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SPRING COLLEGE IN MATERIALS SCIENCE ON 'CERAMICS AND COMPOSITE MATERIALS'
(17 April - 26 May 1989)

OPTICAL PROPERTIES AND SPECTROSCOPIC TECHNIQUES IN SOLIDS MATERIALS

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OPTICAL PROPERTIES AND SPECTROSCOPIC TECHNIQUES IN SOLIDS MATERIALS

1. Basic Concepts
   A. MACROSCOPIC APPROACH
   B. MICROSCOPIC APPROACH
2. Main spectroscopic techniques
   A. ABSORPTION

   B. REFLECTIVITY

   C. LUMINESCENCE

3. Typical examples of spectroscopic data

MACROSCOPIC APPROACH

We formalize the problem of light-matter interaction in the framework of CLASSICAL electromagnetic theory:

PROPAGATION OF E.M. RADIATION IN SOLIDS

$$\text{div}\,\vec{D} = 0$$
$$\text{div}\,\vec{B} = 0$$
$$\text{rot}\,\vec{E} = -\frac{1}{c}\frac{\partial \vec{B}}{\partial t}$$
$$\text{rot}\,\vec{H} = \frac{1}{c}\frac{\partial \vec{D}}{\partial t} + \frac{4\pi}{c}\vec{J}$$

Maxwell eqs.
for an UNCHARGED, POLARIZABLE medium

where

$$\vec{D} = \vec{E} + 4\pi\vec{P}$$
$$\vec{B} = \vec{H} + 4\pi\vec{M}$$

with $\bar{P}$ electric polarization per unit volume
$\bar{M}$ magnetic pol. per unit volume
$\bar{J}$ current per unit area

We shall consider only NON FERROMAGNETIC materials so that $\vec{M}$ is negligible and

$$\vec{B} = \vec{H}$$

Remaining in the LINEAR APPROXIMATION

$\vec{P} = \chi \vec{E}$ χ polarizability

$\vec{J} = \sigma \vec{E}$ σ conductivity

$\Downarrow$

in general TENSOR but becomes SCALAR in isotropic media.

$$\vec{D} = \vec{E} + 4\pi\vec{P} = (1 + 4\pi\chi)\vec{E}$$

$$\Downarrow$$

$$\vec{D} = \underset{\substack{\uparrow \\ \text{dielectric function}}}{\epsilon}\;\vec{E}$$

> The polarizability χ and the conductivity σ contain the RESPONSE OF THE MEDIUM to the electromagnetic field

[illegible]

solve the Maxwell eqs.

$$\operatorname{div}\vec{D} = \operatorname{div}\vec{E} = 0$$

$$\operatorname{div}\vec{B} = \operatorname{div}\vec{H} = 0$$

$$\operatorname{rot}\vec{E} = -\frac{1}{c}\frac{\partial\vec{H}}{\partial t}$$

$$\operatorname{rot}\vec{H} = \frac{\epsilon}{c}\frac{\partial\vec{E}}{\partial t} + \frac{4\pi\sigma}{c}\vec{E}$$

using the relation

$$\operatorname{rot}\operatorname{rot}\vec{E} = \underset{=0}{\underbrace{\operatorname{grad}\operatorname{div}\vec{E}}} - \nabla^2\vec{E}$$

$$= -\nabla^2\vec{E} = \operatorname{rot}\left(-\frac{1}{c}\frac{\partial\vec{H}}{\partial t}\right)$$

$$\nabla^2\vec{E} = \frac{1}{c}\frac{\partial}{\partial t}\operatorname{rot}\vec{H}$$

$$\nabla^2\vec{E} = \frac{\epsilon}{c^2}\frac{\partial^2\vec{E}}{\partial t^2} + \frac{4\pi\sigma}{c^2}\frac{\partial\vec{E}}{\partial t}$$

This equation represents a propagating with dumping [illegible] inside oscillation of Electric Field (light)

$$\vec{E} = \vec{E}_0\, e^{i(\bar{K}\cdot\bar{r} - \omega t)}$$

as a solution of equation we obtain

$$-\vec{K}^2 = \epsilon\frac{\omega^2}{c^2} - i\frac{4\pi\sigma}{c^2}\omega$$

that is COMPLEX VALUE

$$\bar{K} = \frac{\omega}{c}\left(\epsilon - i\frac{4\pi\sigma}{\omega}\right)^{1/2}$$

$$K = \frac{\omega}{c}N$$

N is a COMLEX INDEX of REFRACTION

We can also write explicit form of N

$$K = \frac{\omega}{c}(n + ik)$$

with relations

$$n^2 + k^2 = \epsilon_1 = \epsilon_0\ 1 + 4\pi\chi$$

$$2nk = \epsilon_2 = \text{[illegible]}$$

ALL OPTICAL BEHAVIOR OF SOLIDS IS CONTAINED IN N COMPLEX INDEX OF REFRACTION

In a plane [illegible] polarization in the x direction, propagation into the sample along the z-direction.

$$E = E_{z_0}\,\underbrace{e^{i\left(\frac{\omega}{c}nz - \omega t\right)}}\ \underbrace{e^{-\frac{\omega}{c}kz}}$$

oscillating solution with group velocity $v = \frac{c}{n} < c$ (and depending to ω)

DISPERSION

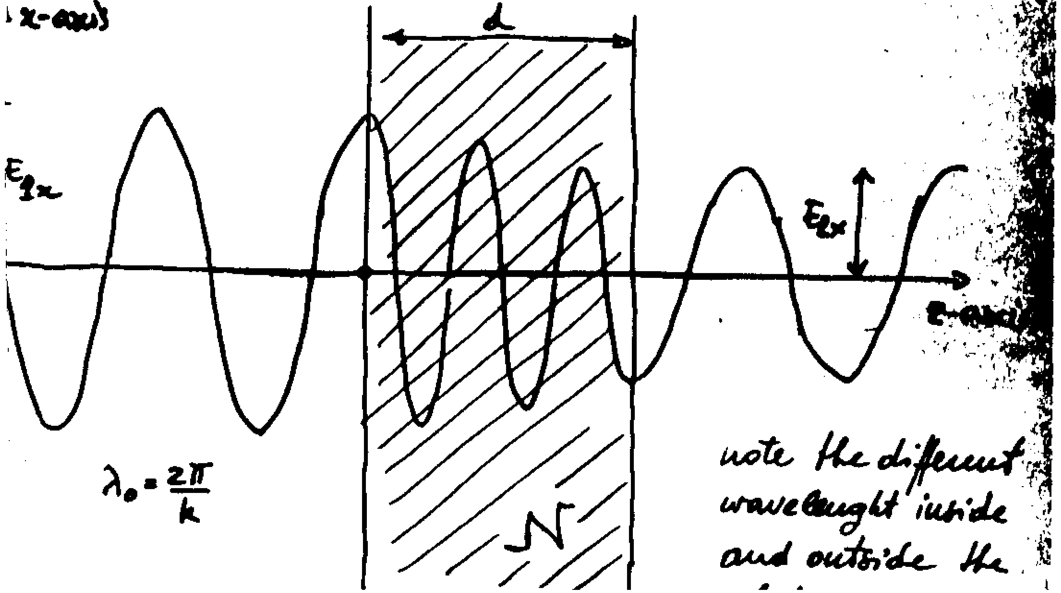
ATTENUATION FACTOR for Electric Field related to ABSORPTION the first case that we consider

IDEAL ABSORPTION neglecting reflection

consider an electromagnetic plane wave of frequency ω linear polarized on the x-axis and propagating in the vacuum along the z-axis. The eq. of this wave is

$$E = E_{x1} e^{i\left(\frac{\omega z}{c} - \omega t\right)} = E_{x1} e^{i\left(\frac{2\pi}{\lambda_0} z - \omega t\right)}$$

This e.m. wave goes through a slab of dielectric solid material with optically polished surfaces placed orthogonally to the z-axis. Let N the complex index of refraction of the dielectric



note the different wavelength inside and outside the

inside the material we have

$$E = E_{x1} e^{-\frac{\omega}{c} k z} \, e^{i\left(\frac{\omega}{c} n z - \omega t\right)}$$

$\downarrow$

OSCILLATING FACTOR

$\lambda = \lambda_0 / n$

$v = c/n$

for $z > d$ we have

$$E = E_{x2} e^{i\left(\frac{2\pi}{\lambda_0} - \omega t\right)}$$

with

$$E_{x2} = E_{x1} e^{-\frac{\omega k d}{c}}$$

considering the "intensity" of the light

$I = \overline{E}^2$ (time average)

$$I_0 = E_{x1}^2$$

$$I = E_{x2}^2 = E_{x1}^2 e^{-\frac{2\omega k d}{c}}$$

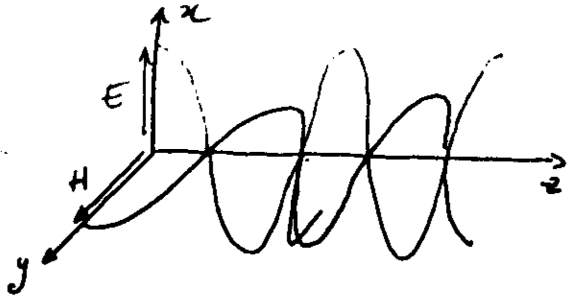
the ratio $\frac{I_0}{I}$ is $e^{\frac{2\omega k d}{c}}$

we can define α ABSORPTION COEFFICIENT

$$\alpha = \frac{1}{d} \ln \frac{I_0}{I} = \frac{2\omega k}{c} = \frac{4\pi\sigma}{n c}$$ in agreement with

in a semplified [illegible]

BOUNDARY CONDITION IN MAGNETIC FIELD



using Maxwell eqs. $\text{rot}\,E = -\frac{1}{c}\frac{\partial H}{\partial t}$

with $\bar{E} = E_{x_0} e^{i\left(\frac{\omega N z}{c} - \omega t\right)}$

$\bar{H} = H_{y_0} e^{i\left(\frac{\omega N z}{c} - \omega t\right)}$

$$\text{rot}\,\vec{E} = \left(\frac{\partial \bar{E}_z}{\partial y} - \frac{\partial E_y}{\partial z}\right)\hat{x} + \underbrace{\left(\frac{\partial \bar{E}_x}{\partial z} - \frac{\partial E_z}{\partial x}\right)}_{\downarrow}\hat{y} + \left(\frac{\partial E_y}{\partial x} - \frac{\partial E_x}{\partial y}\right)\hat{z}$$

$$\bar{E} \cdot i\frac{\omega N}{c} = \frac{\cancel{i}\,\omega N}{\cancel{c}} E_{x_0} \cancel{e^{i\left(\frac{\omega N z}{c} - \omega t\right)}}$$

$$N E_{x_0} = H_{y_0} \leftarrow \textcircled{=}$$

$$-\frac{1}{c}\frac{\partial H}{\partial t} = +\frac{1}{c} i\omega \bar{H} = \frac{\cancel{i}\,\omega}{\cancel{c}} H_{y_0} \cancel{e^{i\left(\frac{\omega N z}{c} - \omega t\right)}}$$

$$\frac{\partial}{\partial z} E_{x_1} e^{i\left(\frac{\omega z}{c} - \omega t\right)} = \frac{i\omega}{c} E_{x_1} \textcircled{=} -\frac{1}{c}\frac{\partial}{\partial t} H_{y_1} e^{i\left(\frac{\omega z}{c} - \omega t\right)} = \frac{1}{c} i\omega H_{y_1}$$

