

ELECTROLUMINESCENCE IN NaI AND NaI(Tl) CRYSTALS

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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.

#### ACKNOWLEDGEMENT

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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<sup>(1)</sup> 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<sup>(2,3)</sup>. Some other early studies of the phenomenon had been reported in reviews by Curie<sup>(4)</sup>, Henisch<sup>(5)</sup>, and Ivey<sup>(6)</sup>.

Destriau<sup>(7)</sup> was first to observe and describe electroluminescence in ZnS powders. He was studying the scintillation produced by  $\alpha$ -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  $\alpha$ -particles. Conducting this experiment, he observed the illumination of the sulfide under the action of the field and in the absence of  $\alpha$ -particle excitation<sup>(4)</sup>. 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<sup>(6)</sup> 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 <sub>2</sub>
CaS	CaF <sub>2</sub>
SrS	Al <sub>2</sub> O <sub>3</sub>
BaS	Cu <sub>2</sub> O
GROUP III - V COMPOUNDS	SnO <sub>2</sub>
GaP	TiO <sub>2</sub>
GaN	BaTiO <sub>2</sub>
GaSb	CaWO <sub>4</sub>
GaAs	SrTiO <sub>2</sub> , CaTiO <sub>2</sub>
InP	KNbO <sub>3</sub>
InSb	PbZrO <sub>3</sub>
BN	Zn <sub>2</sub> SiO <sub>4</sub>
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<sup>(8,9,10)</sup>. Georgobiani<sup>(11)</sup> 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<sup>(9)</sup> reported the phenomenon in NaCl, Georgobiani and Golubeva<sup>(8)</sup> in CsI and CsI(Tl) and Unger and Teegarden<sup>(10)</sup> in KI. Andrianov and Kats<sup>(39)</sup> 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<sup>(33)</sup>.

## 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<sup>(6)</sup>. 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<sup>(12)</sup> 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<sup>(13,14)</sup>. 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<sup>(6)</sup>.

The phenomenon of electric breakdown in alkali halides was recently studied by Hanscomb<sup>(15)</sup>. He observed by studying NaCl, NaCl (MnCl<sub>2</sub>) and KCl (SrCl<sub>2</sub>) crystals that the presence of impurities (MnCl<sub>2</sub>, SrCl<sub>2</sub>) 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<sup>(16)</sup> the "electrically excited glow curves". If the liberated electrons produce luminescence, the result is the Gudden-Pohl effect<sup>(1)</sup> 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<sup>(6)</sup> 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<sup>(18)</sup> 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
- $\epsilon$  = depth of the level
- k = Boltzman constant
- T = temperature
- s = constant

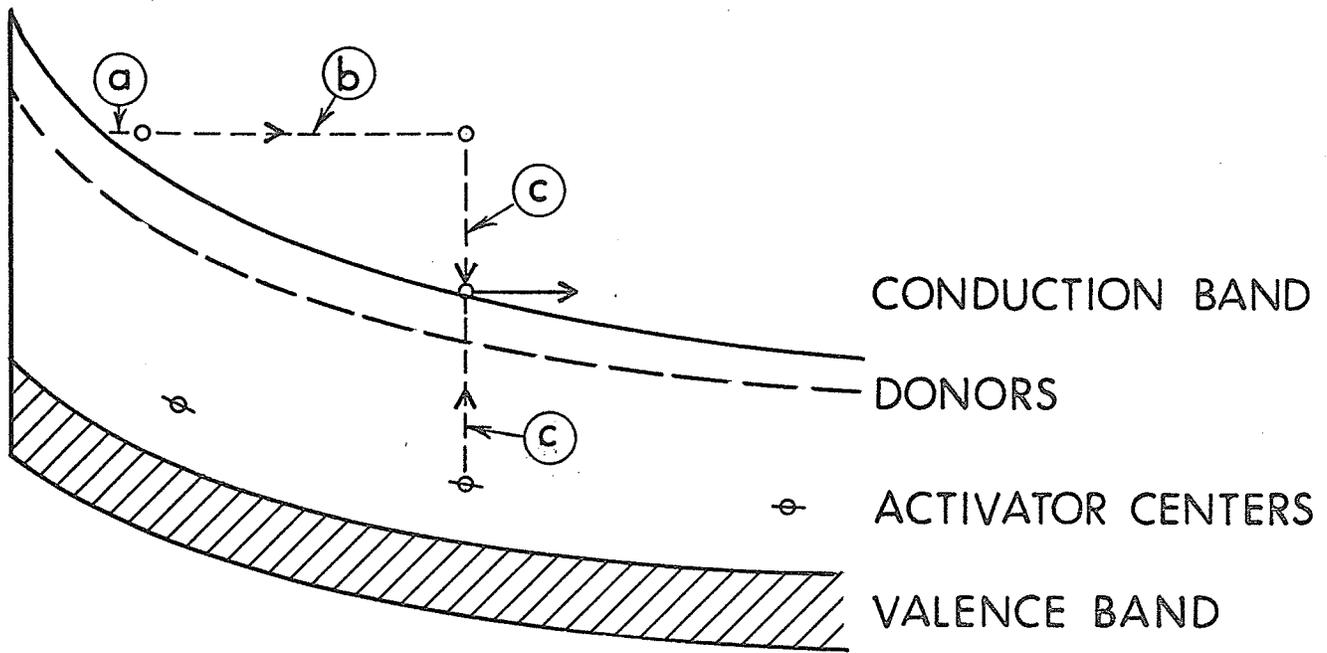


Figure 1

Schematic representation of acceleration-collision mechanism of electroluminescence<sup>(6)</sup>

It is apparent that  $p$  is very small if  $\epsilon$  is large. In the presence of the field,  $\epsilon$  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<sup>(4)</sup>.

b. Acceleration of electrons by the field.

According to Curie<sup>(4)</sup> 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<sup>(4)</sup> 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<sup>(11)</sup>.

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<sup>(4)</sup>. 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<sup>(4)</sup> 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

$\alpha$  = constant

The variation of brightness with applied voltage is significant. Destriau<sup>(7)</sup> 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<sup>(43)</sup> proposed a new form

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

which was modified by Taylor and Alfrey<sup>(19)</sup> 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)<sup>(4,5,6,17,42)</sup>. 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<sup>(6)</sup> 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<sup>(5)</sup> 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<sup>(5)</sup>. Ivey<sup>(6)</sup>, Curie<sup>(4)</sup> and Alfrey and Taylor<sup>(31)</sup> 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<sup>(37)</sup> 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<sup>(43)</sup>. The peaks (normally two) that occur during each cycle of applied AC voltage are not necessarily of the same height.

