductors**
Springer
- T. S. Moss, G. J. Burrell, B. Ellis: **Semiconductor opto-electronics**
Butterworth Group
- H. Kuzmany: **Festkörperspektroskopie**
Springer
- C. Klingshirn: **Semiconductor optics**
Springer
- R. J. Bell: **Introductory Fourier transform spectroscopy**
Acad. Press
- Editor. M. Cardona: **Light scattering in solids – I & II**
Springer
- A. Abragam & B. Bleaney: **Electron paramagnetic resonance of transition ions**
Oxford Univ. Press

1 Electromagnetic waves in media

1.1 Electromagnetic spectrum

Units

$$\begin{aligned}\frac{[\text{meV}]}{0.124} &= [\text{cm}^{-1}], \\ \frac{1.24}{[\mu\text{m}]} &= [\text{eV}], \\ 11.6 \times [\text{meV}] &= [\text{K}].\end{aligned}\tag{1}$$

Table 1: The electromagnetic spectrum.

| | Wavelength | Energy, eV | Wave number, cm^{-1} | T, K |
|----------------|-------------------------------|---------------------------------|-------------------------------|----------------------------------|
| EM waves | $\geq 0.03 \text{ cm}$ | $\leq 400 \times 10^{-6}$ | | ≤ 5 |
| Far IR | $3000\text{--}40 \mu\text{m}$ | $0.4\text{--}50 \times 10^{-3}$ | 3–400 | 5–350 |
| IR | $40\text{--}0.8 \mu\text{m}$ | 0.03–1.6 | 250–12500 | $(0.35\text{--}18) \times 10^3$ |
| Visible | $0.8\text{--}0.4 \mu\text{m}$ | 1.6–3 | 12000–25000 | $(18\text{--}36) \times 10^3$ |
| UV | $400\text{--}10 \text{ nm}$ | 3–120 | | $(3.6\text{--}140) \times 10^4$ |
| X-rays | $10\text{--}0.01 \text{ nm}$ | $0.1\text{--}120 \times 10^3$ | | $(1.4\text{--}1400) \times 10^6$ |
| γ -rays | $10\text{--}0.1 \text{ pm}$ | $0.1\text{--}12 \times 10^6$ | | $(1.4\text{--}140) \times 10^9$ |

1.2 Maxwell equations

$$\nabla \times \mathbf{E} = -\frac{1}{c} \frac{\partial \mathbf{B}}{\partial t}, \quad \nabla \times \mathbf{H} = \frac{1}{c} \frac{\partial \mathbf{D}}{\partial t} + \frac{4\pi}{c} \mathbf{j},\tag{2a}$$

$$\nabla \cdot \mathbf{B} = 0, \quad \nabla \cdot \mathbf{D} = 4\pi\rho,\tag{2b}$$

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} = \mathbf{E} + 4\pi\alpha\mathbf{E} = \epsilon\mathbf{E},\tag{3a}$$

$$\mathbf{B} = \mu\mathbf{H},\tag{3b}$$

$$\mathbf{j} = \sigma\mathbf{E}.\tag{3c}$$

Plane wave (ebene Welle) and nonmagnetic material ($\mu = 1$, $\rho = 0$, $\mathbf{H} = \mathbf{B}$)

$$\mathbf{E} = \mathbf{E}_0 \exp(i\mathbf{k}\mathbf{r} - i\omega t).$$

From Eqs (2) obtain that

$$\begin{aligned}\mathbf{k} \times \mathbf{E} &= \frac{\omega}{c} \mathbf{H}, \\ \mathbf{k} \times \mathbf{H} &= -\frac{\omega}{c} \mathbf{D} - i\frac{4\pi\sigma}{c} \mathbf{E},\end{aligned}$$

and

$$\mathbf{k} \times \mathbf{k} \times \mathbf{E} = -\frac{\omega^2}{c^2} \mathbf{D} - i\frac{4\pi\sigma\omega}{c^2} \mathbf{E}\tag{4a}$$

$$k^2 \mathbf{E} - \frac{\omega^2}{c^2} \epsilon(\omega) \mathbf{E} - i\frac{4\pi\sigma\omega}{c^2} \mathbf{E} = \mathbf{k}(\mathbf{k} \cdot \mathbf{E}).\tag{4b}$$

| $\mathbf{k} \perp \mathbf{E}$ & $\sigma = 0$ | $\mathbf{k} \parallel \mathbf{E}$ |
|--|---|
| Transverse wave $\omega^2 \epsilon(\omega)/c^2 = k^2$ $k = \omega n/c$ | Longitudinal wave (plasmon) $\epsilon(\omega) = 0$ |

