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High Intensity Excitations in Ionic Compounds

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Introduction

The optical properties of some ionic compounds under the action of conventional irradiation with relatively low intensity of light are well known. These compounds however exhibit optical properties which may be substantially different when irradiated with light of very high intensity.

Some of these properties appearing only when the intensity of light becomes very high will be studied in this paper.

A first property which is observable with high intensity irradiation is the simultaneous absorption of two photons. Such an absorption was assumed by Planck many years ago but has been observed only recently with laser technics; this property will be discussed in some details in this paper.

A second category of properties may become important when the intensity of light is very high even disregarding double photon absorption. When the flux of incident photons is very high a certain accumulation of excited states in the irradiated material may become important and this circumstance may modify the optical properties in a kind of phototropic effect.

The theory of the first category of effects has been studied recently and some experimental observations, though not very numerous, have been reported.

I. Simultaneous Absorption of two Photons

I. Band to band transitions with double photon absorption

Results of the theory of simultaneous absorption of two photons will be given in this section. The details of the calculations are out of scope of this paper.

Consider a crystal having an energy gap E_g . Two monochromatic light beams of two different light sources are sent on to the same part of the crystal. Let the energy of the photons be $\hbar\omega_1$ and $\hbar\omega_2$ for both beams. Let us consider now the case when

$\hbar\omega_1 < E_g > \hbar\omega_2$. Therefore, the crystal is transparent to both beams when taken separately and at low value of the photon flux. However there is a limited probability of absorption by the crystal of both photons simultaneously if $\hbar\omega_1 + \hbar\omega_2 > E_g$.

Such a process has been calculated by Göppert-Mayer in 1931 [1] for atoms and recently by Braunstein [2] and London [3] for crystals. If such a process acquires some importance in high intensity irradiation, the crystal will not be transparent any more for the photons $\hbar\omega_1$ or $\hbar\omega_2$, though it was transparent to both at low intensities of light.

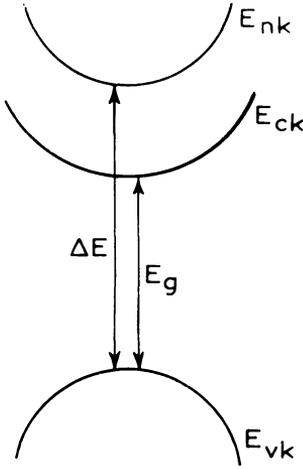


Fig. 1.

The calculations of Braunstein concern band to band transitions. The calculation must be carried out according to the second order perturbation theory. It is well known that if the transition matrix element for a transition between states n and m vanishes for a given process in the first order perturbation, in the second order of perturbation process an intermediate state is introduced, say $n \rightarrow k$ and $k \rightarrow m$ and the correspondent matrix element may not vanish. The conservation of energy is satisfied only for the final result and not for the intermediate transitions ($n \rightarrow k$ or $k \rightarrow m$). The transition to the intermediate state is virtual though the intermediate states are the quantum states of the system. A classical example for such a second order process is the atomic light diffusion theory in quantum mechanics.

We are going to consider a solid in which the band structure is that represented on Fig. 1.

For simplicity this model contains only two conduction bands and one valence band. We suppose that the extrema of all bands are at $\vec{k} = 0$. The second band E_{cn} is the intermediate state. It is virtually excited by one of the photons. One intermediate state only will be considered, though in fact all the higher states should be taken into account.

The absorption coefficient for the frequency ω_1 in the double photon absorption process is:

$$K_1 = -\frac{2n_0}{c} \frac{1}{N_1} \frac{dN_1}{dt} = -\frac{2n_0}{c} \frac{1}{N_1} \sum_{\mathbf{k}} P_{\mathbf{v}\mathbf{k}\mathbf{c}\mathbf{k}} \quad (1)$$

where N_1 is the density of photon $\hbar\omega_1$, n_0 the refractive index and c the velocity of light.

$$P_{\mathbf{v}\mathbf{k}\mathbf{c}\mathbf{k}} = \frac{2\pi}{\hbar} \left[\frac{H_{\mathbf{v}\mathbf{n}} H_{\mathbf{n}\mathbf{c}}}{\Delta E + E_{\mathbf{n}\mathbf{k}} + E_{\mathbf{v}\mathbf{k}} - \hbar\omega_1} + \frac{H_{\mathbf{v}\mathbf{n}} H_{\mathbf{n}\mathbf{c}}}{\Delta E + E_{\mathbf{n}\mathbf{k}} + E_{\mathbf{v}\mathbf{k}} - \hbar\omega_2} \right]^2 \times \delta(E_g + E_{\mathbf{c}\mathbf{k}} + E_{\mathbf{v}\mathbf{k}} - \hbar\omega_1 - \hbar\omega_2) \quad (2)$$

Here $H_{\mathbf{v}\mathbf{n}}$ and $H_{\mathbf{n}\mathbf{c}}$ are the optical matrix elements for a transition from the valence and conduction bands to an intermediate band n . $E_{\mathbf{c}\mathbf{k}}$, $E_{\mathbf{v}\mathbf{k}}$ and $E_{\mathbf{n}\mathbf{k}}$ are energies of the conduction, valence and intermediate bands counted from the top or bottom of the bands. ΔE is the difference of the energies of the valence and of the intermediate bands for $\mathbf{k} = 0$.

From (1) and (2) and after slight transformations one can write:

$$K_1 = \frac{16\pi^3 n_0 \hbar c^4}{cm^4 \omega_1 \omega_2} \int \frac{d^3k}{2\pi^3} \left[\frac{P_{vn}^1 P_{nc}^2}{\Delta E + E_{nk} + E_{vk} - \hbar\omega_1} + \frac{P_{vn}^2 P_{nc}^1}{\Delta E + E_{nk} + E_{vk} - \hbar\omega_2} \right]^2 \times \delta(E_g + E_{ck} + E_{vk} - \hbar\omega_1 - \hbar\omega_2) \quad (3)$$

where P_{vn} and P_{nc} are the appropriate momentum matrix elements. The subscripts 1 and 2 indicate the components in the direction of polarisation of $\hbar\omega_1$ and $\hbar\omega_2$.

In order to obtain an explicit expression of K_1 it is necessary to make assumptions on the dependence of the energies on k and to calculate the transition moments. Assuming spherical bands:

$$E_{vk} = \alpha_v \hbar^2 k^2 / 2m, \quad E_{nk} = \alpha_n \hbar^2 k^2 / 2m, \quad E_{ck} = \alpha_c \hbar^2 k^2 / 2m \quad (4)$$

where the α 's are ratios of the electron mass to the effective mass in the correspondent band.

For allowed transition from an initial state i to a final state f the momentum matrix element is related to the oscillator strength by the relation:

$$\text{allowed} \quad |P_{if}|^2 = \frac{m\hbar\omega_{if}}{2} f_{if}, \quad f_{if} = \text{oscillator strength} \quad (5)$$

For forbidden transitions the matrix element is proportional to k .

$$\text{forbidden} \quad |P_{if}|^2 = \left(\frac{m}{m_T} \right)^2 \hbar^2 (\vec{e}_q \cdot \vec{k}_i)^2 \quad (6)$$

Here \vec{e}_q is the unit vector in direction of polarisation of the correspondent photon; \vec{k}_i is the wave vector of the initial state; m_T is an effective mass for transition.

