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Theoretical approach to the tunneling mechanoluminescence produced during cleavage of II-VI semiconductors

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This paper describes the tunneling mechanoluminescence (ML) produced during fracture of II-VI semiconductors. The electric potential surrounding the charged dislocations bends, valence band and conduction band strongly and consequently, the electron centres float up in synchronism with the band bending as the dislocations core approaches starting distance from the dislocation core the process of electron tunneling from the centre into the conduction band becomes significant. Thus, a moving dislocation can transfer electrons form deep traps to the conduction band. These electrons subsequently recombine with the holes at impurity centres and give rise to luminescence, which is the characteristic of the centres. When a II-VI semiconductor is fractured or cleaved initially the mechanoluminescence (ML) intensity increases with time attains a peak value I_m at the time t_m corresponding to completion of the fracture of semiconductors. After the completion of fracture, the ML intensity decay with time, whereby the initial fast decay is controlled by the pinning time of dislocations and the subsequent slow decay is controlled by the lifetime of electrons in the shallow traps. In the ML produced during the fracture of II-VI semiconductors, both I_m and I_T increase directly with the area of the newly created surfaces of the crystals. The ML intensity of II-VI compounds decreases with temperature. Expressions are derived for the rise of ML intensity, and the total ML intensity. A good agreement is found between the theoretical and experimental results related to the ML produced during the cleavage of II-VI semiconductors.

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The visible trails of light are emitted, when the surface of mineral zinc sulphide (ZnS) was rubbed, is known long back. The study of ML produced from natural and synthetic zinc sulphide (ZnS) was studied in depth only in the past century. The rough measurements of the ML spectra of sulphide (largely ZnS:Mn) was made by Levison[1]. He observed by naked eye that the ML spectrum was extended from 550-650 nm Karl[2,3] fused zinc sulphide with a number of other compounds, e.g., oxides of manganese, tin and silicon and observed ML intensities of new solids by naked eye. Wagganer[4] measured the ML spectra of different samples of ZnS:Mn and compared them with the phosphorescent spectra produced under X-ray excitation. It was observed that the ML spectra of each one of the samples had the maximum intensity at a mean value of 557±5 nm, which compared well with the mean value of 552±3 nm at which maximum intensity was found to occur in the phosphorescent spectrum. Thus, the similarity between mechanoluminscence and photoluminescence spectroscopy was established by this fact.

The ML in plastically deformed semiconductors has been investigated by Vardanyan *et al.*[5], particularly in II-VI compounds. Radioactive electron transition from the conduction band to deep point centers created during plastic deformation of a crystal in the field of a charged dislocation was reported. The present paper reports the theory of ML produced during cleavage of fracture of II-VI semiconductors.

Theory

It is known that the dislocations in II-VI semiconductors are charged[6]. The electric fields at a distance r for the core of charged dislocations is given by $F = 2q/\varepsilon_0 r$ where q is the linear charge density of dislocation and ε_0 is the dielectric permittivity. At q = 0.35 e/units, where e is the electric charge, the electric field at a distance r=10^{-1} cm from the dislocation core is given by E=3.4×10^{6} V cm^{-1}. This field is sufficient to cause the tunneling of the trapped electrons.

Figure 1 shows the electrical potential surrounding the charged dislocation bends the valence band and the conduction band strongly, and consequently electron center “floats up” in synchronism with the band bending as the dislocation core approaches. Starting with a certain distance from the dislocation core, the process of electron tunneling from the center

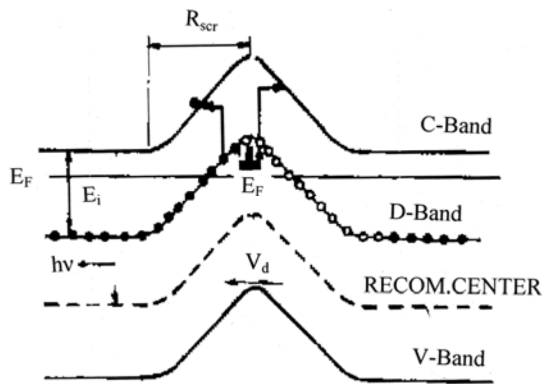
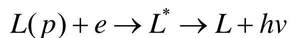