1.3 Optical constants

Transverse wave (Transversalwelle) from Eq. (4b)

$$k^2 - \frac{\omega^2}{c^2} \epsilon(\omega) = \frac{4\pi\sigma\omega}{c^2} i. \quad (5)$$

Here we assume that $\text{Im}(\epsilon(\omega)) = 0$ and $\epsilon(\omega) > 0$. Represent k as

$$k = N \frac{\omega}{c}, \quad (6)$$

where $N = n + i\kappa$. Then

$$n^2 + 2in\kappa - \kappa^2 - \epsilon(\omega) = \frac{4\pi\sigma}{\omega} i \quad (7)$$

or

$$n^2 - \kappa^2 = \epsilon, \quad (8a)$$

$$n\kappa = \frac{2\pi\sigma}{\omega}. \quad (8b)$$

Finally we get

$$2n^2 = \epsilon \left[1 + (4\pi\sigma/\epsilon\omega)^2 \right]^{1/2} + \epsilon, \quad (9a)$$

$$2\kappa^2 = \epsilon \left[1 + (4\pi\sigma/\epsilon\omega)^2 \right]^{1/2} - \epsilon. \quad (9b)$$

Reflectivity R at the interface air/sample is

$$R = \frac{(1-n)^2 + \kappa^2}{(1+n)^2 + \kappa^2}. \quad (10)$$

Absorption of electromagnetic waves (EMW) is determined by parameter k . Since intensity I of the EMW is proportional to \mathbf{E}^2 we obtain that

$$I \propto \exp(-2\kappa\omega z/c) \quad (11)$$

Absorption coefficient α is inversely proportional to the penetration depth δ

$$\alpha = \delta^{-1} = 2\kappa\omega/c \quad (12)$$

Examples

| Insulators $\sigma = 0$ | Metals $4\pi\sigma/\epsilon\omega \gg 1$ | Semiconductors $\sigma \neq 0$ |
|--|---|--|
| $n = \sqrt{\epsilon}, \kappa = 0$ $R = (1-n)^2/(1+n)^2$ | $n \approx \kappa$ $R \approx 1 - 2/n \approx 1$ | $n > \kappa \neq 0$ R depends on doping |

- Intrinsic Si ($\epsilon = 12$ for $\lambda < 1 \mu\text{m}$), $n_e = n_h \approx 10^{10} \text{ cm}^{-3}$, $\rho = 1/\sigma \approx 400000 \Omega\text{-cm}$, $n \gg \kappa \approx 0$, thus $R \approx 30 \%$.
- Strongly doped Si, $n_e = 10^{19} \text{ cm}^{-3}$, $\rho = 1/\sigma \approx 10^{-3} \Omega\text{-cm}$, $n = \sqrt{15}$, $\kappa = \sqrt{3}$, then $R \approx 40 \%$.

Skin-effect In metals at low frequencies, i.e. $4\pi\sigma/\epsilon\omega \gg 1 \Rightarrow k = \sqrt{2\pi\sigma/\omega}$ and

$$\boxed{\delta = \frac{c}{4\pi\sqrt{\sigma\nu}}}. \quad (13)$$

Here we took into account that $\omega = 2\pi\nu$. That is, current flows on the surface of a wire (*Skin-effect*).¹

- For Cu $\rho = 1/\sigma \approx 10^{-6} \Omega\cdot\text{cm}$. If we take $\nu = 1 \text{ MHz}$, then $\delta \approx 25 \mu\text{m}$.

