

ELECTROLUMINESCENCE IN NaI AND NaI(Tl) CRYSTALS

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by
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ABSTRACT

A total of twenty-three pure NaI single crystals and nine thallium doped (0.2 mole % Tl) crystals whose thickness varied between 0.8 and 2.4 mm were tested in order to study electroluminescence processes in those materials.

The electroluminescence emission was observed in both NaI and NaI(Tl) crystals when the 1000 - 2500 volts AC was applied across the crystals at liquid nitrogen temperature. The electroluminescence bands were observed at 295 nm (4.20 eV) and 375 nm (3.30 eV) in pure NaI crystals, and at 430 nm (2.88 eV) in NaI(Tl) crystals. A very weak band at 325 nm (3.80 eV) was observed in some NaI(Tl) crystals. The intensity of dominant bands, 375 nm in NaI and 430 nm in NaI(Tl) was found to be voltage dependent. A linear dependence between the logarithm of intensity and the inverse square root of the applied voltage was observed. The 375 nm band in pure NaI and both 325 nm and 430 nm bands in NaI(Tl) crystals are believed to be impurity electroluminescence bands, while the 295 nm band in NaI is an intrinsic band due to the acceleration-collision mechanism.

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INTRODUCTION

The emission of light quanta is the last stage of any luminescence. Energy can be converted into photons in a variety of ways. The conversion of heat into light is called thermoluminescence. Another process, cathodoluminescence, is the creation of light by fast electron bombardment. The cathodoluminescence has wide application in the communications field (radar, television). If we subject different types of crystals to light beams, they will emit light of another wavelength. This process is called photoluminescence and is of considerable importance as a means of investigating the properties of such crystals. Recently the conversion of chemical energy-chemoluminescence has found application in the laboratory production of intense light sources - chemical lasers. Finally, but by no means least, there is electroluminescence. This is the direct conversion of electric energy into light.

The objective of the research project reported in this Thesis was to observe and investigate electroluminescence processes in pure NaI and NaI(Tl) crystals. There were three reasons for choosing these particular alkali halides as the object of our studies.

1. Electroluminescence studies in alkali halides became a subject of wide interest only very recently and there is no published evidence that the phenomenon had been observed in either NaI or NaI(Tl) crystals.
2. NaI crystals are very important for the study of impurity and

other defect centers in solids and energy transport mechanisms.

3. Considerable work on the luminescence centers in NaI and NaI(Tl) has been done in the Physics Department at the University of Manitoba under the supervision of Dr. I. Cooke. As a result of this work, highly sophisticated equipment for detecting and quantitatively measuring the observed luminescence was constructed and a wide experience was gained in handling highly hygroscopic NaI crystals.

This Thesis is in two parts. In the first part after giving a brief historical background there is a discussion of the theoretical aspects of mechanisms responsible for the occurrence of electroluminescence as suggested in published literature. In the second part some experimental work is presented, experimental results are discussed and conclusions are drawn from this work.

PART 1

THEORETICAL ASPECTS OF ELECTROLUMINESCENCE

1. HISTORICAL BACKGROUND

The important effects of an applied electric field on the behaviour of certain types of solids were observed as early as the late nineteenth century. However the phenomenon became a subject of wider studies only after 1920 when Gudden and Pohl⁽¹⁾ reported the transient luminescence occurring when an electric field is applied to a phosphor previously excited by ultra-violet or X-radiation. This phenomenon of enhanced luminescence became known as a Gudden-Pohl effect or electrophotoluminescence. Electroluminescence resulting directly from the application of an electric field to a solid was first observed in SiC by Lossev^(2,3). Some other early studies of the phenomenon had been reported in reviews by Curie⁽⁴⁾, Henisch⁽⁵⁾, and Ivey⁽⁶⁾.

Destriau⁽⁷⁾ was first to observe and describe electroluminescence in ZnS powders. He was studying the scintillation produced by α -particles in Zinc Sulfide. In order to explain some discrepancies he observed, he wanted to compare the ionization of crystal lattices by an intense electric field with that produced by the α -particles. Conducting this experiment, he observed the illumination of the sulfide under the action of the field and in the absence of α -particle excitation⁽⁴⁾. He attributed the phenomenon to electroluminescence, a direct conversion of electric energy into light. Since then pure ZnS and ZnS phosphors doped with small quantities of other elements (Cu, Sb, Cd, Mn) have become the most important materials for electroluminescence studies.