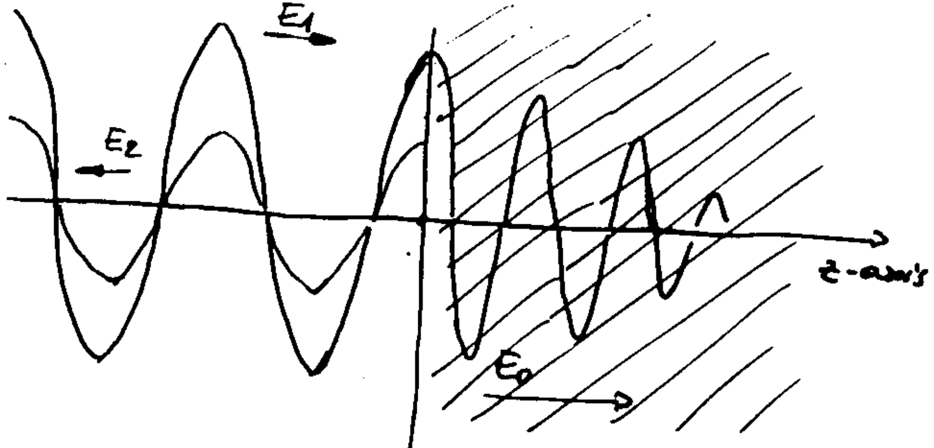
$$E_{x_1} = H_{y_1}$$

$$\frac{\partial}{\partial z} E_{x_2} e^{i\left(\frac{\omega z}{c} + \omega t\right)} = -\frac{i\omega}{c} E_{x_2} \textcircled{=} -\frac{1}{c}\frac{\partial}{\partial t} H_{y_2} e^{i\left(\frac{\omega z}{c} + \omega t\right)} = \frac{1}{c} i\omega H_{y_2}$$

$$-E_{x_2} = H_{y_2}$$

$$H_{y_1} + H_{y_2} = H_{y_0}$$

REFLECTION and TRASMISSION case:



in this region

$$E_x = E_1 e^{i\left(\frac{\omega z}{c} - \omega t\right)} + E_2 e^{-i\left(\frac{\omega z}{c} + \omega t\right)}$$

in this region

$$E_x = E_0 e^{-\frac{\omega}{c} k z} e^{i\left(\frac{\omega}{c} n z - \omega t\right)}$$

using continuity conditions for Electric and Magnetic Fields at the dielectric surface

$$E_0 = E_1 + E_2$$

$$-N E_0 = E_2 - E_1$$

we obtain directly

$$R = \frac{E_2}{E_1} = \frac{1 - N}{1 + N}$$

ratio of the Electric Fields in the left region

To obtain the measurable ratio between incident and reflected *intensity* we must take the square of the ratio R.

$$|R|^2 = \frac{(1-N)^2}{(1+N)^2} = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}$$

which goes to 1 when n goes to zero that is the case of TOTAL REFLECTION:

all energy is reflected if no transmission in the crystal can take place -

BY SIMPLE MEAUSURE OF ABSORPTION and REFLECTION WE CAN OBTAIN COMPLETE INFORMATION on $N = n + ik$

THIS ANALYSIS CAN BE PERFORMED EVERY FREQUENCY ω TO HAVE A SPECTRUM OF n AND k AS A FUNCTION OF THE LIGHT FREQUENCY ω -

The two OPTICAL CONSTANT n and k are not completely independent-

THE COMPLETE KNOWLEDGE OF ONE OF THEM OVER ALL FREQUENCIES INCLUDES THE KNOWLEDGE OF THE OTHER ONE-

They are related by DISPERSION RELATIONS called Kramers-Kronig dispersion relations

This is a *general feature*:

The relationship between REAL and IMAGINARY part of ANY CAUSAL response function is very general and can be used for any linear response.

for the Real and Imaginary part of the DIELECTRIC FUNCTION ε for instance appears:

$$\epsilon_1(\omega) = 1 + \frac{2}{\pi} \mathcal{P}\int_0^\infty \frac{\omega' \epsilon_2(\omega')}{\omega'^2 - \omega^2}\, d\omega'$$

$\mathcal{P}$ means the Cauchy Principal value of the integral

$$\epsilon_2(\omega) = -\frac{2}{\pi} \mathcal{P}\int_0^\infty \frac{\epsilon_1(\omega')}{\omega'^2 - \omega^2}\, d\omega'$$

that substituting $n^2 - k^2 = \epsilon_1$
$2nk = \epsilon_2$ becomes

$$n^2(\omega) - k^2(\omega) = 1 + \frac{4}{\pi} \mathcal{P}\int_0^\infty \frac{\omega' n(\omega') k(\omega')}{\omega'^2 - \omega^2}\, d\omega'$$

$$2n(\omega) k(\omega) = -\frac{2\omega}{\pi} \mathcal{P}\int_0^\infty \frac{n^2(\omega') - k^2(\omega')}{\omega'^2 - \omega^2}\, d\omega'$$

<u>In particular</u> for STATIC ELECTRIC FIELD

$$\epsilon_1(0) = 1 + \frac{2}{\pi} \mathcal{P}\int_0^\infty \frac{\epsilon_2(\omega')}{\omega'}\, d\omega'$$

IF the static real dielectric function is different from 1 THEN there must be some absorption ($\epsilon_2 \neq 0$ for some frequency)

We conclude this section giving some illustrative examples -

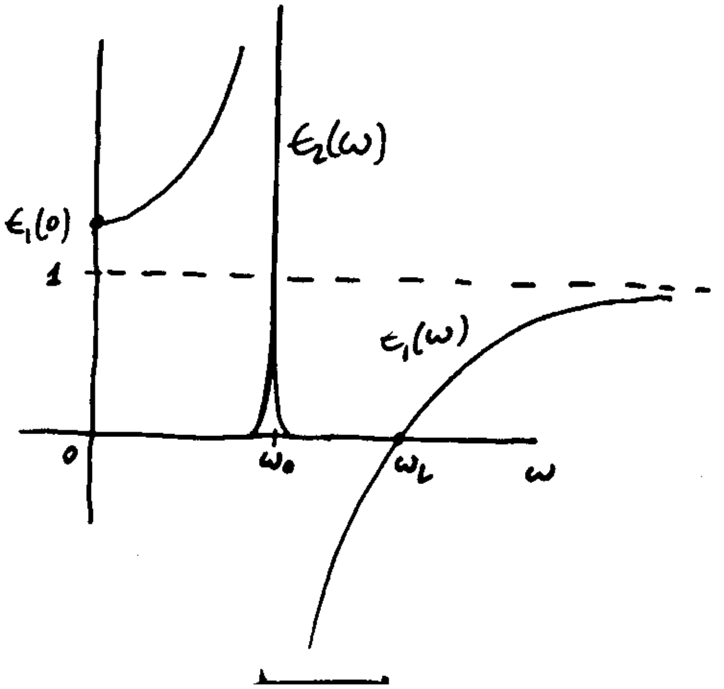
VERY SHARP SINGLE ABSORPTION PEAK at $\omega = \omega_0$

$$\epsilon_2(\omega) = C\,\delta(\omega_0 - \omega)$$

where C is the strenght of the transition

$\uparrow$ is related to static dielectric value because $\epsilon_1(0) = 1 + \frac{2}{\pi}\frac{C}{\omega_0}$

$$\epsilon_1(\omega) = 1 + \frac{\omega_0^2 \left[\frac{2}{\pi}\frac{C}{\omega_0}\right]}{\omega_0^2 - \omega^2}$$



The branch of $\epsilon_1(\omega)$ for $\omega > \omega_0$ crosses the axis at $\omega = \omega_L$ and increases asintoptically to the value 1 for ω going to infinity.

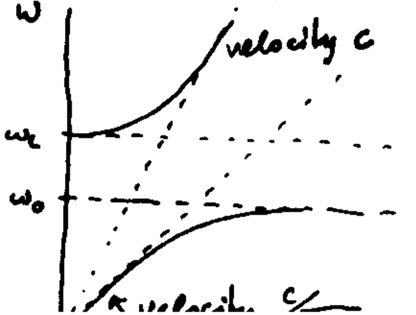
$$\omega_L = \omega_0 \sqrt{\epsilon_1(0)} = \omega_0 \sqrt{1 + \frac{2}{\pi}\frac{c}{\omega_0}}$$

$$\omega_L^2 - \omega_0^2 = \omega\, 2c/\pi$$

in the region $\omega_0 < \omega < \omega_L$ the index of refraction is PURE IMMAGINARY $N = ik$ and we can not have any wave propagation in the material:

condition of TOTAL REFLECTION

If we plot the dispersion ω vs $q = \frac{\pi}{\lambda}$ for the electromagnetic wave



} Region of ANOMALOUS DISPERSION

index of refraction is strongly frequency

This means that the electromagnetic field is strongly influenced by the polarization of the medium.