Problems

1. Energy gap of GaAs at room temperature is 1.42 eV. Calculate a frequency, wave length, and wave number of the corresponding energy transition.
2. What wave length does room temperature (300 K) correspond?
3. Find the values of n , k , and R for silicon at $\lambda^{-1} = 1000 \text{ cm}^{-1}$ ($\epsilon = 12$) if the material has a resistivity of 10 and 0.001 $\Omega\cdot\text{cm}$. What are wave length, energy, and frequency of an electromagnetic wave with $\lambda^{-1} = 1000 \text{ cm}^{-1}$?
4. Conductivity of Ag at 0 °C is $6.7 \times 10^7 \text{ S/m}$. Find the skin depth for the *ac* current with frequencies of 1 kHz and 1 MHz.
5. What are the losses of light with $\lambda = 0.55 \mu\text{m}$ upon reflection from silver, gold, copper, and aluminum? Resistivities of Ag, Au, Cu, and Al are 1.49×10^{-6} , 2.06×10^{-6} , 1.55×10^{-6} , and $2.5 \times 10^{-6} \Omega\cdot\text{cm}$, respectively.

¹Note that in the literature the skin depth δ corresponds to the extinction of \mathbf{E} rather than $|\mathbf{E}|^2$ and is, therefore, a factor of 2 larger than that of given in Eq. (13).

2 Dielectric function

2.1 Free carriers (metals)

If an electron moves with a speed below the speed of light in the media, it can neither absorb nor emit photon.



$$\mathbf{p}_2 = \mathbf{p}_1 + \hbar\mathbf{k} \quad (14a)$$

$$E(p_2) = E(p_1) + \hbar\omega \quad (14b)$$

$$\hbar\omega = \hbar ck \quad (14c)$$

$$E(p_1 + \hbar k) - E(p_1) = \hbar ck \quad (14d)$$

$$\frac{\partial E}{\partial p} \hbar k \approx E(p + \hbar k) - E(p) \quad (14e)$$

$v = \partial E / \partial p$ is a group velocity. Hence, for $v < c$ absorption and emission of photons by electrons without scattering are forbidden. This means, that only interacting electrons can contribute to the dielectric function. How to model this?

$$m \frac{d\mathbf{v}}{dt} = e\mathbf{E}e^{-i\omega t} - m\mathbf{v}/\tau \quad (15a)$$

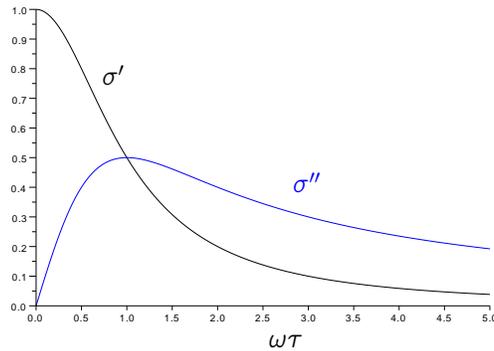
$$\mathbf{v} \propto e^{-i\omega t} \quad (15b)$$

$$\mathbf{j} = eN_e\mathbf{v} = \frac{N_e e^2}{m} \frac{1}{-i\omega + \tau^{-1}} \mathbf{E} = \sigma \mathbf{E}. \quad (15c)$$

$$\sigma = \frac{N_e e^2}{m} \frac{\tau}{1 + \omega^2 \tau^2} + i \frac{N_e e^2}{m} \frac{\omega \tau^2}{1 + \omega^2 \tau^2} = \sigma'(\omega) + i\sigma''(\omega) \quad (15d)$$

Substituting the last equation into Eq. (5) obtain

$$k^2 = \left(\frac{\omega}{c}\right)^2 \epsilon \left(1 - \frac{4\pi\sigma''}{\epsilon\omega} + \frac{4\pi\sigma'}{\epsilon\omega} i\right) \quad (16)$$



For Si with $\mu = e\tau/m = 1450 \text{ cm}^2/\text{Vs}$ $\tau = 10^{-12} \text{ s}$. Thus, $\nu = 1/2\pi\tau = 160 \text{ GHz}$.

Case of $\omega\tau \ll 1 \Rightarrow \sigma' \gg \sigma''$ Absorption dominates, see *skin-effect* above.