Thornton<sup>(38)</sup> 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<sup>(20)</sup>. 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<sup>(6)</sup>. 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)

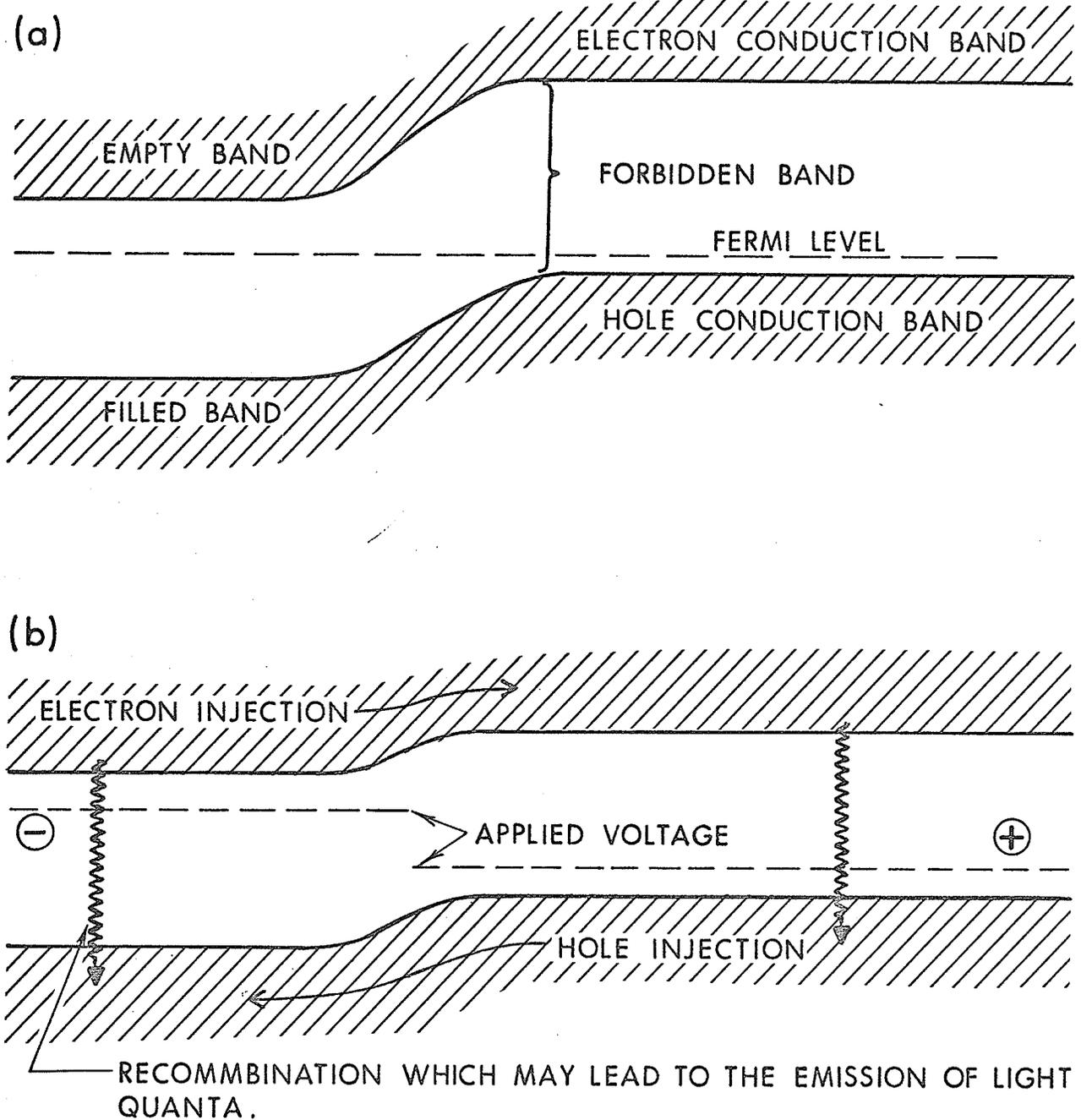


Figure 2

Energy level diagram for a p-n barrier<sup>(4)</sup>

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<sup>(5)</sup>, 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<sup>(21)</sup>. He started from an idealized model proposed by Shockley<sup>(22)</sup> 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<sup>(21)</sup> 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  $\epsilon_i$  corresponds to the Fermi energy in intrinsic material<sup>(23)</sup> 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  $\phi$  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  $\phi$  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  $\Delta n$  electrons/cm<sup>3</sup> and  $\Delta n$  holes/cm<sup>3</sup>, 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<sup>(21)</sup>.

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

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

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<sup>(22)</sup> 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  $\phi_n$  and  $\phi_p$  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<sup>(22)</sup> 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<sup>(21)</sup> 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<sup>(24)</sup> 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  $\tau_n$  and  $\tau_p$  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<sup>(24)</sup> 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<sup>(41)</sup> 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<sup>(4)</sup>. 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<sup>(21)</sup> 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<sup>(21)</sup> 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.

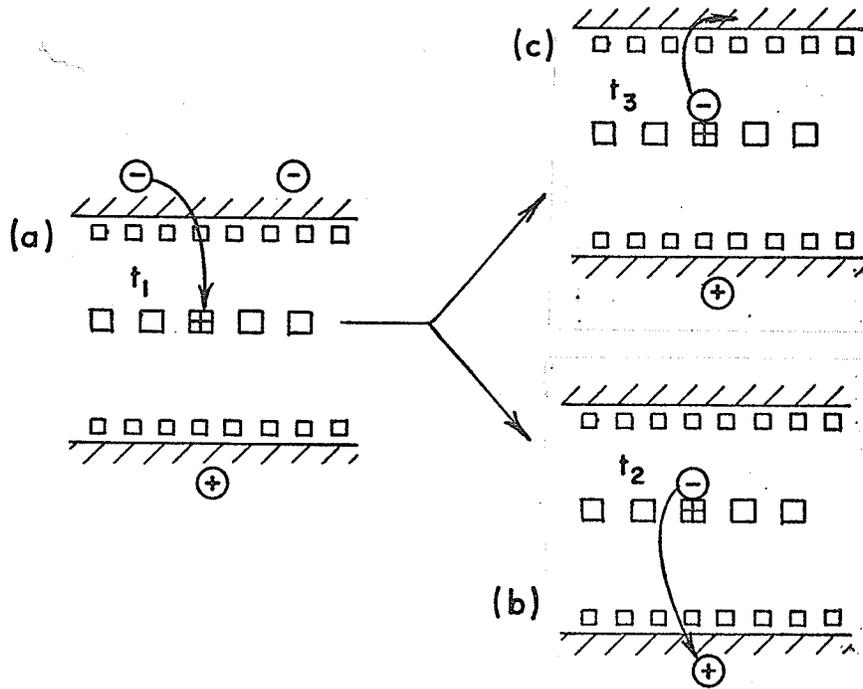


Figure 3  
Illustration of the difference between recombination and trapping action,  
(a) electron capture, (b) hole capture, and (c) thermal ionization of  
filled level(21).

From a theoretical point of view, the role of the "holes" in the perfect crystal lattice in enhancing the electroluminescence was studied by Morgan<sup>(25)</sup>. He observed strong electrostatic potential fluctuations in the p region and attributed them to the high density of charged impurities. The band edge and impurity levels following these potential fluctuations are presented schematically in Figure 4.

