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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 II)

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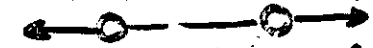
Raman coupling mechanism:

Theory of scattering efficiencies

Response of solid to em field given by dielectric constant $\overleftrightarrow{\epsilon}(\omega,q)=\overleftrightarrow{\epsilon}(\omega)$ or susceptibility $\overleftrightarrow{\chi}(\omega)$ in dipole approximation.

Consider optical phonons of S: (e.g.)



if $\Omega \ll$ electronic transition frequencies which are responsible for $\chi(\omega)$ we can use static approximation: $\chi=\chi(\omega,u)$

$$\vec{P}(\omega,u)=\chi(\omega,u)\,\vec{E}_L$$

We have a radiating dipole. Let us expand in power series of u:

$$\vec{P}(\omega,u)=\left[\chi(\omega)+\frac{d\chi}{du}u+\frac{d^2\chi}{du^2}u^2+\dots\right]\times E_L$$

$u=u_0 e^{\pm i\Omega t}$

$E_L \uparrow E e^{-i\omega_L t}$

Hence we find radiating dipole of the form:

$$\vec{P}_1 = e^{-i(\omega_L\pm\Omega)t}\left(\frac{d\chi}{du}\right)\cdot\vec{E}\,u_0$$

$$\vec{P}_2 = e^{-i(\omega_L\pm\Omega_1\pm\Omega_2)t}\left(\frac{d^2\chi}{du_1 du_2}\right)\vec{E}\,u_1 u_2$$

.....

Hence we see where first and second order scattered radiation come from: Radiating dipoles. Radiated power proportional to square of dipole magnitude:

$$\frac{dS}{d\Omega_{\text{solid angle}}}=\frac{\omega_s^4}{c^4}\left|\hat{e}_s\cdot\frac{d\chi}{du}\cdot\hat{e}_L\right|^2\langle u^2\rangle$$

$$\langle u^2\rangle=\langle n|u^2|n\rangle=\sum_m\langle n|u|m\rangle\langle m|u|n\rangle=$$

$$=\langle n|u|n+1\rangle\langle n+1|u|n\rangle+\langle n|u|n-1\rangle\langle n-1|u|n\rangle$$

$$=\underbrace{|\langle n|u|n+1\rangle|^2}_{\text{Stokes}}+\underbrace{|\langle n|u|n-1\rangle|^2}_{\text{Anti-Stokes}}$$

$$\Rightarrow |\langle n|u|n+1\rangle|^2=(n+1)\frac{\hbar}{2M\Omega};\quad n=\frac{1}{e^{\frac{\hbar\omega}{kT}}-1}$$

Coupling mechanism is the fact that u modulates the susceptibility χ. (for ir-absorption u produces dipole moment $\frac{dM}{du} \cdot u$).

Selection rules for Raman are contained in the so-called Raman tensor $\underset{\sim}{R} \sim \frac{d\underset{\sim}{\chi}}{du}$: (second Rank tensor)

$$\frac{dS}{d\Omega_s} \sim \left| \hat{e}_s \cdot \underset{\sim}{R} \cdot \hat{e}_L \right|^2$$

Since χ is symmetric $\underset{\sim}{R}$ is a symmetric tensor (there are cases not treated here in which $\underset{\sim}{R}$ can have antisym. component). Symmetric R can have at most six independent components. Usually less

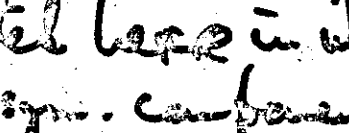
In a cubic crystal at most three independent components (irreducible components):

Γ_1^+, Ag $\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & a \end{pmatrix}$

Γ_{12}^+; Eg $3^{1/2}\begin{pmatrix} b & -b & 0 \end{pmatrix}$; $\begin{pmatrix} b & b & -2b \end{pmatrix}$

$\Gamma_{25'}^+$; T_{2g} $\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$; $\begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}$; $\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}$

One given Raman active phonon must have one of the symmetries above. In the case of crystal silicon



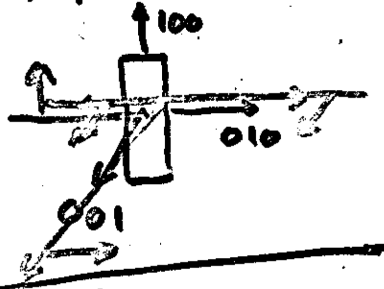
there are 3 degenerate phonons hence symmetry must be $\Gamma_{25'}^+$ (check as an exercise that it transforms under point group as $\Gamma_{25'}^+$ tensor given above)

Examples of Selection rules for Si:

Assume laser polarized along 100

$$\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} ; \begin{pmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix} ; \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & d \\ 0 & d & 0 \end{pmatrix}\begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} = 0$$

Hence scattered light exists only if $\hat{e}_s$ has component perpendicular to 100.



Isotropic and amorphous (gases) materials

If $q \to 0$ amorphous and isotropic

Rotate axes and put z along x+y. Rest remains same

$$\begin{pmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \longrightarrow \begin{pmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{pmatrix}$$ hence Π_{2g} and $\Gamma_{25'}$

are not independent. $d = \Gamma_{25'}$ only two independent parameters a and d

(a gives only polarized scattering (11, 11); d gives both polarized and depolarized ...)

By averaging the Π_{2g} tensors over all possible directions we find:

$$\left[\frac{S_{depol}}{S_{pol}}\right]_d = \frac{3}{4}$$

If we happen to have any a scattering around (ratio decreases):

$$\left[\frac{S_{depol}}{S_{pol}}\right]_{d+a} \leq \frac{3}{4}$$ (In a-Si, a-Ge 0.5; for Si-H 0.17)

Resonance Phenomena:

$$\frac{d\chi}{du} \qquad \chi \sim \sum_0 \frac{A_0}{\omega_0^2 - \omega^2}$$

simplest mechanism: ω_0 is changed by u through electron-phonon interaction: $\frac{d\omega_0}{du}$ = electron-phonon coupling ...

$$\frac{d\chi}{du} = \sum \frac{2\omega_0 A}{(\omega_0^2 - \omega^2)^2} \left(\frac{d\omega_0}{du}\right)$$

χ has critical points or singularities

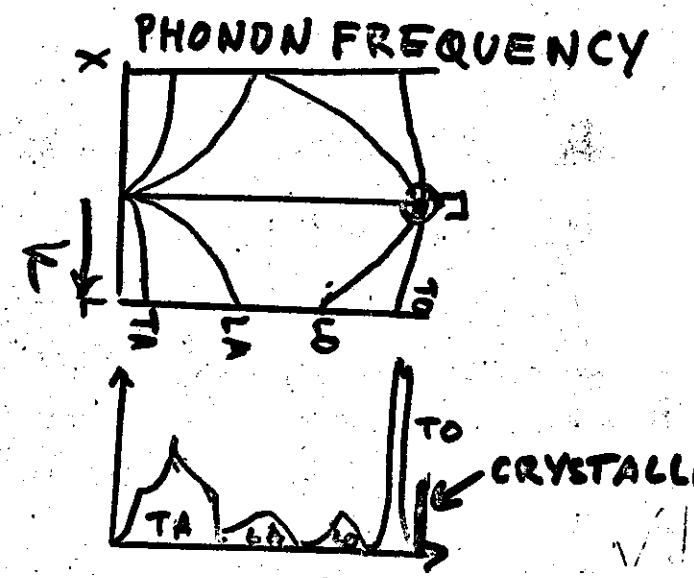
wavenumber: $\chi = F(\omega - \omega_0) + \text{background}$

$$\frac{d\chi}{du} \simeq \frac{d\chi}{d\omega_0} \cdot \frac{d\omega_0}{du}$$

If true $\frac{dS}{d\Omega_s} \propto \left|\frac{d\chi}{d\omega_0}\right|^2 \simeq \left|\frac{dp}{d\omega}\right|^2$

We can from these measurements determine electron-phonon coupling.

Exercise: Show that for Brillouin scattering $\frac{d\chi}{du}$ must be replaced by a linear combination of elasto-optic constants.



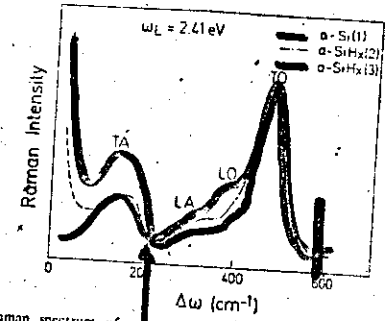


Fig. 1. Stokes Raman spectrum of pure amurphous silicon obtained for parallel (∥) and perpendicular (⊥) scattering configurations. These and all subsequent data were taken at room

?