Fig. 1—Bending of bands near a dislocation and schematic diagram of electronic transition.

into the conduction band becomes significant. Thus, a moving dislocation can transfer electrons from the deep traps to the conduction band. These electrons subsequently recombine with the holes at impurity centers and give rise to luminescence, which is the characteristic of centers. Thus, in II-VI semiconductors the electric field due to moving charged dislocation (D) ionizes the electrons from the filled traps and the subsequent recombination of electrons (e) with the activator centers containing holes, give rise to luminescence characteristic of the activator centers. This process can be represented as follows:

$$C + D \rightarrow C^{+} + e + D$$



$$L(p) + e \rightarrow L^{*} \rightarrow L + h\nu$$

where C is a trap filled with electrons, C^{+} is an empty trap and $L(p)$ is the activator-containing hole.

It has been found that the spectra of ML produced during the fracture of II-VI semiconductors are similar to the corresponding solid-state luminescence spectra. This fact indicates that the ML produced during the fracture is attributed to the continuous ML and not to the pulsed ML, which is due to the gaseous breakdown.

During the cleavage of semiconductors charged dislocations move and also the piezoelectrification of the newly created surfaces may take place, as the crystals are piezoelectric. Thus, the ML excitation in II-VI semiconductors may occur due to the movement of charged dislocations and also due to the piezoelectrification. In II-VI semiconductor, the strength of electric field produced due to the movement of charged dislocations is higher as compared to the strength of the piezoelectric field. Thus, it has been proved that the major contribution to the ML in II-VI semiconductors is from the moving charged dislocations.

If a crystal of length L, breadth W and thickness H is fractured or cleaved along the plane parallel to the breadth side, then the rate of creation of new surface is given by $2Wv$, where v is the average velocity of the separation of cleavage plane or, in other words, the velocity of crack propagation. If F is the number of mobile dislocations produced during the creation of unit surface area, then the rate of generation of mobile dislocations will be $2FWv$.

If τ_{p} is the lifetime of the mobile dislocations, then we can write the following rate equation:

$$\frac{\mathrm{d}N_{\mathrm{m}}}{\mathrm{d}t} = 2FWv - \frac{N_{\mathrm{m}}}{\tau_{\mathrm{p}}}$$

or

$$\frac{\mathrm{d}N_{\mathrm{m}}}{\mathrm{d}t} = 2FWv - \beta N_{\mathrm{m}} \quad \ldots (1)$$

where N_{m} is the number of mobile dislocations at any time t and $\beta = \frac{1}{\tau_{\mathrm{p}}}$. For N_{m} =0, at t=0, the integration of Eq. (1) gives

$$N_{\mathrm{m}} = \frac{2FWv}{\beta}[1 - \exp(-\beta t)] \quad \ldots (2)$$

If N_{m} dislocations each of unit length move through a distance dx in time dt, then they will ionize the traps within the volume $N_{\mathrm{m}} r_{\mathrm{i}} \mathrm{d}x$. If N_t is the concentration of filled traps, then the number of electrons reaching the conduction band from the traps during the time interval dt will be $N_{\mathrm{m}} r_{\mathrm{i}} \mathrm{d}x N_{\mathrm{t}}$. Thus, the rate of tunneling of electrons from the filled traps to the conduction band may be expressed as:

$$g = N_{\mathrm{m}} r_{\mathrm{i}} N_{\mathrm{t}} \frac{\mathrm{d}x}{\mathrm{d}t} = N_{\mathrm{m}} r_{\mathrm{i}} N_{\mathrm{t}} v_{\mathrm{d}} \quad \ldots (3)$$

where v_d is the average velocity of the dislocations.