Case of $\omega\tau \gg 1 \Rightarrow \sigma' \ll \sigma''$ Absorption is weak

$$k^2 = \left(\frac{\omega}{c}\right)^2 \epsilon \left(1 - \frac{\omega_{pl}^2}{\omega^2}\right), \quad (17)$$

where

$$\omega_{pl} = \left(\frac{4\pi e^2 N_e}{\epsilon m}\right)^{1/2} \quad (18)$$

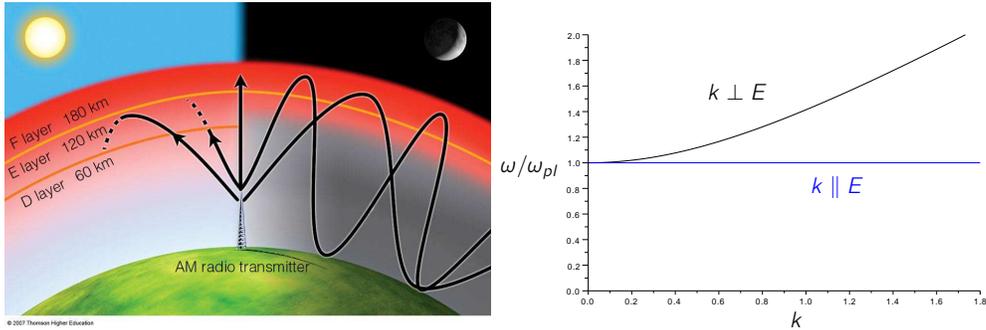
is the plasma frequency.

That is for $\omega < \omega_{pl}$ $k^2 < 0$ and the light is reflected rather than absorbed.

Examples

- In metals $N_e \approx 10^{23} \text{ cm}^{-3}$ and plasma frequency is above visible region. This is why metals reflect light.²
- Communication with satellites is done on the frequencies above ω_{pl} of the ionosphere, so that the radio waves could come through. For $N_e = 10^6 \text{ cm}^3$ plasma frequency is about 9 MHz.
- Radio communication is done on the frequencies below the ω_{pl} , so that radio waves due to many reflections could reach the opposite side of the Earth.

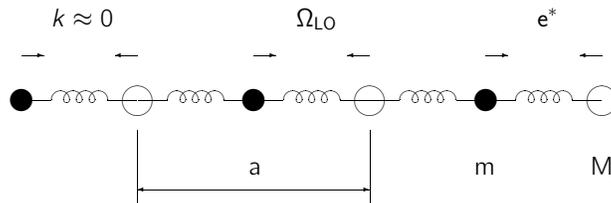
Longitudinal waves



For longitudinal waves in plasma $\epsilon(\omega_{pl}) = 0$ and there is practically no dispersion (blue line in the figure). For transverse waves (black line in the figure).

$$\omega = \omega_{pl} \left(1 + \left(\frac{kc}{\epsilon\omega_{pl}}\right)^2\right)^{1/2} \quad (19)$$

2.2 Damped oscillator



²Color of metals is determined by the intrinsic transitions rather than free electrons.

Equation of motion of a damped harmonic oscillator

$$\mu \frac{d^2 x}{dt^2} = -\mu\gamma \frac{dx}{dt} - \mu\Omega_{\text{TO}}^2 x + e^* E e^{-i\omega t} \quad (20)$$

Here, e^* is the “effective charge”, which is not directly related to the real charge of the oscillator and $\mu = Mm/(m + M)$ is the reduced mass of the oscillator. It depends on the type of the chemical bond: the more ionic, the bigger e^* . Looking for solution in the form of $x = x_0 e^{-i\omega t}$ and obtain

$$x_0 = \frac{e^*}{\mu} \frac{E}{\omega^2 - \Omega_{\text{TO}}^2 - i\omega\gamma}. \quad (21)$$

Since dipole moment $\mathbf{d} = e^* \mathbf{x} = \alpha \mathbf{E}$ get

$$\alpha = \frac{e^{*2}}{\mu} \frac{1}{\omega^2 - \Omega_{\text{TO}}^2 - i\omega\gamma} \quad (22)$$

Per definition $\epsilon = 1 + 4\pi N\alpha$, where N is the concentration of oscillators, hence

$$\epsilon = 1 + \frac{4\pi e^{*2} N}{\mu} \frac{1}{\Omega_{\text{TO}}^2 - \omega^2 - i\omega\gamma} \quad (23)$$

If we take into account other contributions to the dielectric function ϵ , we have to write that for $\omega \gg \Omega_{\text{TO}}$

$$\epsilon = \epsilon_\infty + \frac{4\pi e^{*2} N}{\mu} \frac{1}{\Omega_{\text{TO}}^2 - \omega^2 - i\omega\gamma} \quad (24)$$