It has been shown that the density of state of amorphous silicon is nearly the same as that of the crystalline material with sharp structure removed.

$$\left(\frac{dS}{d\Omega}\right)_{Stokes} \sim |C|^2 N_1(\Omega) \frac{\hbar}{4M\Omega}(n+1)d\Omega$$

$C \sim \frac{dX}{du(\omega)}$ one tends to set C = constant but one must be careful. For $\omega \to 0$ ($q \to 0$ in elastic limit) uniform translation and hence $dX/du \equiv 0$ hence $C \sim \omega + \ldots$

$$\left(\frac{dS}{d\Omega}\right)_{Stokes} \sim N_1(\Omega)\left[\frac{1}{e^{\hbar\Omega/kT}-1}+1\right]\frac{\hbar}{4M\Omega}\cdot\Omega^2 d\Omega$$

for $\Omega \ll kT \to \frac{kT}{\hbar\Omega} \gg 1$

hence $\left(\frac{dS}{d\Omega}\right)_{Stokes} \sim N_1(\Omega) \times \frac{kT}{\hbar\Omega}\Omega^2 d\Omega \sim N_1(\Omega) d\Omega$

$\hbar\Omega \ll kT$

Sometimes one define a reduced Raman efficiency:

$$\left(\frac{1}{d\Omega}\right)\frac{1}{n+1}\left(\frac{dS}{d\Omega}\right)_{Stokes} \sim N_1(\Omega) C^2 d\Omega$$

Infrared absorption

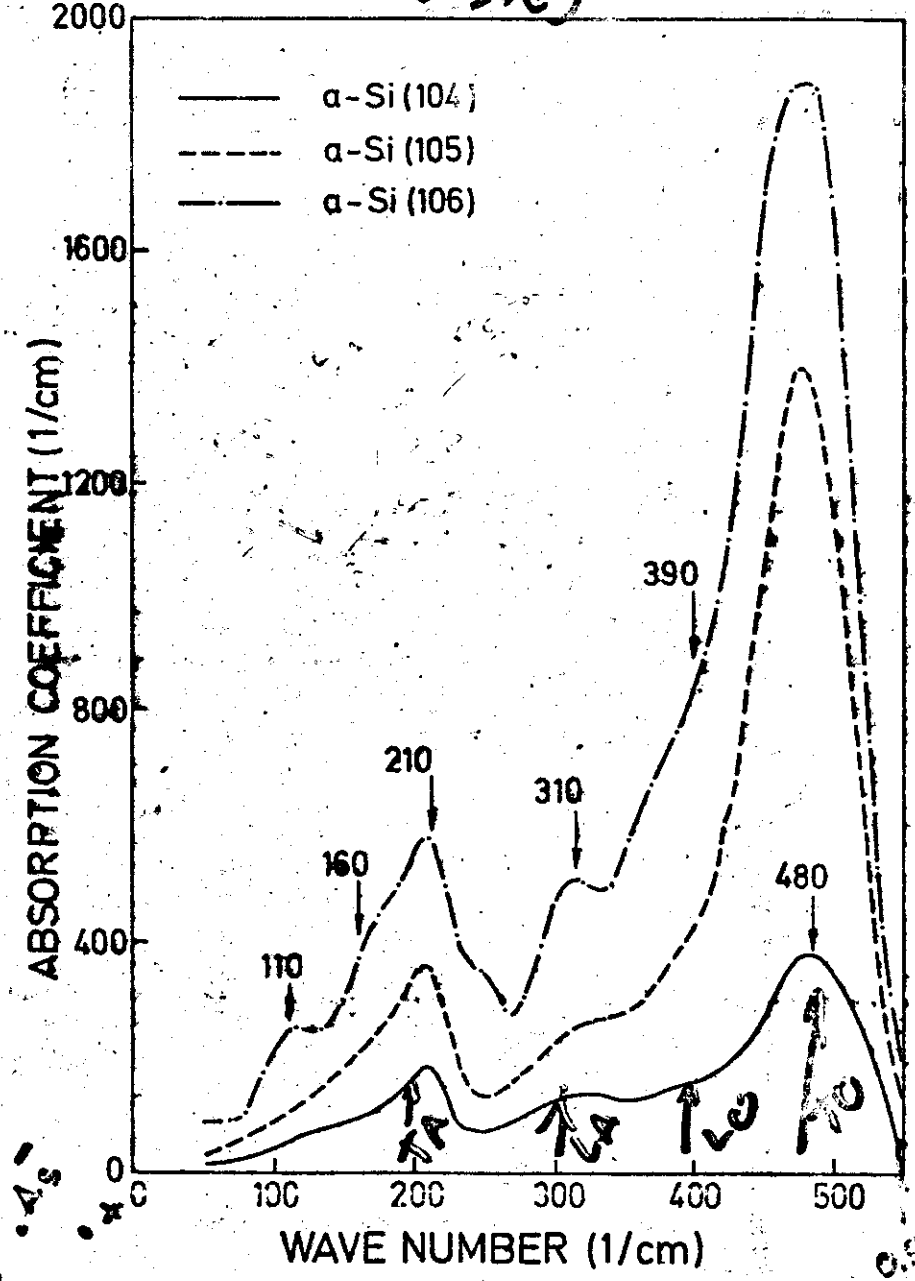
Zero for x-tal. For amorphous $\neq 0$ as local inversion symmetry does not exist also, $q=0$ selection rule does not hold (q has no meaning in general). Absorption determined by dynamical charge of dipole

$$e^* = \frac{dM}{du} = A + Bq + Cq^2 + \ldots$$
(in elastic limit)

- because of translation and inversion sym. $B=0$, hence $e^* \sim cq^2$ and coupling constants $\left|\frac{dM}{du}\right|^2 \sim q^2 \sim \omega^4$ (for $\omega \to 0$).

Contrary to Raman, absorption is expected to depend on preparation, defects, ... No absorption in expt!

a-Si(P)



Samples on X-tal Si

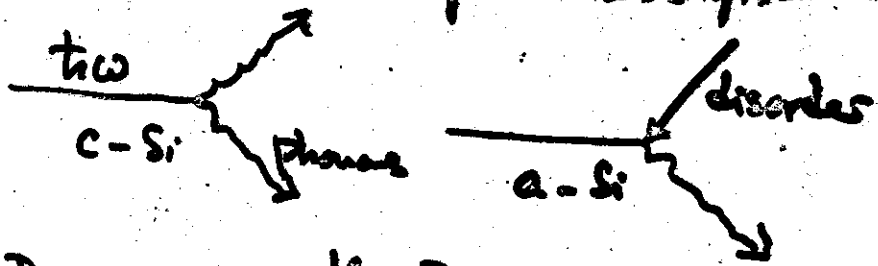
Absorption mechanism not exactly known. Possibilities:

Bond charge: dipole cancels in crystal but not in a-Si as charge not all same because of e.g. bond length:

$e_b^* = \frac{2}{\epsilon} \sim \frac{2}{d^3}$ ← Harrison

↑ Phillips

Other possibility is dangling bonds. It is related to 2-phonon absorption in c-Si:



Increases with P or B-doping as these things introduce a charge (dynamical charge of Si-P or Si-B bond can be treated with Harrison's theory.

• effect increases strongly with doping

For polar GaAs or SiC

$$\epsilon_i = \frac{2\pi^2 N e_T^{*2}}{M \omega_0 \epsilon_0}\,\delta(\omega-\omega_0)$$

⇓

$$e_T^{*2} = \frac{c n \omega_0 M}{2\pi^2 N}\int \frac{\alpha(\omega)}{\omega}\,d\omega$$

We obtain from ↑ for a-Si $e_T^* \simeq 0.5$

for a-Si with ~ 20% P $e_T^* \simeq 1.2$

not unreasonable considering that charge of Si–P bond ≃ 2

Extrinsic spectrum: The Si–H bond.

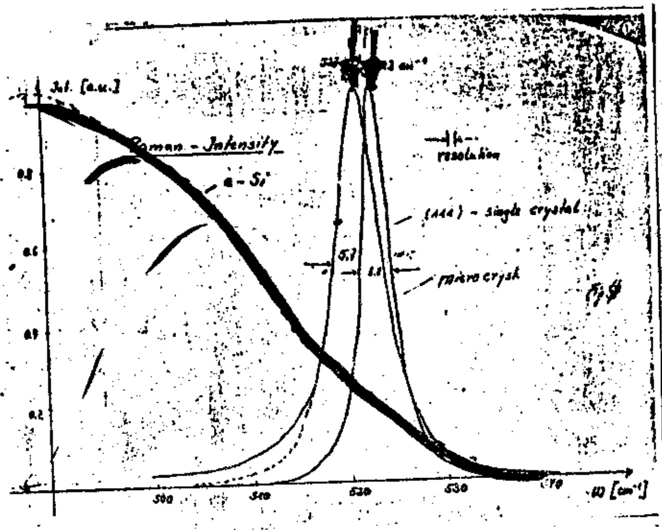
Basically bond-stretching and bond bending (wagging, rocking, rolling, twisting) vibrations.