From Eqs (2) and (3), we get

$$g = \frac{2FWvv_{\mathrm{d}} r_{\mathrm{i}} N_{\mathrm{t}}}{\beta}[1 - \exp(-\beta t)] \quad \ldots (4)$$

ZnS is a *N*-type semiconductor where a large number of electrons are captured in traps. When dislocations move during the deformation, they release some of the electrons from the traps due to the tunneling process. These free electrons recombine with the hole trapped at the hole centers. As only a few electrons are released during the deformation and the deformation does not cause significant change in the number of trapped holes, the rate of recombination may be assumed to follow the linear law. In the case of sphalerite or ZnS:Mn crystal, the energy released during the electron-hole recombination excites the Mn centers, in which the emission takes place from Mn centers. Thus, the rate equation for the change in number of electrons in the conduction band may be written as

$$\frac{d\Delta n}{dt} = g - N_a\sigma_a v_e\Delta n - \gamma\Delta n$$

or

$$\frac{d\Delta n}{dt} = \frac{2FWvv_d r_i N_t}{\beta}[1-\exp(-\beta t)] - \gamma'\Delta n \qquad \ldots (5)$$

where $\gamma' = (N_a\sigma_a v_e + \gamma)$, N_a and σ_a are the concentration and capture cross-section of the activator containing holes respectively v_e is the velocity of the electrons in the conduction band and γ is the rate constant for the transfer of the electrons form the conduction band to the shallow traps in the crystals.

Integrating Eq. (5) and taking $\Delta n = 0$, at t = 0, we get

$$\Delta n = \frac{2FWvv_d r_i N_t}{\beta\gamma'}[1-\exp(-\gamma' t)] +$$

$$= \frac{2FWvv_d r_i N_t}{\beta(\gamma'-\beta)}[\exp(-\gamma' t) - \exp(-\beta t)] \qquad \ldots (6)$$

as γ' is very large and the lifetime $\tau(=1/\gamma')$ of the electrons in the conduction band is very short of the order of 10^{-8} s, one can assume $\gamma' >> \beta$ and Eq. (6) may be expressed as

$$\Delta n = \frac{2FWvv_d r_i N_t}{\gamma'\beta}[1-\exp(-\beta t)] \qquad \ldots (7)$$

Rise of ML intensity

If η is the probability of radiative recombination of electrons with the hole centers, then the rise of transient ML intensity may be expressed as

$$I_r = \eta N_a\sigma_a v_e\Delta n$$

or

$$I_r = \frac{2\eta N_a\sigma_a v_e FWvv_d r_i N_t}{\gamma'\beta}[1-\exp(-t/\tau_p)] \qquad \ldots (8)$$

or

$$I_r = I_0[1-\exp(-t/\tau_p)] \qquad \ldots (9)$$

where

$$I_0 = \frac{2\eta N_a\sigma_a v_e FWvv_d r_i N_t}{\gamma'\beta} \qquad \ldots (10)$$

It is evident from Eq. (9) that when a II-VI semiconductor will be fractured or cleaved, initially the ML intensity should rise linearly with time, and if crack moves for a long time t then I_r should attain a saturation value given by Eq. (10).

Value of I_m

For the crystals of small dimensions $t_m << \tau_p$. Thus, from Eq. (8) the ML intensity at $t = t_m$ (the time at which the complete cleavage or fracture of crystal in two parts takes place) is given by

$$I_m = \frac{2\eta N_a\sigma_a v_e FWvv_d r_i N_t t_m}{\gamma'} \qquad \ldots (11)$$

as

$vt_m = H$, we get

$$I_m = \frac{2\eta N_a\sigma_a v_e Fv_d r_i N_t WH}{\gamma'}$$

or

$$I_m = \frac{\eta N_a\sigma_a v_e Fv_d r_i N_t A}{\gamma'} \qquad \ldots (12)$$

where A=2WH is the area of newly created surfaces.

It is evident from Eq. (12) that I_m increases linearly with the increase area of newly created surfaces A.