LORENTZ-DRUDE theory for charged oscillator and for free electron

$$\omega_0 = \sqrt{\frac{k}{m}}$$
← Hook's constant
← mass

motion equation is

$$m\frac{d^2y}{dt^2} + \underbrace{m\gamma\frac{dy}{dt}}_{\text{dumping}} + ky = eEe^{-i\omega t}$$

solution is $y = \frac{e}{m}Ee^{-i\omega t}\frac{e^{i\varphi}}{\sqrt{(\omega_0^2-\omega^2)^2+\gamma^2\omega^2}}$

φ = phase angle between $\vec{E}$ and y

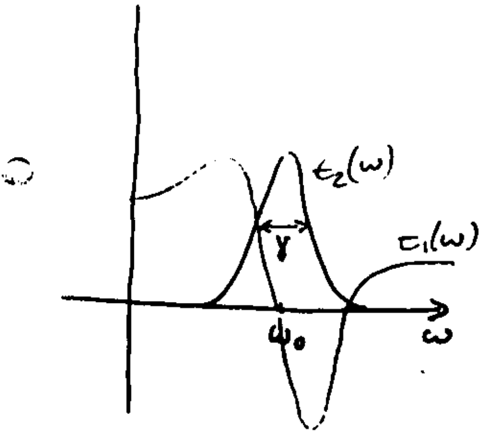
for a system with oscillator density n_0 we will have

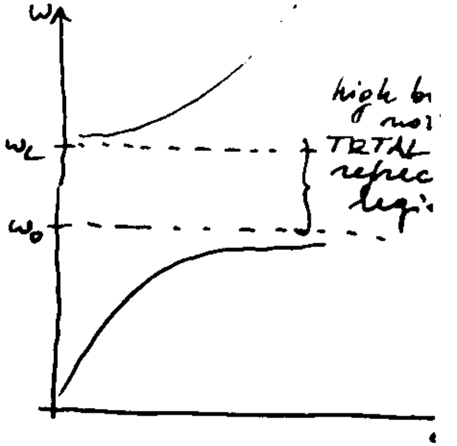
$$\epsilon(\omega) = 1 + 4\pi\chi = 1 + \frac{4\pi e^2 n_0}{m}\frac{1}{(\omega_0^2-\omega^2)-i\omega\gamma}$$

$$\Downarrow$$

$$\epsilon_1(\omega) = 1 + \frac{4\pi e^2 n_0}{m}\frac{\omega_0^2-\omega^2}{(\omega_0^2-\omega^2)^2+\omega^2\gamma^2}$$

$$\epsilon_2(\omega) = \frac{4\pi e^2 n_0}{m}\frac{\gamma\omega}{(\omega_0^2-\omega^2)^2+\omega^2\gamma^2}$$





in the case of FREE ELECTRON $k = 0$ (Hook's c

$$\Downarrow$$

$\omega_0 = 0$

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2+\gamma^2}$$

$$\epsilon_2(\omega) = \frac{\omega_p^2\gamma}{\omega^3+\omega\gamma^2}$$

with $\omega_p^2 = \frac{4\pi e^2 n_0}{m}$

ω_p = Plasma frequency

for high frequencies $\omega \gg \gamma$

$$\epsilon_1(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$$

$$\epsilon_2(\omega) = 0$$

for low frequencies $\lim_{\omega\to 0}\epsilon_2(\omega) = \frac{\omega_p^2}{\omega\gamma} = \frac{4\pi\sigma_0}{\omega} =$

$\sigma_0 = \frac{n_0 e^2}{m\gamma} = \frac{\omega_p^2}{4\pi\gamma}$ for STATIC CONDUCTIVITY

$\downarrow$

Relates optical behavior to an electric properties

MICROSCOPICAL APPROACH

For a description of the Optical Properties of Matter we now take a different point of view, treating quanto-mechanically the problem of RADIATION-MATTER interaction in the framework of PERTURBATION THEORY -

We formalize the interaction taking

$$\underset{\nearrow\atop\text{total system}}{H} = \underset{\uparrow\atop\text{matter}}{H_0} + H' \longleftarrow \text{perturbative term}$$

Shoedinger eq. $H\Psi = i\hbar \frac{\partial \Psi}{\partial t}$

Ψ is the wavefunction of the total system

for semplicity we consider only one atom as MATTER. Let $\psi_n(\bar{r},t)$ and E_n the eigenstates and eigenvalues of the atom respectively

We can expand $\Psi(\bar{r},t)$ in terms of $\psi_n(\bar{r},t)$

$$\Psi(\bar{r},t) = \sum_n a_n(t)\,\psi_n(\bar{r},t) = \sum_n a_n(t)\,u_n(\bar{r})\,e^{-i\frac{E_n}{\hbar}t}$$

where $|a_n(t)|^2$ are the probability for the system to be in the state n at time t.

Solving the Schroedinger eq. we obtain (considering the system in the state i for $t=0$)
$\hookrightarrow$ ground state

$$a_n^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \langle \psi_n(\bar{r},t)\,|\,H'\,|\,\psi_i(\bar{r},t)\rangle\, d\tau$$

Using for H' the interaction of the type $e\bar{E}\cdot\bar{r}$ with $\bar{E} = \bar{\eta}\,E\,e^{i(\bar{k}\bar{r}-\omega t)}$ in DIPOLE APPROXIMATION

η = polarization vector

$$|a_n^{(1)}(t)|^2 = \frac{\pi e^2 E^2}{\hbar}\,|\langle u_n|\bar{\eta}\cdot\bar{r}|u_i\rangle|^2\,\delta(E_n - E_i - \hbar\omega)\,t$$

time derivative gives the probability per unit time that system goes to initial to n state due to $\bar{E}$.

$$W_{in} = \frac{\pi e^2 E^2}{\hbar}\,|\langle u_n|\bar{\eta}\cdot\bar{r}|u_i\rangle|^2\,\delta(E_n - E_i - \hbar\omega)$$

The energy removed from the electromagnetic field in time unit is

$$\Delta I = W_{in} \underbrace{\hbar\omega}_{\text{energy of ~~the~~ very absorbed photon}}$$

For the <u>absorption coefficient</u> $\alpha(\omega)$

$$\alpha(\omega) = \frac{\Delta I}{I}$$

if we expres the intensity of the light beam

$$I = \rho(\omega)\frac{c}{n} = \frac{n^2 E^2}{4\pi}\frac{c}{n}$$

if the system is in a omogeneous medium

$$\alpha(\omega) = \frac{4\pi^2 e^2 \omega}{\boxed{n}c} \underbrace{\left|\langle u_n|\bar{\eta}\cdot\bar{r}|u_i\rangle\right|^2}_{\text{SELETION RULES}} \underbrace{\delta(E_n - E_i - \hbar\omega)}_{\text{ENERGY CONSERVATION}}$$

The selection rules are SYMMETRY CONDITION in order to have different from zero value of the transition probabilities (and α) –

Infact they depend on SPATIAL MATRIX ELEMEN

The GROUP THEORY gives a lot of information about selection rules.

GENERAL CONDITION:

Direct product of irreducible representations of the symmetry of initial state and the symmetry of the perturbation must contain the irreducible representation of the symmetry of the final state

$$\Gamma_f \subset \Gamma_i \otimes \Gamma_p$$

or

$$\Gamma_i \otimes \Gamma_p \otimes \Gamma_f \supset A_{1g}$$

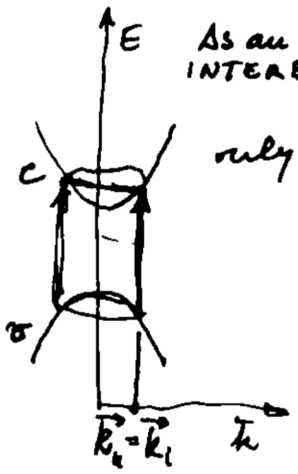
[illegible]

In the microscopic approach we have seen the behavior of a localized center (and only two-level system) but it is easy to extend the theory to a systems with distributed states as a solids.

$$\alpha(\omega) = \frac{4\pi^2 e^2 \omega}{mc} \sum_{ij} \left| \langle u_n | \bar{\eta} \cdot \bar{r} | u_i \rangle \right|^2 \delta(E_n - E_i - \hbar\omega)$$

↑

The sum is extended to all transition that can occur at frequency ω



As an example
INTERBAND TRANSITION

only vertical transitions : FRANCK-CONDON principle

can be shown
that, if we assume the dipole
matrix element varies little with k

$$\alpha(\omega) \propto J_{cv}(\omega) = \int \frac{d\bar{k}}{4\pi^3} \delta(E_n - E_i - \hbar\omega)$$

Both electrons and ions contribute to optical absorption spectrum.

As we will see we can describe the absorption according to the type of transitions that produces it.

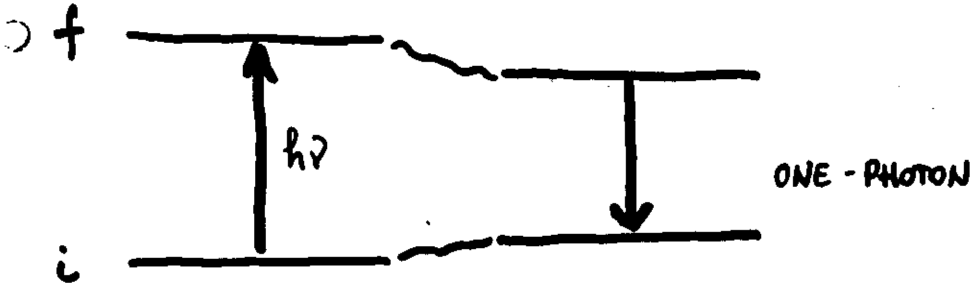
IR OPTICAL PHONONS

VIS - UV {EXCITONS
INTERBAND TRANSITIONS
IMPURITY TRANSITIONS

VUV CORE EXCITONS

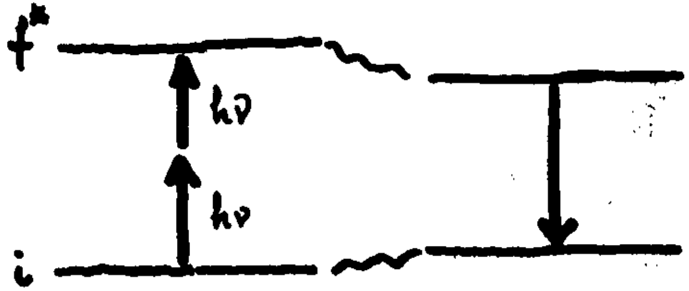
The microscopical approach permits to extend in a direct way the matter-light interaction problem to
NON-LINEAR regime.