First identification done by comp. with Silanes (Germanes ..)

DiSilane SiH_4 Bethke + Wilson J. Chem Phys. 26, 1107 (1957)

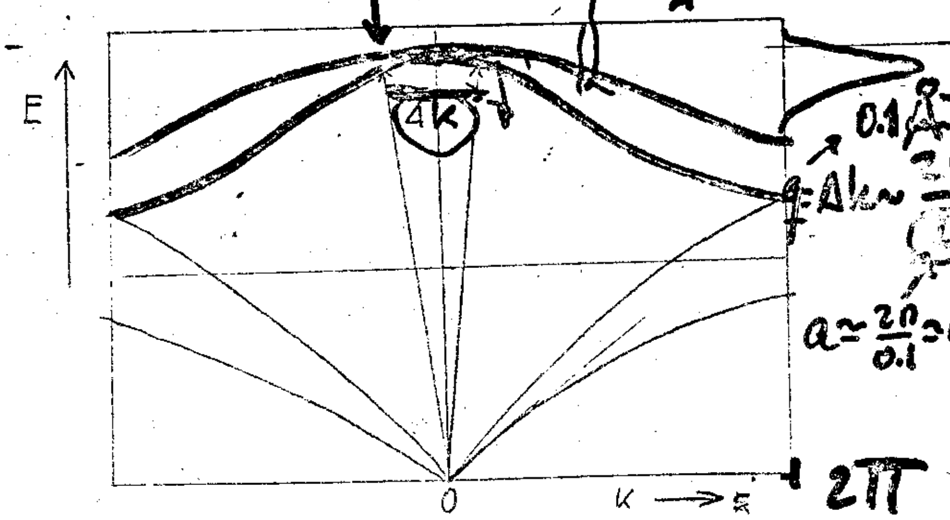
Di Germane GeH_4 ibid 40, 321 (1964)

Silane, Methane Gases on Surf. Armstrong + ... 1971



$\Delta k = \frac{2\pi}{L}$

$\Delta\omega_R(\text{cm}^{-1}) = -200\, q^2$ (q in $Å^{-1}$)



$0.1\ Å^{-1}$

$\Delta k \approx \frac{2\pi}{L}$

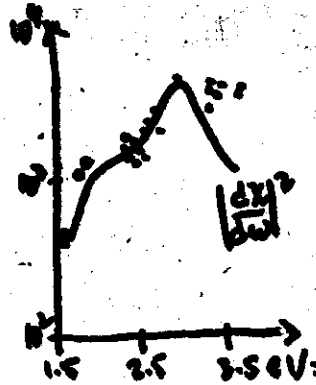
$a \approx \frac{2\pi}{0.1} \approx 60\ Å$

$\frac{2\pi}{a}$

$\Delta K \cdot L \approx 1$

Polycrystalline Si

Broadening and shift



Resonant scattering in a-Si.

But maximum scattering intensity not at ~3 eV

Because observed intensity ~ $\alpha^{-1} \times \left|\frac{d\chi}{d\omega}\right|^2$ (α = absorption coefficient)

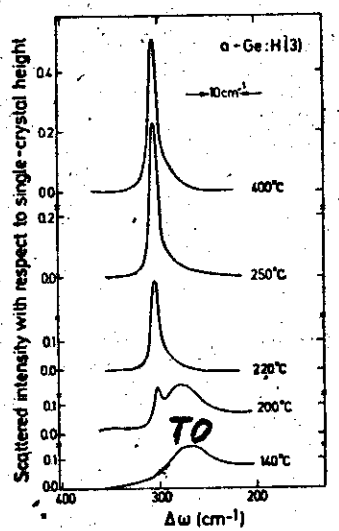
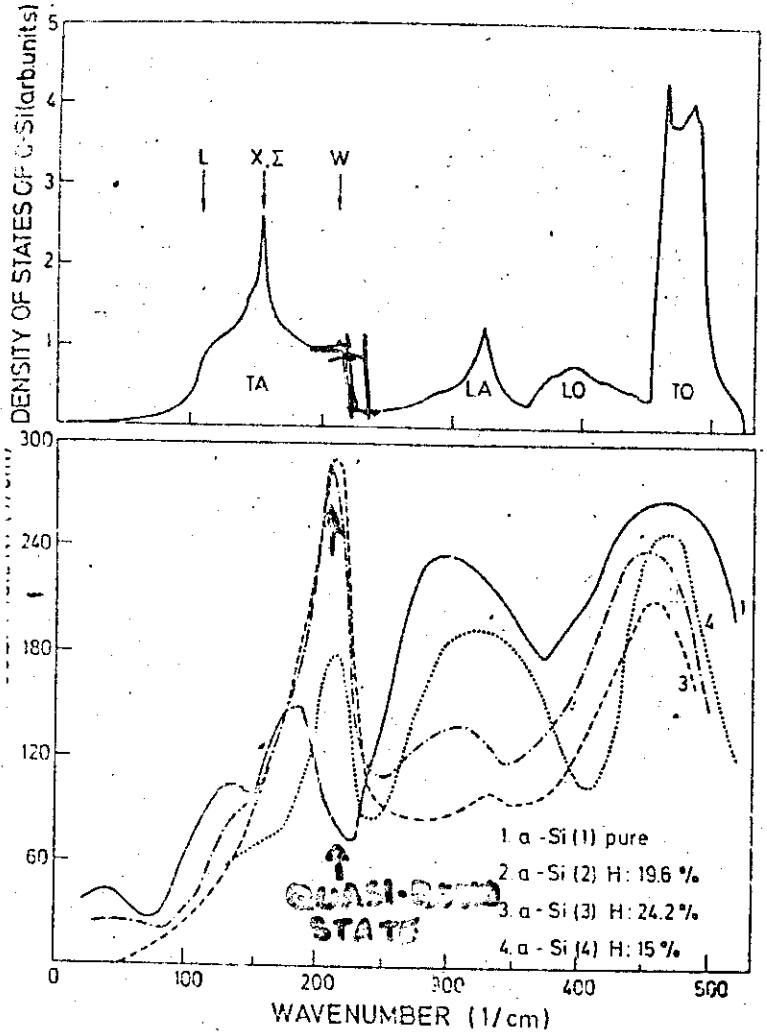
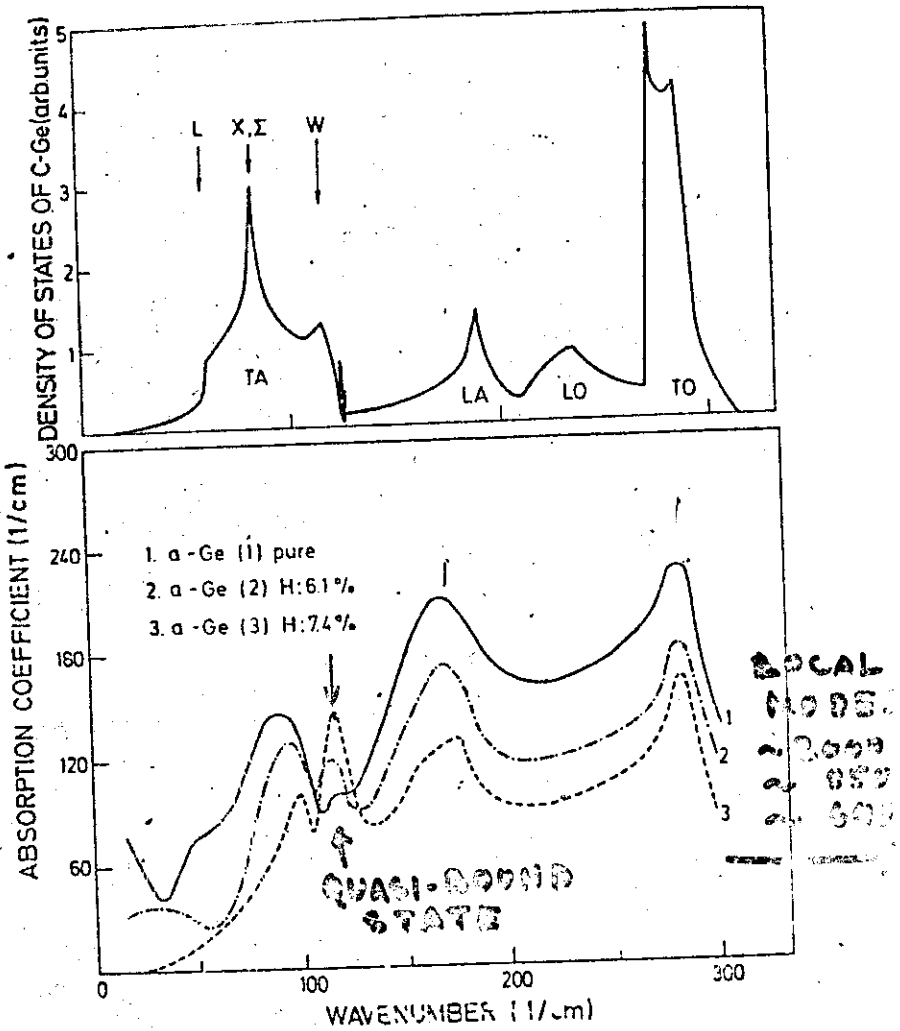
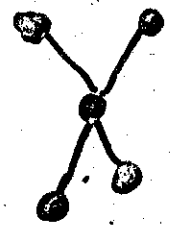


Fig. 4. Raman spectra of a-Ge(3) for five annealing temperatures showing the appearance of the Γ-phonon of the crystal with a low-frequency tail.