Static $\epsilon_0 \equiv \epsilon(0)$, that is

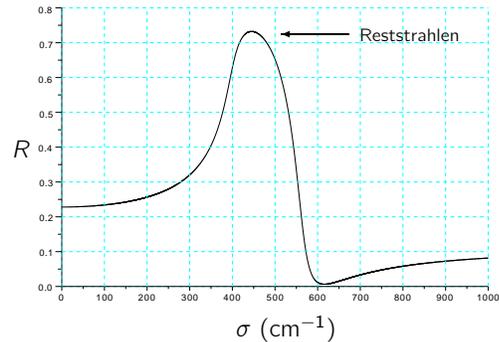
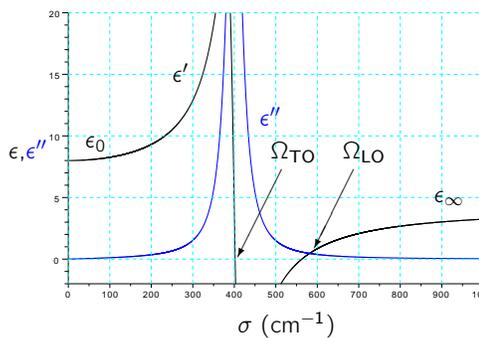
$$\epsilon_0 = \epsilon_\infty + \frac{4\pi e^{*2} N}{\mu\Omega_{\text{TO}}^2}. \quad (25)$$

Finally we get

$$\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \frac{\Omega_{\text{TO}}^2}{\Omega_{\text{TO}}^2 - \omega^2 - i\omega\gamma} \quad (26a)$$

$$\epsilon = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) \frac{(\Omega_{\text{TO}}^2 - \omega^2)\Omega_{\text{TO}}^2}{(\Omega_{\text{TO}}^2 - \omega^2)^2 + (\omega\gamma)^2} + i(\epsilon_0 - \epsilon_\infty) \frac{\gamma\omega\Omega_{\text{TO}}^2}{(\Omega_{\text{TO}}^2 - \omega^2)^2 + (\omega\gamma)^2} \quad (26b)$$

$$\epsilon \equiv \epsilon'(\omega) + i\epsilon''(\omega) \quad (26c)$$



From Eqs. (7) and (8) with $\sigma = 0$ we get

$$n^2 - \kappa^2 = \epsilon'(\omega) \quad (27a)$$

$$2n\kappa = \epsilon''(\omega). \quad (27b)$$

Consequently, we obtain

$$2n^2 = \sqrt{\epsilon'^2 + \epsilon''^2} + \epsilon' \quad (28a)$$

$$2\kappa^2 = \sqrt{\epsilon'^2 + \epsilon''^2} - \epsilon' \quad (28b)$$

Figure shows typical behavior of n , κ , and reflectivity R (see Eq. (10)) as a function of EVW frequency. Note that for $\gamma = 0$ in the frequency range $\Omega_{\text{TO}} < \omega < \Omega_{\text{LO}}$ $n^2 < 0$, which means that there are not states of light in the media with this frequencies, that is, all of it is reflected, but not absorbed (for absorption one needs $\epsilon'' \neq 0$). This band is called *Reststrahlen band*. Here,

$$\boxed{\left(\frac{\Omega_{\text{LO}}}{\Omega_{\text{TO}}}\right)^2 = \frac{\epsilon_0}{\epsilon_\infty}} \quad (29)$$

is the famous LYDDANE-SACHS-TELLER relation.