We will see only a rapid survey to a particular aspect of the problem in the case of atomic localised system but extension to distributed lattice systems is direct



$$\mu^{(1)}(\nu) \propto \delta(E_f - E_i - h\nu) \left| \langle f | \bar{\varepsilon}_\nu \cdot \bar{p} | i \rangle \right|^2$$

Symmetry for one-photon interaction:
T_{1u}



$$\mu^{(2)}(\nu) \propto \delta(E_f - E_i - 2h\nu) \left| \Sigma_p \frac{\langle f^* | \bar{\varepsilon} \cdot \bar{p} | p \rangle \langle p | \bar{\varepsilon} \cdot \bar{p} | i \rangle}{E_p - E_i - h\nu} \right|$$

Symmetry for two-photon interaction:
$T_{1u} \otimes T_{1u} = A_{1g} + E_g + T_{1g} + T_{2g}$

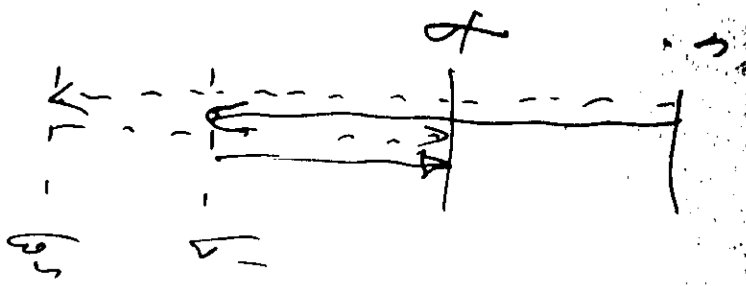
BIBLIOGRAPHY

Many books on optical spectroscopy and optical properties of solids are available for instance:

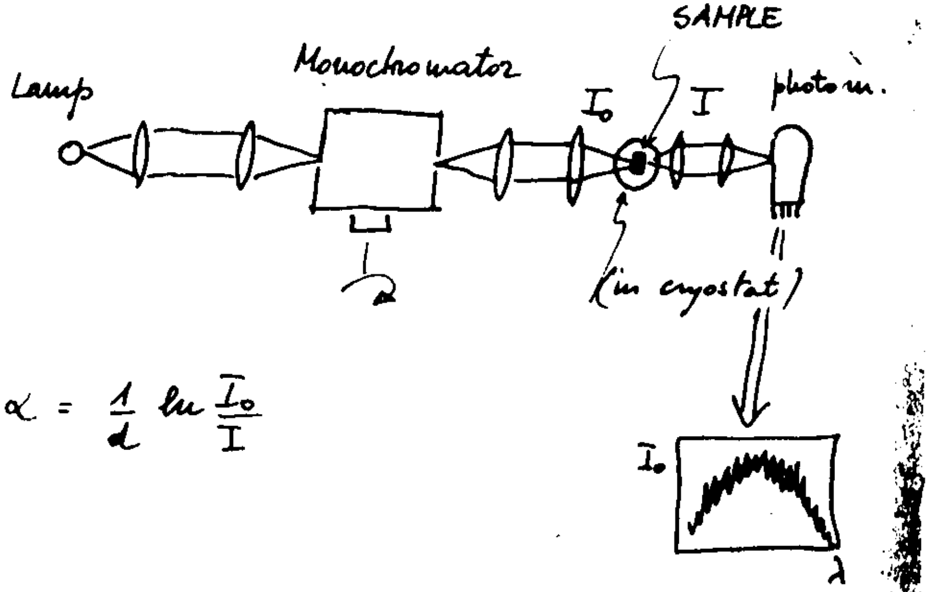
Ziman	Principles of theory of Solids Cambridge University Press UK
Kittel	Introduction to Solid State Physics John Wiley & Son
Nudelman & Mitra, Ed.	Optical Properties of Solids Plenum Press

For a more deep description of optical properties and experiments in the case of one and two-photon spectroscopy in solids

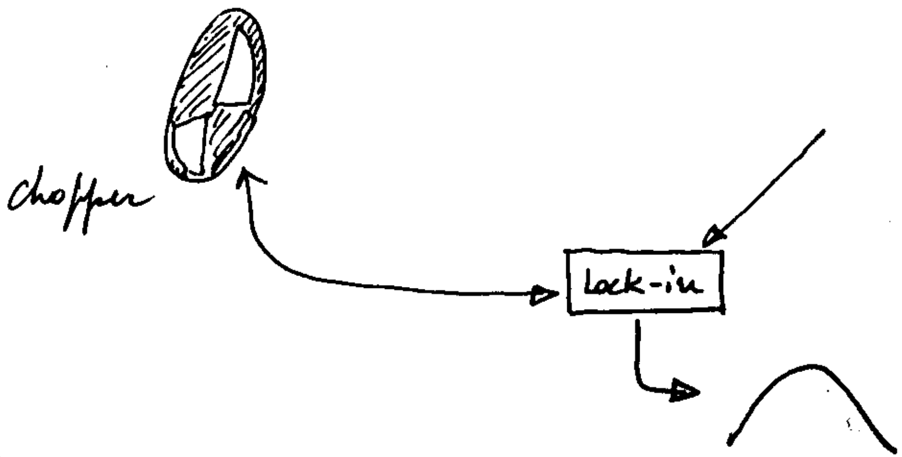
Bassani Parravicini-Pastori	Electronic States and Optical Transitions in Solids Pergamon Press.

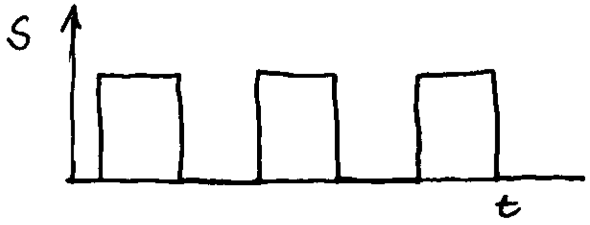


TYPICAL ABSORPTION SET UP



$$\alpha = \frac{1}{d} \ln \frac{I_0}{I}$$





Lock-in reveals signals with same frequency and phase respect to a reference signal coming from chopper

$$\frac{N}{S} \sim 10^{-5}$$

SPECTROPHOTOMETER :

simultaneous measurement of I and I_0 is done using TWO-BEAM TECHNIQU

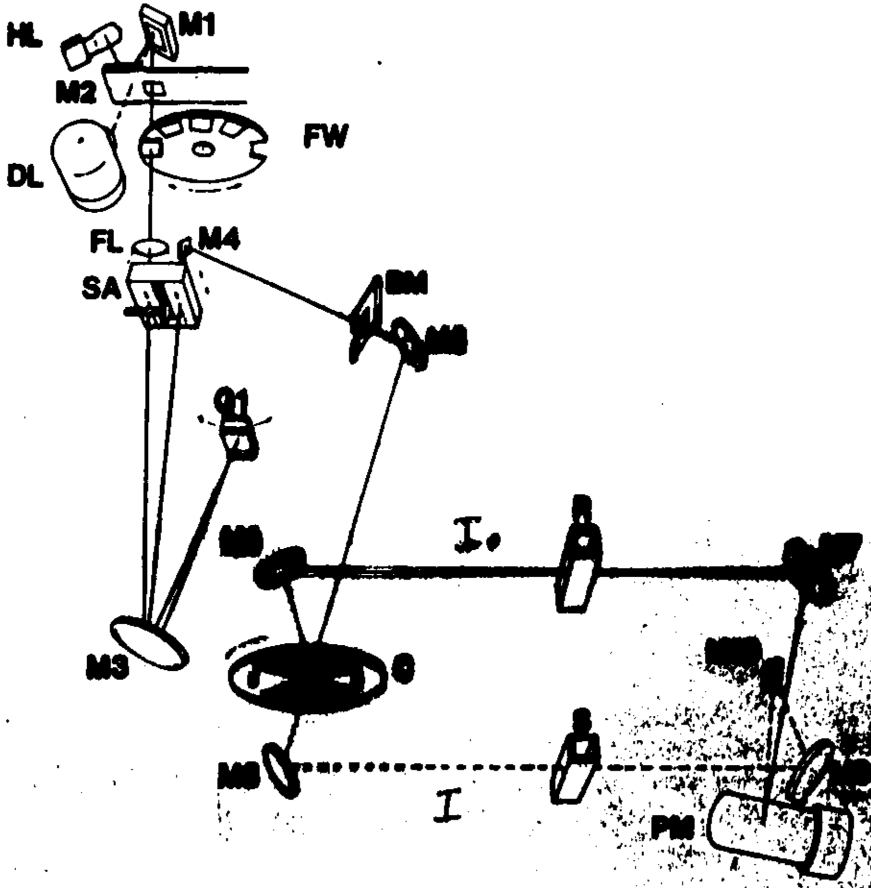
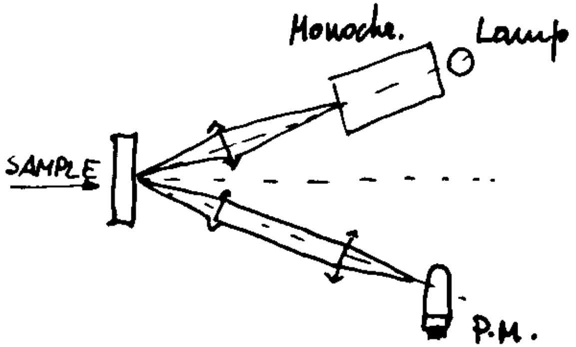


Figure 4-1. Optical System Pictorial Diagram - Lambda 19

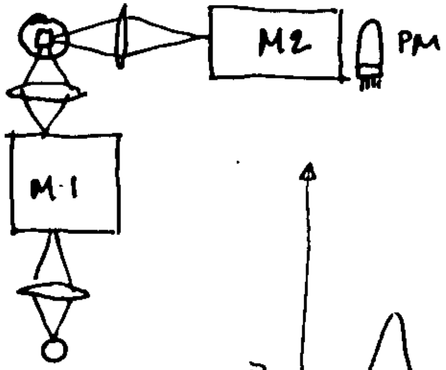
REFLECTIVITY SET-UP

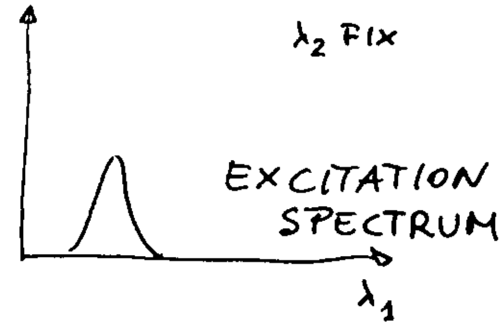
in near normal geometry



In order to taking in account of the spectral distribution of the lamp the reflectivity is often normalized on the reflectivity of Al sample that has almost flat response in a large energy range.

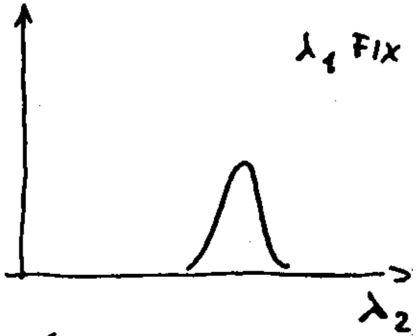
A typical set-up for LUMINESCENCE measurements



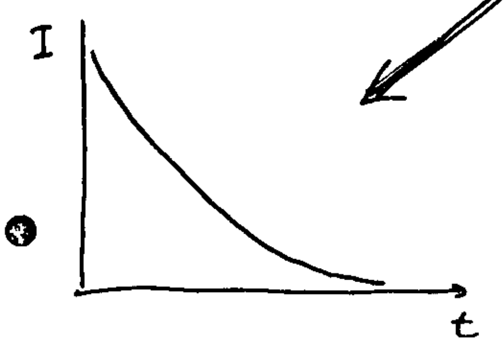


EXCITATION SPECTRUM

Similar to absorption



EMISSION SPECTRUM

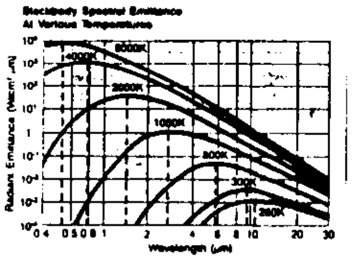


time analysis can be done

SOURCES FOR SPECTROSCOPY

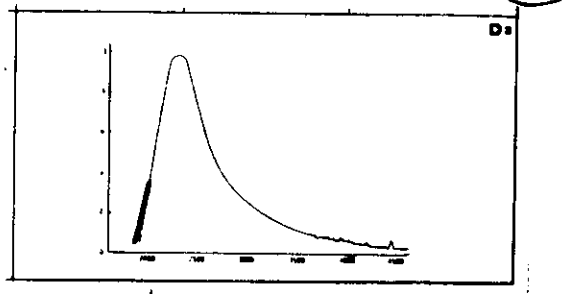
tungsten lamps

- **Blackbody (BB)**
An ideal radiator whose radiant emittance, W, follows the Stefan-Boltzmann law. The relationship is shown below.