In the last thirty years electroluminescence was widely

studied and has been observed in a large number of materials and crystalline chemical compounds. Ivey⁽⁶⁾ gives a list of materials in which electroluminescence has been observed prior to 1963. These materials are listed in the table below:

GROUP II - VI COMPOUNDS	OTHER MATERIALS
ZnS	Ge
CdS	Si
ZnSe	C (diamond)
CdTe	SiC
ZnO	NaCl
BeO	AgCl
MgO	ZnF ₂
CaS	CaF ₂
SrS	Al ₂ O ₃
BaS	Cu ₂ O
GROUP III - V COMPOUNDS	SnO ₂
GaP	TiO ₂
GaN	BaTiO ₂
GaSb	CaWO ₄
GaAs	SrTiO ₂ , CaTiO ₂
InP	KNbO ₃
InSb	PbZrO ₃
BN	Zn ₂ SiO ₄
AlN	Ice
AlP	Organic materials

The table indicates that the majority of the electroluminescence studies have been undertaken on semi-conductors. Electroluminescence in the alkali halides was observed and studied only very recently^(8,9,10). Georgobiani⁽¹¹⁾ tried to give possible reasons why crystals with covalent bonds are more suitable for electroluminescence than those with ionic bonds. He stated that conditions for electron acceleration and concentration of the electric field are more favorable in covalent crystals. He attributed this to the fact that in ionic crystals, where the ions of opposite sign alternate, the strength of the local field may greatly exceed the strength of the fields which are produced in the crystal by an applied external field.

Consequently, electroluminescence was studied and observed in comparatively few alkali halides. Torbin⁽⁹⁾ reported the phenomenon in NaCl, Georgobiani and Golubeva⁽⁸⁾ in CsI and CsI(Tl) and Unger and Teegarden⁽¹⁰⁾ in KI. Andrianov and Kats⁽³⁹⁾ reported electro and x-ray luminescence in KBr, but their observations are apparently closer to electrophotoluminescence than to true electroluminescence. Electrophotoluminescence was widely studied in NaCl(Ag) by Onaka et al⁽³³⁾.

2. MECHANISMS OF ELECTROLUMINESCENCE

As indicated earlier, electroluminescence was observed in a wide variety of materials and for a wide variety of conditions. Many possible mechanisms for electroluminescence have been proposed by different authors but we will restrict our discussion only to the

three which are universally accepted:

1. Acceleration - collision electroluminescence
2. Injection electroluminescence
3. Impurity electroluminescence.

Before starting a detailed discussion of electroluminescence mechanisms, we will briefly mention some other effects of electric field on solids.

One of the earliest observed effects of an electric field on solids, other than conduction current, was dielectric breakdown⁽⁶⁾. The mechanisms of dielectric breakdown can be, according to published literature, divided into two groups: intrinsic breakdown and thermal breakdown. Modern theory assumes an electronic nature of intrinsic breakdown. Zener⁽¹²⁾ suggested quantum-mechanical electron tunnelling from the filled valence band to the empty conduction band as the source of electrons responsible for dielectric breakdown. The mechanisms of intrinsic breakdown were later studied in detail by Frölich and Seitz^(13,14). They proposed a model described as the "low temperature case", where the collisions between electrons are rare compared to those between electrons and the base lattice (or defect centers). In the other limiting model called the "high temperature case" the interelectron collisions are much more important than collisions between electrons and lattice vibrations.

The theory behind thermal breakdown is much simpler. Heat is generated by passage of a current and since the conductivity

of insulators and semi-conductors increases with increasing temperature a regenerative effect may occur and thus cause thermal breakdown⁽⁶⁾.

The phenomenon of electric breakdown in alkali halides was recently studied by Hanscomb⁽¹⁵⁾. He observed by studying NaCl, NaCl (MnCl₂) and KCl (SrCl₂) crystals that the presence of impurities (MnCl₂, SrCl₂) increases the breakdown strength. All breakdowns in the above mentioned crystals that occurred at temperatures below 200°C were attributed to the thermal mechanism.

There are several other effects of a strong electric field on solids. The electrons liberated from centers and traps can be detected by conductivity measurements and produce what is called by Böer and Kümmel⁽¹⁶⁾ the "electrically excited glow curves". If the liberated electrons produce luminescence, the result is the Gudden-Pohl effect⁽¹⁾ or electrophotoluminescence. These and other possible effects of electric fields on solids found application at one time or another in the explanation of the complex phenomenon of electroluminescence. However, as we stated earlier, our discussion will be restricted to the three universally accepted mechanisms of electroluminescence.