Examples

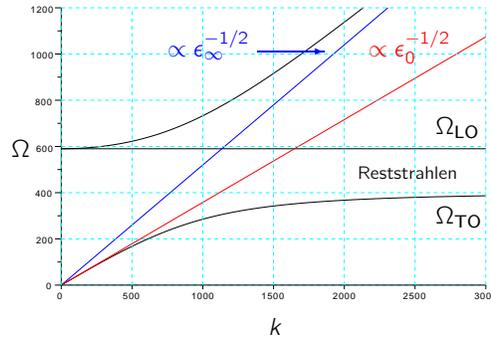
| Material | ϵ_0 | ϵ_∞ | $\epsilon_0/\epsilon_\infty$ | Ω_{TO} (cm ⁻¹) | Ω_{LO} (cm ⁻¹) | $(\Omega_{\text{LO}}/\Omega_{\text{TO}})^2$ |
|----------|--------------|-------------------|------------------------------|--|--|---|
| GaAs | 12.9 | 10.89 | 1.18 | 268 | 285 | 1.13 |
| GaP | 11.1 | 9.11 | 1.22 | 365 | 402 | 1.21 |
| ZnO | 7.8 | 3.7 | 2.11 | 402 | 590 | 2.15 |

Consider dispersion curve of light in media. In the simplest case, $\gamma = 0$, i.e. $\epsilon = \epsilon'$. For the longitudinal waves $\epsilon(\omega) = 0$ (see Eq. (4)). From Eq. (26) obtain that this condition is fulfilled for $\omega = \Omega_{\text{LO}}$, where Ω_{LO} is found from Eq. (29). We see that, indeed, this is a longitudinal wave with $\mathbf{k} \parallel \mathbf{E}$.

For the transverse plane wave to exist, k must be real. That is

$$k^2 = \left(\frac{\omega}{c}\right)^2 \epsilon(\omega). \quad (30)$$

Substituting $\epsilon(\omega)$ from Eq. (26) we obtain the dispersion curve for all



The states with a strong mixing between phonons and light at around Ω_{TO} and Ω_{LO} are called *polaritons*.

2.3 Damped oscillator and free carriers

In insulators with free carriers (for example, doped semiconductors) the total dielectric function includes both contributions: damped oscillator part and free carriers. Since both LO phonon and plasmon are longitudinal waves, they interact, which results in the changes of their frequencies. In order to find out we consider Eqs. (17) and (26) with $\gamma = 0$ to obtain an expression for ϵ . Longitudinal modes are found from the condition $\epsilon(\omega) = 0$.

$$\epsilon = \epsilon_\infty - \epsilon_\infty \left(\frac{\omega_p}{\omega} \right)^2 + \epsilon_\infty \frac{\Omega_{LO}^2 - \Omega_{TO}^2}{\Omega_{TO}^2 - \omega^2} = 0 \quad (31)$$

The solution of this equations gives us two frequencies³

$$\omega_{\pm}^2 = \frac{1}{2} \left(\omega_p^2 + \Omega_{LO}^2 \pm \sqrt{(\omega_p^2 + \Omega_{LO}^2)^2 - 4\omega_p^2\Omega_{TO}^2} \right)^{1/2} \quad (32)$$

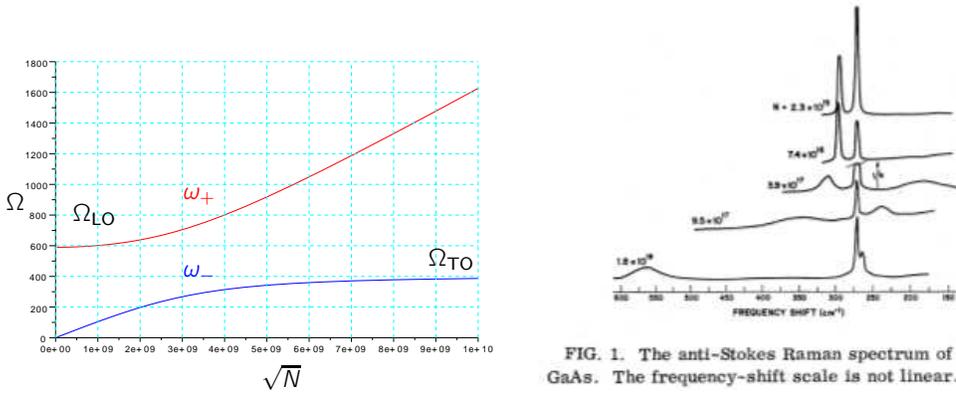


FIG. 1. The anti-Stokes Raman spectrum of *n*-type GaAs. The frequency-shift scale is not linear.

