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Photoinduced Optical Absorption and Conductivity in In-doped CdF_2 Crystals

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In their normal condition CdF_2 crystals are transparent and insulating with resistivities about 10^7 to 10^{14} Ohm cm at room temperature. But when doped with rare earth ions — like Ytterbium, Gadolinium and so on — and annealed in Cd metal vapour at temperatures about 500°C, the crystals become coloured and semiconducting with resistivities smaller than 1 Ohm cm. During annealing the fluorine interstitials normally compensating the charge of the trivalent rare earth ions are replaced by electrons. This process is denoted "conversion". These electrons do not recharge the trivalent ions to divalent ones but have a weak hydrogenlike bond to them, and a small thermal energy is sufficient to excite them into the conduction band.

Besides these ions other trivalent ones exist — like Chromium and Vanadium —, which are recharged to divalent ions when annealing the doped CdF_2 crystals in Cd vapour.

Trautweiler, Moser and Khosla [1] discovered that Indium — and to a smaller extent Europium — is a specially interesting doping material inasmuch as both ground states occur after annealing, the recharged In^{2+} — state and the hydrogenlike In^{3+} e^- — state with a loosely bound electron (see Fig. 1). The two ground states differ from each other by their optical absorption and electric conduction properties.

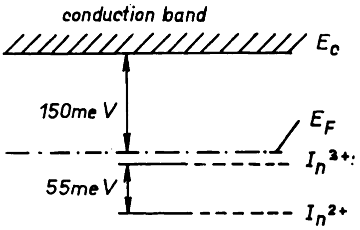

Fig. 1. Energy levels of In *in* CdF_2: In *crystals*

Curve 1 in Fig. 2 shows the absorption coefficient at room temperature of a CdF_2 crystal doped with 100 ppm In and annealed. There is an absorption in the ultraviolet and visible region with a peak at 3,2 eV and a broad absorption in the infrared region with a peak at 160 meV. After cooling to liquied hydrogen temperature the infrared absorption has disappeared and the ultraviolet absorption is little increased (curve 2). After irradiation with light of high intensity absorbed in this band, at least 99 per cent of this absorption has disappeared in favour of a strong infrared absorption (curve 3).

If we assume that the ultraviolet absorption is caused by the In^{2+} states, whereas the infrared absorption comes from the electrons in the $In^{3+}: e^-$-states, we can explain these results. At room temperature the electrons are distributed over the two ground states and the conduction band following the conditions of thermal equilibrium. Both bands are present. After cooling the electrons are localized in the lowest energy level, the In^{2+}-state. The infrared absorption has disappeared. Irradiation of the sample with ultraviolet or visible light excites the electrons from the

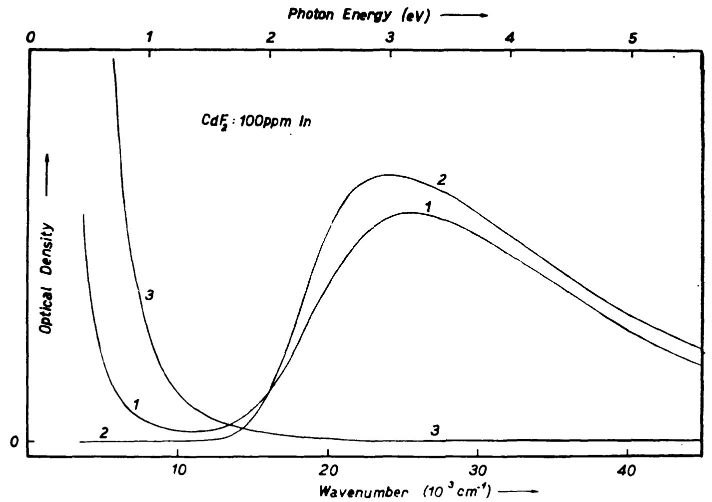

Fig. 2. Optical absorption of a Cd *annealed* CdF_2 : In *crystal 1) at room temperature, 2) after cooling to liquid hydrogen temperature, 3) after irradiation with visible light at liquid hydrogen temperature*

In^{2+}-ground state into a higher state from where they get into the conduction band and recombine to $In^{3+}: e^-$. The ultraviolet band disappears and the infrared band is built up. Below 50 °K the electrons cannot return to the "atomic" ground state and the photoinduced infrared absorption is completely stable.

With some assumptions about the temperature dependence of the two absorption bands we calculated the distance of the two energy levels and obtained 55 meV.