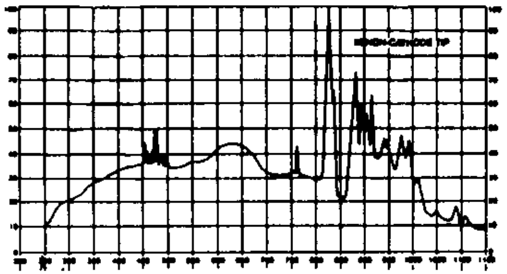
VIS ; NIR

D₂ UV

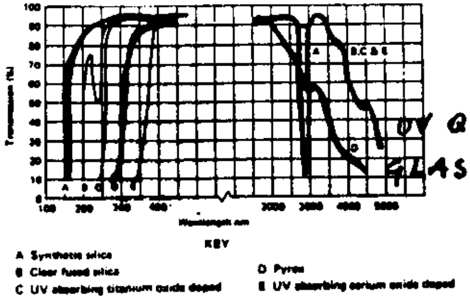


Synchrotron Radiation VUV

Spectral Emission Curve for Xenon Compact Arc Lamps



these structures makes difficult using in absorption



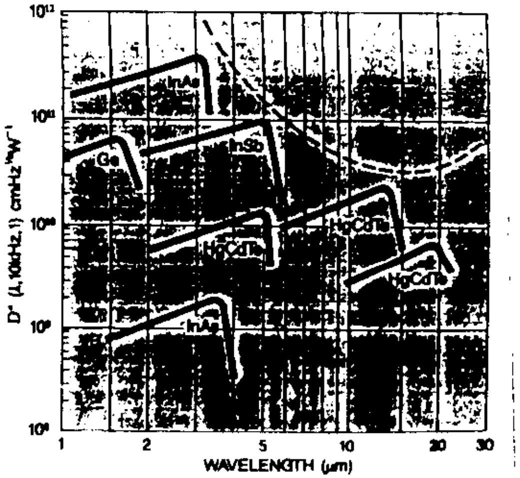
UV QUARTZ
GLASS

optical lens
filters
cryostat windows

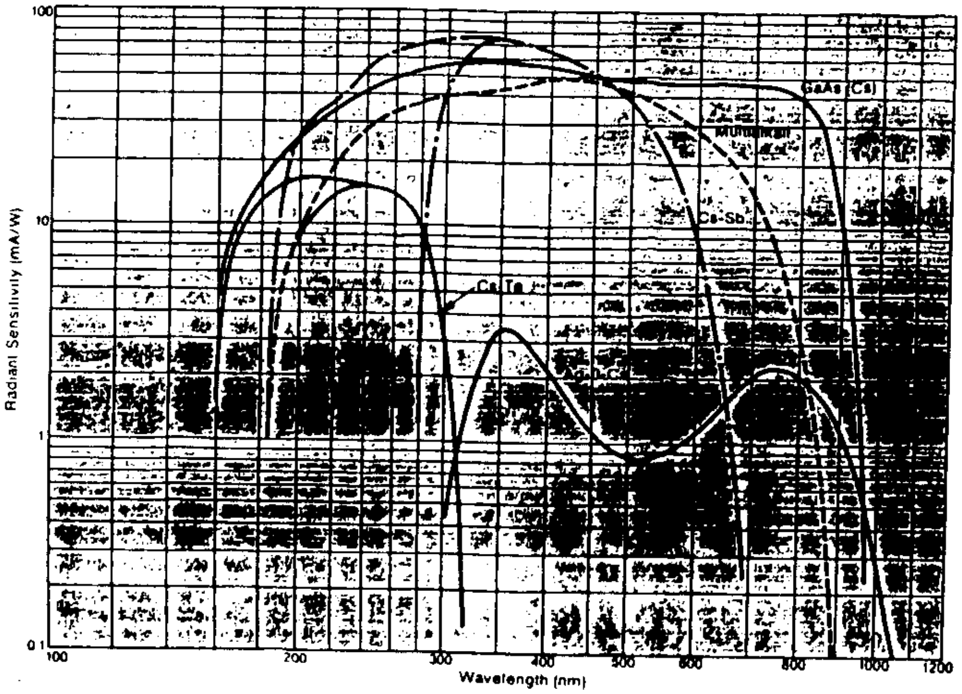
MUST BE OF SUITABLE MATERIALS

Side-on or Head-on Types	Nominal Diameter (mmDia.)	Vacuum or Gas Types	Cs-Te		Cs-Sb		Multialkali		GaAs(Cs)	Ag-O-Cs
Spectral Response (nm)			—	—	S-4	S-5	—	—	—	—
			185 ~ 320	160 ~ 320	280 ~ 650	185 ~ 650	280 ~ 850	185 ~ 850	160 ~ 910	400 ~ 1100
Window Material			UV-glass	Fused Silica	Borosilicate glass	UV-glass	Borosilicate glass	UV-glass	Fused Silica	Borosilicate glass
Side-on Types	18	Vacuum			PV13	R491		R518		PV11
		Gas			PG14A P250					PG12
	18 (Top cathode)	Vacuum			PV16	R370				
	30 (OT types)	Vacuum			IP39	R630		R520, R314	R807	R321
		Gas			4409					6953
	30 (Top cathode)	Vacuum				935				
	19	Gas			90AG					
Head-on Types	2L or smaller	Vacuum	R788 (21Dia.)	R765 (14Dia.)	R413 R927 (9.5Dia.) (21Dia.)	R840, R721 (40ia.) (21Dia.)		R645 (21Dia.)		R925 (21Dia.)
	25	Vacuum						R330-02		
	30	Vacuum.	R403					R647		
	Biplaner	Vacuum				R617-02	R617-03			R617-01

Detectivity for Judson Detectors



Spectral Response Characteristics



○ Normally the must be cooled to decrease their noise.

○

From absorption measurement we can expect, in a broad energy range, for an insulator like ALKALI HALIDE :

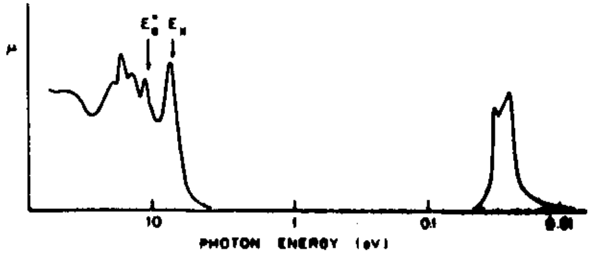


FIG. 1-4. Absorption spectrum of a typical alkali halide crystal over a wide range. The mechanisms responsible for the various peaks are discussed in the text.

GAP REGION

exciton
+
band to band
transition

TRANSPAR. REGION

IR

OPTICAL PHONONS

We saw that for Alkali Halides Around 10 eV appear big structures due, in first approximation, to transitions from VALENCE band to CONDUCTION band.

Electron - hole couples are created with the electron free in the conduction band and the hole free in the valence band.

Measuring the absorption in the gap energy region we can have information about the band structure of the material

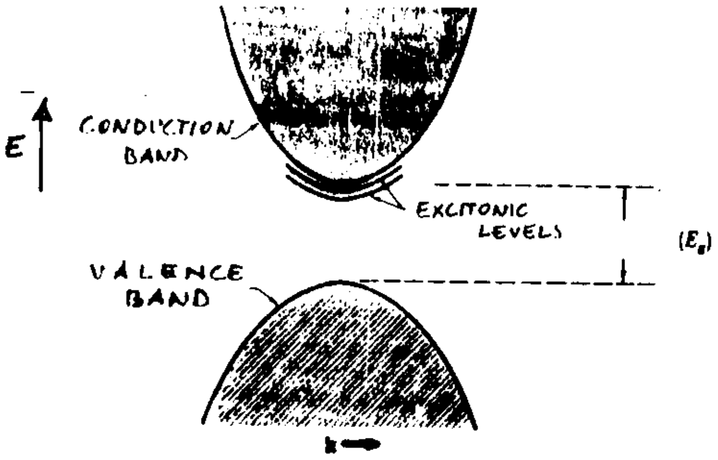
In particular the value of E_g energy distan between bottom of conduction band and top of valence band

Furthermore a very interesting aspect can be studied :

EXCITONIC STRUCTURES appear.

EXCITON: bound state due to residual interaction between an electron and his hole.

It can move in the crystal and its deexcitation gives rise to emission of photon (RECOMBINATION)



To illustrate EXCITONS we will show some examples of absorption spectra

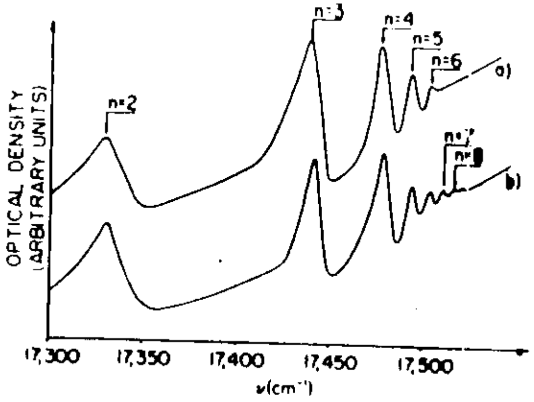
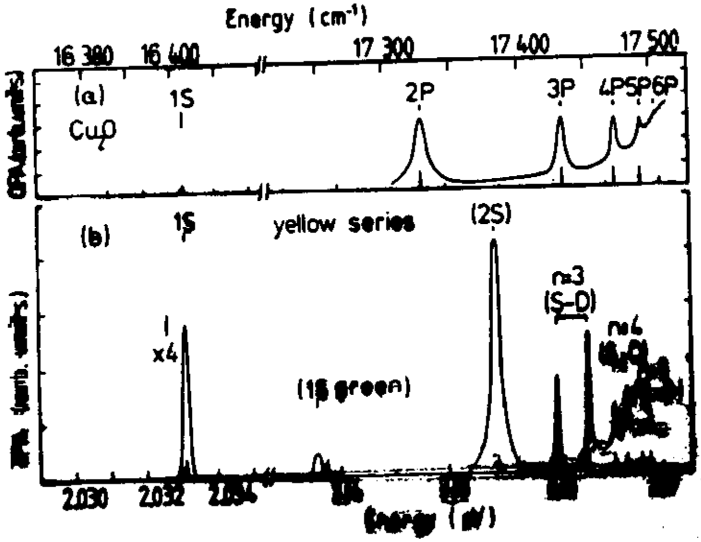


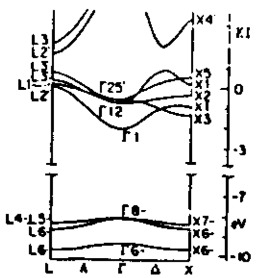
FIGURE 11. The so-called yellow series of excitons in Cu_2O at 4.2°K

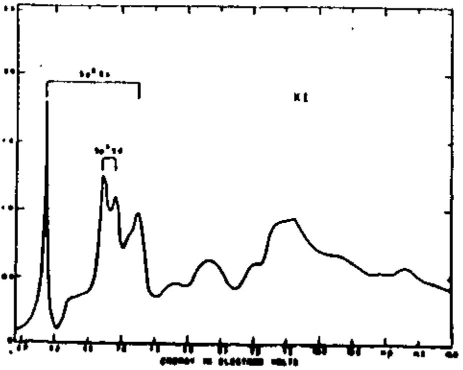
the $n=1$ peak is forbidden in linear absorption measurement due to symmetry.