2.1 ACCELERATION - COLLISION ELECTROLUMINESCENCE

The mechanism which has been most generally accepted to explain the electroluminescence of zinc sulfide is the acceleration of electrons in the conduction band followed by collision excitation of luminescence centers. The schematic presentation of this process

according to Ivey⁽⁶⁾ is given in Figure 1. As Figure 1 indicates the mechanism involves three steps:

- a. Raising of electrons for acceleration into the conduction band.
- b. Acceleration of some of these electrons by the field.
- c. Collisions of these electrons with centers causing the excitation or ionization of the latter.

As a consequence radiative or non-radiative recombination of electrons with centers will occur. We will discuss briefly each of the three steps that occur in the acceleration-collision electroluminescence mechanism.

- a. Raising of electrons into conduction band.

The electrons raised into the conduction band come from donor levels which are deeper than traps but not as deep as the center levels. Frankel et al⁽¹⁸⁾ suggested that the field and phonons mutually assist each other in producing ionization. They proposed the formula for probability of ionization,

$$p = s \exp \left(- \frac{\epsilon}{kT} \right) \quad (1)$$

where

- p = probability of ionization per second
- ϵ = depth of the level
- k = Boltzman constant
- T = temperature
- s = constant

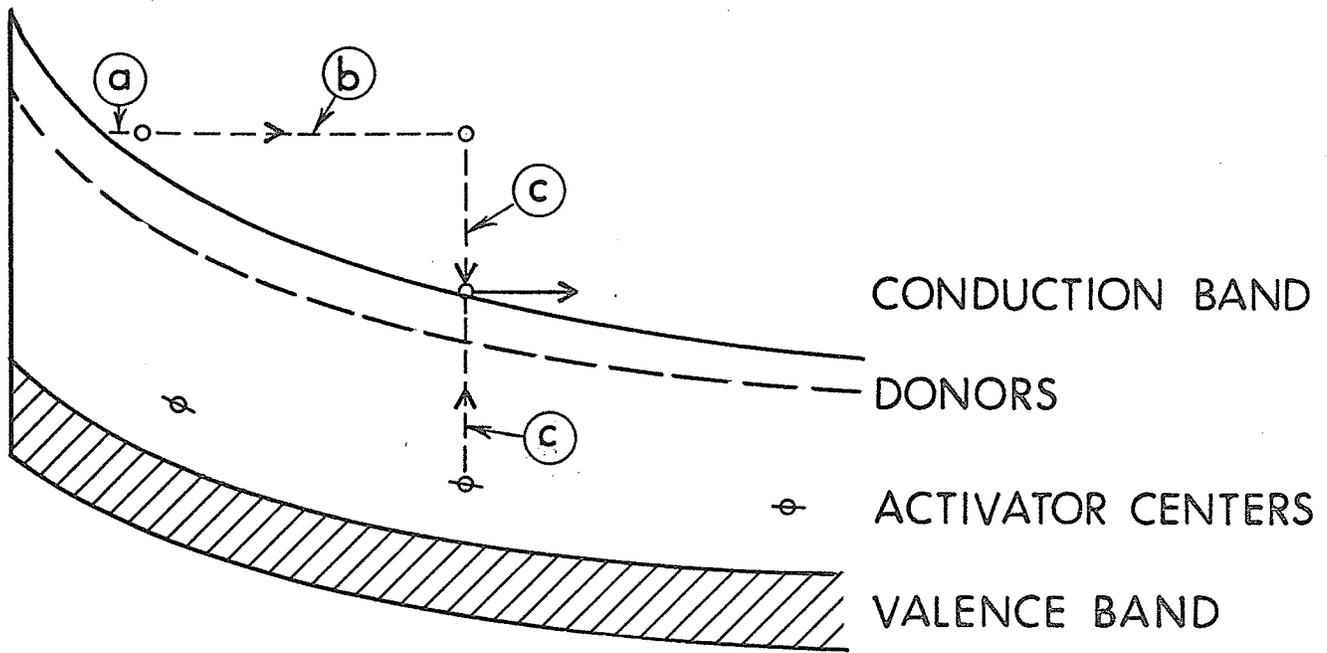


Figure 1

Schematic representation of acceleration-collision mechanism of electroluminescence⁽⁶⁾

It is apparent that p is very small if ϵ is large. In the presence of the field, ϵ the depth is reduced to

$$\epsilon^* = \epsilon - f(E) \quad (2)$$

and probability of ionization becomes

$$p = s \exp - \left(\frac{\epsilon - f(E)}{kT} \right) \quad (3)$$

During the first few cycles of an applied field the electro-luminescence brightness is very low and then gradually as electrons fall into traps, the ionization of the latter soon plays a dominant role in the supply of electrons to the conduction band⁽⁴⁾.

b. Acceleration of electrons by the field.