The results of the electrical measurements confirm this interpretation of the optical behaviour. Curve a in Fig. 3 shows the temperature dependence of the conductivity of a CdF_2 crystal doped with 1890 ppm In and annealed. The curve has two linear parts. In the upper temperature range the electron concentration in the conduction band is determined by the thermal equilibrium between the In^{2+} levels, the $In^{3+}: e^-$ levels and the conduction band. An activation energy of 160 meV is measured for this part. With decreasing temperature the recombination to In^{2+} becomes more and more improbable, and below 50°K it is not noticeable. In this temperature range the electron concentration in the conduction band is determined by the thermal equilibrium between the $In^{3+}: e^-$ levels and the conduction band. The activation energy in this range is about 70 meV.

At hydrogen temperature the conductivity of unirradiated samples is too small to be measured. But exposure to light absorbed in the ultraviolet band raises the conductivity to measurable values. This photoinduced conductivity is completely stable below 50°K. Curves b to f of Fig. 3 show the temperature dependence of the photoinduced conductivity. The slopes of the curves become smaller with increasing exposure. Above 50°K the curves go through a maximum and then fall into the temperature curve of the unexposed sample.

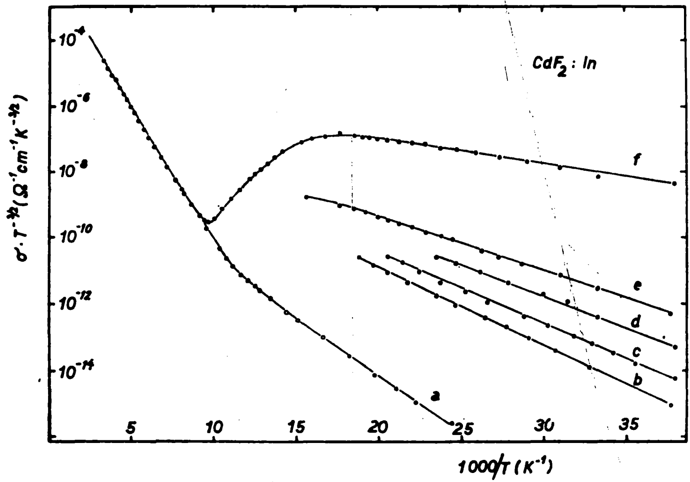

Fig. 3. Temperature dependence of the conductivity of a Cd *annealed* CdF_2 : In *crystal a) unirradiated, b–f) after increasing exposure to visible light at liquid hydrogen temperature*

The explanation is the same as in the case of the optical measurements. The electrons from the In^{2+} states are excited by the light absorbed in the ultraviolet band, they get into the conduction band and are trapped into the $In^{3+} : e^-$ states. Temporary thermal release of them causes the photoinduced conductivity. Longer or stronger irradiation increases the number of electrons in $In^{3+} : e^-$ states and the photoinduced conductivity. In Fig. 4 the photoinduced conductivity is plotted against the time of irradiation with constant intensity (curve 1). As the log-log-plot shows, the steep part of the curve can be described by a power law with an exponent near 5. Later on a saturation value is reached.

The photoinduced state is insensitive to irradiation with light absorbed by the electrons in the $In^{3+} : e^-$ states. The current can be strongly enchanced during irradiation with infrared light, but after switching off the initial photoinduced conductivity is restored. Below 50°K the excited electrons do not return into In^{2+} states. It seems that there is a potential barrier around the In^{3+}, and the probability that the free electrons overcome this barrier becomes negligeably small below 50°K. From our measurements we calculated a barrier heigth of 250 meV. The position of the impurity from the electrical measurements levels below the bottom of the