DENSITY OF STATES OF C-Si(arbunits)
L
X,Σ
W
TA
LA
LO
TO
ABSORPTION COEFFICIENT (1/cm)
1. a -Si (1) pure
2. a -Si (2) H: 19.6 %
3. a -Si (3) H: 24.2 %
4. a - Si (4) H: 15 %
QUASI-BOUND STATE
WAVENUMBER (1/cm)

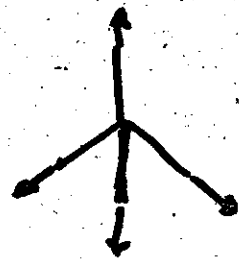

DENSITY OF STATES OF C-Ge(arbunits)
L
X,Σ
W
TA
LA
LO
TO
ABSORPTION COEFFICIENT (1/cm)
1. a -Ge (1) pure
2. a -Ge (2) H:6.1 %
3. a -Ge (3) H:7.4 %
QUASI-BOUND STATE
WAVENUMBER (1/cm)

Vibrational spectrum of XY_4 (tetrahedral) 3d.



$5 \times 3 - 6 = 9$ modes

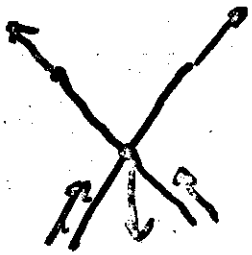
(5 atoms, 3 vector comp. per atom, 6 rot. + trans.)



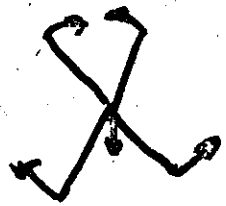
$\nu_1 : A_1(\Gamma_1)$ — Symmetry — Frequency (cm^{-1}) — 2187

A_1 Raman active, ir-inactive

$\nu_2 : E(\Gamma_{12})$ — 972 — Raman active, ir-inactive

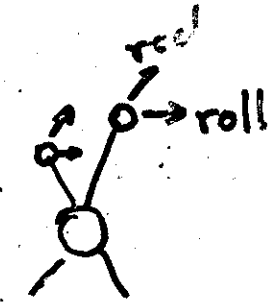


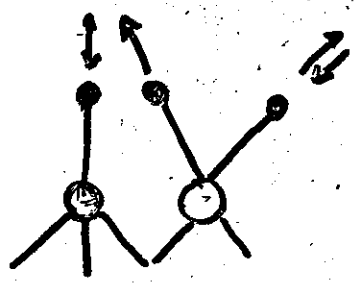
$\nu_3 : T_2(\Gamma_{15})$ — 2189

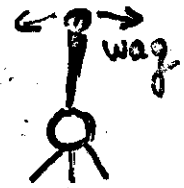


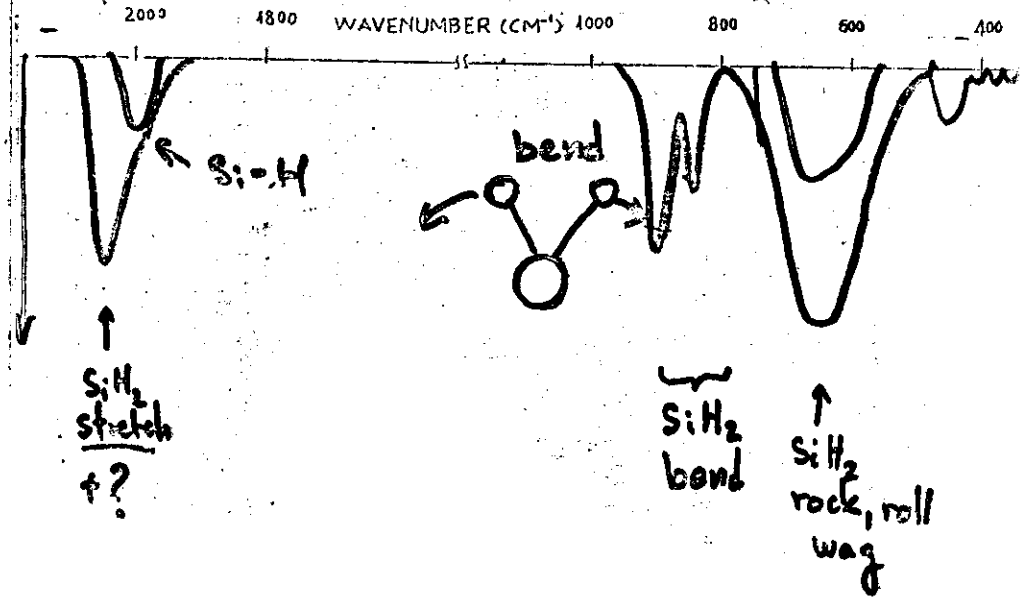
$\nu_4 : T_2(\Gamma_{15})$ — 913

ν_3, ν_4: Raman + ir-active









Hydrogen in a-Si

It is customary to describe vibrations in terms of valence force field constants:

(K) bond stretching k_r: $\Delta U = \frac{1}{2} k_r (\Delta l)^2$

H bond bending k_θ: $\Delta U = \frac{1}{2} k_\theta (\Delta\theta)^2$

k_r force along bond: $f = -k_r \Delta l$

k_θ force $\perp$ bond in θ-plane $f_\perp = -k_\theta \frac{\Delta l}{l^2}$

It is easy (but an exercise) to show that

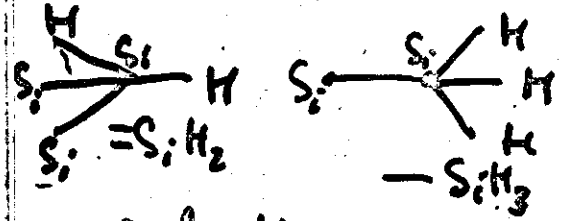
$\omega_1 M_H = k_r$; $\omega_2 M_H = 3 k_\theta / l^2$

do as exercise (Herzberg's Boole)

$M_1 (\omega_1^2 + \omega_2^2 + \omega_3^2) = k_r \left(1 + \frac{2M_H}{3M_{Si}}\right)$

$M_1^2 \omega_1^2 \omega_2^2 \omega_3^2 = \frac{3 k_r k_\theta}{l^2} \left(1 + \frac{4M_H}{M_{Si}}\right)$

For Ge and Sn we can neglect M_H / M_X; for Si, diamond not. In any case we can extract from experimental frequencies k_r, k_θ (over determined) and use them to calculate vibrations of



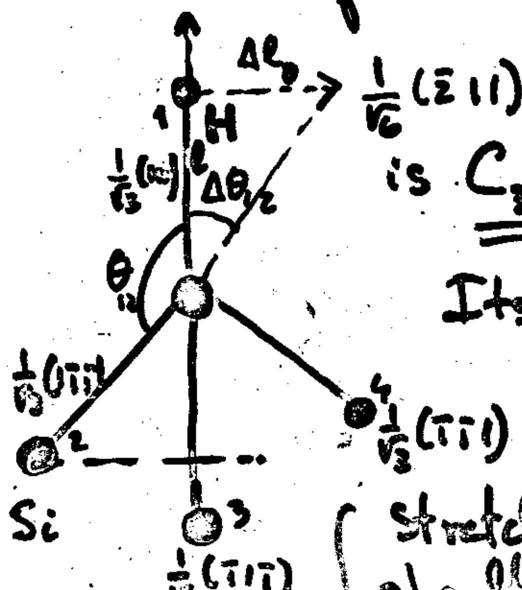
neglect $\frac{M_H}{M_{Si}} \simeq 0$

Then $\omega_2 = \sqrt{\frac{3}{3}}\,\omega_4 = 1.22\,\omega_4$ ←

	SiH4	SiH3D	SiH2D2
ω_3	932	923	903
ω_4	913	821	657
ω_2/ω_4	1.06	1.13	1.19

comparison gives idea of error of our model, about 10%

Vibrations of $\equiv Si-H$



The point group is $\underline{\underline{C_{3v}}}$ (identity, threefold rot., 3 reflection planes)