For double photon transition three types of band to band transitions have to be considered. The designation is obvious and derives from the matrix elements. It can be shown that the absorption coefficients are in the three cases as follows:

a) *Allowed-allowed transitions*

$$K_1 = \frac{2^{3/2} \pi n_0 e^4 \omega_{vn} \omega_{nc} f_{vn} f_{nc}}{cm^{1/2} (\alpha_c + \alpha_v)^{3/2} \omega_1 \omega_2} (\hbar\omega_2 + \hbar\omega_1 - E_g)^{1/2} \left(\frac{1}{B} + \frac{1}{C} \right) N_2 \quad (7)$$

b) *Allowed-forbidden transitions*

$$K_1 = \frac{2^{7/2} \pi n_0 e^4 \omega_{vn} f_{vn}}{3c(m_T)^2 (\alpha_c + \alpha_v)^{5/2} \hbar\omega_1 \omega_2} (\hbar\omega_2 + \hbar\omega_1 - E_g)^{3/2} \left(\frac{1}{B} + \frac{1}{C} \right) N_2 \quad (8)$$

c) *Forbidden-forbidden transitions*

$$K_1 = \frac{2^{11/2} \pi n_0 e^4 m^{7/2}}{9c(m_T)^4 (\alpha_c + \alpha_v)^{7/2} \hbar^2 \omega_1 \omega_2} (\hbar\omega_2 + \hbar\omega_1 - E_g)^{5/2} \left(\frac{1}{B} + \frac{1}{C} \right) N_2 \quad (9)$$

$$\text{Here: } B = \left[\Delta E + \left(\frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} \right) (\hbar\omega_2 + \hbar\omega_1 - E_g) - \hbar\omega_1 \right]^2$$

$$C = \left[\Delta E + \left(\frac{\alpha_n + \alpha_v}{\alpha_c + \alpha_v} \right) (\hbar\omega_2 + \hbar\omega_1 - E_g) - \hbar\omega_2 \right]^2$$

In deriving these expressions the square of the sum of matrix elements has been replaced by the sum of the squares.

2. Transitions to exciton states

Loudon has calculated the non-linear exciton absorption. In the case of exciton lines it is more appropriate to calculate the oscillator strength of the correspondent exciton line: the calculations lead to the formula for allowed-allowed transitions.

$$f_j^{(1)} = \frac{4\pi c^2 N_2}{\varepsilon_1 m^3 \omega_1 \omega_2} \left| \sum_n \frac{P_{cn}^1(\mathbf{o}) P_{nv}^2(\mathbf{o})}{\Delta E_{nk=0} - \hbar \omega_2} + \frac{P_{vn}^2(\mathbf{o}) P_{nc}^1(\mathbf{o})}{\Delta E_{nk=0} - \hbar \omega_1} \right|^2 |U_j(\mathbf{o})|^2 \quad (10)$$

In the formula ε_1 is the dielectric constant for the frequency ω_1 ; the sum is extended to different higher intermediate states; U_j is the envelope exciton function at $\vec{k} = 0$ for the exciton state j .

$$|U_j^{(0)}|^2 = \frac{1}{\pi a_0^3} \frac{1}{j^3} \quad (11)$$

where a_0 is the Bohr radius of the first quantum state of the exciton,

$$a_0 = \frac{\hbar^2 \varepsilon}{\mu e^2}$$

and j the quantum number of the exciton state; finally

$$\mu = \frac{m_e^* \bar{m}_h^*}{m_e^* + \bar{m}_h^*}$$

For allowed-forbidden transitions the expression for the oscillator strength is according to Mahan [4]

$$f_j \approx \frac{j^2 - 1}{j} \quad (12)$$

as in the forbidden transitions of Elliotts theory [5]. The forbidden transitions of Elliott are still dipole transitions. Therefore, 2^d class transitions is a more adequate name, as suggested by Nikitine.

The oscillator strength is furthermore related to the absorption coefficient by the well known formula

$$f_j^{(1)} = \frac{m c n_0}{2\pi^2 c^2 N} \int K(\omega_1) d\omega_1 \quad (13)$$

where N is the number of atoms per unit volume and m the mass of an electron.

3. Discussion of the above theory

The above formulae show an amount of new properties which are predicted for *non-linear absorption*.

1. In a crystal with inversion center in double photon absorption the transition takes place between states of *same parity*. For example, the transitions we have qualified

allowed-allowed must have p_{vn} and p_{nc} both different from zero. This means that v and n on one band and n and c on the other are states of different parity. So the final transition from v to c must involve states of same parity. The selection rules are therefore different in double photon absorption as compared to single photon absorption.

For crystals lacking inversion symmetry the situation is somewhat more complicated. The selection rules must be carefully analysed for different polarisation of incident light. In particular, transitions allowed in single photon absorption may be also allowed-allowed in double photon absorption.

2. If in the band to band transition in single photon absorption:

$$K \simeq (\hbar\omega_1 - E_g)^x$$

in double photon absorption:

$$K_1 \simeq (\hbar\omega_1 + \hbar\omega_2 - E_g)^x$$

This means that the absorption spectrum is shifted to lower energies by $\hbar\omega_2$. This may be of great interest in studying the absorption with high values of E_g (absorbing in the far ultraviolet). However, it has to be remembered that in this case the transition does not involve the same states and therefore one would not expect to observe the *same* structure in the shifted spectrum as in the spectrum observed in the ultraviolet unless the states are degenerate.

The same conclusion can be derived for exciton spectra.

3. The non-linear absorption being a second order effect, is small. In linear absorption the absorption coefficient is of the order of 10^5 or 10^6 cm^{-1} . On account of that the thickness of the sample under investigations must be very small, 10^{-5} or 10^{-6} cm . Samples of this thickness and of good quality are difficult to obtain.

In non-linear absorption investigations this difficulty is avoided; thick samples are used, which is a considerable simplification.

4. The absorption coefficient K_1 for the beam ω_1 in formulae (7), (8), (9), (10) is a function of the density of photons of frequency ω_2 , conversely K_2 is a function of N_1 .

A direct consequence of this is that Lamperts law does not apply for double photon absorption [8].

Let us take $\hbar\omega_1 = \hbar\omega_2$, so $N_1 = N_2$, and express $K_{\text{non-linear}}$ in function of I :

$$K = 2\hbar\omega a \cdot I$$

K is defined as:

$$K = -\frac{1}{I} \frac{dI}{dx}$$

So we can write:

$$\frac{dI}{dx} = 2\hbar\omega a I^2 - \alpha I.$$

The term αI is introduced to take into account the residual linear absorption. (α is the coefficient of *linear* absorption.) The solution of the equation is:

$$I(x) = \frac{I_0 e^{-\alpha x}}{1 + 2 \frac{I_0 a \hbar}{\alpha} (1 - e^{-\alpha x})} \quad (14)$$

Now α is usually very small for the frequency ω in the kind of experiments performed in *non-linear* absorption. So we can assume $\alpha x \ll 1$. Formula (14) becomes in this case:

$$I(x) = \frac{I_0}{1 + aI_0x 2h\omega} \quad (15)$$

It is important to note that in non-linear absorption $I(x)$ does *not* decrease as an exponential with the thickness of the absorbing medium but as an inverse of a linear function of x : this is a much slower decrease than in linear absorption.