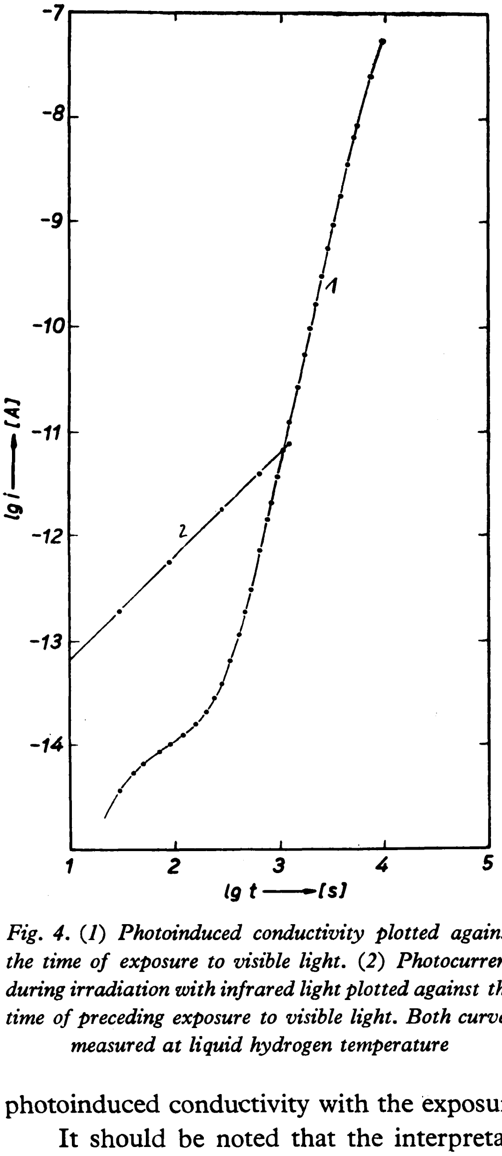

Fig. 4. (1) Photoinduced conductivity plotted against the time of exposure to visible light. (2) Photocurrent during irradiation with infrared light plotted against the time of preceding exposure to visible light. Both curves measured at liquid hydrogen temperature

conduction band can be determined. To this aim we used an effective mass value of 0.9 electron masses reported by Khosla [2] and assumed that the number of electrons introduced during annealing is equal to the number of In^{3+} ions at lattice sites, i.d. complete conversion. Then at room temperature the Fermi level is 150 meV below the conduction band and the In^{3+} : e^- level is 4 meV lower. But we have reasons to believe that the conversion is incomplete. In^{3+} ions charge-compensated by interstitial fluorine ions instead of electrons probably exist in a considerable quantity still in the annealed crystal and produce a random electric field which influence the ionisation energies of the hydrogenlike donors. The resulting energy spectrum of the donors is the reason why the slope of the temperature curves of the photoinduced conductivity diminishes with increasing excitation (Fig. 3). After small excitation only the lowest part of the donor level spectrum is occupied. With increasing excitation the upper levels become occupied too and the activation energy to the conduction band decreases. This model also explains the steep increase of the photoinduced conductivity with the exposure time and intensity.

It should be noted that the interpretation of our conductivity measurements on the base of a trap-controlled transport is not unambigous. Our results can also be explained on the base of hopping processes between the In impurity centres. We hope to obtain some elucidation about this point by measurements in magnetic fields.

Our work will be published in more detail in phys. stat. sol.

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To the Phenomenological Theory of Impact Triboluminescence

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The theoretical conciderations are based on the following experimental facts:

(1) Triboluminescence (TBL) is induced by the impact of the luminescent powder particles and monocrystal realised by the sandblasting or by shock respectively

(2) TBL spectra of the luminescent solids are the same as their band luminescent ones

(3) The line spectra of the nitrogen or another elements observed in some TBL experiments will not be considered here

(4) TBL will be generated due the time change of the outer mechanical action

(5) TBL intensity and the mechanical action on the solid are in phase or shifted together so that both are synchronic or the TBL intensity lags after the applied strass

(6) The TBL materials belong as so to the crystalline or as to amorphous solids

(7) The crystalline solid shows the stronger TBL as the amorphous one

(8) At this time the strongest TBL materials is zinc sulphide activated with managenese

(9) The luminescent materials without center of symetry show stronger TBL than with the center.

The problem is to put out elementary relation between the mechanically acting stress and to give a formula which can be compared with experiments made and give the stimulation to futher measurements.

From this point of view some formulae for the TBL intensity I_{TBL} on the dependence on the applied pressure p and its time change dp/dt were derived by Dr. Chudáček, by prof. Alzetta and prof. Meyer which give the following relations between TBL respons on the applied pressure:

$$I_{\mathrm{TBL}} \sim p\ dp/dt \tag{1}$$

$$I_{\mathrm{TB-}} \sim \exp\,(\alpha\, p^2) \tag{2}$$

$$I_{\mathrm{TBL}} \sim \exp\,(\beta/p^{1/2}) \tag{3}$$

where α and β are the quantity not explicitly dependent on the pressure. The last two formulae are based on the supposition that the intermediate phase of TBL cykle is electroluminescence. This means that for the nonelectroluminescent materials to which belongs also the strongest known manganese activated zinc sulphide and others materials, the forgoing two formulae are not applicable.

In the first step we shall derive the general formula close related to experiment. We will for the simplicity suppose that the TBL has its origin as other kinds of the luminescence through the radiation transition between two energetic levels E_1, E_2 so that $E_2 - E_1 > 0$. The crystalline particle or the monocrystal driven into the motion with velocity v collides with the obstacle. In each point of the material the inner stress field $\sigma = \sigma(\varepsilon(r))$ will be generated by the impact depending on the deformation ε.