Problems

1. For the *E* layer of ionosphere the concentration of electrons is around $5 \times 10^4 \text{ cm}^{-3}$. What is the plasma frequency $f_{pl} = \omega_p/2\pi$ for such a system? What is a penetration depth of electromagnetic waves with frequencies of 0.5, 0.9, 0.95, and $0.99f_{pl}$?
2. For InAs $\epsilon_0 = 15.15$ and $\epsilon_\infty = 12.3$, whereas $\Omega_{TO} = 217 \text{ cm}^{-1}$. What is the Reststrahlen band for this material?
3. Under conditions from the previous problem find the reflectivity for the electromagnetic waves with frequencies of $\Omega_{TO}/2$ and $2\Omega_{LO}$ assuming that $\gamma = 0$.
4. GaP has $\epsilon_\infty = 9.11$, $\epsilon_0 = 11.1$, and $\Omega_{LO} = 402 \text{ cm}^{-1}$. Assuming that $\gamma = 0$ find a frequency at which the light is not reflected from this material.
5. For ZnO the values of ϵ_0 and ϵ_∞ are approximately equal 7.8 and 3.7, respectively, whereas $\Omega_{TO} = 402 \text{ cm}^{-1}$. Assuming that concentration of oscillators is $5 \times 10^{22} \text{ cm}^{-3}$ and reduced mass is $\mu = m_{Zn}m_O/(m_{Zn} + m_O)$ estimate the effective charge of the oscillator e^* . Does it make sense?
6. Frequency of LO phonon in strongly doped GaAs was found to be 400 cm^{-1} compared to the value of 285 cm^{-1} observed in undoped material. Find the concentration of conducting electrons in this material taking into account that $\epsilon_0 = 12.9$ and $\epsilon_\infty = 10.89$. What is the frequency ω_- of the low energetic plasmon? Assume that the effective mass of electrons in GaAs is equal to that of the free electron.

³A. Mooradian and G. B. Wright, Phys. Rev. Lett. **16**, 999 (1966).

3 Experimental equipment

3.1 Light sources

3.1.1 Broad band sources

3.1.2 Lasers

3.2 Detectors

3.2.1 Photomultiplier

3.2.2 Photodiodes

3.2.3 Bolometer

3.3 Spectral analysis of light

3.3.1 Monochromators

3.3.2 Fabry-Perot interferometer

3.3.3 Fourier spectroscopy

4 Spectral line shapes

4.1 Lorentzian

4.2 Gaussian

4.3 Fano-resonance

Problems

4.4 Apparatus function & convolution

5 Symmetry and selection rules

5.1 Representation of groups and selection rules

5.2 Influence of perturbation: magnetic & electric field, stress

6 IR spectroscopy

6.1 Absorption

6.2 Reflection

6.3 Photoconductivity

7 Scattering of light

7.1 Raman scattering: CARS, SERS, micro-Raman

7.2 Scattering by: phonons/plasmons, defects, free carriers, Brillouin scattering

8 Luminescence

8.1 Types of recombination: band-band, band-impurity, impurity-impurity, excitons

8.2 Photo-, cathodo-, electro-, etc. luminescence, excitation spectroscopy

9 Magnetic resonance spectroscopy

9.1 EPR, NMR

9.2 ODMR

10 Dipole-dipole interactions

Appendices

A Tables

Table A: SI vs. CGS units.

| Quantity | SI | CGS |
|-------------------------|---------------------|--|
| Force | 1 Newton (N) | 1 dyne (dyn) = 10^{-5} N |
| Work, energy | 1 Joule (J) | 1 erg = 10^{-7} J |
| Dynamic viscosity | 1 Pa·s | 1 Poise (P) = 0.1 Pa·s |
| Kinematic viscosity | 1 m ² /s | 1 Stokes (St) = 10^{-4} m ² /s |
| Pressure | 1 Pascal (Pa) | 1 barye (ba) = 0.1 Pa |
| Charge | 1 Coulomb (C) | 1 esu = $10/c \approx 3.3356 \cdot 10^{-10}$ C |
| Current | 1 Amperes (A) | 1 esu/s = $10/c \approx 3.3356 \cdot 10^{-10}$ A |
| Voltage | 1 Volt (V) | 1 Statvolt = $10^{-8}c \approx 300$ V |
| Resistance | 1 Ohm (Ω) | 1 s/cm = $10^{-9}c^2 \approx 9 \cdot 10^{11}$ Ω |
| Capacitance | 1 Farad (F) | 1 cm = $10^9/c^2 \approx 10^{-11}/9$ F |
| Magnetic field strength | 1 A/m | 1 Oersted (Oe) = $10^3/(4\pi) \approx 79.6$ A/m |
| Magnetic flux density | 1 Tesla (T) | 1 Gauss (G) = 10^{-4} T |
| Magnetic flux | 1 Weber (Wb) | 1 Maxwell (Mx) = 10^{-8} Wb |

