Chapter 10 Solution Manual

Written by: Albert Liu

10.1:

(a) Water molecules are highly polar, with the hydrogen atoms being positively charged and the oxygen atom being negatively charged. They thus form highly polar hydrogen bonds in an ice crystal, which should show strong infrared absorption.

(b) Solid germanium is composed of covalent bonds between germanium atoms, which should show weak infrared absorption.

(c) Because argon has a filled outer shell, an argon solid is bound by only van der Waals forces. It should therefore show weak infrared absorption.

(d) The Zn and Se atoms in ZnSe are bound by ionic bonds, which should show strong infrared absorption.

(e) SiC is bound by triple bonds of primarily covalent character. However, the silicon atoms have a slightly positive charge and the carbon atoms have a slightly negative charge. SiC should therefore show modest infrared absorption.

10.2:

The dielectric constant with no damping is given by:

$$\epsilon_r(\nu) = \epsilon_\infty + (\epsilon_{st} - \epsilon_\infty) \frac{\nu_{TO}^2}{(\nu_{TO}^2 - \nu^2)} \tag{1}$$

At the frequency $\nu = \sqrt{\frac{\epsilon_{st}-1}{\epsilon_{\infty}-1}}\nu_{TO}$, the dielectric constant becomes unity:

$$\epsilon_r = \epsilon_{\infty} + (\epsilon_{st} - \epsilon_{\infty}) \frac{\nu_{TO}^2}{\nu_{TO}^2 \left(1 - \frac{\epsilon_{st} - 1}{\epsilon_{\infty} - 1}\right)}$$
$$= \epsilon_{\infty} + \frac{(\epsilon_{st} - \epsilon_{\infty})(\epsilon_{\infty} - 1)}{\epsilon_{\infty} - \epsilon_{st}}$$
$$= \epsilon_{\infty} + 1 - \epsilon_{\infty}$$
$$= 1$$
(2)

The reflectance then becomes zero:

$$R = \left| \frac{\sqrt{1} - 1}{\sqrt{1} + 1} \right|^2$$
$$= 0 \tag{3}$$

10.3:

The lower and upper bounds of the Reststrahlen region are $\nu = \nu_{TO}$ and $\nu = \nu_{LO}$, which result in $\epsilon_r = \infty$ and $\epsilon_r = 0$ respectively. For $\epsilon_{st} = 8.9$, $\epsilon_{\infty} = 1.9$, and $\nu_{TO} = 9.2$ THz, the two lower and upper bounds are $\nu_{TO} = 9.2$ THz and $\nu_{LO} = \sqrt{\frac{\epsilon_{st}}{\epsilon_{\infty}}}\nu_{TO} = 2.16\nu_{TO} = 19.9$ THz. This corresponds to bounds of $\lambda = 15 \ \mu m$ and $\lambda = 33 \ \mu m$.

10.4:

The dielectric constant with damping is given by:

$$\epsilon_r = \epsilon_\infty + (\epsilon_{st} - \epsilon_\infty) \frac{\nu_{TO}^2}{\nu_{TO}^2 - \nu^2 - i\gamma\nu} \tag{4}$$

For $\nu_{TO} = 10$ THz, $\epsilon_{st} = 12.1$, and $\epsilon_{\infty} = 10$, the LO phonon frequency is $\nu_{LO} = \sqrt{\frac{\epsilon_{st}}{\epsilon_{\infty}}}\nu_{TO} = 11$ THz. In the middle of the Reststrahlen region ($\nu \approx 10.5$ THz), we find reflectivities (a) R = 0.894 and (b) R = 0.427 for $\gamma = 10^{11} \text{s}^{-1}$ and $\gamma = 10^{12} \text{s}^{-1}$ respectively. The two cases are plotted below:



where the dashed lines indicate the boundaries of the Reststrahlen region.

10.5:

(a) The frequencies of the TO and LO phonons represent the boundaries of the Reststrahlen region. From the figure, we can estimate that the upper and lower boundaries are $\lambda = 32 \ \mu m$ ($\nu_{TO} = 9.38 \ \text{THz}$) and $\lambda = 29 \ \mu m$ ($\nu_{LO} = 10.34 \ \text{THz}$).

(b) The low and high frequency reflectivities are $R_{st} \approx 0.3$ and $R_{\infty} \approx 0.25$. This corresponds to $\epsilon_{st} = 11.7$ and $\epsilon_{\infty} = 9$.

(c) We see that the peak reflectivity is approximately 90%. Comparison with the figure above in

the solution to problem 10.4, we see that the peak reflectivity for $\gamma = 10^{11} \text{ s}^{-1}$ is also approximately 90%. We thus estimate that here, γ is also approximately 10^{11} s^{-1} . The ratio between the TO and LO phonons from part (a) is $\frac{\nu_{LO}}{\nu_{TO}} = 1.1$. This does not completely match the ratio from part (b) $\sqrt{\frac{\epsilon_{st}}{\epsilon_{\infty}}} = 1.3$.