The TBL transfer of the energy is supposed to be as in each kind of luminescence three step cycle process: excitation of charge carrier (*e*), their transport through material (*t*) and recombination (*r*) (Fig. 1).

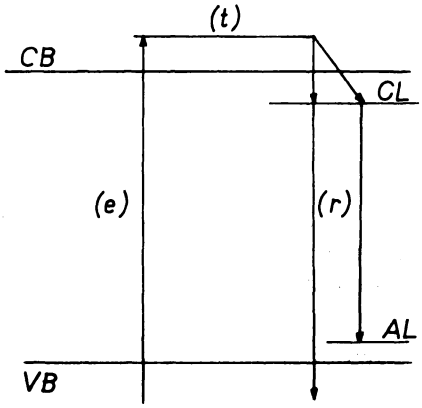

Fig. 1. The three cykles model of the luminescence mechanism. CB conduction band, VB valence band, CL coactivator level, AC activator level, (e) excitation,(t) transport, (r) recombination

For the simplification the stress applied will be considered only as uniaxial.

If we consider the single step of the luminescence mechanism with probabilities P_e, P_t and P_r respectively as independent the total probability P of the whole TBL process can be expressed as

$$P = P_e P_t P_r . \tag{4}$$

The energy of the individual crystalline particle or monocrystal from the unit area E_p can be expressed through

$$E_p = h\nu \langle N_p \rangle = (E_2 - E_1) \langle N_p \rangle \tag{5}$$

where $\langle N_p \rangle$ is the average number of the emited photons. For the $\langle N_p \rangle$ we use

$$\langle N_p \rangle = N_p P = N_p P_e P_t P_r . \tag{6}$$

If in the experiment the number of n particles participate on TBL, the total emited energy E is

$$E = n E_p. \tag{7}$$

The total TBL intensity is obtained by differentiation of the energy E as follows:

$$dE/dt = (dE_p/dt)n + E_p (dn/dt) . \tag{8}$$

The both term of the relation can by easely put out through the parameters of the experiment as

$$I_{\mathrm{TBL}} = Sn_0 l(dE_p/dt) + Sn_0 E_p v , \tag{9}$$

where S is the cross section and l is the lenght of the tube used in the experiments, n_0 is the concentration of the flowing particles moving with the velocity v. The linear dependence of TBL intensity on velocity as expressed by the second term in (9) is in agreement with the forgoing experiment made [4]. From this we see that for the total theoretical estimation of the TBL intensity we have a need to calculate the E_p and dE_p/dt. This will be done with following simplified supposition:

(1) the studied solid is luminescent with homogenously distributed lumininescent centers over the whole volume of the luminophor with concentration N_c

(2) only two energetic levels E_1 and E_2 with the statistical weight 1 participate in the TBL mechanism

(3) for the number of atom activators with elektron occupation on the energetic level E_1 holds the Boltzmann statistical formula

$$N_1 = N_c \exp(-E_1/kT) \tag{10}$$

(4) the excitation is primary caused by the inner stress in the material which is generated through the outer mechanical action and through the inner origin stress state of the luminophor. The inner stress is a funkcion of the deformation

$$\begin{aligned} \sigma = \sigma(\varepsilon) &= \sigma_0 + (d\sigma/d\varepsilon)\varepsilon + (d^2\sigma/d\varepsilon^2)\varepsilon^2 + \ldots \\ &= \sigma_0 + E\varepsilon + F\varepsilon^2 + \ldots \\ &= \sigma_0 + \sigma_1 + \sigma_2 + \ldots \end{aligned} \tag{11}$$

(5) for the our discussion only two term for the $\sigma(\varepsilon)$ will be used

$$\sigma = \sigma_0 + \sigma_1 \tag{12}$$

(6) the time dependence of the applied pressure is supposed harmonic

$$\sigma = \sigma_0 \sin \omega t \tag{13}$$

with phase shifted deformation ε [5]:

$$\varepsilon = (\sigma_m/E) \sin(\omega t - \delta) ; \tag{14}$$

δ is the phase shift constant between the stress and deformation.