II. Experimental Evidence of Double Photon Absorption

I. Experiments on double photon absorption

Some definite evidence of double photon absorption has been obtained experimentally. Two kinds of experiments will be discussed in this paper.

a) In a first class of experiments the absorption spectrum in double photon absorption have been measured for several substances. The variation of the absorption as a function of the depth of penetration has also been investigated.

b) In a second class of experiments the radiative recombination (luminescence) excited by a double photon absorption is investigated. This type of experiment is simpler than a) and leads to new information on highly excited crystals. However these experiments give only a qualitative information on double photon absorption. They consist in exciting luminescence with a frequency ω for which the crystal at low intensities is transparent; but the crystal absorbs $2h\omega > E_g$.

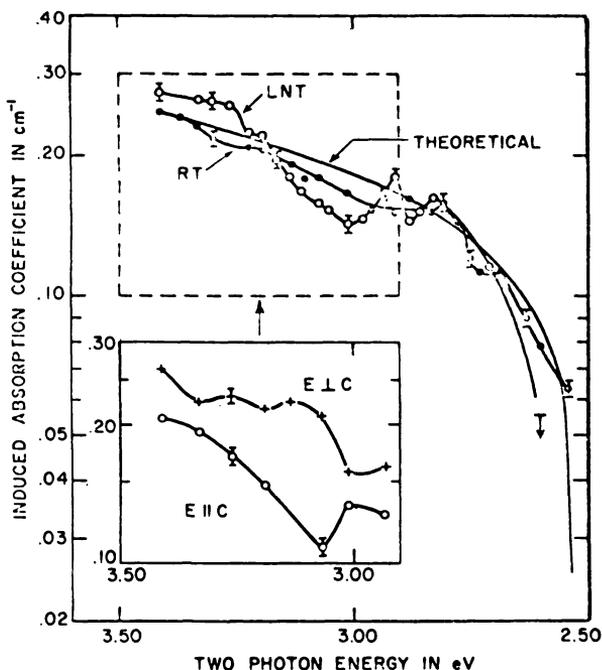


Fig. 2. Double-photon absorption spectrum of CdS at 77°K (LNT) and 300°K (RT). The dichroism at 300°K is also shown (after Regensburger).

A. Absorption Experiments

2. Double photon absorption — Band to band transitions

Double photon absorption has been measured only on a few substance (9, 10, 11, 12, 13). In these experiments the induced absorption of a light beam of frequency ω_2 is measured when the crystal is illuminated by a laser pulse of frequency ω_1 . By varying ω_2 , one gets an absorption spectrum. Both photons are such that $\hbar\omega_2 < E_g$ and $\hbar\omega_1 < E_g$, but $\hbar\omega_1 + \hbar\omega_2 > E_g$.

To our knowledge no exciton spectra have been observed* till now with two photon absorption technics on inorganic crystals.

Band to band transitions have been observed for KI and CsI (Hopfield and Warlock) TlCl (Matsuoka and Yasima) CdS (Regensberger and Parrizza) KBr, RbBr (Fröhlich, Staginnus).

The results of the measurements in CdS are illustrated by Fig. 2. The experimental results (K_{exp}) have been compared to the theory of Braunstein for the case of an allowed-allowed transition.

3. Non-linear absorption and Lamberts law

Non-linear absorption coefficients have been measured by Basov and al. In order to perform these measurements it is necessary to know the residual absorption coefficient in linear absorption which is given by

$$\lim_{I(0) \rightarrow (0)} \frac{I(x)}{I(0)} = e^{-ax}$$

It is possible then to calculate the absorption coefficient a in Basow's law.

$$\text{This is given by } \frac{K_{\text{non-linear}}}{2\hbar\omega} = a$$

Basov and al. [8] have found following values:

$$\text{CdSe } \frac{K_{nL}}{I} \approx 1 \text{ cm}^{-1}/\text{MW}$$

$$\text{GaAs } \frac{K_{nL}}{I} \approx 5 \text{ cm}^{-1}/\text{MW}$$

4. The expected exciton spectra

Double photon experiments would be of particular interest for Cu_2O on account of the various exciton transitions observed for this substance in single photon absorption technic.

Cu_2O has a cubic structure with inversion symmetry. It is well known that it

* Note added in proof — Recently excitonic lines have been observed in double photon absorption for CuCl (D. Fröhlich, B. Staginnus and E. Schönherr — to be published).

exhibits several series of exciton lines. Let us consider the yellow series. The exciton lines form a hydrogen like series of second class, the first line corresponds to $n = 2$ (Nikitine and al., Gross and al.). According to Elliott the oscillator strength in this serie decreases with n as $f \simeq (n^2 - 1)/n^5$. The excitons formed are in a P state (Fig. 3).

The $n = 1$ line has also been observed but this line is weak and it has been shown by Gross and al. and Nikitine and al. to belong to a quadrupole transition. The band

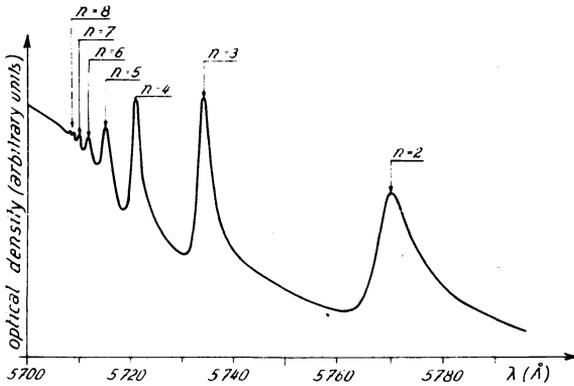


Fig.3. Single photon absorption spectrum of Cu_2O at 4.2°K .

structure has recently been calculated by Dahl and al. It so happens that at $\mathbf{K} = 0$ the band gap is between two bands formed of $\text{Cu}/3d$ orbitals and the transitions from the highest valence conduction band are forbidden for $\vec{\mathbf{K}} = 0$. They are weakly allowed for k small, but $\neq 0$ on account of overlap.

Loudon has calculated the oscillator strength of exciton transitions in double photon absorption. As in single photon absorption the transitions are

to P exciton states, they will be to S states in double photon absorption; in this case the oscillator strength will be according to Elliott proportional to n^{-3} .