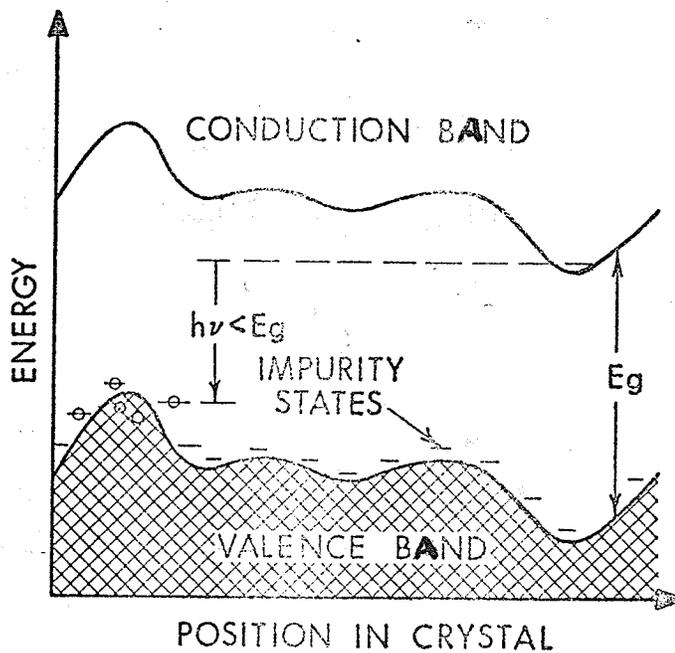


Figure 4  
Model for radiative recombination in closely compensated  
p type material with deep impurity center<sup>(40)</sup>

At equilibrium, in compensated p type material the few holes reside near the top of the band or in the highest energy impurity states. An injected electron drops into the lowest available energy states of the conduction band tail. Now the deepest states in these bands act like localized potential wells. While the wells for electrons are potential maxima, so that the two types of wells are necessary spatially separated<sup>(40)</sup>. Ashley and Milnes<sup>(26)</sup> and Lampert<sup>(27)</sup> in their theoretical approach to the problem stated that the cross-section for the hole capture by the deep center is much greater than the cross-section for electron capture. They assumed the diffusion negligible and considered only electron drift. At low currents the voltage drop across the p region is negligible and an exponential current-voltage relation for junction recombination results. At higher currents the voltage drop across the p region ( $V-V_j$ ), becomes comparable with the junction voltage  $V_j$ . The current in the p region is carried by holes resulting in the Ohm's law relation<sup>(40)</sup>.

$$J = \frac{e \mu_p p_o (V - V_j)}{L} \quad (39)$$

where  $e$  = electron charge

$\mu_p$  = hole mobility

$p_o$  = equilibrium density of holes

$L$  = distance from the junction plane to the p contact

Electron drift is at that point negligible and the light is emitted within

the diffusion length of the junction. As the current is further increased, the electrons drift into the p region and electron space charge builds up. A square law characteristic results from the space charge limited current flow and is described by the relation

$$J = (9/8) [ e \tau_n \mu_n \mu_p p_o (V - V_j)^2 / L^3 ] \quad (40)$$

where  $\tau_n$  is the electron combination time from the conduction band to the deep acceptor level and  $\mu_n$  is the electron mobility.

The mechanism for the "hole" impurity electroluminescence can be summarized as follows<sup>(40)</sup>:

- (a) At low currents electrons flow by diffusion and the recombination and emission is within a diffusion length of the junction.
- (b) At intermediate currents a voltage drop appears across the p region comparable to the junction voltage; a space charge of electrons begins to penetrate the p region and the light emission begins to spread.
- (c) At high currents a large space charge of electrons and a considerable number of injected electrons drift across the p region; light emanates from the entire p region.

PART II

EXPERIMENTAL STUDIES OF ELECTROLUMINESCENCE

PROCESSES IN NaI AND NaI(Tl) CRYSTALS

## 1. EXPERIMENTAL PROCEDURES

### 1.1 EXPERIMENTAL EQUIPMENT

With some modifications the experimental equipment was similar to that designed and described by Palser<sup>(28,29)</sup> and Watson<sup>(30)</sup>. The equipment is schematically presented in Figure 5 and the details of cryostat and the crystal holder are given in Figure 6.

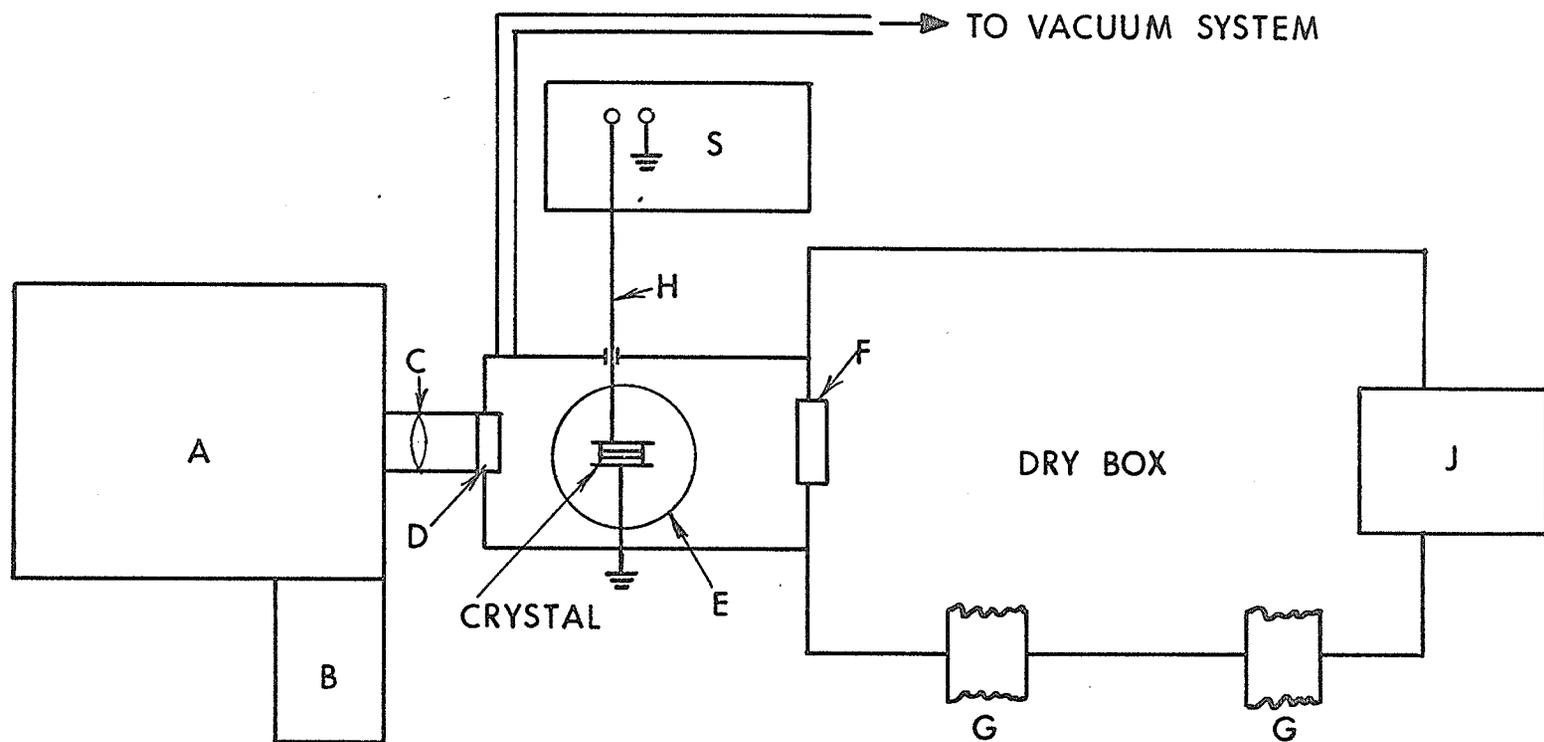
The crystal samples of both NaI and NaI(Tl) were prepared in the dry box. After being mounted in the crystal holders between indium electrodes, the sample was transferred into the vacuum chamber and secured in the cryostat. A high voltage cable was then connected with one of the electrodes and the vacuum chamber was evacuated. In order to assure a good vacuum the system was connected with the mercury diffusion vacuum pump and liquid nitrogen was added to the cryostat. The temperature of the sample was measured by a copper-constantan thermocouple attached to the brass crystal holder. After the sample temperature had stabilized at liquid nitrogen temperature ( $-190^{\circ}\text{C}$ ), the AC voltage was applied across the crystal.