According to Curie⁽⁴⁾ the condition for an electron to cause excitation is that it must gain energy more rapidly in the field than it loses by interaction with phonons. If E is the energy of such an electron,

$$\left(\frac{dE}{dt} \right)_{\text{field}} > \left(\frac{dE}{dt} \right)_{\text{phonons}} \quad (4)$$

must be satisfied.

Curie⁽⁴⁾ further introduced some important ideas about ionic crystals. He stated that in ionic crystals the mean free path increases gradually and is proportional to the energy of the electrons.

If an electric field in the order of tens of thousands of volts per centimeter is applied to such a crystal one can distinguish two electron groups. In the first group the majority of electrons remain at the thermal energies with an electronic temperature greater by a few degrees than the lattice temperature. This temperature is constant except when conditions for dielectric breakdown are approached. In the second group some electrons have considerably higher temperatures.

Higher thermal energies of electrons are responsible for energy losses at a reduced level and for full traps. In this case dielectric breakdown will occur sooner than the ionization of a luminescence center. This agrees with most of the published literature discussing the difficulties of observing electroluminescence in ionic crystals⁽¹¹⁾.

c. Excitation of centers by impact of a fast electron

Impact of a fast electron with a luminescence center involves the loss of the whole or part of its energy and the release of an electron from the center into the conduction band⁽⁴⁾. If the applied field is oscillating between zero and a maximum, the maximum brightness wave occurs when the field is zero, because at a zero field the electrons return to their original centers. The freed electrons recombine with empty centers in each cycle of applied field. Since the freed electrons are removed some distance from the centers in the excitation process, Curie⁽⁴⁾ derived an empirical expression which gives the relationship

between brightness and applied field frequency

$$\frac{1}{B} \propto \frac{1}{n_0^{2\alpha}} \left[1 + \frac{n_0^\alpha}{2f} \right] \quad (5)$$

where B = electroluminescence brightness

n_0 = number of electrons initially excited

f = applied field frequency

α = constant

The variation of brightness with applied voltage is significant. Destriau⁽⁷⁾ originally proposed an empirical formula of the following form,

$$B = B_0 \exp \left(\frac{aV + b}{cV + d} \right) \quad (6)$$

where V = applied voltage

a, b, c, d = appropriate constants

Later he simplified equation (6) to

$$B = B_0 \exp (-c/V) \quad (7)$$

where c = constant

The expression (7) was experimentally confirmed which simultaneously verified the mechanism of excitation of luminescence centers as being caused by the collision of accelerated electrons.

As a modification of equation (6) and (7) Destriau later⁽⁴³⁾ proposed a new form

$$B = B_0 V^n \exp - (c/V) \quad (8)$$

which was modified by Taylor and Alfrey⁽¹⁹⁾ to

$$B = B_0 V^n \exp \left(- \frac{b}{\sqrt{V}} \right) \quad (9)$$

which form is most frequently used today.

ACCELERATION-COLLISION ELECTROLUMINESCENCE IN ZnS PHOSPHORS

As mentioned earlier, a majority of the studies of acceleration-collision mechanisms was done on the pure ZnS phosphors or ZnS phosphors doped with small quantities of some other elements (Cu, Sb, Mn, As, P, Cl)^(4,5,6,17,42). These studies led to some important relationships which are of general interest for electroluminescence studies.

Electroluminescence studies are generally performed on ZnS powders embedded in a dielectric material (to avoid the electric breakdown). Due to this fact some consideration has to be given to the dielectric constant. Ivey⁽⁶⁾ discussing the complex nature of dielectric constants assigned its "imaginary" part (k_1) to the dielectric material used for embedding the electroluminescent powders and the "real" part (k_2) to the ZnS phosphor. For electrically homogeneous spherical powders he derived an empirical expression that related the electric field strength in the sample F to the average applied field strength V/d .

$$\frac{F}{V/d} = \frac{3 k_2/k_1}{(1 + 2 k_2/k_1) - C (1 - k_2/k_1)} \quad (10)$$

where C is a constant (for close packing of equal sized spheres, C has a maximum value, $C_{\max} = \pi/3\sqrt{2} = 0.74$).

