ELECTROLUMINESCENCE IN SODIUM IODIDE SINGLE CRYSTALS

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To Amanda, My Wife

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ABSTRACT

Electroluminescence has been observed in single crystals of sodium iodide when excited by alternating fields of the order of 10^4 V/cm. The emission has been studied over the temperature range 100°K to 300°K and the mechanism is found to be more efficient at low temperatures. At low temperatures the electroluminescence has been studied as a function of voltage, frequency, crystal impurities and electrode materials and the effect of a D.C. field was investigated. The various theories of electroluminescence are discussed in relation to their applicability to the emission observed in the alkali halides. Of these mechanisms, that of excitation by impact ionization is shown to be compatible with the present results. In addition the effect of an electric field on the radioluminescence spectra of these crystals was studied. For the main emission bands a reduction in intensity is observed that is attributed to the electric field increasing the probability of electron trapping by increasing the distance the electron moves through the lattice. Finally the thermoluminescence of the various crystals was studied to determine the presence of trapping centres and their possible relation to the above processes.

CHAPTER I

INTRODUCTION

1-1 Preamble and Definitions

The phenomenon of luminescence can be defined as the emission of electromagnetic radiation in excess of thermal radiation. As pointed out by Guilbault (1967) luminescence was observed as early as 1565 by Monardes for the extract Lignium Nephiticiem in water. From such an early beginning the phenomenon of luminescence had to wait for the advent of quantum mechanics and electron theory of solids to provide bases for the understanding of luminescence. However, valuable work was performed in the latter half of the nineteenth century. Stokes (1852) showed that the colour of the emitted light was different from that of the incident light and that the emitted light had the longer wavelength. This is the well known Stokes' shift. Becquerel (1867) showed that the decay of emission after removal of the exciting radiation could be separated into two types, exponential and hyperbolic. These he attributed to different types of decay mechanisms, monomolecular and bimolecular.

As the study of luminescence has grown, many different modes of excitation have been discovered, all of which lead to the emission of light. The present work is concerned with the excitation of crystals by the application of an electric field, a process known as electroluminescence. The electroluminescence process will be discussed in relation to other types of luminescence. It is convenient to define various luminescence processes so that the following terms can be used unambiguously later in the text.

Electroluminescence -- light produced by application of an electric field. Photoluminescence -- light produced by the absorption of light. Radioluminescence -- light produced by high energy radiation or high energy particles. Electrophotoluminescence -- the effect of an electric field on the photoluminescence and radioluminescence processes. Thermoluminescence -- light produced by increasing the temperature of a crystal after it has been excited initially by another process. Fluorescence -- the emission due to a spontaneous transition after excitation. Phosphorescence -- the emission due to energy that is stored in the crystal and released when additional energy is provided by thermal means.

The luminescence of alkali halides, that is photoluminescence and radioluminescence, will be discussed in the next section to provide a background for the discussion of electroluminescence in alkali halides. Next the possible mechanisms involved in the electroluminescence process in solids will be considered and finally consideration will be given to the theories of thermoluminescence. The study of thermoluminescence provides information about energy storage within crystals, which often plays a vital role in the theories of electroluminescence.

1-2 Luminescence in Alkali Halide Crystals

Alkali halide crystals offer a unique medium for the study of many solid state phenomena because of their simple lattice and electronic structures. On account of this simplicity the alkali halides have been studied extensively and their basic properties are discussed thoroughly in all the standard solid state texts (e.g. Brown, 1967).

The optical properties of the alkali halides have been investigated in the study of colour centres. (Schulman and Compton, 1962; W. B. Fowler, 1968) This is the study of defects and impurities in alkali halides that produce absorption bands in the normally transparent region of the crystal, thus giving the crystal a characteristic colour. The most important of these centres is the F-centre which serves as a basis for the investigation of all other centres. Markham (1966) has recently reviewed the properties of F-centres in crystals.

Strong luminescence is observed in alkali halides in two cases. At low temperatures a luminescence is observed in pure crystals that is characteristic of the crystal lattice and is known as intrinsic luminescence. Second, crystals doped with various impurities produce luminescence characteristic of the impurity centres. These two forms of luminescence will now be discussed and special attention will be given to sodium iodide.

