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SPRING COLLEGE ON AMORPHOUS SOLIDS
AND THE LIQUID STATE

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# OPTICAL SPECTROSCOPY AND PHOTOELECTRON SPECTROSCOPY OF AMORPHOUS SEMICONDUCTORS

(Part I)

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Materials Discussed:

Amorphous Semiconductors with Optoelectronic Applications: Ge, Si

Random tetrahedral network

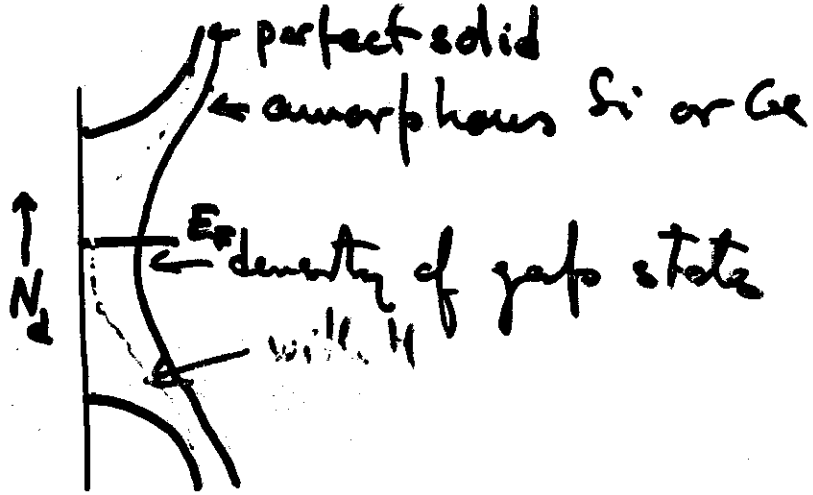
Length fluctuates by ~ 1%

Bond angles by ~ 10%

## Dangling bonds

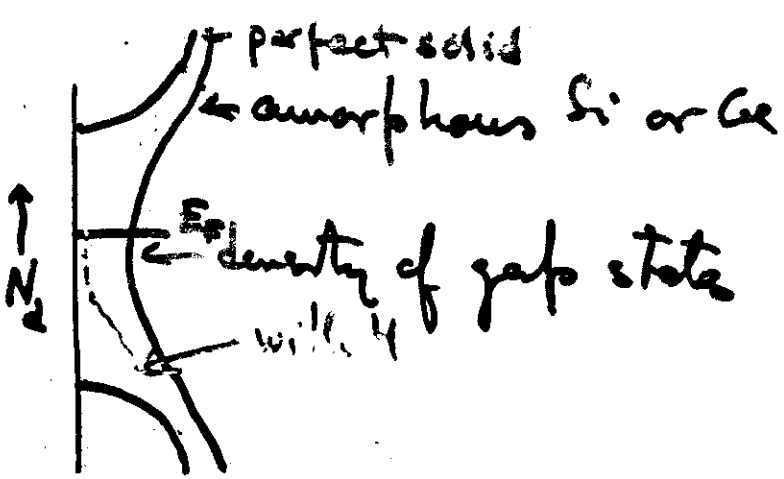
Dangling bonds produce strong density of states in the gap ~ $10^{20} - 10^{21}$ /eV cm$^3$






Under these conditions the material behaves as metallic and cannot be doped with group V elements (donors) or group III (acceptors).

Solution: saturate the dangling bonds with either hydrogen (atomic) or with fluorine (possibly also chlorine)

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the level which was in the middle of the gap moves down to about -5 eV from top of valence band for H, ~ -8 for fluorine and the gap is cleaned up. Doping becomes possible.

Preparation techniques

Vacuum deposition

Sputtering of a Si (Ge) target in Ar + [(H) + {$PH_3$ (n-type), $B_2H_6$ (p-type)}] ($SiF_4$)

Contents of the Lecture.

Study of vibrational spectra of Si:(H), (F) and Si:(H) doped with P or B

Study of electronic states in these materials.

Methods: Spectroscopy

Vibrational Spectroscopy (non-stimulated)

ir, Raman, Hyperraman, Brillouin

General principles, selection rules for solids, molecules, amorphous materials: Parity

Raman tensor.

Cross Section

Resonance phenomena

Intrinsic spectra of a-Si:(a-Ge)

Spectra of defects (H, F, B, P.....)

Detailed discussion of the vibrations of Si-H bonds.

Photoelectron Spectroscopy

General Principles and Experimental methods: Synchrotron radiation spectroscopy

Fermi Energies and Doping

Valence bands

Gap States: Threshold spectroscopy

Intrinsic spectra of a-Si:(a-Ge)

Spectra of defects
(H, F, B, P .....)

Detailed discussion of the vibrations of Si-H bonds.