The dependence of the electroluminescence intensity upon the applied voltage in ZnS powders was studied widely and we have discussed it earlier. The electroluminescence intensity is also a function of frequency and temperature. Its variation with frequency is greater at high voltages than at low voltages. Henisch⁽⁵⁾ claims that as far as the frequency dependence is concerned there is no significant difference between electroluminescent powders and single crystals. If the spectrum consists of more than one band, the change in brightness with frequency is accompanied by a change in the spectral composition of the light towards shorter wave lengths⁽⁵⁾. Ivey⁽⁶⁾, Curie⁽⁴⁾ and Alfrey and Taylor⁽³¹⁾ showed that high frequency has a similar effect to low temperature. Both these variables were studied simultaneously and it was found that

$$f = C \exp (- F/KT) \quad (11)$$

where f = frequency
 T = temperature
 k = Boltzman constant
 E = electric field

The changes in the emission color in ZnS phosphors were found to be a function of both variables in the equation (11). Roberts⁽³⁷⁾ studied a mixed ZnS-ZnSe phosphor and found only slight electroluminescence intensity variations between -100°C and +50°C. Several authors reported a strong temperature dependence of the electroluminescence intensity, but apparently there is no general agreement on the matter.

Another important feature of electroluminescence in ZnS powder are so-called "brightness waves". The existence of brightness waves and the fact that their frequency is twice the frequency of the applied AC voltage was first reported by Destriau⁽⁴³⁾. The peaks (normally two) that occur during each cycle of applied AC voltage are not necessarily of the same height.

Thornton⁽³⁸⁾ studied the differences between the electroluminescence intensities for AC and DC voltages. His study covered a wide range of ZnS doped powders. He found that there was no appreciable difference in the electroluminescence intensity when AC or DC voltages were applied. However when a DC voltage was superposed on the AC voltage in some cases the intensity was enhanced as much as two hundred and fifty times. This enhancement was attributed to the recombination at the DC ionized luminescence centers.

After this brief discussion we can conclude that the electroluminescence intensity and the spectral composition of ZnS type phosphors depends upon the applied voltage, frequency and to a certain degree upon the temperature. The superposition of a DC voltage on the

applied AC voltage can significantly enhance the electroluminescence intensity.

2.2 INJECTION ELECTROLUMINESCENCE

Electroluminescence due to charge injection arises from entirely different mechanisms from those of collision-acceleration electroluminescence discussed in Chapter 2.1. The injection of majority charge carriers occurs either at an electrode contact or a p-n junction. In the absence of an applied voltage, Figure 2(a), thermal production and subsequent recombination of electron-hole pairs is in dynamic equilibrium⁽²⁰⁾. When the voltage is applied and additional carriers injected the rate of recombination is increased. As indicated in Figure 2(b), this upsets the equilibrium and may result in recombination which can lead to the emission of light quanta. Contrary to the acceleration-collision electroluminescence, for the injection electroluminescence mechanism, no high electric field is required.

Once the majority carriers are injected, a variety of recombination mechanisms are possible⁽⁶⁾. Some of these mechanisms do not lead to luminescence and thus contribute to the low efficiency usually observed. An important parameter is the depth for which the majority carriers penetrate into the semi-conductor. The depth is proportional to the current and carrier "life-time". If the "life-time" of the carrier is very short, the injection may be very difficult to detect. If however the "life-time" is sufficiently long, the presence

N TYPE
(Electron conductor)

P TYPE
(Hole conductor)