Fast decay of ML intensity

Suppose the cleavage of crystal is completed at $t = t_m$, then creation of new surfaces will become zero beyond $t = t_m$ and from Eq. (1), we get

$$\frac{dN_m}{dt} = -\beta N_m \quad \ldots (13)$$

For $N_m = N_{mo}$ at $t = t_m$, the integration of Eq. (13) gives

$$N_m = N_{mo} \exp[-\beta(t - t_m)] \quad \ldots (14)$$

Thus, the fast decay of ML intensity may be expressed as

$$I_d = \frac{\eta N_a \sigma_a v_e v_d r_i N_t N_{mo}}{\gamma'} \exp[-\beta(t - t_m)] \quad \ldots (15)$$

At $t = t_m$, $I = I_m$ and Eq. (15) can be written as

$$I_d = I_m \exp[-\beta(t - t_m)] \quad \ldots (16)$$

$$I_m = \frac{\eta N_a \sigma_a v_e v_d r_i N_t N_{mo}}{\gamma'} \quad \ldots (17)$$

In Eq. (16) at $t = t_m$, the quantity under exponential becomes 1 and $I_d = I_m$. Thus Eq. (16) indicates exponential decay of the ML intensity, where the decay time is controlled by the lifetime τ_p of the dislocations, which is also called the pinning time of dislocations.

The comparison of Eq. (12) and (17) indicates that $N_{mo} = FA$. This is true for a crystal of small dimension, in which the number of mobile dislocations pinned up to t_m may be negligible.

Decay of delayed ML

Using Eqs (13) and (14), the rate of tunneling of electrons from filled traps to the conduction band after $t = t_m$, is given by

$$g = N_{mo} \exp[-\beta(t - t_m) v_d r_i N_t \quad \ldots (18)$$

As $N_{mo} = FA = 2FWH$, Eq. (18) may be expressed as

$$g = 2FWHv_d r_i N_t \exp[-\beta(t - t_m)] \quad \ldots (19)$$

Now, using Eqs (5) and (19) the rate equation for the change in number of electrons in the conduction band may be written as

$$\frac{d\Delta n}{dt} = 2FWHv_d r_i N_t \exp[-\beta(t - t_m)] - \gamma'\Delta n \quad \ldots (20)$$

In equilibrium, Δn may be expressed as

$$\Delta n = \frac{2FWHv_d r_i N_t}{\gamma'} \exp[-\beta(t - t_m)] \quad \ldots (21)$$

As γ is the rate constant for the transfer of electrons from conduction band to shallow traps, the rate of generation of electrons to the shallow traps is given by

$$G = \gamma \Delta n \quad \ldots (22)$$

Using Eqs (21) and (22), we get

$$G = \frac{2\gamma FWHv_d r_i N_t}{\gamma'} \exp[-\beta(t - t_m)] \quad \ldots (23)$$

If δ is the rate of release electrons from the shallow traps to the conduction band, then we can write the following rate equation

$$\frac{dN}{dt} = \frac{2\gamma FWHv_d r_i N_t}{\gamma'} \exp[-\beta(t - t_m)] - \delta N \quad \ldots (24)$$

where N is the number of electrons in the shallow traps at any time t.

Integrating Eq. (24) and taking $N = N_0$ at $t = t_m$, we get

$$N = \frac{2\gamma FWHv_d r_i N_t}{\gamma'(\beta - \delta)} [\exp\{-\delta(t - t_m)\} - \exp\{-\beta(t - t_m)] \quad \ldots (25)$$

From $\beta >> \delta$, Eq. (25) may be expressed as

$$N = \frac{2\gamma FWHv_d r_i N_t}{\gamma'\beta} [\exp\{-\delta(t - t_m)\}] \quad \ldots (26)$$

Thus, the decay of ML intensity involving the release of electrons from the shallow traps may be given by

$$I_d' = \eta N_a \sigma_a v_e \delta N$$

$$I_d' = \frac{2\eta N_a \sigma_a v_e \delta_r \gamma FWHv_d r_i N_t}{\gamma'\beta} \exp[-\delta(t-t_m)] \quad \ldots (27)$$

or

$$I_d' = I_o' \exp\left[\frac{-(t-t_m)}{\tau_e}\right] \quad \ldots (28)$$

where

$$I_o' = \frac{2\eta N_a \sigma_a v_e \delta\gamma FWHv_d r_i N_t}{\gamma'\beta} \quad \ldots (29)$$

and

$$\delta = 1/\tau_e \,.$$

Equation (28) indicates the exponential decay of ML, where the decay time will be controlled by the lifetime of electrons in the shallow traps in the crystals.

Thus, it seems that after the completion of the cleavage, initially the ML intensity should decay at a rate controlled by the rate constant β, and latter on it should decay at rate controlled by the rate constant δ.