The electroluminescent radiation from the sample was collected by the quartz lens, focussed on to the entrance slit of the analyzer monochromator and its intensity measured by the photomultiplier. Due to the large number of spectra required in the earlier work<sup>(28,29)</sup> the system had been automated. The analyzer monochromator was equipped with a reversible synchronous motor which drove the grating through an appropriate gear train. A number of cams attached to each grating drive

shaft triggered microswitches which in turn set ring counters in the automatic control unit<sup>(28)</sup>. The analyzer monochromator scanned the emission spectrum until the region of interest was reached. At this point a microswitch closed causing the control unit to feed the photomultiplier output to the digital voltmeter, which fed its binary coded decimal output through a parallel to serial convertor into the tape punch. At the end of the spectral region of interest another microswitch closed causing the control unit to stop output. The output was then transferred onto a card prior to correction and analysis by an IBM 360/65 computer. The correction programme was identical to one described by Palser<sup>(29)</sup>. The computer output resulted in a corrected electro-luminescence spectrum.

The following is a list of model number or origins of various items of equipment used.

Analyzer monochromator	Bausch and Lomb No. 33-86-45
Photomultiplier	E.M.I. No. 6256
High Voltage Supply	Keithley Model 242
Amplifier	Magnetic Instruments Model 759-5
Digital Voltmeter	Vidar Model 500
Parallel to Serial Converter	Designed and built in the laboratory from DEC Modules
Paper Tape Punch	Tally Model 420
Vacuum System	Mercury Diffusion Pump
500 Hz High Voltage Supply	Designed and built in the Physics Department, University of Manitoba



- A - ANALYZER MONOCHROMATOR
- B - PHOTOMULTIPLIER
- C - QUARTZ LENS
- D - QUARTZ WINDOW
- E - CRYOSTAT
- F - VACUUM CHAMBER ENTRANCE
- G - GLOVE PORTS
- H - HIGH VOLTAGE CABLE
- J - ENTRANCE PORT
- S - HIGH VOLTAGE SUPPLY

Figure 5

Electroluminescence apparatus  
(schematic)

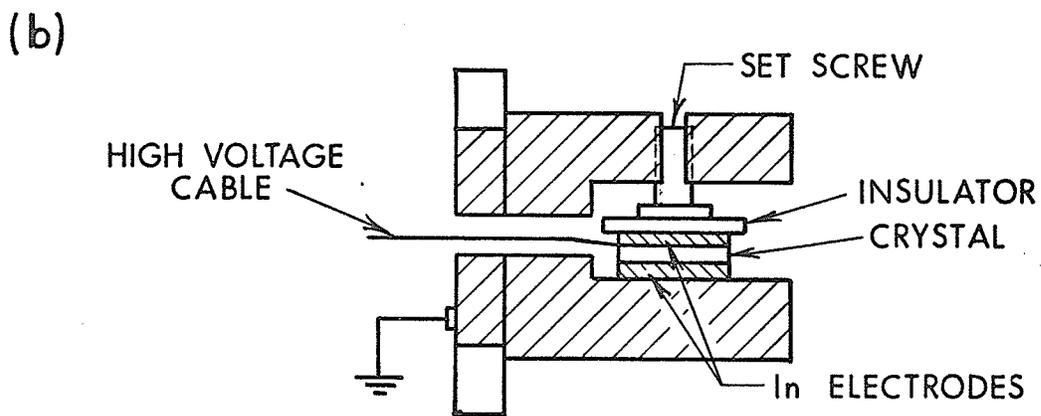
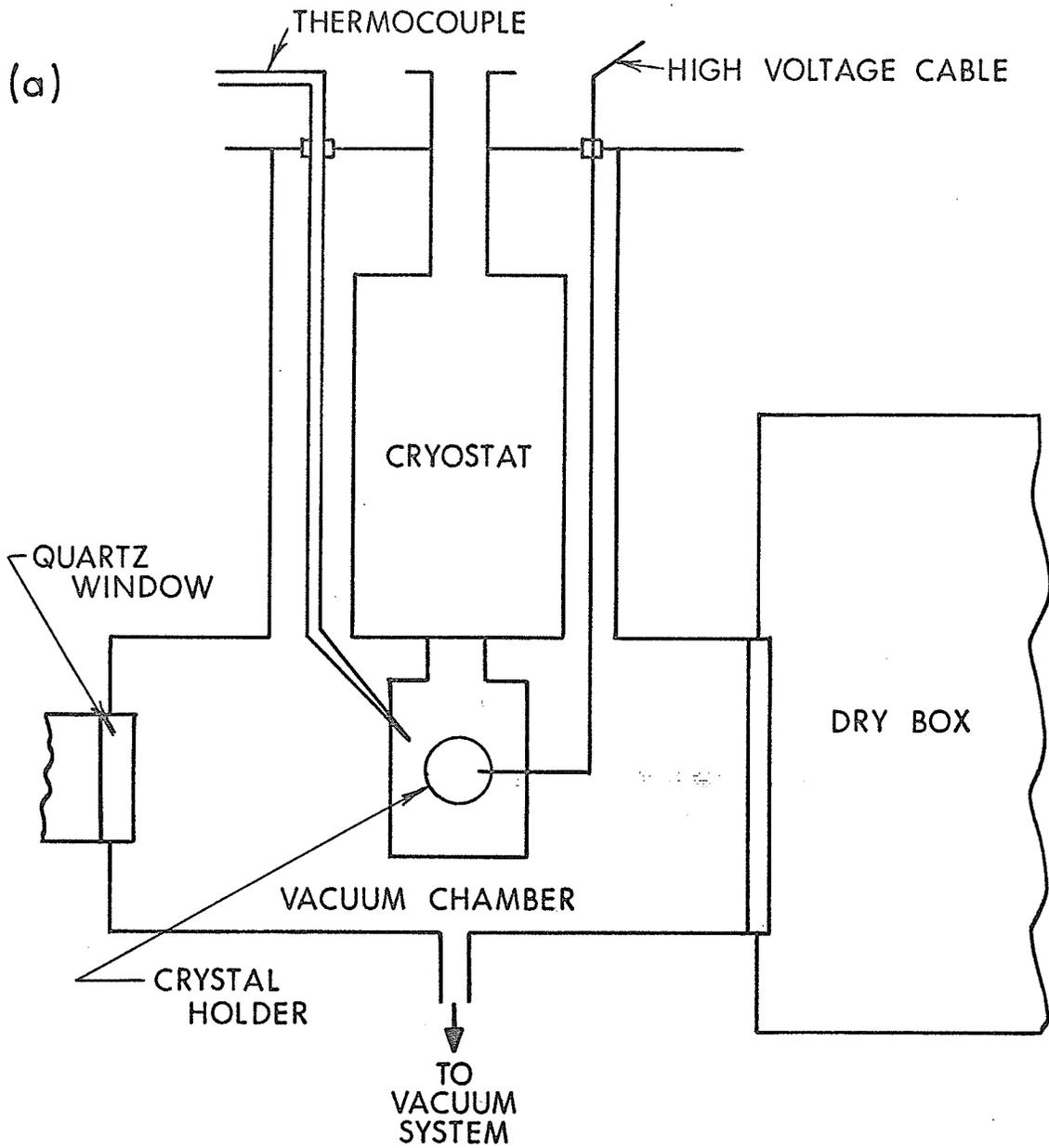


Figure 6

The details of (a) vacuum chamber and cryostat (b) crystal holder.