Its reps are

A_1, A_2, E (2-fold)

Stretching mode A_1 sym. should have same frequency as A of SiH_4 $M\omega_1^2 = k_r$

Bending mode E-sym. Two-fold degenerate

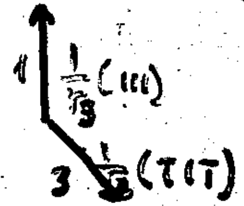
Calculation: Move H along $\frac{1}{\sqrt{6}}(\bar{2}11)$ an amount Δl_0; $\Delta\theta_{12} = \frac{\Delta l_0}{l}$ [contribution of θ_{12} to rest. force]

Calculate contribution of θ_{13} and θ_{14} (both the same):

$[\cos\theta_{13}] = \frac{1}{\sqrt{3}}(\bar{1}1\bar{1})\cdot\frac{1}{\sqrt{3}}\left[-(1-\sqrt{2}\Delta l), 1+\frac{\Delta l}{\sqrt{2}}, -\left(1+\frac{\Delta l}{\sqrt{2}}\right)\right] =$

$= \frac{1}{3}\left[-1+\sqrt{2}\Delta l\right] = -\frac{1}{3} - \sin\theta_{13}\,\Delta\theta_{13} = -\Delta\theta_{13}\times\frac{2\sqrt{2}}{3} - \frac{1}{3}$

Direction of force:



Must be contained in this plane and be ⊥ to (111), hence $\frac{1}{\sqrt{6}}(1\bar{2}1)$; For 1-4 bond angle $\frac{1}{\sqrt{6}}(11\bar{2})$ total

$$\vec{f} = -\frac{k_\theta}{l}\frac{\Delta l}{l}\left[\frac{1}{\sqrt{6}}(2\bar{1}\bar{1}) + \frac{1}{2}\times\frac{1}{\sqrt{6}}\left[(1\bar{2}1)+(11\bar{2})\right]\right]$$

$$= -\frac{k_\theta}{l}\frac{\Delta l}{l}\frac{1}{\sqrt{6}}(2\bar{1}\bar{1})\left(1+\frac{1}{2}\right)$$

Hence frequency given by

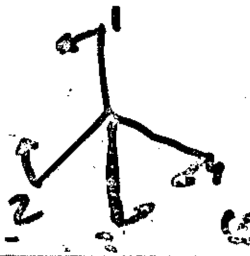
$$M_H\omega_E^2(SiH) = k_\theta l^{-2}\left(1+\frac{1}{2}\right)$$

(1 ← 1-2; $\frac{1}{2}$ ← 13 + 14)

We can estimate k_θ from SiH_4 (ω_2) (assume $l^{-2}k_\theta$ same in both cases!)

$M_H\omega_2 = k_\theta l^{-2}\left[2+\frac{1}{4}\right]$

[Note: 1 is doubled because 2 masses. Also $\frac{1}{4}$ is doubled because 3, 4 move]. Hence approximately

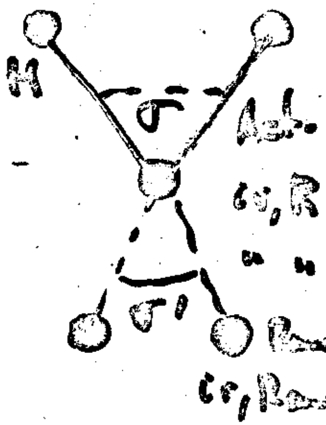


$\omega_E \simeq \sqrt{\frac{4}{6}}$ $\omega_2(SiH_4) \simeq 972/\sqrt{\ldots}$

Actually app. = 660, hence excellent

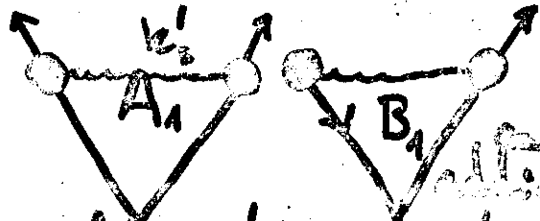
660 is the wagging (E) mode of ≡Si–H !!!. { A_1 and E both Raman and ir-active!

Consider =SiH_2 : Point group C_{2v}
2-fold axis + 2 refl. planes.



	E	C_2	σ	σ'	
A_1	1	1	1	1	stretch, Bend
B_1	1	-1	1	-1	stretch, Bend
A_2	1	1	-1	-1	Twist
B_2	1	-1	-1	1	Roll

Stretch modes



With the force constants chosen they are degenerate. k_s' splits it by adding e.g. a small neighbour force constant between H and H. It affects A_1 but not B_1.

It is easy to see that k_s' introduces in perturbation theory (do it!)

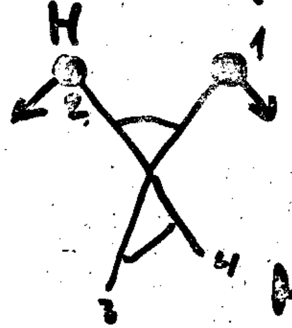
$$M\Delta(\omega^2) = \frac{4}{3} k_s'$$

There is also a sym.-antisym. splitting for the stretching of –SiH_3 equal to

$M\Delta(\omega^2) = 2k_s'$. This splitting can be estimated to be ≈ 15 cm⁻¹ from disilane $H_3Si-SiH_3$. Hence we estimate sym.-antisym. stretch splitting of SiH_2 ≈ 10 cm⁻¹ to small to be seen (linewidths ≈ 100 cm⁻¹). Note $k_s' < 0$ as antisym > sym.

SiH_2, C_{2v}

A_1 bending mode



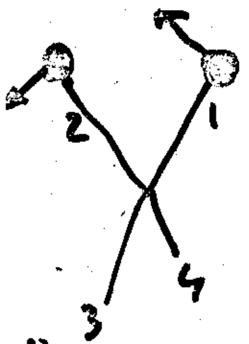
Looks like wag of SiH except that 1-2 force has been doubled:

$$M_H \omega_E^2(SiH) = \frac{k_\theta}{l^2}\left[1+\frac{1}{2}\right]$$ ← Take same

$$M_H \omega_{A_1}^2(SiH_2) = \frac{k_\theta}{l^2}\left[2+\frac{1}{2}\right] = \frac{5}{3} M_H \omega_E^2(SiH)$$

From $\omega_E(SiH) = 660$ we find $\omega_{A_1}(SiH_2) = \underline{852}$ not bad! exp. around $\underline{875}$

B_1, rocking mode.

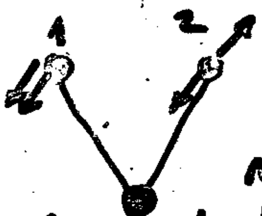


opposite to case above

1-2 force is ... 13, 14 cancelled, hence ↙ 660 cm^{-1}

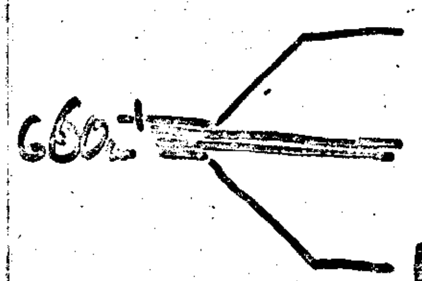
$$\omega_{B_1}^2(SiH_2) = \frac{1}{3}\omega_E^2(SiH)$$

Rolling (B_2) and Twisting (A_2)

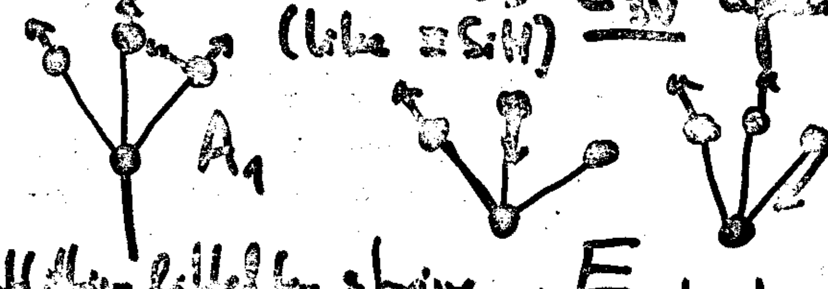


The angle 1-2 is not changed to first order by motion. If we stop 2 rolling happens. Hence same frequency as wagging Si-H (660 cm^{-1})

Assume we consider the wagging of 1 and of 2. In total 4 modes

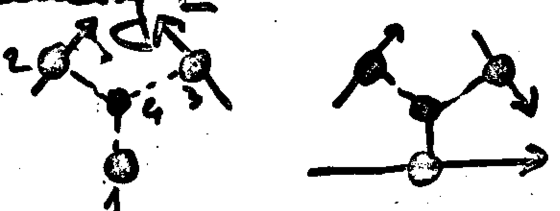


SiH_3 stretch modes (like ≡SiH) C_{3v} again



... lifted by spring ...