Ch. Uihlein, D. Fröhlich and R. Kenklis
Phys. Rev. B 23, 2735 (1981)

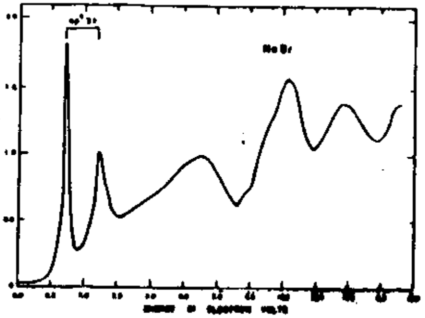


Cu_2O

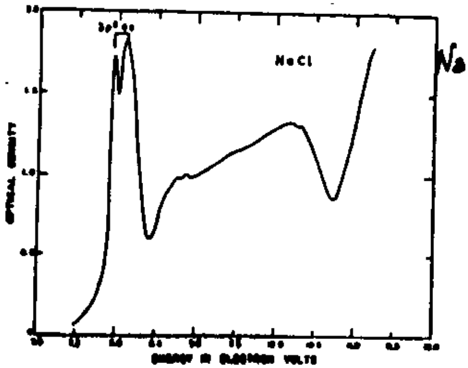




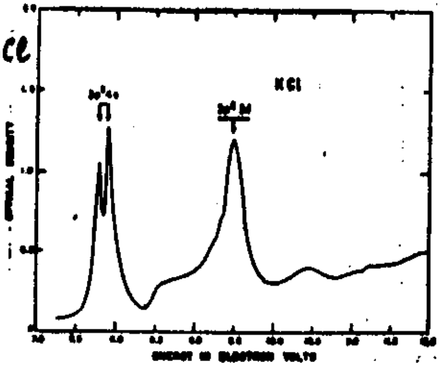
KI



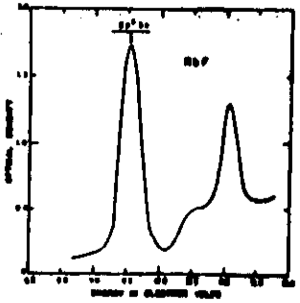
NaBr



NaCl



KCl



RbF

KI

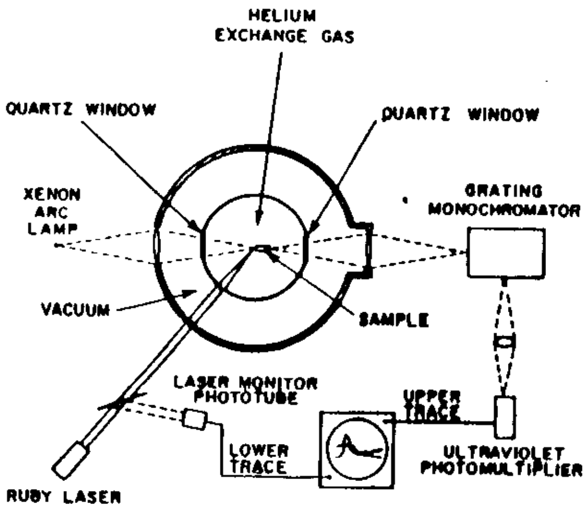
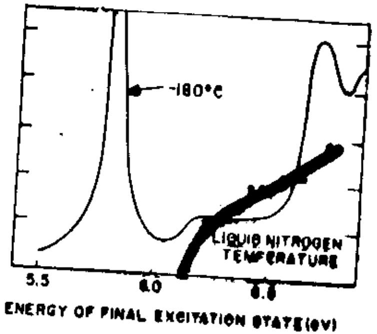


Fig. 4. Schematic diagram of two-photon absorption experiment (after Hopfield et al. 1963)

was really no further work, either theoretical or experimental, in this field until the invention of the laser. Then it was suddenly clear that nonlinear optical phenomena were observable. The first demonstration of double-photon absorption was the work of Kaiser and Garrett (1961), who were able to excite a blue fluorescence in an ion of europium in a crystal of CaF$_2$ by irradiating it with a red ruby laser. Almost

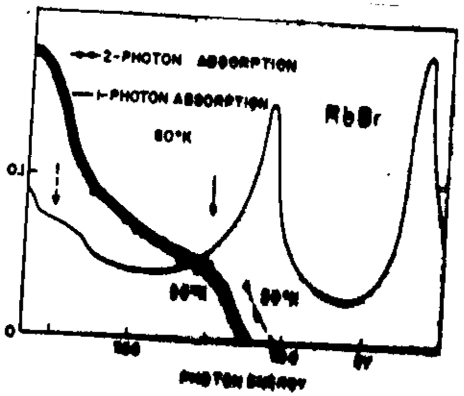
KI [illegible]I RbI RbBr [illegible] [illegible]Br CsBr [illegible]
iodides