## 1.2 SAMPLE PREPARATION

Both NaI and NaI(Tl) single crystals having a nominal thallium concentration of 0.2 mole % were obtained from Harshaw Chemical Company. Because of the extreme hygroscopic nature of these crystals the samples were prepared in the dry box. Samples generally one centimeter square by 0.8 - 2.4 mm thick were cleaved from a single crystal block. After that the crystals were mounted between metal electrodes in the brass crystal holder. In the preliminary tests various combinations of indium, aluminum and brass were used as electrode material. There was no difference in the emission observed with various types of metal electrodes, but because of its mechanical flexibility indium was used in the majority of the tests. Special precaution was taken when the set screw was tightened (Figure 6a). We wanted to have a tight and uniform contact between crystal surface and electrodes, but on the other hand we had to be very cautious not to cause mechanical damage to the crystal. On several occasions we mechanically cracked the crystal which led to the abortion of a particular test. After the crystal was mounted in the crystal holder one of the electrodes was connected to the high voltage cable and the holder transferred into the vacuum chamber for the test. After the electroluminescence test was completed the crystal was demounted and examined for possible surface contamination and for mechanical defects. In some cases this visual examination was helpful in the interpretation of test results.

## 2. EXPERIMENTAL RESULTS AND DISCUSSION OF RESULTS

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. Electroluminescence has been observed in both pure NaI and thallium doped NaI(Tl) crystals at liquid nitrogen temperature (-190°C) when excited by 1000 - 2500 V AC voltage. The observed electroluminescence spectra for pure NaI and NaI(Tl) are presented in Figures 7 and 8 and summarized in the table below:

### Electroluminescence Bands in NaI and NaI(Tl) Crystals

	<u>295 nm</u>	<u>325 nm</u>	<u>375 nm</u>	<u>430 nm</u>
NaI (pure)	small	-	dominant	-
NaI(Tl)	-	very small	-	dominant

As indicated in Figure 7 a typical electroluminescence spectrum of pure NaI consists of a dominant band centered at 375 nm (3.30 eV) and a smaller band centered at 295 nm (4.20 eV). The 295 nm band was not observed in all tested crystals. In thallium doped crystals (Figure 8) the broad emission band at 430 nm (2.88 eV) was dominant and in some crystals a very small band centered at 325 nm (3.80 eV) was observed. All four bands were reported earlier in the photoluminescent studies of NaI and NaI(Tl) crystals. Van Sciver<sup>(34)</sup> discusses all four bands in detail. According to him the 295 nm band occurs in all crystals