Bending E



consider motion of only 3. It is wagging

$M\omega_w^2 = k \cdot 1.5$

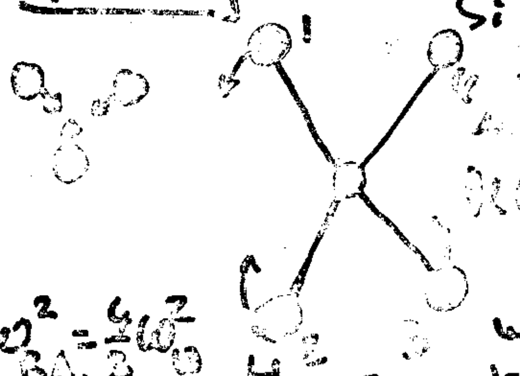
This has only 3-2 and 3-1 contributing as 3-4 hence our mode is

$$M\omega^2_{BE}(SiH_3) = \frac{k_\theta}{\ell^2}\left[\underset{3-1}{\frac{1.5}{2}} + \underset{3-2}{1.5}\right]$$

$$= \frac{k_\theta}{4\ell^2}\left[3+6\right] = \frac{3}{2}M\omega_w^2$$

$$\simeq 808\ cm^{-1}$$

A1 Bending



If 2,3 do not wag:

$$M\omega^2 = \frac{k_\theta}{\ell^2}\left[\underset{1-4}{4} + \underset{1-2,\ 1-3}{\frac{1}{2}}\right]$$

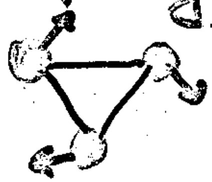
we must multiply 1-2 and 1-3 by 2

$\omega^2_{BA_1} = \frac{4}{3}\omega_0^2$

For these bending modes, however, we must increase the force constants as we are dealing largely with H–Si–H angles instead of H–Si–Si

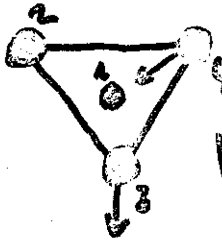
Experimentally one observes one mode only at ~ 907 cm^{-1}.

The A_1-like twist mode has zero frequency (from disilane ~ 200 cm^{-1})



Wagging E mode of SiH_3

$$M\omega^2_{wag}(SiH) = \frac{k_\theta}{\ell^2}\left[\underset{4-1}{1} + \underset{4-2}{\frac{1}{4}} + \underset{4-3}{\frac{1}{4}}\right]$$



in SiH_3 4-3 disappears

hence $M\omega^2_{wag} = \frac{k_\theta}{\ell^2}\left[1 + \frac{1}{4}\right]$

$\omega_{wag}(SiH_3) = \omega_{wag}(SiH)\sqrt{\frac{5}{6}} \simeq 607\ cm^{-1}$

	stretch	wag		
SiH	2000	687		
	2000	660		
	stretch	Rock B_1	Bend A_1	Bend(B_2) Twist(A_2)
SiH_2	A_1 (sym) 2088	B_1 (asym) 2080	396	887 687
	2100	2100	—	875 660
	Stretch	Bend A_1	Bend E	Wag T_2
SiH_3	A_1 (sym) 2088	E (asym) 2015	793	841 626
	2130	2130	—	907 660
	Stretch		Bend	
SiH_4	A_1 sym.	T_2 asym.	E	T_2
	2186	2189	972	913

Comments and open questions:

These lines narrow (SiH, B_1, SiH_2 T, E)

It [illegible]

Note that for SiH_2 and SiH_3 the stretch lines are about 100 cm^{-1}

Note that SiH_2 and SiH_3 have stretches at ~2100, 100 cm^{-1} higher than SiH and close to SiH_4. Reason: one possibility is lowering SiH by solid state effects

force opposed to ionic force

$$\Delta\omega = -\frac{\epsilon - 1}{2\epsilon + 1}\frac{e^{*2}_T}{R^3 M}$$

for $\epsilon_\infty = 0.5$ and a^3 = bond length of Si (vacancy) we find $\Delta\omega = -90\ \text{cm}^{-1}$

Probably SiH_2 and SiH_3 sit in some open space (R larger, $\Delta\omega$ smaller)

This would explain why at surface of x-tal Si(111) $\omega = 2086$ cm^{-1} and absorption maximum in a-Si: $\omega = 2100$ with [illegible]

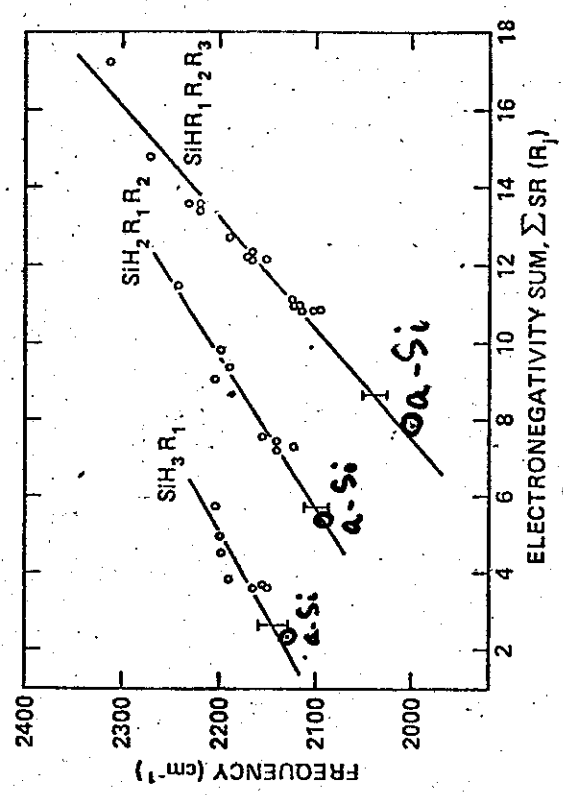


Figure 1

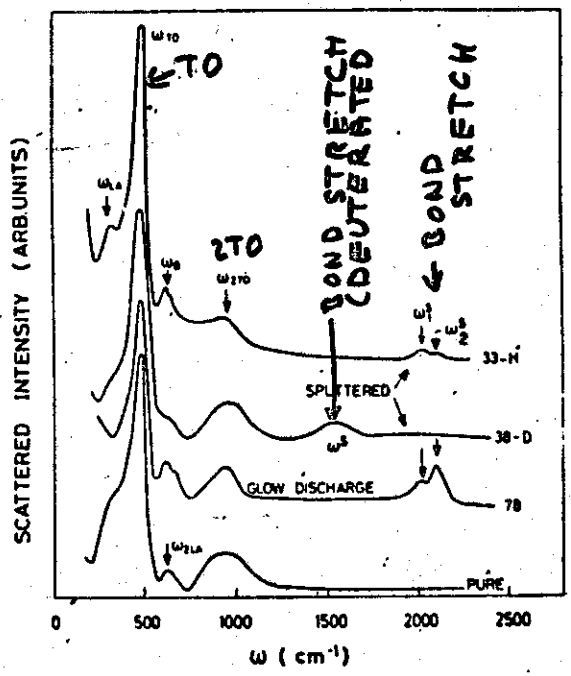
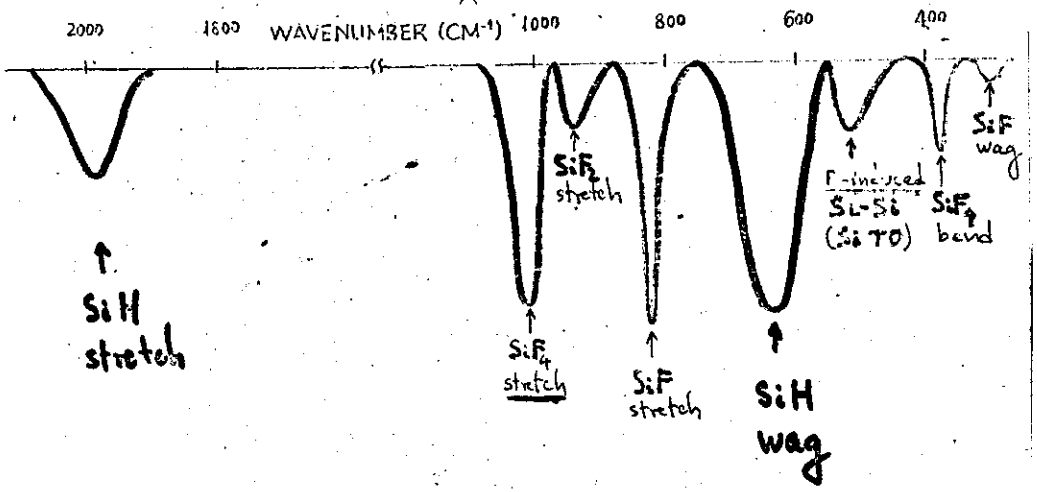


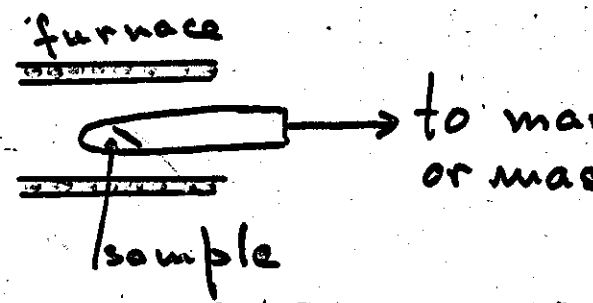
Fig. 11. Raman scattered intensities versus frequency ω for four representative a-Si samples. The PURE sample was sputtered deposited in 100% Ar; the 33-H (38-D) samples were sputtered deposited in 90% Ar - 10% H_2 (-10% D2). Sample 78 was deposited onto a room temperature substrate from a high pressure glow discharge of SiH_4.