HOPFIELD
WORLOCK
1963



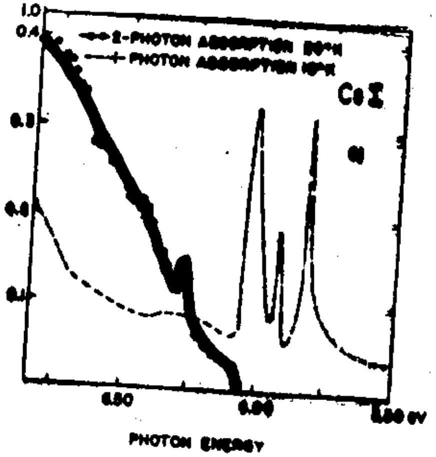
KI

FRÖHLICH
STAGINNUS
1967

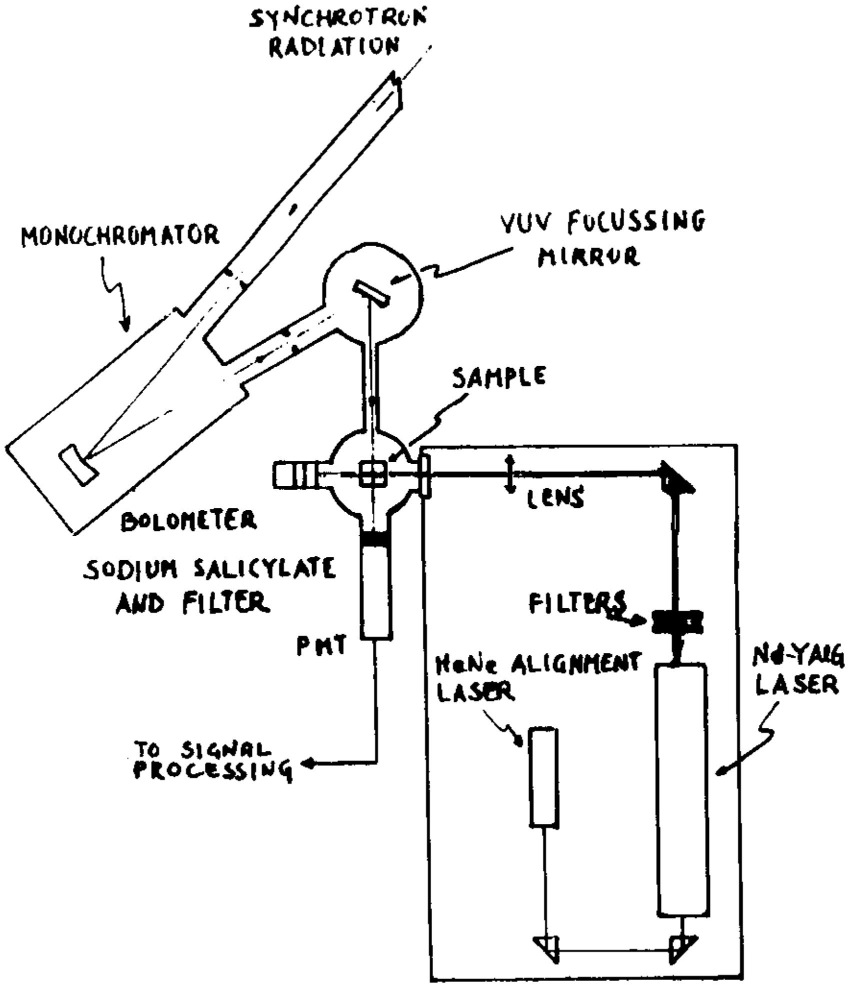


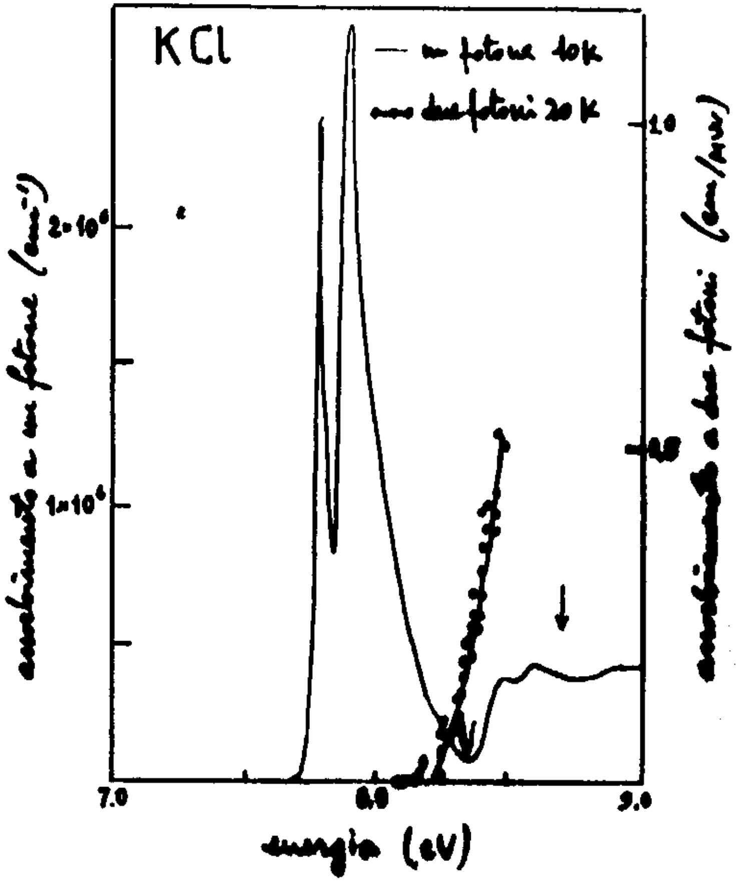
RbBr

FRÖHLICH
STAGINNUS
1969



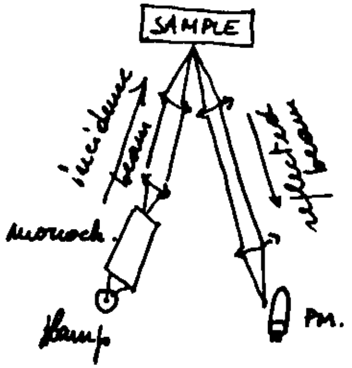
CsI


SYNCHROTRON RADIATION
MONOCHROMATOR
VUV FOCUSSING MIRROR
SAMPLE
LENS
BOLOMETER
SODIUM SALICYLATE AND FILTER
FILTERS
PMT
HeNe ALIGNMENT LASER
Nd-YAG LASER
TO SIGNAL PROCESSING


KCl
— un fotone 10K
due fotoni 20 K
assorbimento a un fotone (cm⁻¹)
2×10⁶
1×10⁶
assorbimento a due fotoni (cm/MW)
1.0
0.5
7.0
8.0
9.0
energia (eV)

the reflectance spectra of a ceramics $La_{2-x}Sr_xCuO_{4-y}$ solid solution is shown.

REFLECTANCE SPECTRA AT NEAR NORMAL INCIDENCE



Using Kramers Kronig relation can be extract optical function.

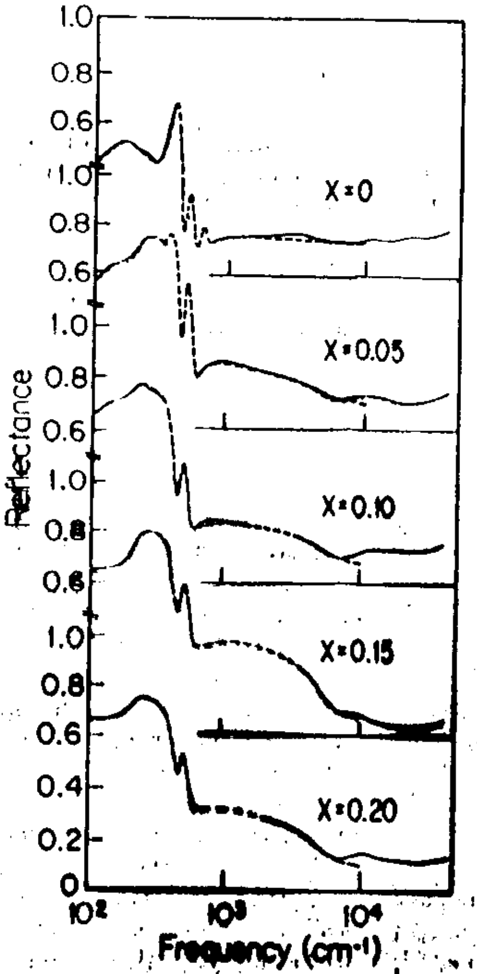


FIG. 1. Reflectance spectra of $La_{2-x}Sr_xCuO_{4-y}$ taken at room temperature in a near-normal-incidence geometry. The dashed lines are fits to the data using the effective-medium anisotropy model given in Eq. (1). The optical parameters of the fits are gathered in Table I. The normal-mode eigenvectors shown schematically in the figure are appropriate to K_2MnF_4 (Ref. 21) and a force-constant model is required to find the appropriate modes for La_2CuO_4.

this approach, since another loss mechanism (i.e., low-frequency phonons, etc.) may be responsible for the inability to fit the data at low energy to a Drude form.

A comparative study of the dc conductivity deduced from the optical measurements ($\sigma_0 = \omega_p^2 \tau / 4\pi$) and the direct resistively measured dc conductivity (σ_{dc}) on the same set of samples is shown in Fig. 6. Good agreement is obtained between these independent measurements of σ_0 and σ_{dc}, indicating that the Drude parameters obtained from our model provide consistent estimates for the optical conductivity of the *ab* planes, and for the large anisotropy in σ_{dc} (parallel and perpendicular to the *ab* planes).

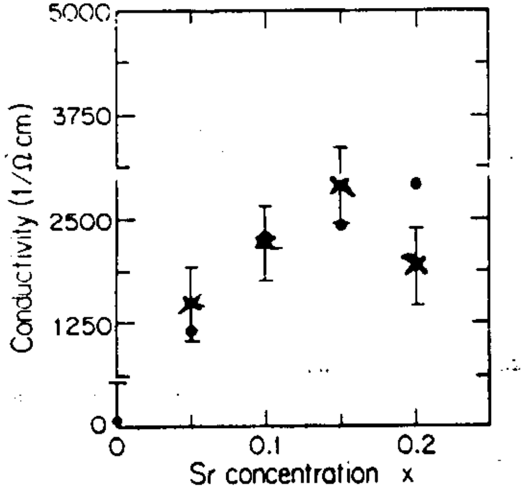


FIG. 6. dc conductivity obtained from the optical measurements $\sigma_0 = \omega_p^2 \tau / 4\pi$ (✖) and directly (resistively) measured conductivity σ_{dc} (●) plotted vs Sr concentration at room temperature.

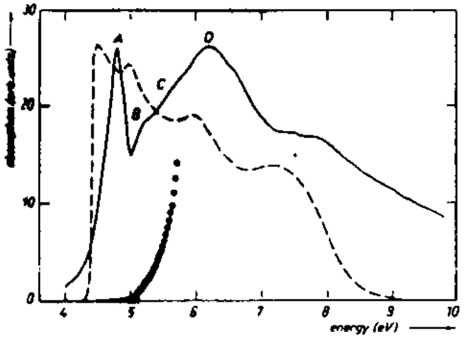


Fig. 3. Two-photon absorption coefficient (○ present measurements, ● [6]), one-photon excitation spectrum (– – – [3]), and one-photon absorption coefficient derived from reflectivity measurements (——— [4]) as a function of energy

OPTICAL PROPERTIES OF DOPED MATERIALS

Very important from a technological as well as theoretical point of view.

TWO MAIN TYPES of IMPURITIES:

A. Defect of the lattice structure like F and F-aggregates centers

B. Substitutional ions like Tl^+-type ion (Tl^+, Ag^-, Cr^{3+}, Eu^{3+})

The impurities or lattice defects concentrations usually range between 10^{16} to 10^{18} center/cm^3

Especially for very low concentrations the sensitivity of the measurements can be increased using LUMINESCENCE techniques

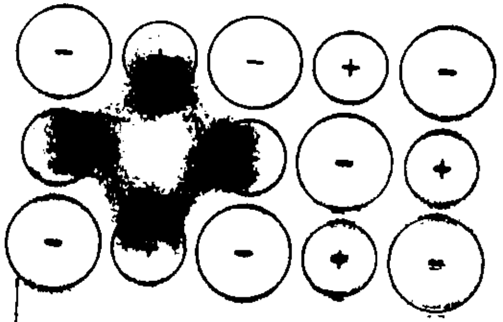
Furthermore this technique gives a number of very important information about relaxation process and time behaviour of the center.

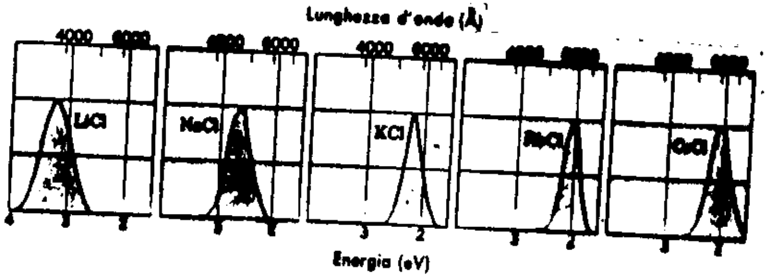
Alkali Halides can be colored

1. putting [illegible] at temperature near the melt temp. in a alkaline metal vapour

2. irradiating the pure crystal with x-ray, γ-ray or electron

In both these way are produced negative ion vacancies with an electron.





This system is strongly dependent on the vibrations of the surrounding ions.

Adiabatic Potential Energy Surfaces in a simplificated scheme

NOTE: in the 1° excited state the APES has a different equilibrium position

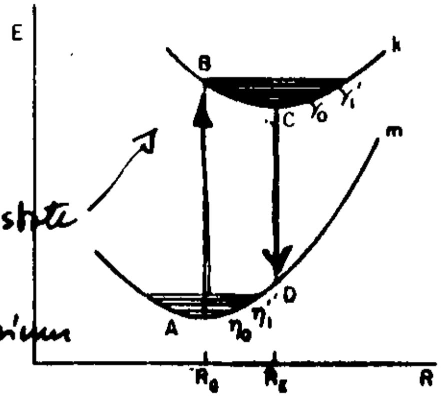
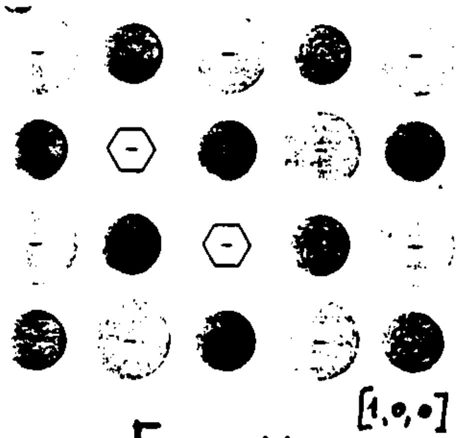
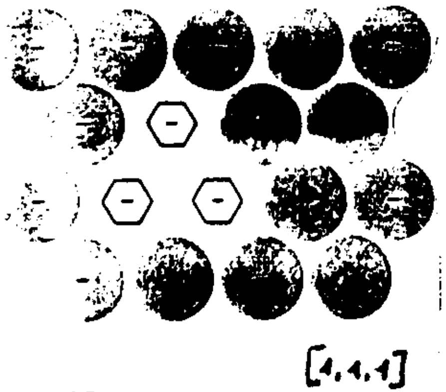


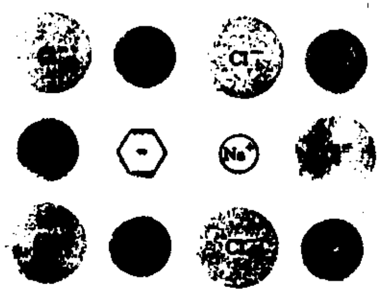
FIG. 2-6. Schematic configuration-coordinate diagram. See text for details (aft Fowler and Dexter, 1965).