B Solutions to the problems

B.1 Electromagnetic waves in media

1. From Eq. (1) obtain that the wave length and the wave number of the corresponding energy transition are $0.87 \mu\text{m}$ and 11452 cm^{-1} , respectively. The frequency of the transition is equal to

$$\nu = c/\lambda = 3.45 \times 10^{14} \text{ Hz.}$$

2. From $E = k_{\text{B}}T$ obtain that 300 K is 26 meV in energy units, which from Eq. (1) corresponds to $48 \mu\text{m}$.
3. As follows from Eqs. (9) and (10), for $\rho = 10 \Omega\cdot\text{cm}$ the values of n , κ , and R at $\lambda^{-1} = 1000 \text{ cm}^{-1}$ are equal to $n = 3.46$, $\kappa \approx 0$, and $R = 0.3$, whereas for $\rho = 0.001 \Omega\cdot\text{cm}$ $n = 6.1$, $\kappa = 5$, and $R = 0.68$.
4. Directly from Eq. (13) obtain that the skin depth in silver at 10^3 and 10^6 Hz equals 1 mm and $30 \mu\text{m}$, respectively.
5. For the given parameters $4\pi\sigma/\omega \gg 1$ and, hence $n \approx \kappa$. From Eqs. (9) and (10) obtain the values of R and subsequently the losses of light $(1 - R)$, which for Au, Cu, and Al are 6 , 6 , and 7.5% , respectively.

B.2 Dielectric function

1. $f_{pl} = 2 \text{ MHz}$, that is $\lambda_{pl} = 150 \text{ m}$. For frequencies $f = af_{pl}$ penetration depths δ in units of λ_{pl} are

| | | | | |
|-----------------------|------|------|------|------|
| a | 0.5 | 0.9 | 0.95 | 0.99 |
| δ/λ_{pl} | 0.13 | 0.26 | 0.36 | 0.8 |

2. Reststrahlen band is between 217 and 241 cm^{-1} .
3. Since $\gamma = 0$, we get that $\epsilon'' = 0$, $\kappa = 0$, $n = \sqrt{\epsilon'}$, and consequently

$$R = \left(\frac{1 - n}{1 + n} \right)^2.$$

Substituting the values of $\omega = \Omega_{\text{TO}}/2$ and $2\Omega_{\text{LO}}$ into Eq. (26) obtain that $R(\Omega_{\text{TO}}/2) = 0.36$, and $R(2\Omega_{\text{LO}}) = 0.3$.

4. Since $\gamma = 0$, the reflectivity is given by the simple formula from the previous problem. For $R = 0$ to occur, n must be equal to 1. After simple calculations we obtain that the frequency at which the reflectivity equals 0 is

$$\Omega = \Omega_{\text{LO}} \sqrt{\frac{\epsilon_{\infty}(\epsilon_0 - 1)}{\epsilon_0(\epsilon_{\infty} - 1)}} > \Omega_{\text{LO}},$$

which for GaP is 406.4 cm^{-1} .

5. From Eq. (25) we obtain that $e^* = 1.9e$, where e is the elementary charge. Taking into account that ZnO is a II-VI compound, the value of e^* seems to be plausible.
6. From Eq. (31) we obtain that

$$\omega_{pl}^2 = \omega_{\pm}^2 \frac{\Omega_{\text{LO}}^2 - \omega_{\pm}^2}{\Omega_{\text{TO}}^2 - \omega_{\pm}^2} = \frac{4\pi e^2 N_e}{\epsilon_{\infty} m},$$

which gives us the concentration of electrons $N_e = 1.7 \times 10^{19} \text{ cm}^{-3}$. After that from Eq. (32) we obtain the frequency of the low energetic plasmon $\omega_- = 243 \text{ cm}^{-1}$.