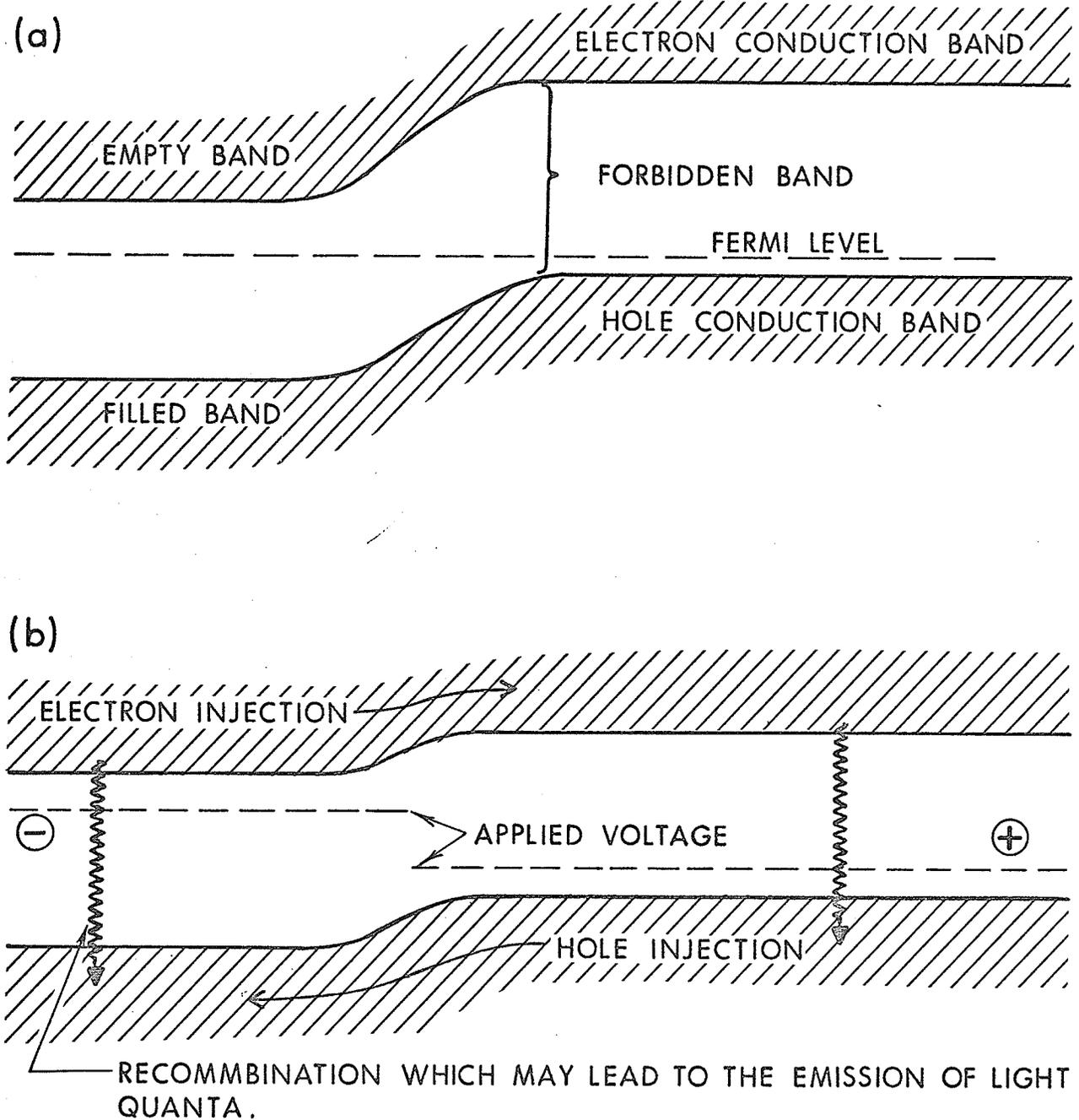


Figure 2

Energy level diagram for a p-n barrier⁽⁴⁾

of injected carriers can be detected by the effects of injected carrier density on the bulk conductivity, the properties of metal contacts and the optical absorption. According to Henisch⁽⁵⁾, the effective bulk conductivity will increase and a metallic contact behaves practically the same way as if it had been illuminated. The optical properties are influenced by the absorption on the long wavelength side of the absorption edge. This absorption occurs when free electrons and holes are generated through the injection process.

The quantitative dependence of carrier injection on the applied voltage was widely studied by Thornton⁽²¹⁾. He started from an idealized model proposed by Shockley⁽²²⁾ which neglects carrier recombination and generation. Later both recombination and generation of carriers were incorporated and the model became physically meaningful. Considering the relationship between carrier density, electrostatic potential and the Fermi level, Thornton⁽²¹⁾ concluded that in the absence of a current flow the Fermi level should be constant throughout the system and the Fermi level should relate the local carrier densities to the electrostatic potential. If $\Psi = (-\epsilon_i/e)$ represents the electrostatic potential where ϵ_i corresponds to the Fermi energy in intrinsic material⁽²³⁾ it can be shown that

$$n = n_i \exp \{e(\Psi - \phi) / kT\} \quad (12)$$

$$p = n_i \exp \{-e (\Psi - \phi) / kT\} \quad (13)$$

where ϕ is a potential related to the Fermi energy by $\epsilon_F = -e\phi$.

From equation (12) and (13) the build-up or diffusion voltage V_0 can be derived. In the n type region at a point remote from the junction and in the p type region far from the junction we obtain

$$n = n_n, \Psi = \Psi_n \quad \text{and} \quad p = p_p, \Psi = \Psi_p \quad (14)$$

respectively. Since $V_0 = |\Psi_n - \Psi_p|$ and ϕ is a constant, we obtain

$$n_p p_p / n_i^2 = \exp \{e(\Psi_n - \Psi_p) / kT\} = \exp \{eV_0/kT\} = \frac{n_n}{n_p} \quad (15)$$