10.6:

At the TO phonon frequency, the dielectric constant is given by:

$$\epsilon_r(\nu_{TO}) = \epsilon_\infty + i(\epsilon_{st} - \epsilon_\infty) \frac{\nu_{TO}}{\gamma}$$
(5)

For $\nu_{TO} = 10$ THz, $\epsilon_{st} = 12.1$, and $\epsilon_{\infty} = 10$, the real and imaginary parts of the dielectric constant are:

$$\epsilon_1 = 10 \qquad \epsilon_2 = \frac{21 \text{ THz}}{\gamma} \tag{6}$$

This is related to the κ variable:

$$\kappa = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}} \tag{7}$$

which then gives the absorption:

$$\alpha = \frac{2\kappa\omega_{TO}}{c} \tag{8}$$

For damping constants (a) $\gamma = 10^{11} \text{ s}^{-1}$ and (b) $\gamma = 10^{12} \text{ s}^{-1}$, we find $\alpha = 4.19 \times 10^6 \text{ m}^{-1}$ and $\alpha = 1.08 \times 10^6 \text{ m}^{-1}$ respectively.

10.7:

From problem 10.4, we know that the peak reflectivity in the middle of the Reststrahl band decreases with increasing damping of the TO phonon. Decrease of the reflectivity of NaCl with increasing temperature is thus due to increasing damping γ .

10.8:

For $\epsilon_{st} = 12.5$, $\epsilon_{\infty} = 9.6$, and $\nu_{TO} = 9.2$ THz, the dielectric constant in the absence of damping at $\nu = 8$ THz is given by:

$$\epsilon_r = 9.6 + (12.5 - 9.6) \frac{(9.2 \times 10^{12})^2}{(9.2 \times 10^{12})^2 - (8 \times 10^{12})^2} = 21.5$$
(9)

The corresponding polariton wavevector is thus:

$$q = \frac{\sqrt{\epsilon_r}\omega}{c} = 776904 \text{ m}^{-1} \tag{10}$$

10.9:

(a) The maximum absorption between the cyclotron energy levels occurs at a wavelength:

$$\frac{hc}{\lambda} = \frac{e\hbar B}{m^{**}} \tag{11}$$

For B = 3.4 T and $\lambda = 306 \ \mu m$, the polaron mass in n-type CdTe is:

$$m^{**} = \frac{eB\lambda}{2\pi c} = 8.83 \times 10^{-32} \text{ kg} = 0.1m_e$$
 (12)

(b) Given $\epsilon_{\infty} = 7.1$, $\epsilon_{st} = 10.2$, and $\nu_{LO} = 5.1$ THz, we find an electron-phonon coupling constant:

$$\alpha_{ep} = \frac{1}{137} \sqrt{\frac{m^{**}c^2}{2h\nu_{LO}}} \left(\frac{1}{\epsilon_{\infty}} - \frac{1}{\epsilon_{st}}\right) = 0.339 \tag{13}$$

The rigid lattice effective mass can then be found:

$$m^* = m^{**} \left(1 - \frac{\alpha_{ep}}{6} \right) = 8.33 \times 10^{-32} \text{ kg} = 0.09 m_e$$
 (14)

10.10:

Diamond is composed of covalently bonded carbon atoms, and is therefore nonpolar. Recall that for nonpolar materials $\nu_{LO} = \nu_{TO}$, which means that there will only be one peak in the Raman spectrum.

10.11:

For excitation using an argon laser at 514.5 nm (583.1 THz), the peaks at 528.6 nm (567.5 THz) and 501.2 nm (598.6 THz) correspond to Stokes and anti-Stokes scattering processes involving optical phonons of silicon respectively. The optical phonon frequency is found to be $\nu_{TO} = \nu_{LO} = 15.6$ THz. Recall that for nonpolar materials such as silicon the longitudinal and transverse optical phonon modes are degenerate.

The ratio between the two peaks at 300 Kelvin is given by:

$$\frac{I_{\text{anti-Stokes}}}{I_{\text{Stokes}}} = e^{-h(15.6 \times 10^{12})/k_B T} = 0.08$$
(15)

10.12:

Because the bonding mechanism of NaCl is predominantly ionic, the TO phonon modes will be IR-active. Recalling the rule of mutual exclusion, which states that in centrosymmetric materials IR-active modes are not Raman active and vice-versa, the TO phonon modes will not be Raman active.

10.13:

In Fig. 10.11 we are given the peaks seen in the Raman spectra of each material. The peak with the (smaller)larger energy shift corresponds to the (TO)LO phonon mode, and we can estimate their energies directly from the plot:

<u>GaAs</u> :	
TO mode = $260 \text{ cm}^{-1} = 32.24 \text{ meV}$	LO mode = $280 \text{ cm}^{-1} = 34.72 \text{ meV}$
InP:	
TO mode = $300 \text{ cm}^{-1} = 37.20 \text{ meV}$	LO mode = $340 \text{ cm}^{-1} = 42.16 \text{ meV}$
<u>AlSb</u> :	
TO mode = $320 \text{ cm}^{-1} = 39.68 \text{ meV}$	LO mode = $340 \text{ cm}^{-1} = 42.16 \text{ meV}$
<u>GaP</u> :	
TO mode = $360 \text{ cm}^{-1} = 44.64 \text{ meV}$	LO mode = $400 \text{ cm}^{-1} = 49.6 \text{ meV}$

In Fig. 10.5, the bounds of the Reststrahlen band for GaAs are around 270 cm⁻¹ (33.48 meV) and 290 cm⁻¹ (35.96 meV) which correspond to the TO and LO phonon modes respectively. These values are each around 1 meV higher than the values from the Raman spectra, which may be attributed to human error.