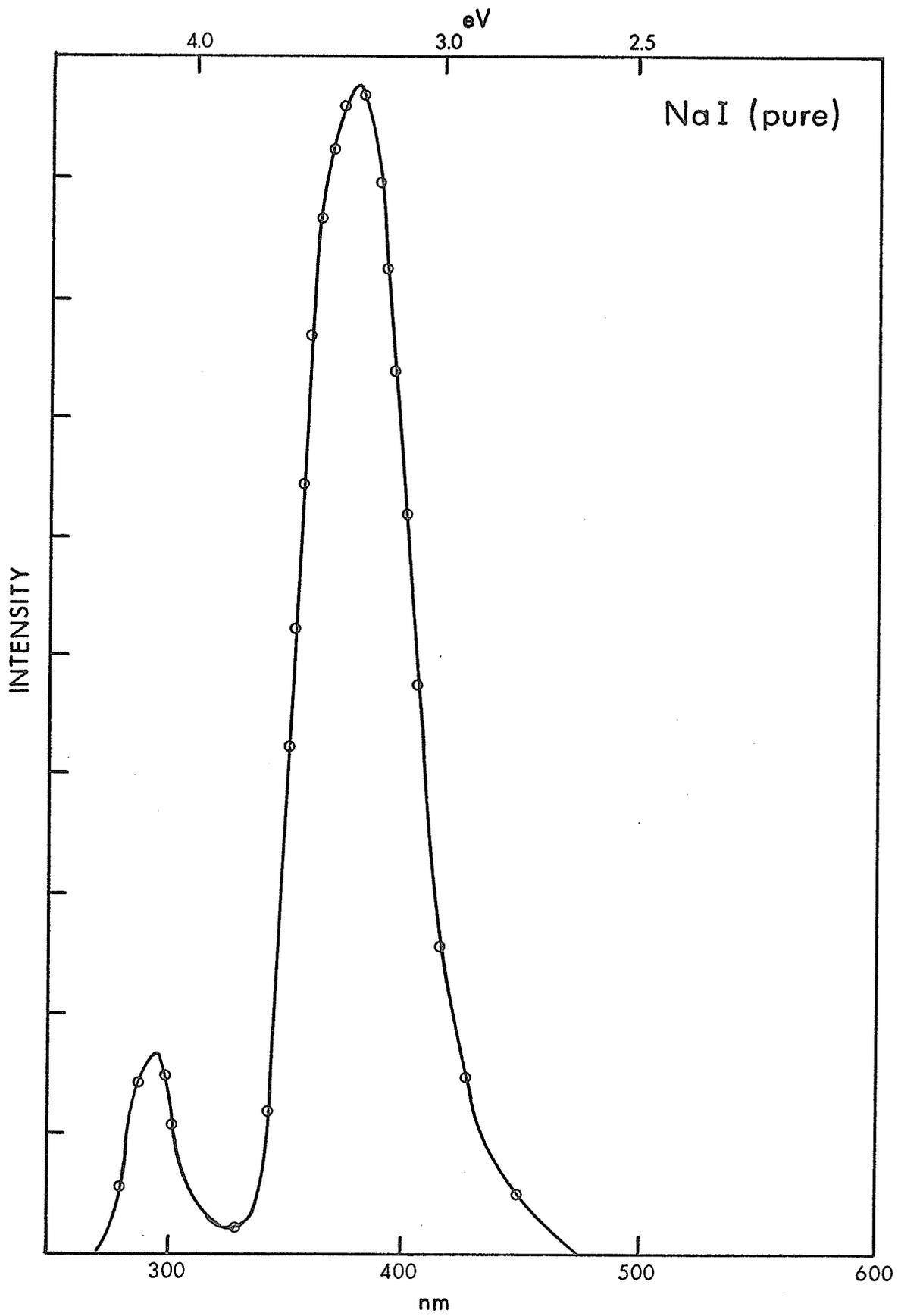


Figure 7

Typical Electroluminescence Spectrum

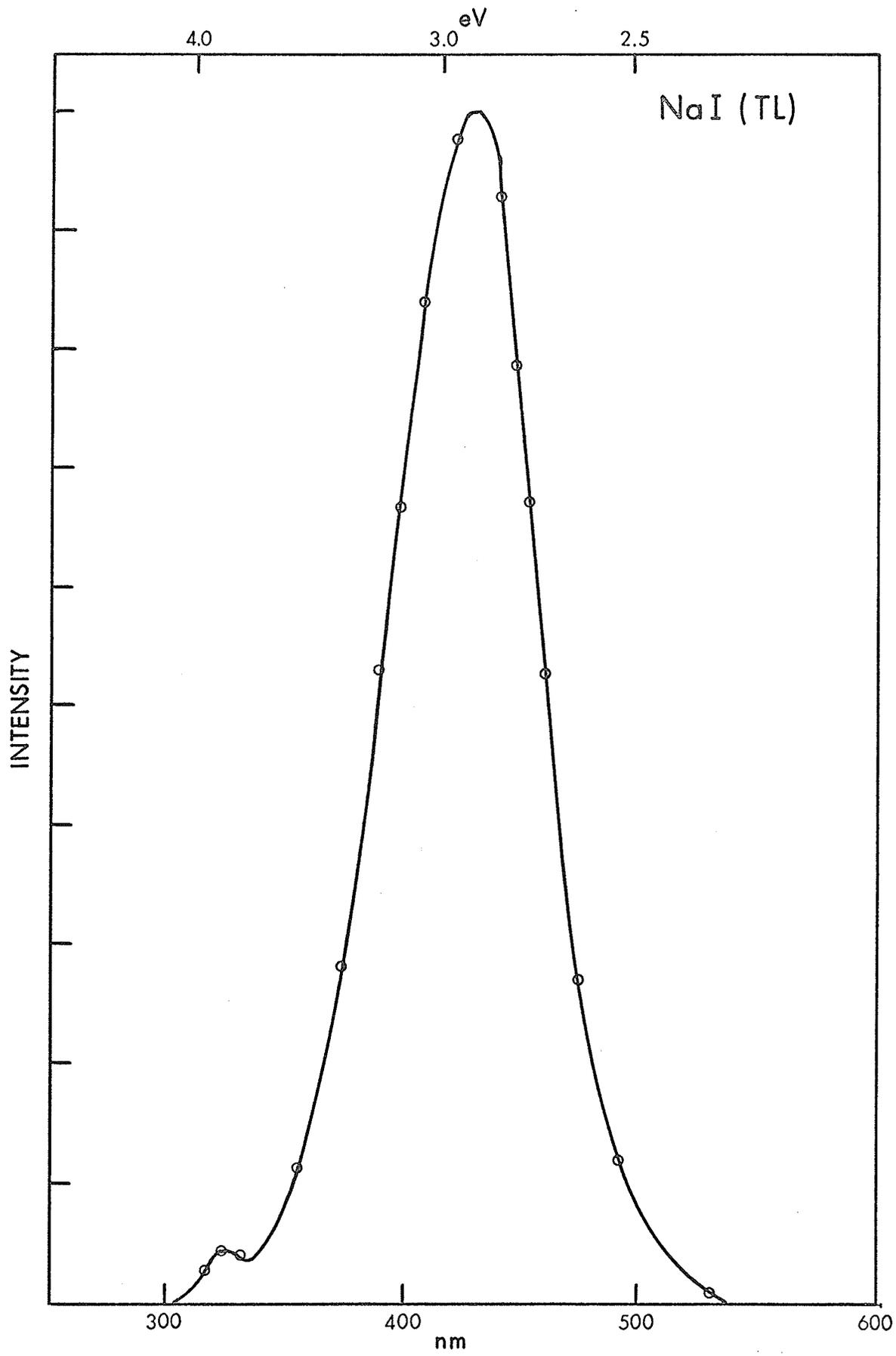


Figure 8

Typical Electroluminescence Spectrum

containing 0.05 or less mole percent of thallium at  $-190^{\circ}\text{C}$ . The 325 nm band appears only in the crystals doped with relatively high concentrations of Tl (over 0.1 mole %). The 375 nm band is attributed to the stoichiometric excess of  $\text{I}_2$ . The 425 nm band is an exclusive property of the crystals containing Tl and no others. Similar coincidence between electroluminescent and photoluminescent spectra was reported by Unger and Teegarden<sup>(10)</sup> when they discussed electroluminescence in the single KI crystals. In our experiments the applied AC voltage varied between 500 and 2500 volts. The first signs of the electroluminescence emission were observed when approximately 1000 volts was applied across the crystal. The intensity gradually increased by increasing the applied voltage. When the applied voltage exceeded 2500 volts the "breakdown" and/or direct contact (via sparking) between the electrodes generally occurred.

In order to study the dependence of electroluminescence intensity upon the applied voltage we have an approach suggested by Taylor and Alfrey<sup>(19)</sup> and used by Unger and Teegarden<sup>(10)</sup> in the electroluminescence studies of KI crystals. The inverse square root of the applied voltage was found to be linearly proportional to the logarithm of the electroluminescence intensity of the dominant bands (Figures 9 and 10).

The linear relationship was expected from the empirical correlation suggested by Taylor and Alfrey<sup>(19)</sup> and discussed earlier in the theoretical section. Henisch<sup>(5)</sup> attributed this electroluminescence