When pure alkali halide crystals are excited by light absorbed in the exciton and band-to-band transitions region at low temperatures then a strong luminescent emission is observed that is characteristic of the pure crystal (Teegarden, 1957; Van Sciver, 1960). The basic observations of intrinsic luminescence were made on the alkali iodides since the emission from these crystals is visible at liquid nitrogen temperatures. Intrinsic emission has been observed in other alkali halides at liquid helium temperatures (Kabler, 1964; Ramamurti and Teegarden, 1966; Kabler and Patterson, 1967) where the radiative efficiencies are high.

The experiments of Weeks (1958), Teegarden and Weeks (1959) and Edgerton (1962) indicated that the intrinsic bands in KI and RbI were due to the recombination of an electron with a trapped hole. They showed that electrons that were released from F-centres produced the same intrinsic emission as observed when exciting in the exciton or band-to-band region. The experiments of Kabler (1964) and Murray and Keller (1965) using polarized light techniques identified the nature of the trapped hole as a V_K centre. The V_K centre was identified by Castner and Kanzig (1957) as two halogen ions, one of which has lost an electron, covalently bonded together. This constitutes a halogen molecule ion X_2^-, where X refers to any halogen, and these centres are oriented randomly among the $\langle 110 \rangle$ directions of the crystal. The optical properties of these centres were investigated by Delbecq et al. (1958), Hersch (1959) and Delbecq et al. (1961), who showed that it was possible to selectively orient these centres along certain ⟨110⟩ directions. This technique allowed Kabler (1964) and Murray and Keller (1965) to show that electrons, recombining at oriented V_K centres emitted light that was polarized with respect to the axis of the V_K centre. A tabulation of the polarizations of the intrinsic emissions as either parallel to the direction of the axis of the V_K centre (σ polarized) or perpendicular to this axis (π polarized) is given by Knox and Teegarden (1968).

Thus the intrinsic emission in alkali halides has been identified as due to an electron trapped at a V_K centre returning to the ground state. Using the nomenclature of Wall (1968) we will designate the centre formed by an electron trapped at a V_K centre as a V_{Ke} centre. As soon as this centre returns to the ground state, radiatively with the emission of intrinsic light, or non-radiatively, then the two halogen ions relax to become part of the normal crystal lattice. Thus the term V_{Ke} centre refers only to the excited state and the ground state immediately after the radiative transition.

Theoretically the V_{Ke} centre has been considered by analogy to an X_2^{--} molecule (Kabler, 1964). Kabler and Patterson (1967) have indicated that the two bands normally observed in the intrinsic emission can be assigned to two states of this system, one of which is predominantly singlet while the other is triplet in character. Wood (1965, 1966) has considered theoretically the relationship between excitons and V_{Ke} centres while the experimental results of Ramamurti and Teegarden (1966) indicate that the lower energy emission band can be excited directly from an exciton in KI and RbI. However Teegarden (1966) indicates that V_{Ke} centres are formed more easily from free electrons and holes than by excitons.

In pure sodium iodide the investigations of Van Sciver and Hofstadter (1955) and Van Sciver (1960) showed that the intrinsic luminescence consists of a single band at 295 nm. Murray and Keller (1967) showed that this band was due to the recombination of electrons at a V_K centre and that it was polarized. This was characterised as a transition from the triplet excited state by Kabler and Patterson (1967). Murray and Keller (1967) found that the luminescence intensity was a maximum at 70^oK, decreased 20% on cooling to 7^oK and decreased by a factor of 11 when the temperature was increased from 70^oK to 273^oK. This decrease they attribute to a decrease in luminescence efficiency that is described by a function of the form

$$\eta = \frac{p}{p+s\ \exp(-E/kT)} \qquad (1.1)$$

where p is the radiative-transition probability, s is a frequency factor and E is the thermal activation energy necessary to allow nonradiative decay. p is assumed to be independent of the temperature and E = 0.06 eV provided a fit to the experimental data.

Consideration will now be given to luminescence in the alkali halides containing impurities. Reviews of the various impurities studied have been given by Klick and Schulman (1957), McClure (1959a, b), Teegarden (1966) and Fowler (1968). Most work has been performed on two groups of heavy metal ions, those ions isoelectronic with Tl^+ and Ag^+, and the interpretation of their properties based on the work of Seitz (1938) for Tl^+ ions and Seitz (1951) for the Ag^+ ions. In the following, the discussion will be limited to the spectra of Tl^+ ions and certain other centres that contribute to the luminescence of sodium iodide.