F + H in a-Si

H dosage

evolution or desorption



TECHNIQUE DESTRUCTIVE!

infrared absorption

$$N_H = A \int \alpha(\omega) d\omega \qquad A\ (e^{19})$$

one can use any of the Si-H bands but must calibrate

A. Nuclear reactions

$^{15}N\ (6.4\ MeV) + {}^1H = {}^{12}C + \alpha + \gamma\ (4.4\ MeV)$ ↙ count!

Profiling ~ 50Å

Question is calibration constant A constant for a given mode or does A depend on N, type of preparation, additional doping (eg F, C, B, P...) etc?

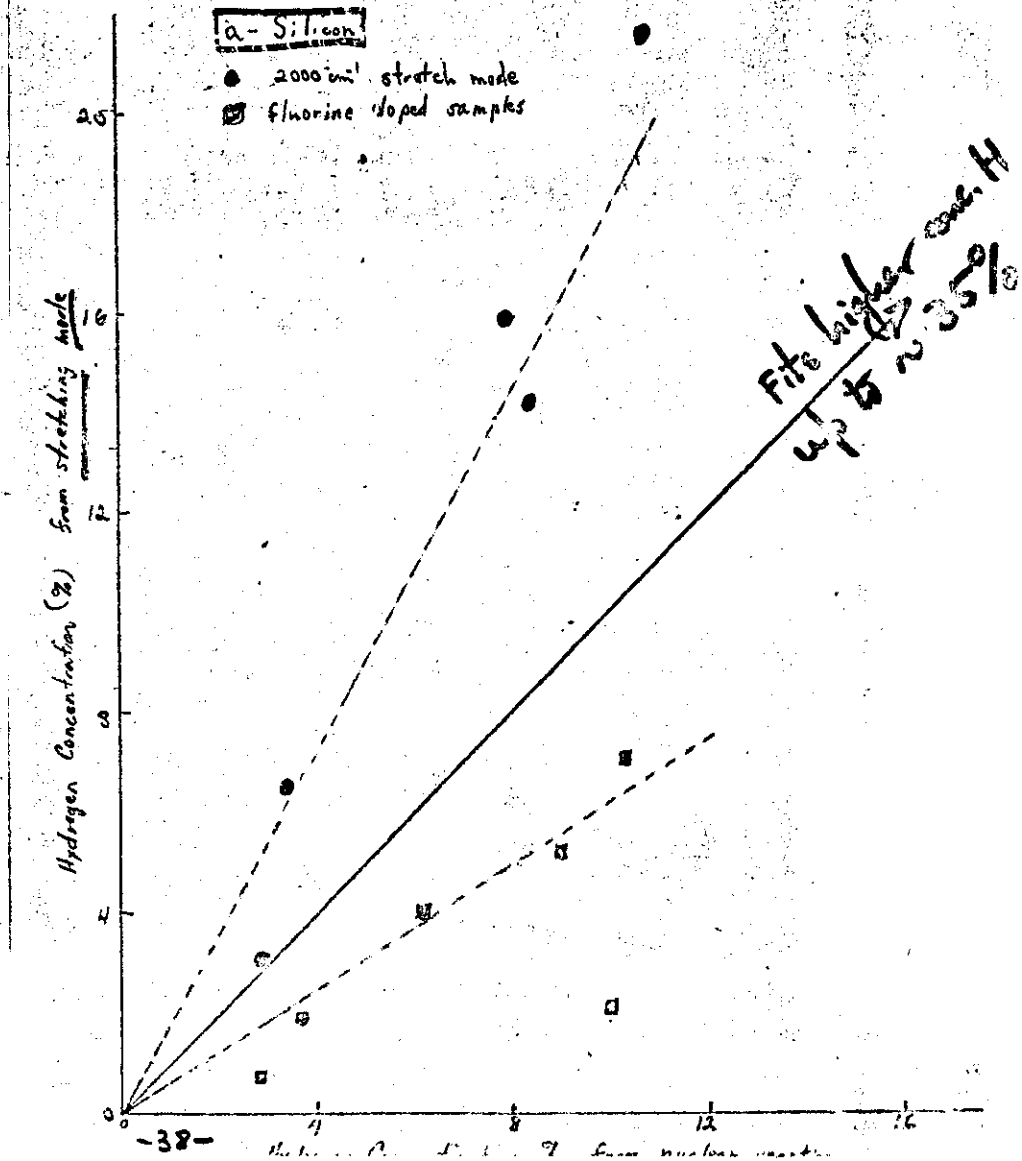
Answer:

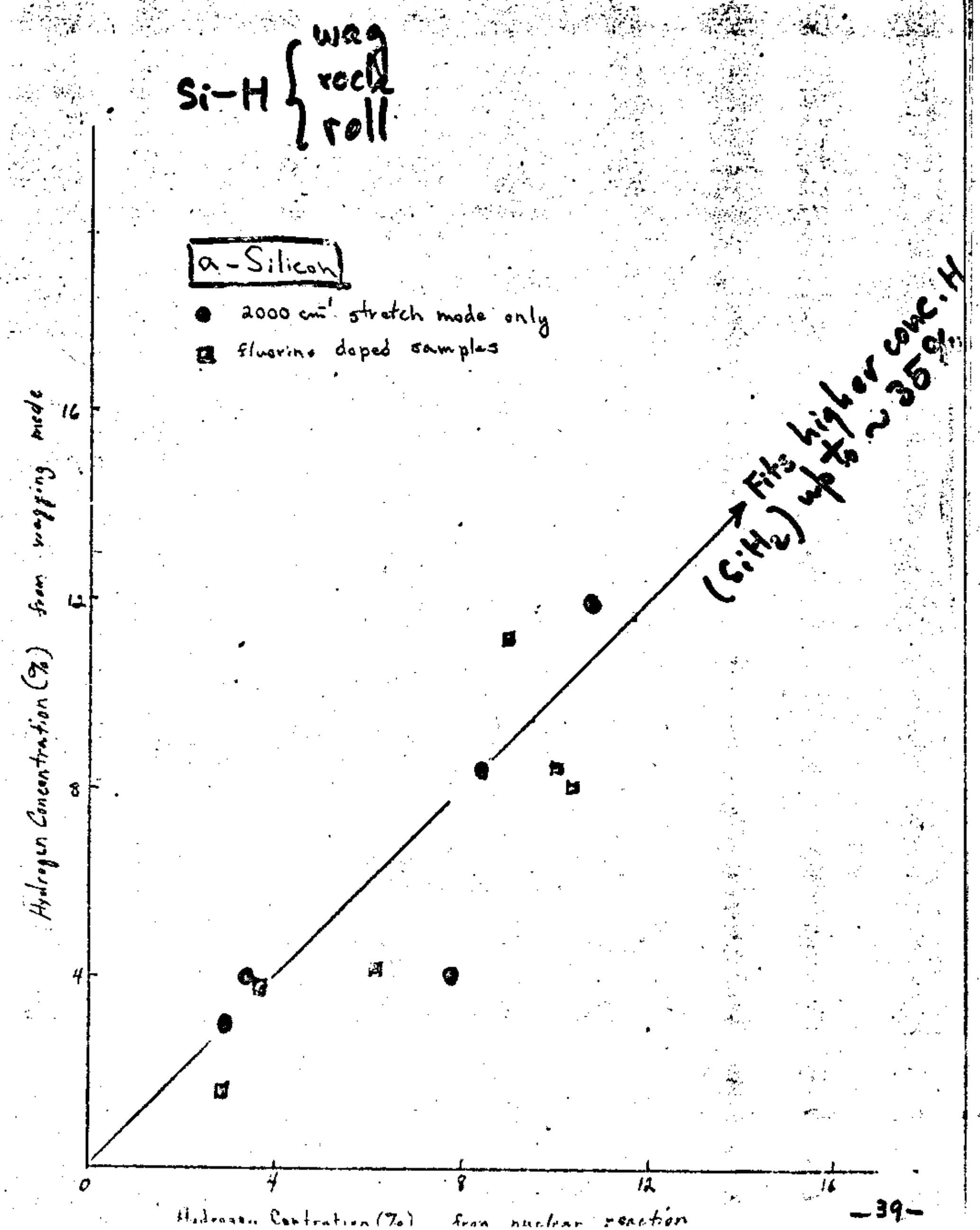
A is constant for { wag rock. bands + bend roll 640 cm^{-1}. energy ↑ weak