Value of total intensity I_T

The value of total intensity I_T, which is summation of rise in ML intensity component due to radiative recombination of electron and holes, fast decay and delayed decay may be expressed as

$$I_T = \int I\mathrm{d}t = \int_0^{t_m} I_r \mathrm{d}t + \int_{t_m}^{\infty} I_d \mathrm{d}t + \int_{t_m}^{\infty} I_d' \mathrm{d}t \quad \ldots (30)$$

From Eqs (8), (15), (27) and (30), we get

$$I_T = \int_0^{t_m} \frac{2\eta N_a \sigma_a v_e FWvv_d r_i N_t}{\gamma'\beta}\{1-\exp(-t/\tau_p)\}\mathrm{d}t + \int_{t_m}^{\infty} \frac{2\eta N_a \sigma_a v_e FWvv_d r_i N_t}{\gamma'}\exp[-\beta(t-t_m)]\mathrm{d}t + \int_{t_m}^{\infty} 2\eta N_a \sigma_a v_e \delta\gamma FWHv_d r_i N_t \exp[-\delta(t-t_m)]\mathrm{d}t \quad \ldots (31)$$

$$I_T = \frac{2\eta N_a \sigma_a v_e FWHv_d r_i N_t}{\gamma'}\left[\int_0^{t_m} \frac{v}{\beta}\{1-\exp(-t/\tau_p)\}\mathrm{d}t + \int_{t_m}^{\infty} H \exp\{-\beta(t-t_m)\}\mathrm{d}t + \int_{t_m}^{\infty} \frac{\delta\gamma H}{\beta} \exp\{-\delta(t-t_m)\}\mathrm{d}t\right]$$

$$I_T = \frac{2\eta N_a \sigma_a v_e FWv_d r_i N_t}{\gamma'}\left[\frac{v}{\beta}.\tau_p t_m^2 + \frac{H}{\beta} + \frac{\delta\gamma H}{\beta\delta}\right]$$

$$I_T = \frac{2\eta N_a \sigma_a v_e FWv_d r_i N_t}{\gamma'}\frac{H}{\beta}\tau_p.t_m + \frac{2\eta N_a \sigma_a v_e FWv_d r_i N_t}{\gamma'}\frac{H}{\beta} + \frac{2\eta N_A \sigma_a v_e FWv_d r_i N_t}{\gamma'}\frac{H\gamma}{\beta}$$

or

$$I_T = \frac{\eta N_a \sigma_a v_e Fv_d r_i N_t A}{\gamma'\beta}[1+\gamma+\tau_p t_m] \quad \ldots (32)$$

Equation (32) indicates that I_T should increase linearly with the area A of newly crated surfaces of the semiconductors.

Temperature dependence of the ML intensity

For photoluminescence (PL), the temperature dependence comes mainly from η. However, as indicated by Eq. (12) for the ML there is an additional factor r_i, depending on the temperature. It should be noted that as the charge on the dislocation decreases with increasing temperature, the strength of electric field and consequently, r_i, should decrease with temperature. As such, there should be faster decrease of ML intensity with increasing temperature as compared to that of the photoluminescence.

Results and Discussion

Since II-VI semiconductor exhibit intense ML during their plastic deformation, most of the work have been done on the ML produced during the plastic deformation of the crystals.

Figure 2 shows the time dependence of ML intensity produced during fracture of ZnS:Mn crystals of different sizes. In this experiment, a small crystal placed on a transparent lucite plate, is fractured in two

parts by giving a pulse to a sharp blade places onto the crystals. The time dependence of ML intensity if measured using an RCA 931A photo-multiplier tube, whose output was connected to storage oscilloscope[7]. Fig. 3 shows the plot of In I versus $(t-t_m)$ for ZnS:Mn crystals. It is seen from this figure that initially the ML intensity decreases at a faster rate and after some time it decrease at a slow rate. It is evident from Eqs (16) and (27) that fast decay of ML intensity is controlled by β, however, the slow decay of ML intensity is controlled by δ. As $\beta > \delta$ (Table 1), initially the ML intensity decays at a faster rate and then later on decays at a slower rate. The values of decay time for the fast and slow decays are shown in Table 1 for ZnS:Mn and Cds:Te crystals. Such results are expected form Eqs (16) and (28).