## Photoelectron Spectroscopy

General Principles and Experimental methods:

Synchrotron radiation spectroscopy

Fermi Energies and Doping

Valence bands

Gap States: Threshold spectroscopy



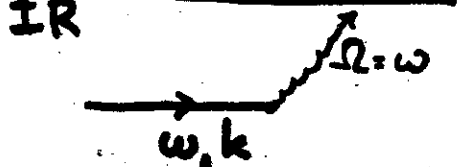
Core levels: charge fluctuations in a-Si

Impurities, Fluorine, hydrogen ...

# Vibrational Spectroscopy



infrared
Raman
Hyperraman
Brillouin




Two types of mechanisms:

Gratings - Prisms ~ 500 cm$^{-1}$

Fourier - Transform ~ 50 cm$^{-1}$

Remember that

Wavenumbers (cm$^{-1}$) $\times 1.24 \times 10^{-4}$ = eV
$1/\lambda$

Selection rules:

In solids (crystalline) k is conserved to a reciprocal lattice vector,



hence $q(\text{excitation}) = k + G$

$G = 0$ if we stay in the first Brillouin zone (reduced zone scheme). We only see phonons of $q \simeq 0$ since

$k = \frac{2\pi}{\lambda} \ll \frac{2\pi}{a_0}$ (size of Brillouin zone)

$\lambda \sim 10^{-4}$ cm, $a_0 \sim 10^{-8}$

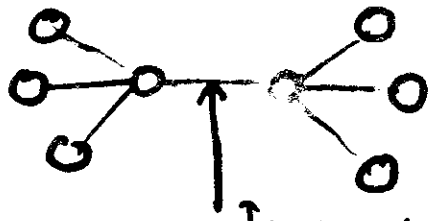
Parity selection rule:

If solid or molecule has inversion symmetry, eigenstates have definite parity, i.e., they are odd or even upon inversion.

Photon is odd (vector, electric field) (dipole approximation) hence couples only to odd excitations

Examples

Si crystal

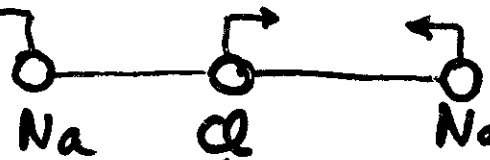


Inversion center

Optical phonons at $q=0$ are <u>even</u> hence ir-forbidden

Material transparent in ir: used as windows and substrate.

NaCl




↑ <u>center of inversion</u>

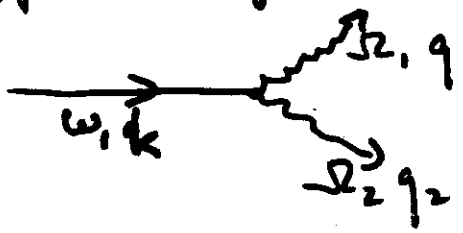
phonon at $q=0$ <u>reverses sign</u> <u>upon inversion</u>, hence odd and ir-allowed.

$$\langle f|\hat{e}\cdot\underline{p}|0\rangle \equiv \langle f|\hat{e}\cdot\underline{M}|0\rangle$$

$-$ $+$ must be $\ominus$

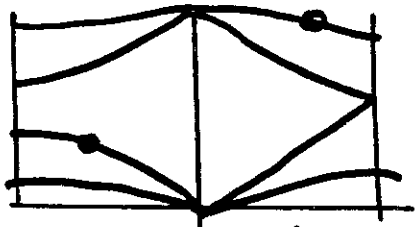


It is possible to couple also to two or more excitations (phonons):




$\omega = \Omega_1 \pm \Omega_2$

$k = q_1 \pm q_2 + G$



$q_1 + q_2 = 0$

but not $q_1 = 0$

In this manner it is in principle possible to see all phonons, not only $q=0$

Absorption measured by absorption coefficient ($cm^{-1}$)

$$I = I_0 e^{-\alpha x}$$

$\alpha \cong 10^5 cm^{-1}$ for 1 phonon allowed

$\alpha \cong 10$ for 2 phonons.