The $n = 1$ line being dipole forbidden in single photon will be allowed in double photon transition. Loudon [3] has estimated the expected value of the oscillator strength for the $n = 1$ line. It can be shown that

$$f_{1s} \simeq 5.10^{-25} \frac{N}{V}$$

$\frac{N}{V}$ is the photon density of the laser beam. If 10^6 watts of a laser pulse are focused on 10^{-3} cm^2 , $\frac{N}{V} \simeq 10^{15}$. Therefore it is shown that in double photon absorption:

$$f_{1s} \simeq 5.10^{-10} \text{ per unit cell}$$

This value with the known line width of about 2 cm^{-1} [14],[15] gives a coefficient of absorption of $K_{\text{max } 1s} \simeq 1 \text{ cm}^{-1}$, a value which is of the same order for the single photon transition for the quadrupole line $n = 1$.

Loudon has also calculated that for the continuum near E_g \mathbf{K} should be of the order of 10^{-3} cm^{-1} .

It might be useful to remember orders of magnitude for the oscillator strength of different characteristic transitions in single photon absorption:

first class transitions	$f_{n=1} =$	$\left\{ \begin{array}{l} 10^{-2} \\ 5,5 \cdot 10^{-3} \end{array} \right.$	$\left\{ \begin{array}{l} \text{violet line of } \text{Cu}_2\text{O} \\ \text{blue line of } \text{Cu}_2\text{O} \end{array} \right.$
	$f_{n=1} \simeq$	$\left\{ \begin{array}{l} 0,3 \cdot 10^{-2} \\ 10^{-2} \end{array} \right.$	$\left\{ \begin{array}{l} \text{for fine series CuCl} \\ \text{diffuse series CuCl} \end{array} \right.$

second class transitions	$f_{n=2} \simeq \begin{cases} 3 \cdot 10^{-6} \\ 3 \cdot 10^{-5} \end{cases}$	yellow series of Cu_2O green series of Cu_2O
quadrupole transition	$f_{n=1} = 0.5 \cdot 10^{-9}$	Cu_2O

The results of the calculation of Loudon have been developed in this section in order to show the expected values for double photon exciton transition. It can be seen that the expected values are very small. They may be difficult to obtain also for another reason. As it was shown before, the non-linear absorption spectrum is shifted towards lower energy compared to the linear absorption spectrum by the quantity $\hbar\omega_{\text{Laser}}$.

The energy of $n = 1$ exciton state is roughly $E_{\text{exc}} \simeq 164 \text{ cm}^{-1}$. For pulsed Q spoiled lasers (which are necessary for such an experiment) the neodymium glass laser frequency is $\nu_{\text{laser}} = 9430 \text{ cm}^{-1}$. Therefore the frequency of the second beam should be about $\nu_2 = 6970 \text{ cm}^{-1}$ or $\lambda = 1.4 \mu$ which is in the near infrared. This may be of some difficulty for the observation.

B. Luminescence Experiments

Another method to put double photon absorption in evidence is to study the subsequent radiative recombination. In this kind of experiments the sample is illuminated with laser light of frequency ω_1 such that: $\hbar\omega_1 < E_g < 2\hbar\omega_1$. The luminescence of the crystal is detected at a frequency $\omega > \omega_1$.

Such a method of investigation gives much less information upon non-linear absorption for several reasons:

- the quantum efficiency is not known, therefore also the value of K_{NL}
- concurrent excitation processes are possible, as we shall discuss later
- one is limited only to a few available laser frequencies

This kind of experiment has been performed with a number of compounds: CdS (Braunstein), ZnO, CuCl, AgCl, etc. [16, 17, 18, 19, 20, 21, 22].

In CuCl, the luminescence spectrum obtained by excitation with double photon absorption is different from the luminescence obtained with a low intensity excitation with photons having an energy greater than the forbidden gap.

It is therefore useful to compare single photon and double photon excitation for the same excitation intensity.

III. Luminescence

We shall first briefly discuss some mechanisms of radiative emission in the vicinity of the absorption edge for "pure" crystals. The luminescence at low temperatures is mostly due to the recombination of excitons, free or bound.

I. Free excitons

For the direct recombination of free excitons both energy and momentum conservation laws must be satisfied.

$$\begin{aligned} E_{\text{phot}} &= E_{\text{exc}} \\ K_{\text{phot}} &= K_{\text{exc}} \\ K_{\text{phot}} &\simeq 0 \\ K_{\text{exc}} &\simeq 0 \end{aligned}$$

The position of the emission line will correspond to the absorption line.

Excitons may also recombine with the cooperation of phonons (simultaneous emission or absorption of one or more phonons). As the excitons are in stronger interaction with longitudinal optical phonons, usually this kind of phonons will be involved in the process. This kind of process has been recently studied by Gross, Razbirin and Permokhorov [23].

The energy conservation will be in the case of the emission of one phonon LO.

$$E_{\text{phot}} + E_{\text{phon}} = E_{\text{exc}}$$

The emission line will be on the lower energy side of the spectrum by the amount of one phonon.

In the case of phonon absorption, the emission line will lie on the higher energy side relative to the zero phonon line. It is not observable at very low temperature since the LO phonon population is negligibly small.

2. Bound excitons

At very low temperatures, bound exciton recombinations due to impurities in the crystal are very important (Lampert, Haynes, Thomas and Hopfield) [24, 25, 26, 27, 28, 29, 30]. Under bound excitons is meant a stable complex consisting of an exciton bound to a defect (for instance a substitutional impurity, a vacancy, etc.).

In that case, excitons have no translation energy, the line width is small and does not increase with increasing temperature.

The position of the lines will be at lower energy than the free exciton line because of the binding energy between impurity and exciton. One will also see the lines in absorption, but weakly.

3. Experimental

Figure 4 shows the experimental set-up. The sample is in direct contact with the cooling liquid. A carefully selected portion of the sample is successively illuminated by the light from:

a) A high pressure mercury lamp. The light is filtered through a Leiss monochromator.

b) The intense ultraviolet light produced by doubling the frequency of the red light from a ruby laser through a KDP crystal ($h\nu = 3.56\text{eV}$). A solution of CuSO_4 after the KDP crystal absorbs all the red light left.

The flux density is about 10^6 watts/cm² unfocused for a pulse duration of about $20 \cdot 10^{-9}$ sec. The light intensity is regulated by means of liquid filters. The filters consist of different concentration of a K_2CrO_4 solution in plane parallel glass cells.

The beam is focused with a cylindrical quartz lens on the sample. Part of the beam is sent on a high speed photocell in order to measure the excitation intensity (CSF 9096 risetime $\approx 3 \cdot 10^{-9}$ sec).

c) The intense red light from a ruby laser ($h\nu = 1.78\text{eV}$). The laser is Q-spoiled by a rotating prism. The output power is of the order of 10^8W/cm^2 unfocused, during a time of $30\text{--}40 \cdot 10^{-9}$ sec. The laser intensity is regulated by means of different concentrations of CuSO_4 .

The image of the illuminated portion of the sample is projected into the entrance slit of a Spex monochromator (linear dispersion = 10 Å/mm in the first order). The luminescence signal is recorded with a high speed photomultiplier (Radiotechnique 56 AVP, risetime $\approx 2 \cdot 10^{-9}$ sec). The signal is sent to a dual-beam oscilloscope (Fairchild 777) and recorded with a high speed camera (Polaroid 10.000 ASA).