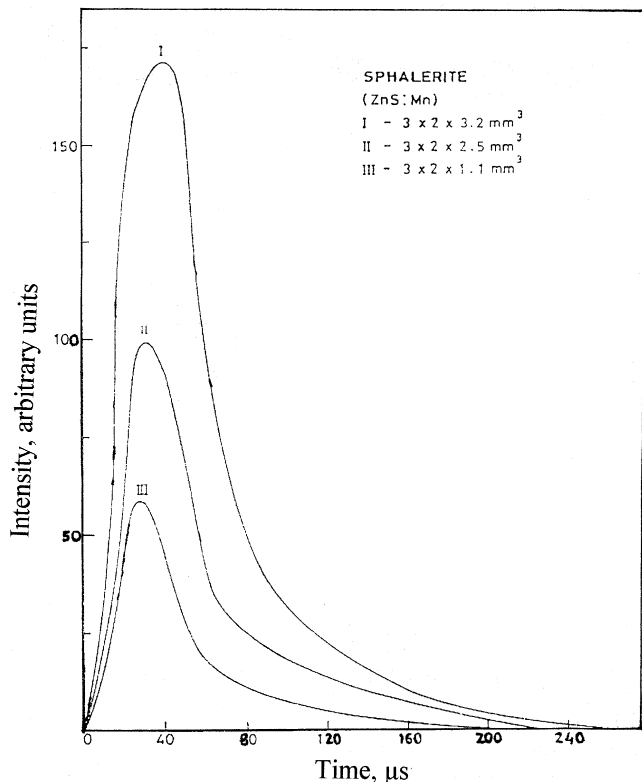


Fig. 2—Intensity versus time curve of ZnS:Mn crystals of different sizes.

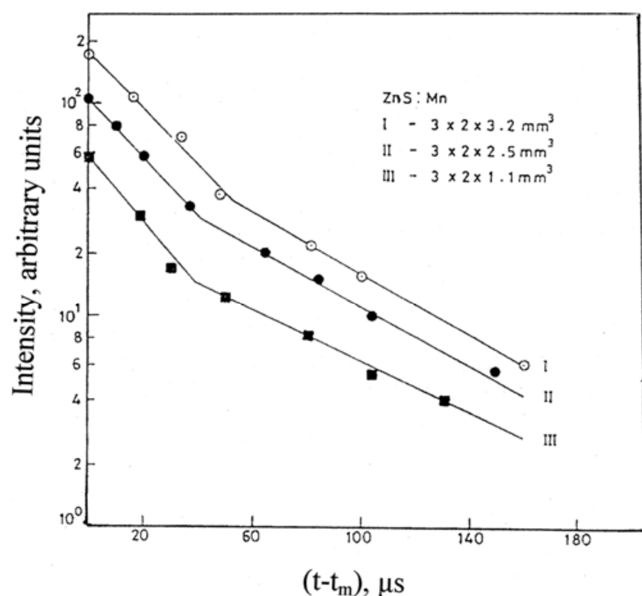


Fig. 3—In I versus time $(t-t_m)$ curve of ZnS:Mn crystals of different sizes.

Both I_m and I_T are found to increase directly with the area of newly created surfaces of ZnS:Mn and CdS:Te crystals as expected from Eqs (11) and (32).

Figure 4 shows the dependence of the total ML and PL intensities of ZnS:Mn crystals. It is seen that the ML intensity decreases faster as compared to the PL intensity according to present theory.

Figures 5-7 show the ML and PL spectra of impurity doped ZnS, CdS, ZnSe and (Zn, Cd) S crystals. It is evident that the ML spectra are similar to their corresponding PL spectra. Fig. 8 shows that effect of CdS content onto the wavelength corresponding to the peaks of both the ML and PL spectra.