and finally solving for V_0

$$V_0 = (kT/e) \ln \{n_n/n_p\} \quad (16)$$

For a homogeneous n type semi-conductor in the absence of any excitation the free carrier densities are given by

$$n_0 = n_i \exp \{e (\Psi - \phi) / kT\} = n_i^2/p_0 \quad (17)$$

If a light spot with $h\nu > e_g$ is scanned across the specimen so that at the spot location (x'), there are Δn electrons/cm³ and Δn holes/cm³, from the equilibrium considerations, equations (12) and (13), we obtain

$$n = (\Delta n + n_0) = n_i \exp e (\psi - \phi_n) / kT \quad (18)$$

and

$$p = (\Delta n + p_0) = n_i \exp \{e(\phi_p - \psi) / kT\} \quad (19)$$

for the concentration of electrons and holes respectively. Equations (18) and (19) represent non-equilibrium situations and define what can be called quasi-Fermi levels⁽²¹⁾.

This idea was applied to the p-n junction. In order to calculate diffusion currents it is necessary to determine electron density in the element dx at x . In the steady state the electron continuity equation gives $dn/dt = 0 = \text{field term} + \text{diffusion term} + \text{net recombination term}$.

By neglecting the field term it can be expressed as

$$D_n \frac{d^2 n}{dx^2} - (n - n_p) / \tau = 0 \quad (20)$$

The solution of differential equation (20) gives

$$n - n_p = (n'_p - n_p) \exp \{ -(x - x_p) / \sqrt{(D_n \tau)} \} \quad (21)$$

for $x \geq 0$ where n'_p is the value of n at $x = x_p$. The electron diffusion current density at $x = x_p$ is equal to

$$(j_n)_{x_p} = D_n e (dn/dx) / x = x_p \quad (22)$$

By combining with (21) it gives

$$(j_n)_{x_p} = e (n'_p - n_p) / L_n \quad (23)$$

Similarly an expression for the holes can be derived

$$(j_p)_{x_n} = e (p'_n - p_n) / L_p \quad (24)$$

In order to relate equations (23) and (24) to the total current in the system the "low recombination" approximation suggested by Shockley⁽²²⁾ is employed

$$(j_p)_{x_p} = (j_p)_{x_n} \quad \text{and} \quad (j_n)_{x_n} = (j_n)_{x_p} \quad (25)$$

$$j = e (n'_p - n_p) / L_n + e (p'_n - p_n) / L_p \quad (26)$$

Now n'_p and p'_n can be evaluated as a function of the applied voltage. In order to do so the ϕ_n and ϕ_p at the edges of high field region are needed. The variation of the minority carrier density near the quasi-Fermi level is assumed to be approximately linear. With this approximation, at any point in the transition layer,

$$p = n_i \exp \{ e (\phi_p - \psi_x) / kT \} \quad (27)$$

$$n = n_i \exp \{ e (\psi_x - \phi_n) / kT \} \quad (28)$$

Since the difference in Fermi levels ($\phi_p - \phi_n$) is equal to the applied voltage we multiply equations (27) and (28) and obtain

$$pn = n_i^2 \exp \{ e (\phi_p - \phi_n) / kT \} = n_i^2 \exp (eV/kT) \quad (29)$$

By applying this equation at the edges of the high field region we obtain

$$p'_n = (n_i^2/n_n) \exp (eV/kT) = p_n \exp (eV/kT) \quad (30)$$

$$n_p' = (n_i^2/p_p) \exp (eV/kT) = n_p \exp (eV/kT) \quad (31)$$

Finally, combining (30) and (31) with (23) and (24) leads to an equation that gives current - voltage characteristics

$$j = e \{ D_{n p} / L_n + D_{p n} / L_p \} [\exp (eV/kT) - 1] \quad (32)$$

The equation (32) is a final equation for Shockley's⁽²²⁾ model, i.e. it does not take into account the recombination and generation of carriers in the depletion layer itself. In order to account for those phenomena that undoubtedly occur, Thornton⁽²¹⁾ first defines the recombination current density, j_{rc} as a function of the local recombination rate $R(x)$ as

$$j_{rc} = e \int_{-x_n}^{x_p} R(x) dx \quad (33)$$

The recombination rate $R(x)$ can be determined in a way suggested by Sah et al⁽²⁴⁾ via recombination through an impurity center

$$R = (pn - n_i^2) / [(n + n_1) \tau_p + (p + p_1) \tau_n] \quad (34)$$

where

$$p_1 = n_i \exp \{ (\epsilon_i - \epsilon_t) / kT \} \quad (35)$$

$$n_1 = n_i \exp \{ (\epsilon_t - \epsilon_i) / kT \} \quad (36)$$

and τ_n and τ_p are minority carrier lifetimes in p and n type materials respectively. For a symmetrical junction with the recombination centers situated at the intrinsic level, i.e. $\epsilon_t = \epsilon_i$, Sah et al⁽²⁴⁾ estimate the recombination current