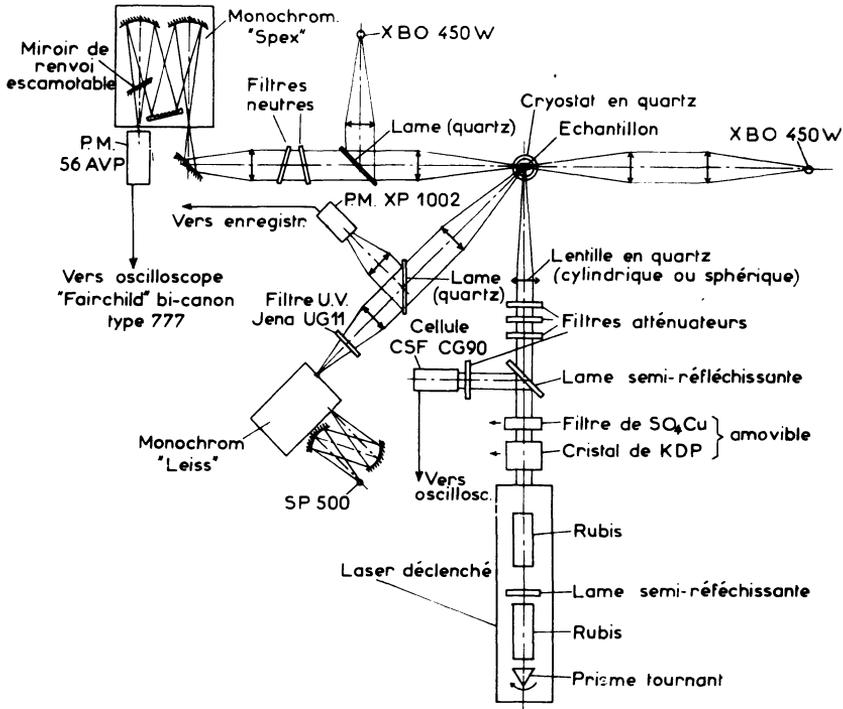


Fig. 4. Experimental set-up.

A system of reflecting mirror inside the monochromator allows to use it as a spectrograph. In that case, the luminescence spectrum is recorded photographically.

4. Experimental results on CdS [35, 37]

A. Spectrophotographical detection

The emission spectrum of CdS has been much studied [26, 32, 33, 35].

a) In Fig. 5a the emission spectrum at 4.2°K is shown when excited by a low density of photons having an energy greater than the forbidden gap (2.5eV). Line A₁ corresponds to the annihilation of a free exciton in the n = 1 state.

Lines I₁, I₂ are interpreted as emission from excitons bound to neutral centers, I₃ an exciton bound to an ionised center (see Thomas and Hopfield for instance).

The lines on the lower energy side have been interpreted as recombinations of excitons with simultaneous emission of LO phonons (Gross [23]).

b) The spectrum shown under B is obtained with very intense ultraviolet light ($h\nu_{ph} > E_g$). The spectrum is detected spectrophotographically. The lines are very intense. 5 to 10 laser shots are sufficient to produce a suitable exposure of the luminescence spectrum.

As one can see, the emission consists of a group of lines, the position of which corresponds well to the phonon assisted lines of A.

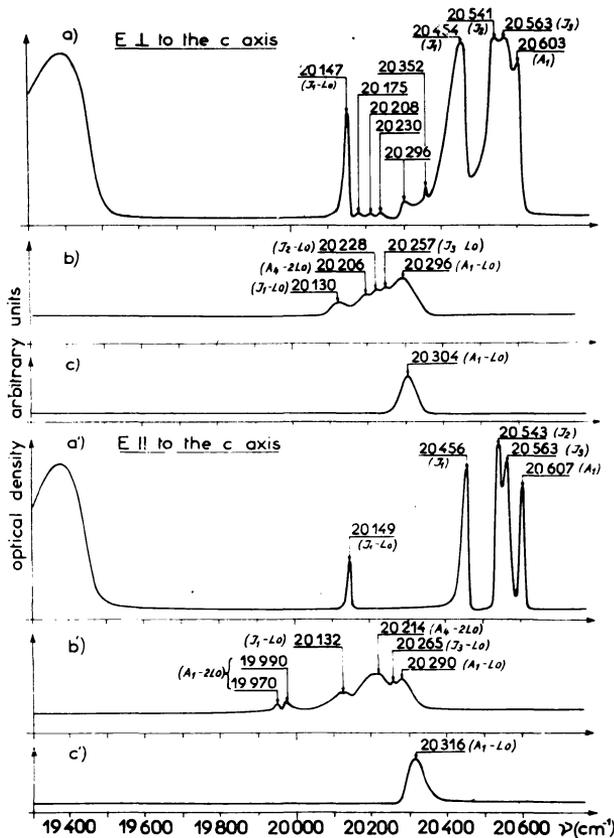


Fig. 5. Luminescence of CdS at 4.2°K for both directions of polarization of the emitted light.

a), a'): excitation by a low density of photons ($h\nu_{phot} > E_g$); b), b'): excitation by a very high density of photons ($h\nu_{phot} > E_g$); c), c'): excitation by a very high density of photons ($h\nu_{phot} < E_g$).

c) The spectrum shown under C is obtained by irradiation with red laser light ($h\nu_{laser} < E_g$).

The obtained intense line corresponds to A_1 -LO. Different mechanisms of excitation are possible in experiment C.

- A two-step transition via an intermediate real state. Such a mechanism is possible in CdS. The intermediate state situated in the forbidden gap is due to copper impurities [38]: a first photon brings an electron from the valence band to the impurity level, a second photon brings the electron from the impurity level to the conduction band. In this case, an infrared luminescence is also observed, due to the decay of electron from the impurity level.

In our experiments, we selected crystals which showed neither blue nor infrared luminescence, when excited by conventional, red light ($1.78 \pm 0.05\text{eV}$), even with photographic exposures of several hours. This experiment rules out the existence of the above intermediate impurity state in our crystals.

- Another possible mechanism is doubling of the frequency of the red-light inside the crystal with subsequent absorption of the ultraviolet light. This possibility has been ruled out by Braunstein and Ockman (doubling of the frequency depends on

the orientation of the light propagation vector relative to the optical axis of the crystal; the luminescence obtained with different orientation of the c -axis of a single crystal relative to the incident light beam did not change in intensity.

– The most probable mechanism of excitation is double photon absorption via an intermediate virtual state.

B. The intensity of the emission as a function of the intensity of excitation [36, 37]

The dependance of the emission intensity upon excitation intensity has been measured for the various emission lines (slide). Figure 6 shows the results at 4.2°K for A_1 and $A_1 - LO$ when the crystal is excited with ultraviolet laser light. A_1 corresponds to the recombination of a free exciton with simultaneous emission of a LO phonon. The direction of polarisation of the emission was chosen parallel to the c -axis of the crystal ($E \parallel C$) where E is the electric vector of light (in this polarisation, line A_1 is better separated from bound exciton recombination lines).