When the outer pressure is acting on the luminophor, the energetic transfer to the luminescent center is realised what makes the energetic dinstance $E_2 - E_1 = \Delta E_{21}$ narrower so that the new energetic distance ΔE is

$$\Delta E = \Delta E_{21} - \Delta E(\sigma) . \tag{15}$$

The second term $\Delta E(\sigma)$ can be expressed through the mechanical energy density

$$\Delta E(\sigma) = (\sigma^2/2E)\Delta V = (\sigma_0^2/2E + \sigma_0\sigma_1/E + \sigma_0^2/2E)\Delta V \tag{16}$$

where ΔV is effective volume around the luminescence center. The first term describes the influence of the internal the third of the external stress acting in the solids. The second term representing the interaction of two external and internal stress fields can be interpreted as the amplification of the internal stress through the external one.

The probability factors P_e and P_r can be calculated using the Einsteins radiation theory formalae as

$$P_e = \{[(8/3)\pi^3/h^2]\, X_{12}^2 + \sigma^2/2E\}\, t \tag{17}$$

$$P_r = (64\pi^4/3h^4c^3)\,(E_2 - E_1)^3\, X_{21}^2 \left[(c^3h^2/8)\,\frac{\varrho((E_2 - E_1)) + 1}{(E_2 - E_1)^3}\right] t, \tag{18}$$

where the X_{12}, X_{21} means the matrix element of the dipol transition between energetic elvels E_2 and E_1, t is the time of the mechanicalaction dur ation and $\varrho((E_2 - E_1))$ is the radiation density of the frequency $h\nu = E_2 - E_1$ in the material.

The transport probability P_t is not expressible so explicitely as the P_e and P_r ones. It can be writen as

$$P = 1 - P_L = 1 - (P_I + P_N)\,, \tag{19}$$

where the P_L denotes the lost energy probability, which can be expressed through ionisation probability P_I and through the nonradiating transition probability P_N which must be known for the each special case. After this the energy E_p can be expressed as

$$E_p = At^2[B\,\varrho(E_2 - E_1)\,(1 + \sigma^2/2E)\exp(\sigma^2/2E)]\,\Delta V \tag{20}$$

where A and B is substituted for

$$\begin{aligned} A &= \frac{512}{3}\,\frac{\pi^7 N_c}{h^6c^3}\,\frac{(E_2 - E_1)^4}{\exp(E_2 - E_1)}\,[1 - (P_I + P_N)]\,X_{12}^2 X_{21}^2 \\ B &= c^3h^2/8\pi(E_2 - E_1)^3 \end{aligned} \tag{21}$$

For the simplicity the quantity P_I, P_N X_{12} and X_{21} are assumed as the pressure and time independent. After differentiation of energy and supposing with experiment the dependence of the TBL intensity on the $d\sigma/dt$, we become for the $I_{TBL} = dE_p/dt$ the following expression:

$$I_{TBL} = 2At^2(B\varrho + 1)\exp(\sigma^2/2E)\,\Delta V \cdot (\sigma/E)(1 + \sigma^2/2E)\, d\sigma/dt\,. \tag{22}$$

The intensity I_{TBL} can be further modified if the quantity $d\sigma/dt$ is expressed using the formulae (12), (13), (14) more explicitely as

$$d\sigma/dt = d\sigma_0(x)/dt + E\, d\varepsilon/dt = (d\sigma_0/dx)u + \sigma_1\omega\cos(\omega t - \delta)\,, \tag{23}$$

to:

$$\begin{aligned} I_{TBL} = {} & 2At^2(B\,\varrho + 1)(\sigma/E)(1 + \sigma^2/2E)\exp(\sigma^2/2E)\,\Delta V \,\cdot \\ & \cdot\, [(d\sigma_0/dx)u + \sigma_1\omega\cos(\omega t - \delta)]\,. \end{aligned} \tag{24}$$

The derived formula based on the simplified assumption has shown the complicated dependence the TBL intensity on the internal stress. The first term in $(B\varrho + 1)$ describes the part of the stimulated emission and in many cases can be neglected. The dependence of the type $\sim \exp(\alpha\sigma^2)$ and $\sim (\sigma/E)\, d\,\sigma/dt$ are in accordance with experiments [2], [6], [7]. The influence of the factor $1 - (P_I + P_N)$ can be sometimes very strong.

It is interesting to note that the dependence I_{TBL} on $(E_2 - E_1)$ explicitely contained in A and B having the form

$$\sim (E_2 - E_1)^4 / \exp (E_2 - E_1) \tag{25}$$

is nonmonoton. The dependence of this type was not tested experimentaly at this time.

The phase shift dependence of the TBL intensity $I = I(\delta)$ explains the experimental facts, that the different phase shift in different experimental conditions was observed.

The amplification of TBL with the pressure action can be achieved at the materials without the center of symetry through the piezoelectric effect. The microscopic mechanisms of the TBL were not be considered in this work and were elementary discussed in [8].

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