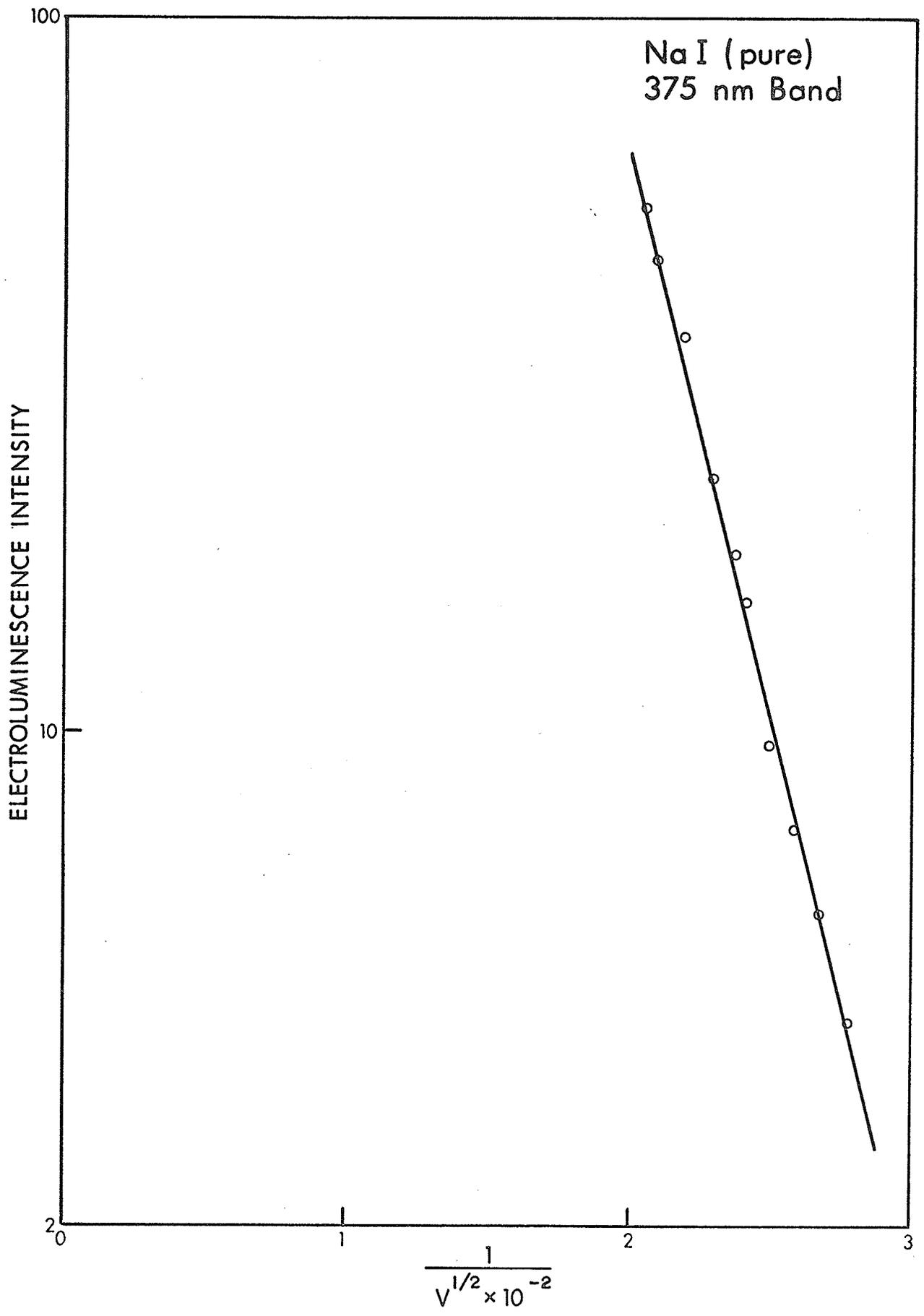


Figure 9

Electroluminescence intensity as a function of applied voltage.

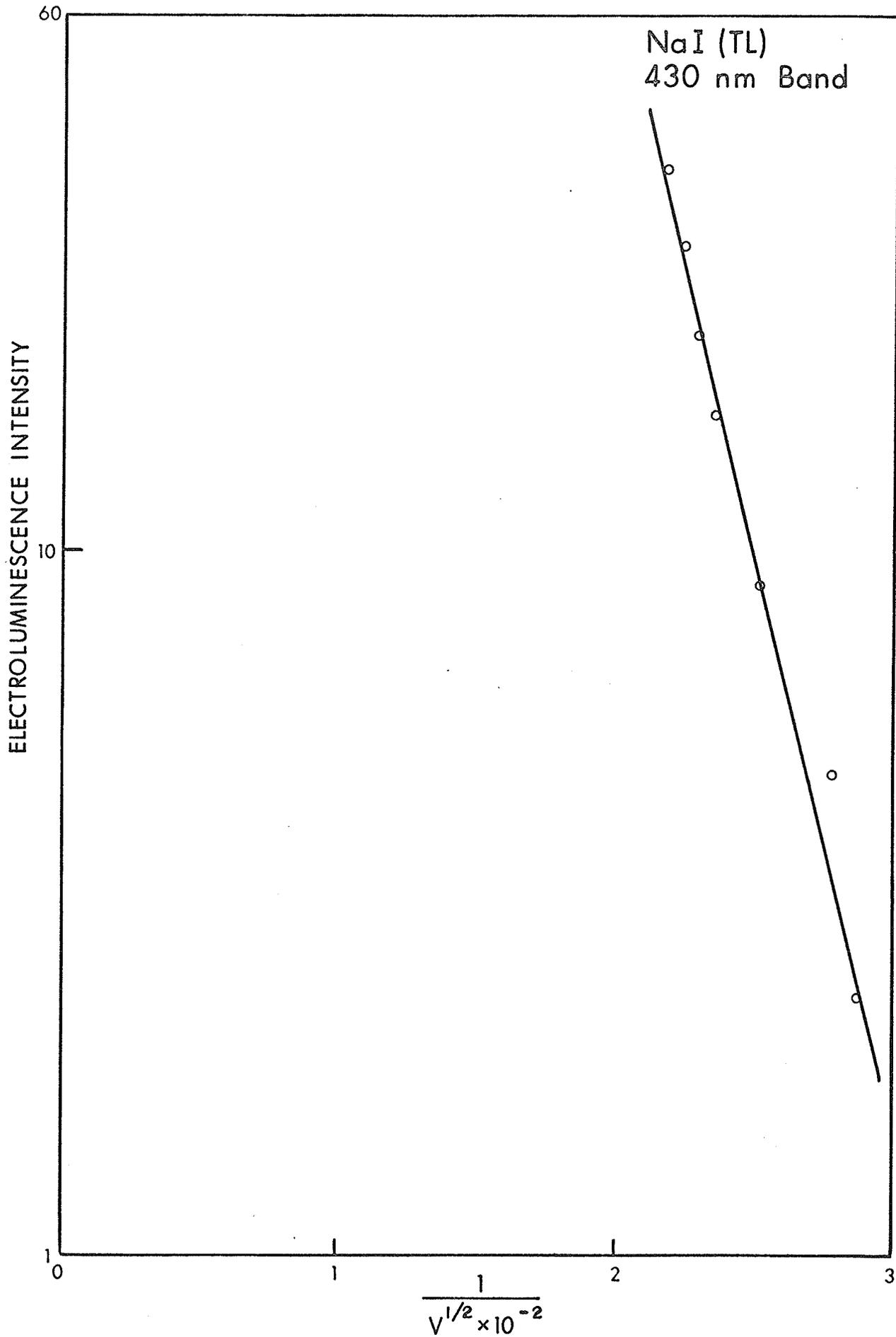


Figure 10

Electroluminescence intensity as a function of applied voltage.

dependence upon the applied voltage to the acceleration of charge carriers to optical energies in a locally high field due to a Mott-Schottky barrier in the vicinity of an electrode or the crystal surface. Georgobiani and Solodovnikova<sup>(32)</sup> reported similar dependence between the applied voltage and the electroluminescence intensity in CsI(Tl) crystals.

In the course of experimental work an apparent decay of the 375 nm peak in the pure NaI crystals was observed when a constant AC voltage was applied over a longer period of time (over 15 minutes). In order to test this decay quantitatively we kept the crystal at liquid nitrogen temperature for 80 minutes. The applied voltage was kept constant at 2300 V. The peak intensity as a function of time is presented in Figure 11.

The "ageing" of electroluminescent phosphors is a well known fact and is widely discussed by Ivey<sup>(6)</sup> and Henisch<sup>(5)</sup>. Ivey<sup>(6)</sup> suggested the use of an empirical relationship, originally proposed by Roberts<sup>(44)</sup> for calculating the electroluminescence intensity at a given time.