For a certain excitation threshold the variation of the intensity of line A_1 becomes sublinear when represented on a double-logarithmic scale; line $A_1 - LO$ becomes super-linear.

Figure 7 shows the dependence of $A_1 - LO$ for E perpendicular to C ($E \perp C$). The pulses of luminescence (left) and laser (right) for a) the superlinear and b) the linear part are also shown (the time scale is 50 nanoseconds per centimeter).

Figure 8 shows the results for bound exciton emission lines I_3 excited by ultraviolet laser light. It should be noticed that the emission intensity of I_3 is strongly dependent, for a given excitation intensity, upon the time interval between two successive laser shots. The behaviour is illustrated in this figure where luminescence signals for different time intervals are shown. The shorter the time interval, the weaker the emission intensity will be. (The time necessary between two laser shots in order to get a reproducible spectrum is of the order of 30 minutes of I_3).

Figure 9 shows the intensity dependence of I_2 and $I_2 - LO$. There is a saturation of I_2 due to the very high concentration of incident exciting photons.

The time interval necessary between successive laser shots is 5 minutes. The dashed curve shows the results obtained for a time interval of 2 minutes between successive laser shots. The dependence of $I_2 - LO$ is also shown.

Figure 10 shows the results for CdS at liquid nitrogen temperature. The intensity dependence of the intense recombination lines has been also measured (Fig. 11). In particular, one can see that the slope of the line $20\,186\text{ cm}^{-1}$ obtained by a double photon absorption mechanism, is twice the slope of the lines obtained by a single photon absorption mechanism.

5. Experiments on CdSe

Figure 12 shows the emission spectrum of CdSe at 4.2°K for a) a low density and b) a very high density of photons ($h\nu_{\text{photon}} > E_g$). Here also, for high excitation intensity, the exciton recombination with simultaneous emission of LO phonons is the most intense [39].

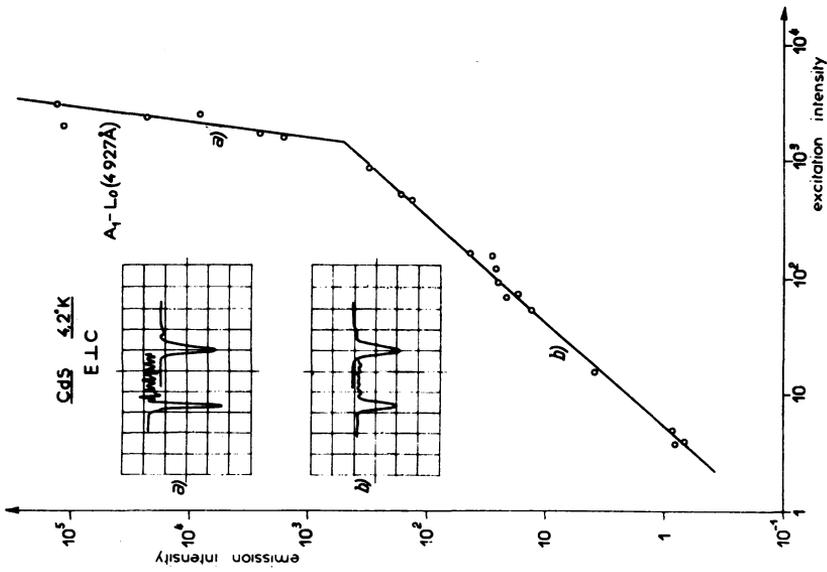


Fig. 6. Intensity dependence of $A_1 - LO$ upon excitation intensity ($E \perp C$) at $4.2^\circ K$. The slope m has following values: region a) $m \approx 8$; region b) $m \approx 1$. The luminescence signal (left) and laser signal (right) are shown for region a) and b) (sweep speed 50 nanosec/cm).

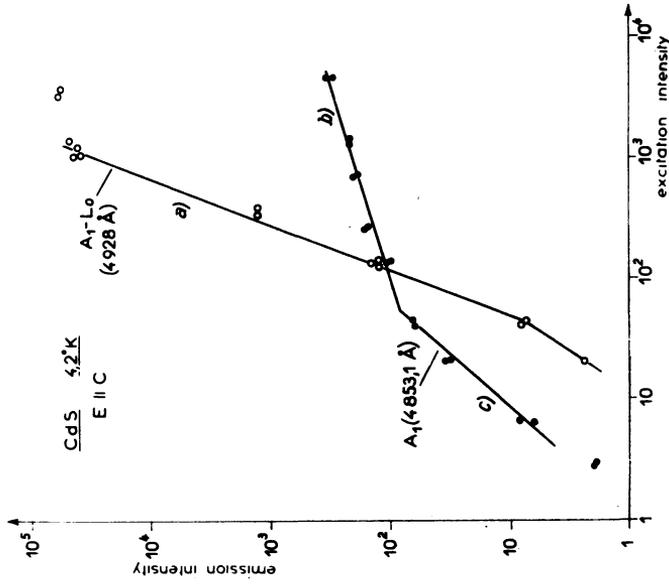


Fig. 7. Intensity dependence of A_1 and $A_1 - LO$ upon excitation intensity ($E \parallel C$) at $4.2^\circ K$. The slope m has following values: region a) $m \approx 3$; b) $m \approx 0.3$ c) $m \approx 1$

6. Experiments on CuCl

The luminescence of CuCl excited in the conventional way has been also much studied.

The results obtained in high intensity and double photon excitation are not as simple

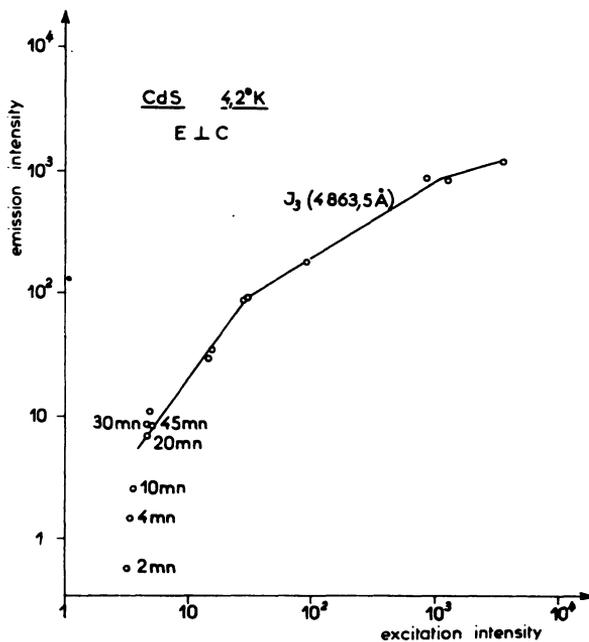


Fig. 8. Intensity dependence of I_3 upon excitation intensity at 4.2°K for $E \perp C$. The effect of the time interval between successive U-V laser shots is also shown.