Table 1—Value of β, δ, τ_p and τ_e for ZnS:Mn and CdS:Te crystals

Crystal	I_T/mm^2 arb unit	β (s^{-1})	δ (s^{-1})	τ_p (μs)	τ_e (μs)
ZnS:Mn	416.7	29.89×10^3	15.49×10^3	33.45	64.55
CdS:Te	12.61	11.51×10^3	2.19×10^3	86.88	456.62

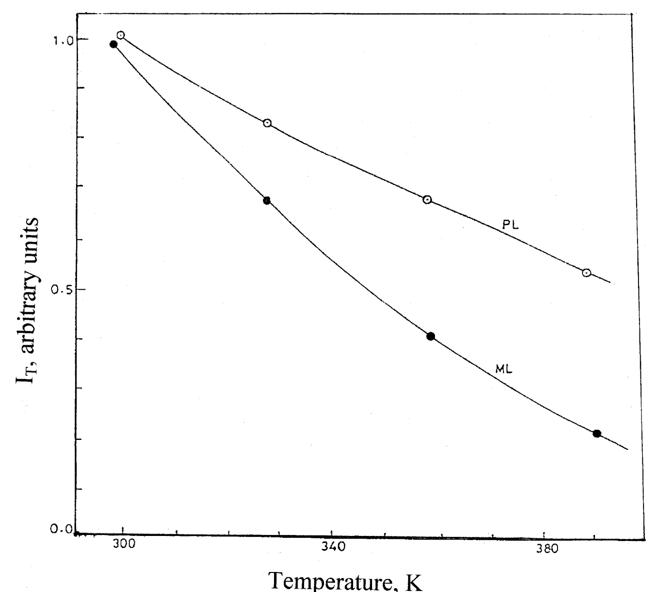


Fig. 4—Temperature dependence of the intensities of the PL and ML of ZnS:Mn crystals.

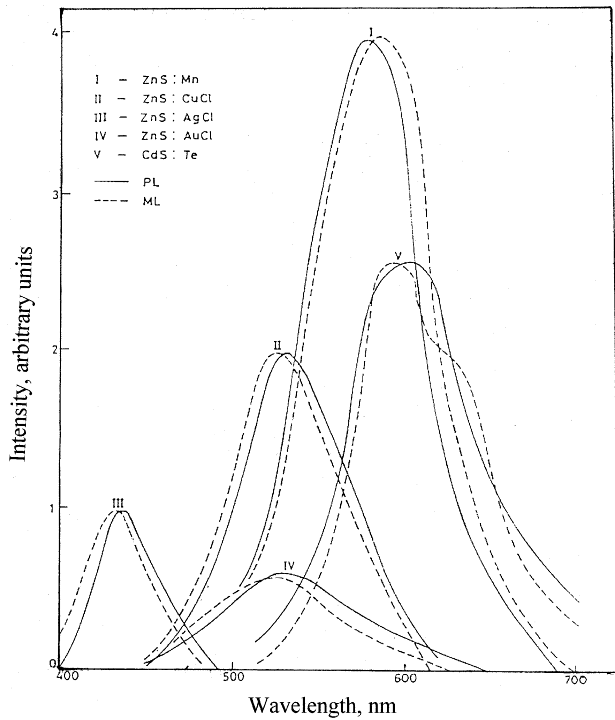


Fig. 5—ML and PL spectra of ZnS:Mn, ZnS:CuCl, ZnS, ZnS:AgCl, ZnS:AuCl and CdSi:Te crystals.

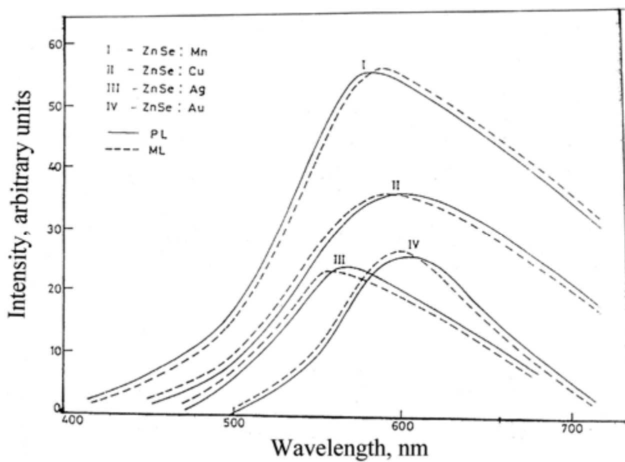


Fig. 6—ML and PL spectra fo ZnSe:Mn, ZnSe:Cu, ZnSe:Ag and ZnSe:Au crystals.