F_2 or M



F_3 or R



F_A

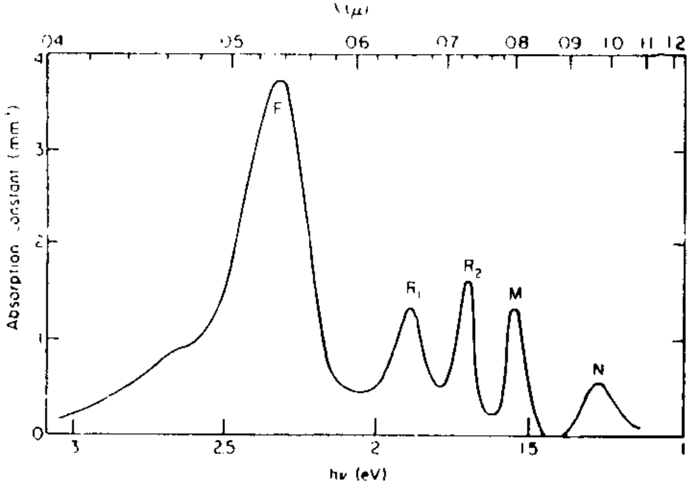


FIG. 2-16. Optical absorption of various electron-excess centers (after **Van Doorn, 1962**).

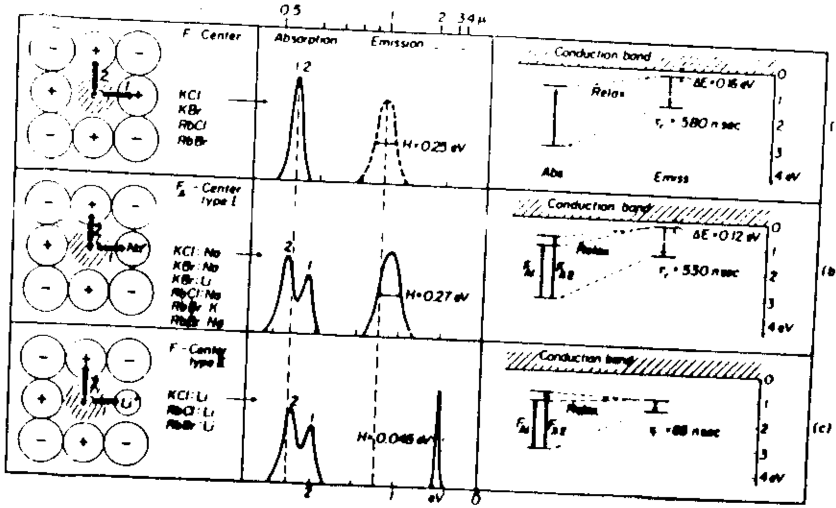


FIG. 3-1. Survey of F- and F_A-center properties as treated in this chapter. Indicated are models for the centers with absorption transition vectors, corresponding absorption and emission spectra, and schematic representations of electron/lattice processes in a level diagram for the electronic energy. (a) F center in KCl. (b) F_A(Na) in KCl [representative of F_A(I) centers]. (c) F_A(Li) in KCl [representative of F_A(II) centers].

USED AS A LASER'S MATERIAL
FOR IR REGION

To illustrate the optical properties of substitutional ions we will show some features of Tl⁺-type ions

wide ranging, including such systems as rare gases in dilute solid solution (e.g., Ar:Xe), ZnTe:O_{Te}, GaP:N_P, Si:Ge, KCl:Tl, KCl:Ag, and AgCl:Br. Almost all such cases show exciton binding at the impurity site.

In KCl:Tl one finds four absorption bands below the crystal band edge (8.7 eV), labeled *A* (4.38 eV), *B* (5.06 eV), *C* (5.30 eV), and *D* (5.50 eV). The *A*, *C*, and *D* bands are strong and rather temperature dependent, whereas the strength of the weaker *B* bands is temperature independent. The ground state of the free Tl^+ ion is $6s^2(^1S_0)$ and the next-highest levels come from the configuration $6s6p(^3P_{0,1,2}, ^1P)$. A qualitative explanation of the observed absorption spectrum was put forward by Seitz (1938), who suggested that the energy levels of the free

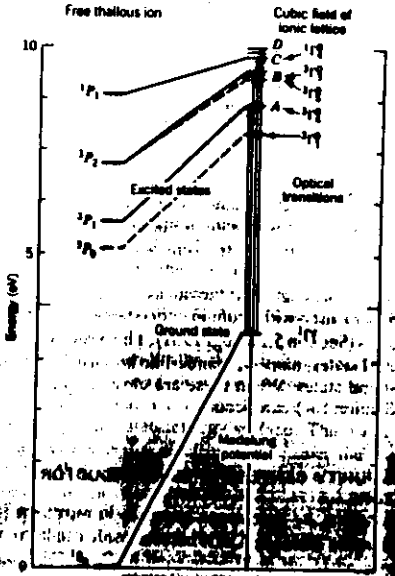
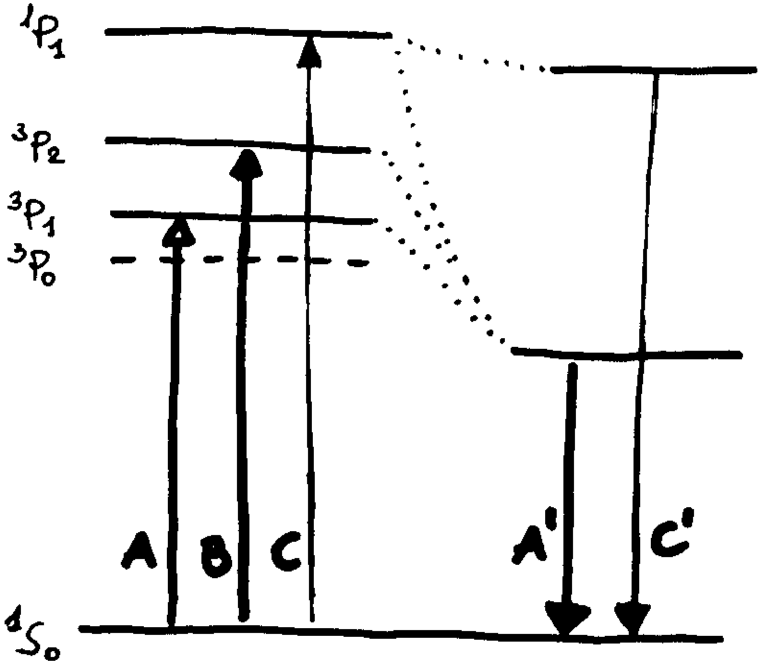


Figure 8.28 Effects of the cubic crystal field [illegible] levels of the Tl^+ ion. All states are raised in energy by the Madelung potential, the ground state probably more than the excited states (after Seitz (1938) [illegible]



cannot be explained by a dependence of the ${}^4T_{2g}$ → ${}^4A_{2g}$ energy gap on glass structure.

3.2. Hydroxyl quenching

Relaxation via quenching by hydroxyl groups is possible in glass since the third harmonic of the hydroxyl stretch at 10500 cm^{-1} is a fair match to the broadband ${}^4T_{2g}$ fluorescence. This transfer is short range so that it is likely that the hydroxyl moiety must be directly coordinated to Cr(III) in order to be effective. The hydroxyl content of our glasses was measured using the infrared absorption of the –OH stretch fundamental at 3500 cm^{-1}. The concentration of hydroxyl was found to be so low that the requirement of direct coordination to Cr(III) should make the hydroxyl mechanism negligible. Nevertheless, a series of soda lime silicates were prepared in which the ratio of hydroxyl to total oxygen present was varied between 4×10^{-5} and 20×10^{-5} by drying procedures. As expected, hydroxyl quenching in this series could not be detected by either absolute yield or lifetime measurements.

3.3. Concentration quenching

Concentration quenching was carefully characterized in soda lime, borate, fluorophosphate and phosphate glasses. In all cases a plateau region in the $\overline{\tau}$ versus chromium concentration curves was found below 0.02 mole% Cr_2O_3. All the glasses listed in table 2 have Cr_2O_3 contents near or below this limit, so that Cr(III) concentration quenching can be dismissed as the cause of low luminescence efficiency.

3.4. Aluminum metaphosphate

Figs. 1 and 2 show the broadband fluorescence decay and spectra for Cr(III) incorporated into two phases of aluminum metaphosphate $Al(PO_3)_3$, an especially interesting host in the present context. Depending on thermal history, $Al(PO_3)_3$ can be prepared as a glass or crystal, and the X-ray powder pattern confirms that the crystalline material in figs. 1 and 2 is the tetrametaphosphate (cubic) phase. A low resolution crystal structure has been reported for this phase, and it is consistent with all Al^{3+} sites being surrounded by a regular octahedron of oxygens [5]. Since

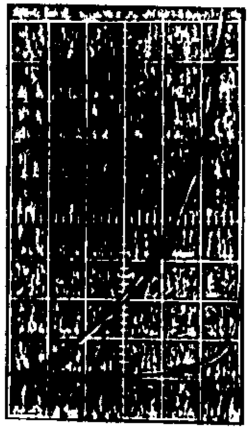


Fig. 1. ${}^4T_{2g}$ → ${}^4A_{2g}$ emission decay of $Al(PO_3)_3$: Cr(III) glass (fast decay) and crystal (slow decay). Oscilloscope settings are 50 mV/div and 50 μs/div and an RCA 4832 PM was used for detection.

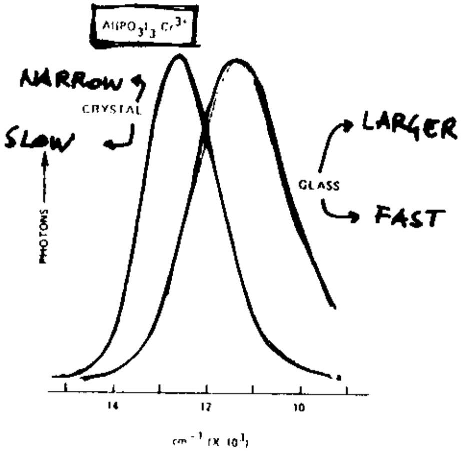


Fig. 2. Corrected fluorescence spectra of $Al(PO_3)_3$: Cr(III) glass and crystal.