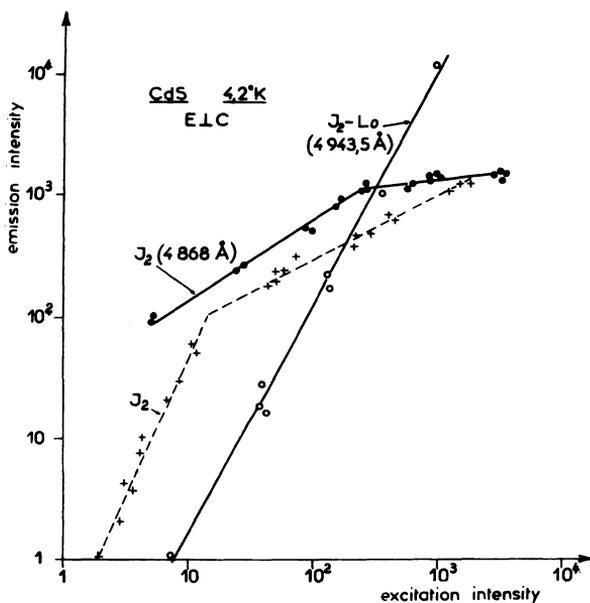


Fig. 9. Intensity dependence of I_2 and $I_2 - \text{LO}$ upon excitation intensity at 4.2°K (time interval between successive laser shots = 5 minutes). Also shown is the curve obtained for a time interval of 2 minutes (dashed curve).

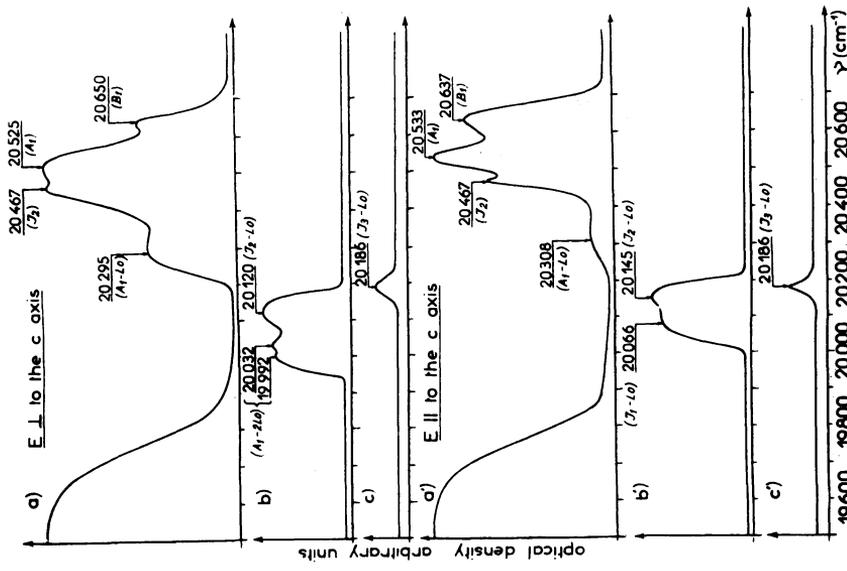


Fig. 10. Luminescence of CdS at 77°K for both directions of polarization of the emitted light. a), a') : excitation by a low density of photons ($h\nu_{\text{phot}} > E_g$); b), b') : excitation by a very high density of photons ($h\nu_{\text{phot}} > E_g$); c), c') : excitation by a very high density of photons ($h\nu_{\text{phot}} < E_g$).

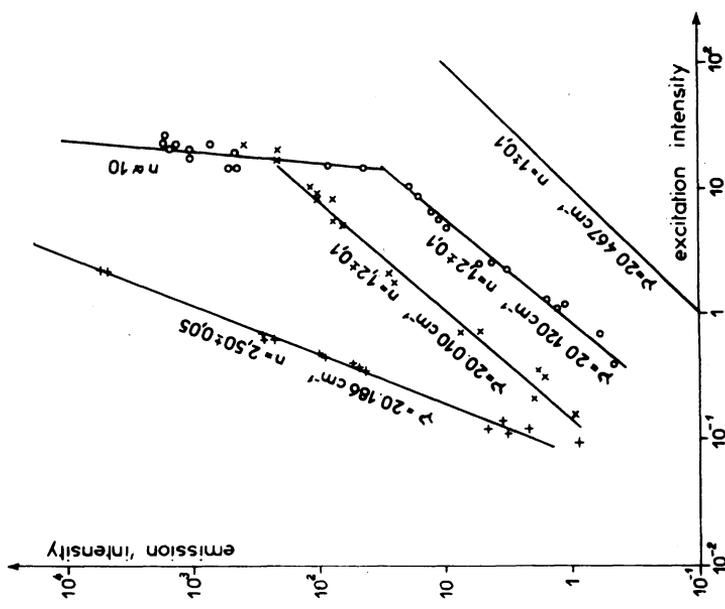


Fig. 11. Intensity dependence upon excitation intensity of emission lines of CdS at 77°K. Lines 20120 cm^{-1} and 20010 cm^{-1} are obtained by excitation with a U-V laser ($h\nu_{\text{phot}} > E_g$). Line 20186 cm^{-1} is obtained by excitation with a red laser ($h\nu_{\text{phot}} < E_g$, double-photon absorption).

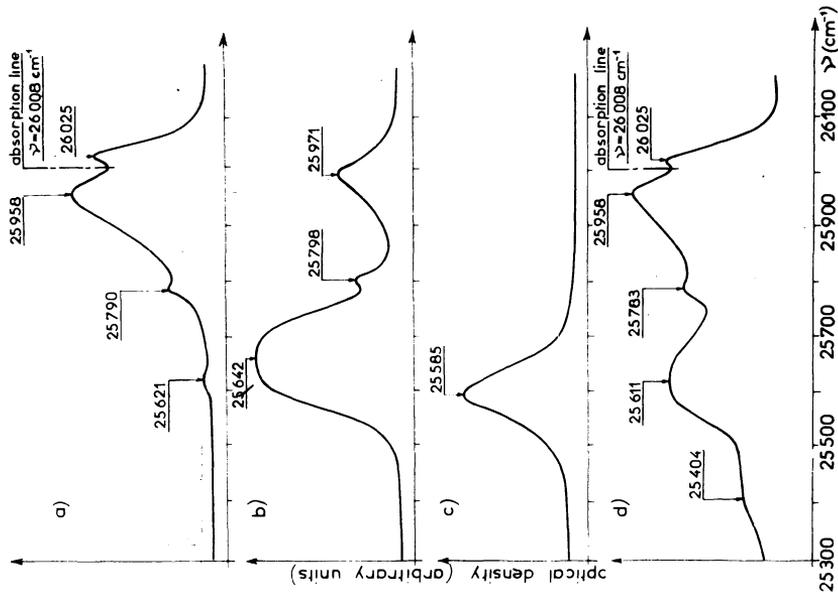


Fig. 13. Luminescence of CuCl at 77°K

- a): excitation by a low density of photons ($h\nu_{\text{phot}} > E_K$);
- b): excitation by a very high density of photons ($h\nu_{\text{phot}} > E_g$);
- c): excitation by a very high density of photons ($h\nu_{\text{phot}} < E_g$);
- d): excitation by a low density of photons ($h\nu_{\text{phot}} > E_g$) after the sample has been irradiated with many red laser shots.