10.14:

The wavevectors of the incoming photon and phonon are $k_{\text{photon}} = \frac{n\omega}{c}$ and $k_{\text{phonon}} = \frac{\Omega}{v_s}$ respectively. We can write down conservation of momentum:

$$\mathbf{k}_{\rm photon}' = \mathbf{k}_{\rm photon} - \mathbf{k}_{\rm phonon} \tag{16}$$

If $\omega \gg \Omega$, the magnitude of the incoming and scattered wavevectors is approximately equal $k'_{\text{photon}} \approx k_{\text{photon}}$. The conservation of momentum relation can thus be written:

$$\sin\left(\frac{\theta}{2}\right) = \frac{k_{\rm phonon}}{2k_{\rm photon}} \tag{17}$$

Rewriting the above equation in terms of the photon and phonon frequencies:

$$\Omega = 2 \frac{n\omega v_s}{c} \sin\left(\frac{\theta}{2}\right) \tag{18}$$

This is identical to equation 10.32, with $\Omega \to \delta \omega$ representing the frequency shift of the scattered photons in a Brillouin scattering experiment.

10.15:

Using equation 10.32, where $\theta = 180$ °C, we have:

$$10 \times 10^9 = \frac{2(3)v_s}{488 \times 10^{-9}} \tag{19}$$

which gives the speed of sound:

$$v_s = 813.33 \frac{\mathrm{m}}{\mathrm{s}}$$
 (20)

10.16:

(a) The r^{-1} is the familiar attractive term between the oppositely charged ions. The r^{-12} term is due to the Pauli exclusion principle, which results in a repulsive force when the electrons get close to each other (this term is seen in the Lennard-Jones potential for neutral atoms as well).

(b) Taking the derivative of U(r):

$$\frac{dU}{dr} = \frac{\alpha e^2}{4\pi\epsilon_0 r^2} - \frac{12\beta}{r^{13}} \tag{21}$$

we can set the derivative equal to zero to find the potential minimum:

$$\frac{\alpha e^2}{4\pi\epsilon_0 r_0^2} = \frac{12\beta}{r_0^{13}}$$
$$\rightarrow r_0^{11} = \frac{48\beta\pi\epsilon_0}{\alpha e^2}$$
(22)

(c) The Taylor expansion of the potential is given by:

$$U(r) = U(r_0) + \left. \frac{dU}{dr} \right|_{r=r_0} (r-r_0) + \frac{1}{2} \left. \frac{d^2U}{dr^2} \right|_{r=r_0} (r-r_0)^2 + \frac{1}{3!} \left. \frac{d^3U}{dr^3} \right|_{r=r_0} (r-r_0)^3 + \dots$$
(23)

By definition, r_0 is the displacement at which $\frac{dU}{dr} = 0$. The Taylor expansion of the potential, with $U(r_0)$ as the reference energy, is thus:

$$U(r) = \frac{1}{2} \left. \frac{d^2 U}{dr^2} \right|_{r=r_0} (r-r_0)^2 + \frac{1}{3!} \left. \frac{d^3 U}{dr^3} \right|_{r=r_0} (r-r_0)^3 + \dots$$
(24)

which we can relate to equation 10.33 by:

$$C_2 = \frac{1}{2} \left. \frac{d^2 U}{dr^2} \right|_{r=r_0} \qquad C_3 = \frac{1}{3!} \left. \frac{d^3 U}{dr^3} \right|_{r=r_0}$$
(25)

To find C_3 , we thus compute the third-order derivative of U(r):

$$\frac{d^2 U}{dr^2} = \frac{156\beta}{r^{14}} - \frac{\alpha e^2}{2\pi\epsilon_0 r^3}$$
(26)

$$\rightarrow \frac{d^3 U}{dr^3} = \frac{3\alpha e^2}{2\pi\epsilon_0 r^4} - \frac{2184\beta}{r^{15}} \tag{27}$$

We can thus write C_3 in terms of r_0 :

$$C_3 = \frac{1}{3!} \left. \frac{d^3 U}{dr^3} \right|_{r=r_0} = \frac{1}{3!} \left(\frac{3\alpha e^2}{2\pi\epsilon_0 r_0^4} - \frac{2184\beta}{r_0^{15}} \right)$$
(28)

10.17:

The spectral width $\Delta \nu$ of a Raman peak is related to the phonon lifetime τ by:

$$\Delta \nu = \frac{1}{2\pi\tau} \tag{29}$$

For a spectral width of 0.85 cm^{-1} (25.48 GHz), we have a lifetime:

$$\tau = \frac{1}{2\pi\Delta\nu} = 6.25 \text{ ps} \tag{30}$$