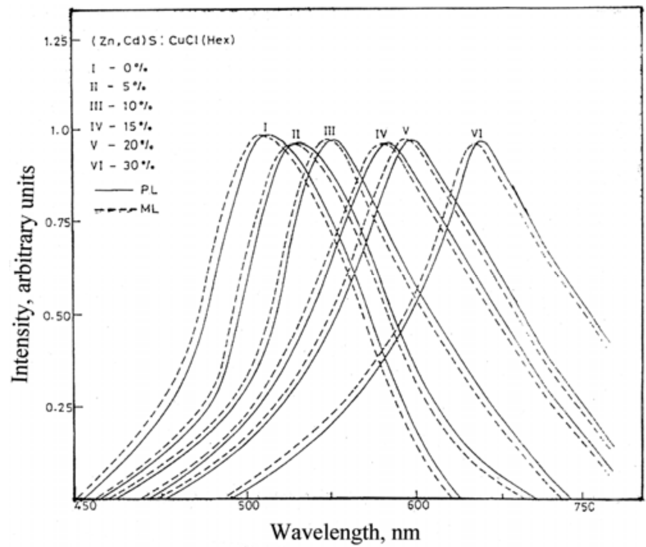


Fig. 7—ML and Pl spectra of (Zn, Cd) S:CuCl crystals.

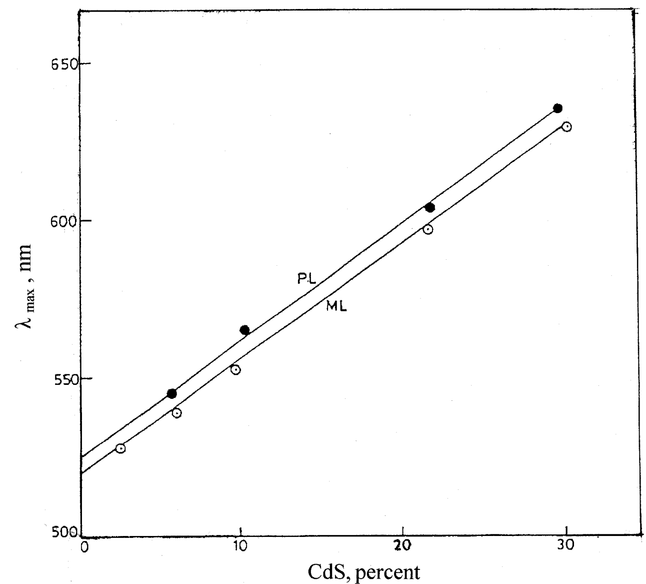


Fig. 8—The effect of the CdS content on the wavelength corresponding to the peak of the ML and PL spectra of (Zn, Cd) S:CuCl crystals.

The wavelength of corresponding to the peaks of both the ML and PL spectra increase linearly with the CdS content in (Zn, Cd) S:CuCl crystals. Since the PL in II-VI semiconductor are related to radiative recombination of electrons with trapped holes the similarity of the ML and PL spectra indicates that the ML emission should also be related to the radiative recombination of free electrons with trapped holes. A good agreement is found between the theoretical and experimental results.

Conclusions

A moving dislocation can transfer electrons from deep traps to the conduction band. These electrons subsequently recombine with the holes at impurity centers and give rise to luminescence, which is the characteristic of the centers. When a II-VI semiconductor is fractured or cleaved, initially the ML intensity increase with time, attains peak value I_m at the time t_m corresponding to completion of the fracture of the semiconductors. After the completion

of fracture, the ML intensity decays with time, whereby the initial fast decay is controlled by the pinning time of dislocations, and the subsequent slow decay is controlled by the lifetime of electrons in the shallow traps. In the ML produced during the fracture of II-VI semiconductors, both I_m and I_T should increase directly with the area of the newly created surfaces of the crystals. The ML intensity of II-VI compounds decreases with temperature.

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