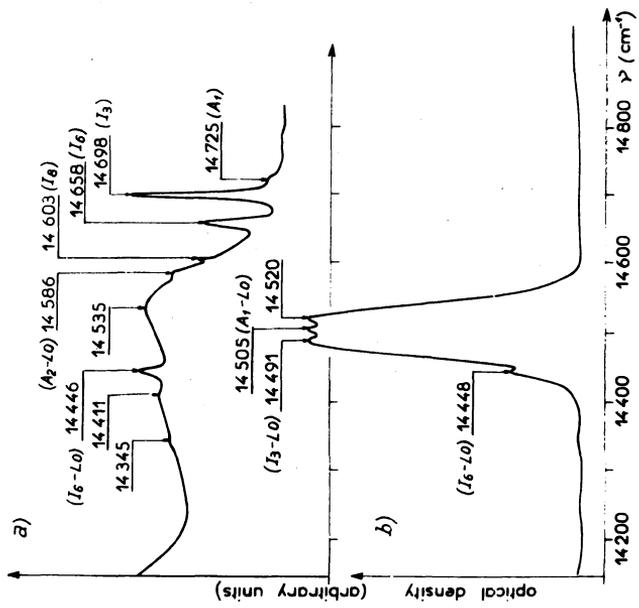


Fig. 12. Luminescence of CdSe at 4.2°K

- a) excitation with low intensity light ($h\nu_{\text{phot}} > E_K$);
- b) excitation with very high intensity light ($h\nu_{\text{phot}} > E_g$).

as for CdS. Even though the theoretical interpretation is not yet satisfactory, we are going to describe the results for CuCl now.

The spectrum of CuCl excited by a low intensity light is rather simple at 77°K [42]. The emission is composed essentially of the inversed resonance line ν_0 and a second line named ν_2 25 790 cm^{-1} which has been proved to be an exciton complex line superimposed to a $\nu_0 - \text{LO}$ line $\nu_{\text{phon}}(\text{LO}) = 215 \text{ cm}^{-1}$ [31], figure 13a).

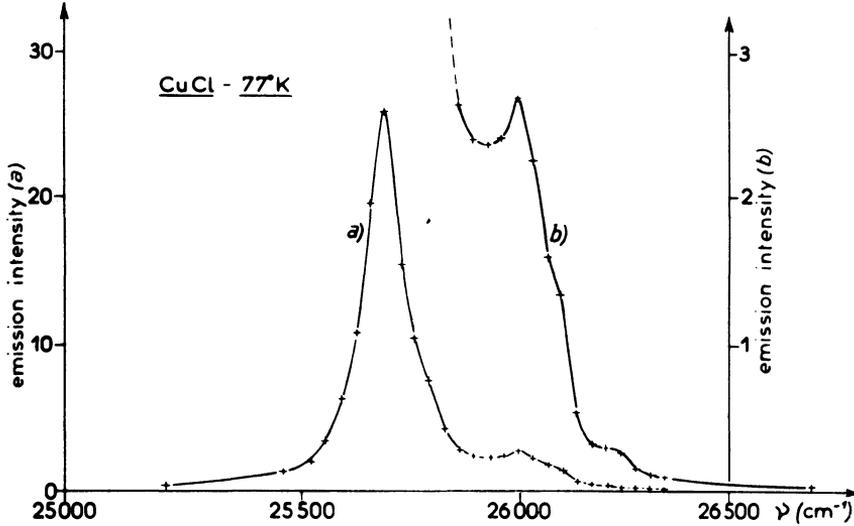


Fig. 14. Luminescence of CuCl at 77°K excited with a U-V laser.

The spectrum obtained when excited by very intense ultraviolet light is shown on figure 13b).

The resonance emission line ν_0 (25 971 cm^{-1}) appears with no reabsorption.

The most intense line is situated on the lower energy side of the spectrum (this line is not well understood).

With double photon absorption excitation, a single intense line 25 585 cm^{-1} appears separated from the excitonic absorption line by the energy of 2 LO phonons, fig. 13d).

In CuCl, recombination of an exciton with simultaneous absorption of one LO phonon has been observed (Fig. 14), at a temperature of 77°K.

The phonons present in the sample are suggested to be produced by the relaxation of the hot carriers created in the crystal by the absorption of the light (the energy of the photons is higher than the minimum of the band gap). It is known that the relaxation of hot electrons is accompanied by LO phonon emission; this explains the oscillatory structure observed in photoconductivity.

Basov and al. [45] and Benoit à la Guillaume [46] have performed experiments on semiconductors with intense excitation with hot electrons. In CdS they could show a laser action; the emission line seems to correspond to a phonon-assisted emission (fig. 15).

Basov has also taken advantage of the fact that a beam of light is attenuated more

slowly in function of the thickness of the sample by a double photon absorption process to produce laser action with optical excitation in a larger volume of a sample.

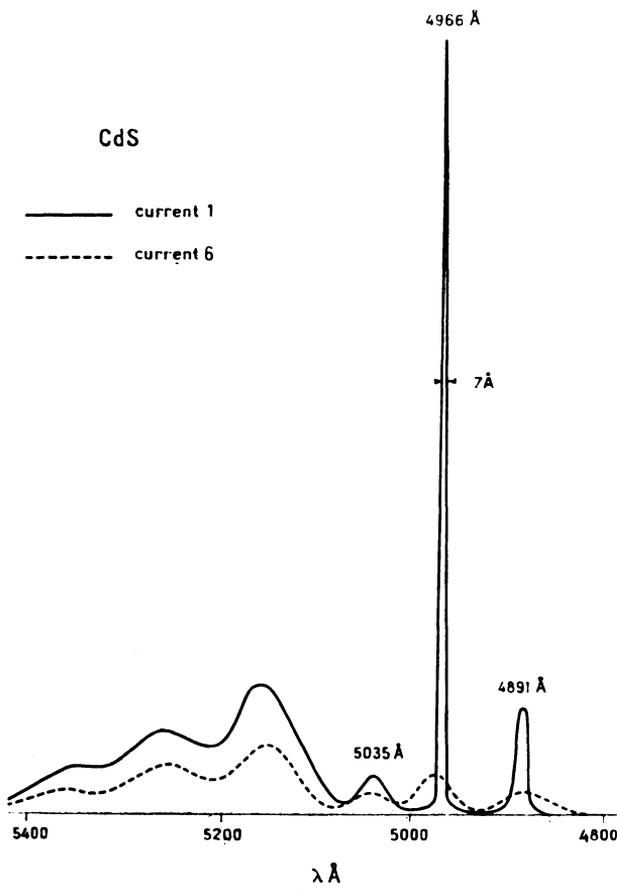


Fig. 15. Emission of CdS excited by fast electrons (after Basov) dashed curve: low current density continuous curve: high current density.

Finally, an interesting characteristic which could be put in evidence by using very intense light sources is the predicted condensation of excitons [47, 48, 49]. Such a condensation, which is a property of particles obeying Bose-Einstein statistics, is responsible for such effects as superfluidity and superconductivity.

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