wavevector sequence and $\in$

$\alpha = \frac{4\pi k}{\lambda}$ $k$: imag. part of ref. index



$n^2 - k^2 = \epsilon_1$

$2nk = \epsilon_2$ $\quad \underline{\epsilon = \epsilon_1 + i\epsilon_2}$

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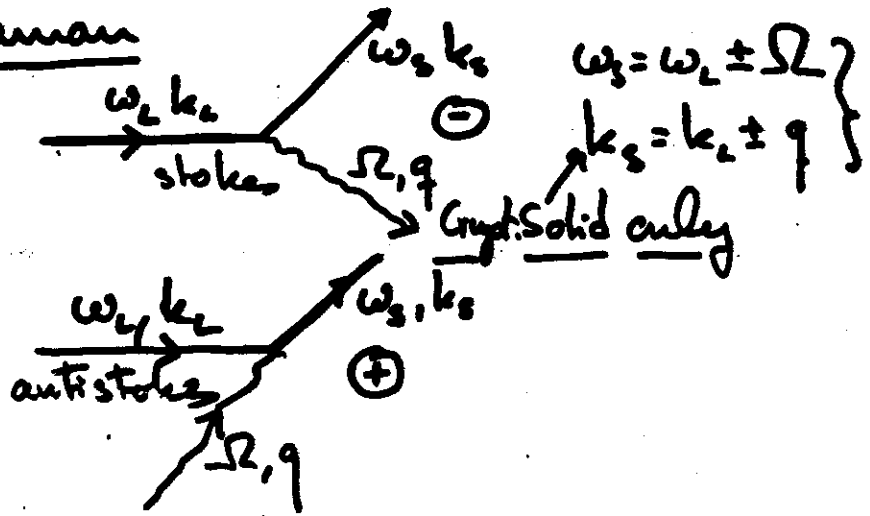
Raman




Parity selection rules:

Now two photons hence:

Raman couples only to even excitations. If parity is good q. n.:

Raman allowed $\equiv$ ir forbidden

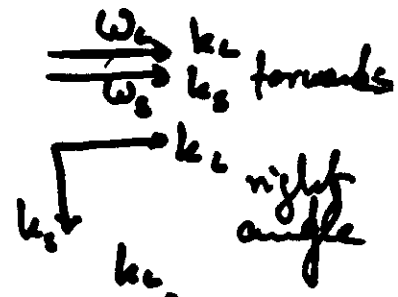
(within dipole approximation)



Solid k - selection rule (crystal, not amorphous)



$k_s = k_L \pm q$




$\Delta k = q \lesssim \frac{4\pi}{\lambda} \simeq 0$

hence also we only couple to $q \simeq 0$

Comparison with neutron scattering

Thermal neutrons

$E \simeq 0.02\,eV = \frac{\hbar^2}{2M} q^2$

in calculation in Hartree (atomic units)

$\hbar = 1 \quad M = 1800$

$E = \frac{0.02}{27}$ Hartree $= \frac{1}{2M} q^2$

$q$ = 2 at units / Brillouin zone $\simeq \frac{2\pi}{a} = 0.6$

Neutron scattering expensive cumbersome and not accurate for frequencies (not better than 1 $cm^{-1}$) Raman $\approx 1\,cm^{-1}$

Typical Raman Efficiency section.

In solids one talks about efficiencies $dS/d\Omega$, per cm and sterradian

For optical mode of crystal Si at $\sim 2\,eV = \omega_L$:

$$\frac{dS}{d\Omega} \simeq 2\times10^{-7}\ sr^{-1}cm^{-1}$$

Hence since absorption coefficient at $\omega_L$ $\alpha \simeq 10^4\,cm^{-1}$

$$\frac{dS}{d\Omega} \times L = 2\times10^{-7}\times10^{-4} = \underline{2\times10^{-11}\ sr^{-1}}$$

very small.

Hard to detect unless very good



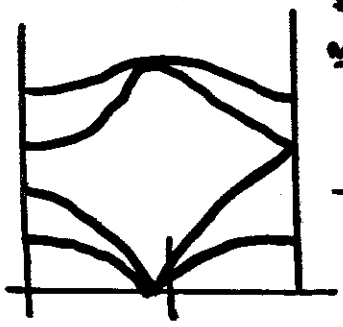
spectrometers using a very high stray light rejection are used.

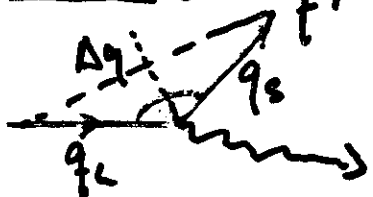
(stray light ≡ elastically (Rayleigh) scattered light)

One uses double or triple mono chromators and photomultipliers with photon counting.

Brillouin Scattering

scattering by acoustic modes $q \neq 0$ important






$$\Delta\omega = v_s \Delta q = \left(\frac{4\pi}{\lambda}\sin\frac{\varphi}{2}\right) v_s$$

$\lambda = \frac{\lambda_0}{n}$

In principle it helps you find $v_s$, i.e., the elastic constants

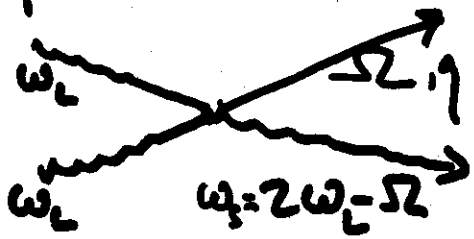
Interesting for a-Si

Techniques

Fabry - Perot interferometer with
[illegible] (1 to 5 x):
J. Sandercock

think by yourselves about selection rules, especially parity (always asked)

Hyperraman scattering




Parity selection rule

Same as for ir scattering
Hyperraman couples to odd excitations.

But it can couple to silent modes, forbidden by symmetry oder than inversion.