A varies by as much as a factor of 4 for stretch modes (2000 - 2100 cm^{-1}) depending on conditions: no good for quick H-concentration determination

The same results hold true for germanium

Si:-H bond stretching vibration





The bond stretching data of Fig. 2 have [illegible] and [illegible] 0.5, the same [illegible] factor used for Fig. [illegible] 0.7 is [illegible] concentration [illegible] increases at [illegible] material. The first [illegible] that the [illegible] are not the [illegible] that [illegible] are very weak [illegible] stretching [illegible] occur by [illegible] attributed to the group IV element [illegible] (1979), [illegible] This result [illegible] a word of [illegible] determined [illegible]. The wagging parts, however, [illegible] for a-Si [illegible] can be used [illegible]

[illegible]

[illegible] controversy has been raised recently about the possible existence [illegible] frequency stretching bands, at [illegible] in a-Si:H and 2000 [illegible] are not associated with =SiH₂ or –SiH₃ radicals, but rather with [illegible] bending) (Bermejo and Cardona (1979), Freeman and Paul (1979)). We have synthesized such a-Si:H samples by annealing samples containing only [illegible] band (see Fig. 3).

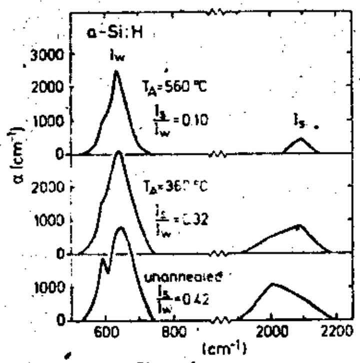
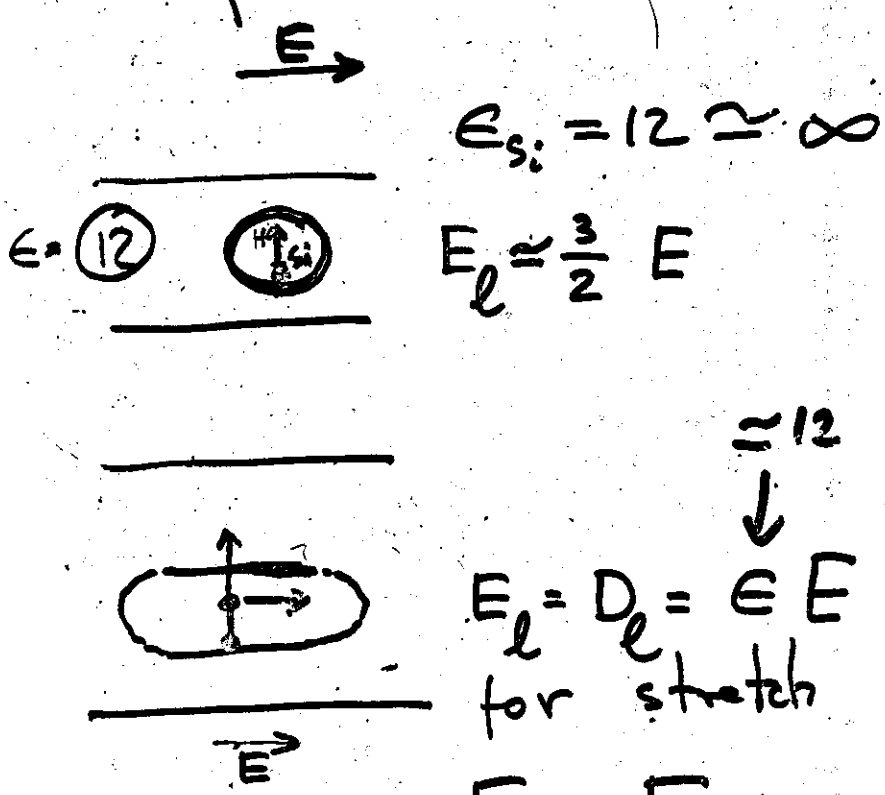


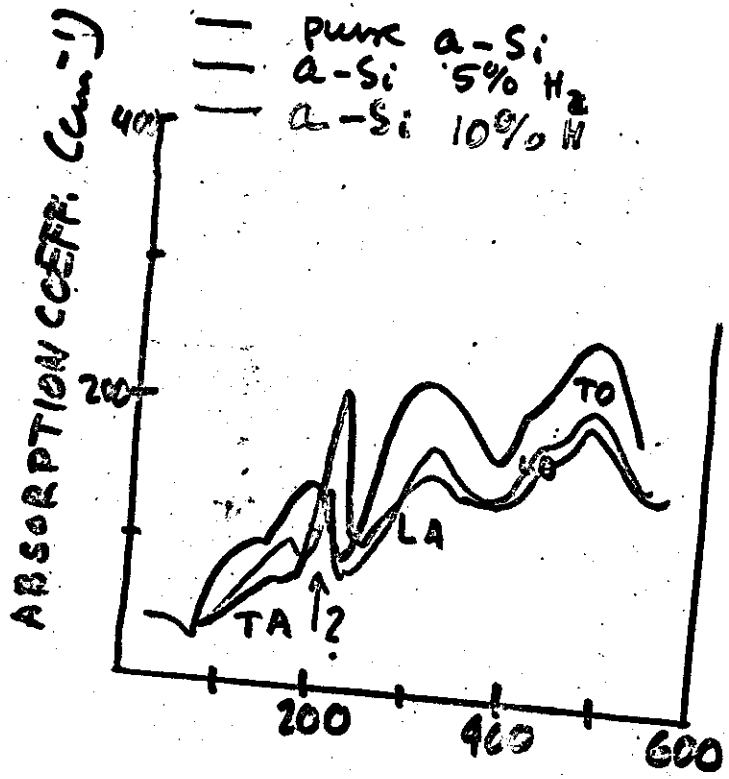
Figure 3

Stretching (I_s) and wagging (I_w) bands of an a-Si:H sample prepared by sputtering with P_{H_2} = 5x10 [illegible] torr. Also, effect of annealing on these bands. I_s/I_w represents the ratio of areas under the peak.

The samples annealed at 560°C have the I_s peak shifted to [illegible] 2200 [illegible] and nevertheless show no trace of bending bands. The ratio I_s/I_w decreases strongly with annealing, a fact which points to the different nature of the I_s peaks in the annealed and unannealed samples. A possible explanation of the I_s peak at 21[illegible] [illegible] (SiH [illegible]. The possibility [illegible] exists [illegible] correspond to neighboring (SiH)₂-bonds while the 21[illegible] [illegible] 2140 [illegible] Freeman and Paul (1979)) corresponds to the isolated SiH bonds. Such bonds are more difficult to break than in (SiH)₂. In the latter, two bonds can be broken with formation of H_2 before effusion.

Local field corrections

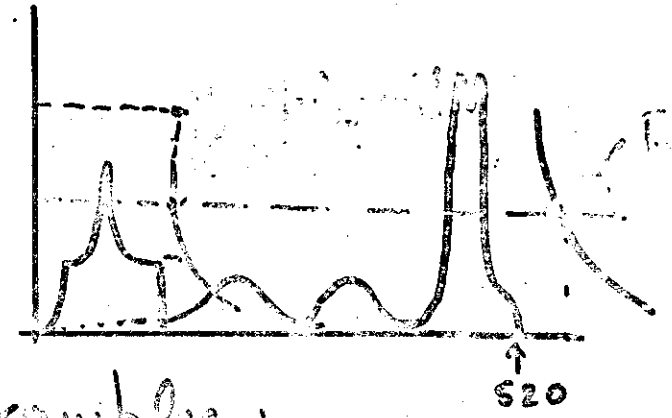




Secular equation for mass defect:

$$\frac{\omega^2}{6}\int \frac{g(\omega')\,d\omega'}{\omega^2-\omega'^2} = \frac{M}{M-M_{imp}}$$

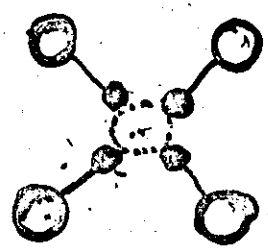
$g(\omega')$ = density of phonon states



examples:

B in c-Si

Si in c-Ge



consider the $(H_4) \equiv$ as replacing one Si

Mass defect $\epsilon = 1 - \frac{4M_H}{M_{Si}} = 0.85$