$$j_{rc} = \pi (kT/eF) en_i / \exp (eV/2kT) / 2\tau_0 \quad (37)$$

As F, the electric field in the junction region is equal to $(V_0 - V) / (X_n + X_p)$, a combination of (32) with (37) finally yields

$$j_{rg}/j_D = (n_i/n_p) (x_n + x_p) / 2L_0 [kT/e(V_0 - V)] \exp (-eV/2kT) \quad (38)$$

Equation (38) enables calculations of relative magnitude of electroluminescent currents under a variety of conditions providing the approximations involved in its derivation are met.

In order to make accurate measurements of the capture cross-sections for holes and electrons Wilson and Brinet⁽⁴¹⁾ recently suggested that consideration must be taken of the extent of the depletion

layer and the doping profile in the specific p-n junction under consideration. They claim their findings are applicable to the inhomogeneously doped p - n junctions.

2.3 IMPURITY ELECTROLUMINESCENCE

The mechanisms of impurity electroluminescence are not as clearly understood and as well explained as the mechanisms of acceleration-collision and injection electroluminescence.

The role of some "impurities" in enhancing both photoluminescence and electroluminescence intensity in ZnS has been reported by Curie⁽⁴⁾. The phosphors of the ZnS(As), ZnS(P) and ZnS(Sb) type showed appreciably different electroluminescence spectra from those of the pure ZnS. Further, some undesired impurities like surface contaminants doubtlessly play an important role as possible "impurity electroluminescence" centers.

Discussing the impurity states Thornton⁽²¹⁾ presented a model which contained shallow donors and acceptors which are fully ionized and atoms in a deeper level of which only a fraction is ionized. Figure 3 illustrates how the free electrons can fall into ionized levels.

According to Thornton⁽²¹⁾ two things can happen to the electron immobilized in such a way. Firstly it can fall from the defect level into the valence band, or secondly it can be thermally activated back into the conduction band. The first process represents the recombination of an electron-hole pair through an impurity state. The second

process is the net result of the free carrier (an electron in this case) being immobilized or trapped for a finite time before continuing its movement through the crystal. The first process is by far the more important in attempting to explain the mechanism of impurity electro-luminescence.

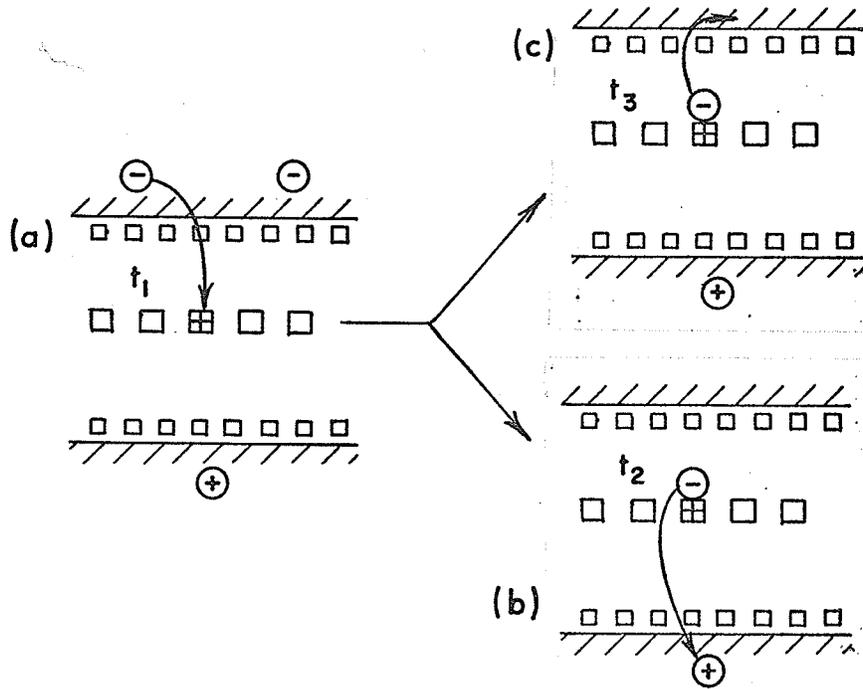


Figure 3
Illustration of the difference between recombination and trapping action,
(a) electron capture, (b) hole capture, and (c) thermal ionization of
filled level(21).