$$L = L_i \left[ 1 + \frac{t}{t_0} \right] \quad (41)$$

where

$L_i$  = initial intensity of electroluminescence

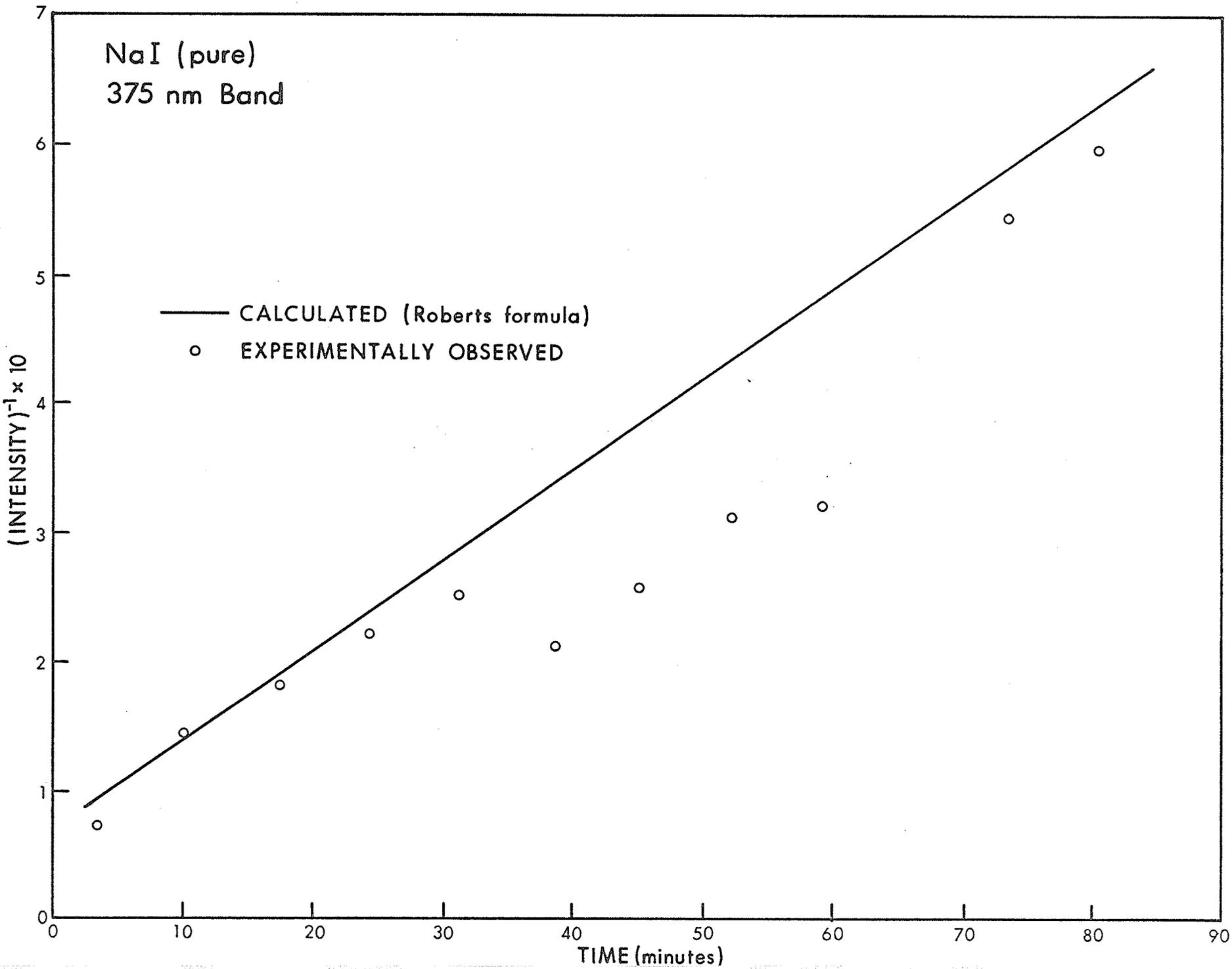
$t_0$  = time to half intensity

$t$  = total time of applied voltage

$L$  = intensity of electroluminescence at time  $t$

Electroluminescence intensity as a function of time.

Figure 11



Although Roberts formula was derived for ZnS type phosphors, we attempted to apply it for calculating "ageing" of the 375 nm band in pure NaI. Figure 11 indicates a fairly good match between calculated and experimentally obtained values. We have concluded that the Roberts formula gives a good estimate for the decay of electroluminescence intensity with time for the 375 nm band in NaI crystals. More experimental work is needed if this finding is to be applied for other electroluminescence bands in NaI crystals and/or for other alkali halides.

The observed electroluminescence emission from pure NaI (except the 295 nm band) and NaI(Tl) crystals discussed above is believed to be impurity electroluminescence. The 375 nm band in NaI which is attributed to the excess iodine can be interpreted as the "hole" electroluminescence as suggested by Ashley<sup>(26)</sup>. There is a possibility that surface contamination due to the highly hygroscopic nature of NaI crystals might have played a certain role in enhancing the 375 nm luminescence. This possibility arose when in the continuation of this work<sup>(30)</sup> the 375 nm band was observed to be much less intensive and the 295 nm band became a dominant one in the pure NaI crystals. Both the very weak 325 nm and a broad and dominant 430 nm bands are attributed to the impurity electroluminescence mechanism. It is well known that small amounts of purposely added "impurities" like Sb, Cu, As, and Mn to ZnS have an appreciable effect on both luminescence and electroluminescence. Onaka et al<sup>(33)</sup> widely studied the mechanisms of electrophotoluminescence for NaCl(Ag). They suggested the possibility that due to the imperfec-

tions (impurities) in the crystal lattice a strong localized field in the order of  $10^5$  volts/cm is provided by a potential barrier near the surface. The enhancement of luminescence in NaCl(Ag) by an applied electric field was attributed to the presence of such a barrier. Such an enhancement can be visualized in other alkali halide crystals containing some "impurities". We believe that trapping the hole at  $Tl^+$  in NaI(Tl) crystals is responsible for the electroluminescence bands observed in NaI(Tl).

The 295 nm band in pure NaI crystals is an intrinsic electroluminescence band and corresponds to the electroluminescence observed by Unger and Teegarden<sup>(10)</sup> in pure KI. The electrons are injected into the conduction band by quantum mechanical tunnelling from the two electrodes on alternate half cycles of the AC field. These electrons are then accelerated by the field to the optical energies which enable them to ionize valence electrons through inelastic collisions<sup>(10)</sup>. The free holes and electrons produced in the above manner then undergo recombination via the  $V_k$  centers which are, according to Murray and Keller<sup>(35)</sup>, responsible for the intrinsic emission bands of the alkali halides. Hersh<sup>(36)</sup> and Murray and Keller<sup>(35)</sup> attribute this vacancy generation in a perfect crystal to the formation of an excited halogenic molecule  $X_2^{-*}$ . This excited molecule may dissociate into a normal halide ion and an unchanged atomic halogen X moving into an interstitial position and leaving behind a vacancy:  $X_2^{-**} \rightarrow X_{int} + X^- + e$ . Capture of an electron and motion of an interstitial

halogen atom ( $X_{int}$ ) results in formation of F, H, and V (halogen centers) which depends on the temperature.

As mentioned earlier the 295 nm band in pure NaI crystals was not a dominant band and was observed only in about 50 percent of the tests when higher voltages (1600 - 2500V) were applied across the crystal.

### 3. CONCLUSIONS

On the basis of experimental result and the discussion of experimental results the following conclusions were drawn:

- (1) The electroluminescence emission was observed in pure and thallium doped (0.2 mole % Tl) NaI single crystals when the 1000 - 2500 V AC voltage was applied across the crystals at liquid nitrogen temperature.
- (2) The electroluminescence bands were observed at 375 nm (3.30 ev) and 295 nm (4.20 ev) in pure NaI 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. All observed bands are identical to the luminescence bands reported earlier in NaI and NaI(Tl) crystals.
- (3) The 375 nm band in pure NaI and both the 325 nm and 430 nm bands in NaI(Tl) crystals are believed to be impurity electroluminescence bands. The 295 nm band in pure NaI is an intrinsic band due to the acceleration-collision mechanism.

- (4) The intensity of dominant bands at 375 nm and 430 nm in NaI and NaI(Tl) respectively is voltage dependent. The logarithm of electroluminescence intensity is proportional to the inverse square root of the applied voltage.
- (5) Roberts formula can be used for predictions of "ageing" of the 375 nm band in pure NaI.

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