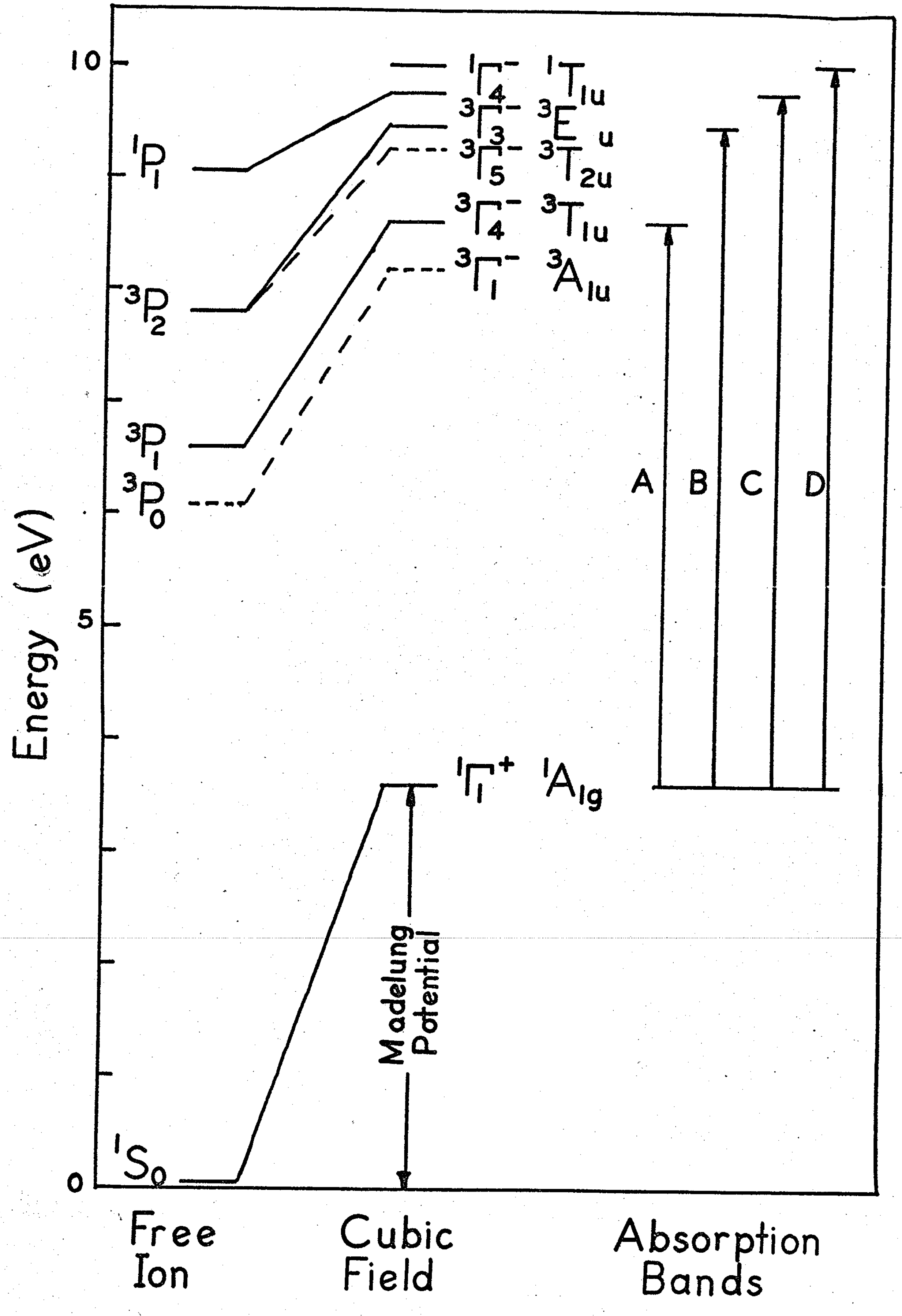
The interpretation of the new absorption and emission bands that result from the addition of impurities can be explained with reference to the possible transitions associated with the free ion. Seitz (1938) proposed a scheme that has provided the basis for the interpretation of the data associated with Tl^+ ions that have been substituted for an alkali ion in the alkali halides. The free thallous ion has a $^1S_0$ ground state ($6S^2$) and four low lying excited states, namely the $^3P_0$, $^3P_1$, $^3P_2$ and $^1P_1$ states, from a 6S6p configuration. When this ion is in a substitutional lattice site, all these states are raised in energy by the Madelung field. This is illustrated in Fig. 1-1 and the two point group symmetry notations of the lattice that are in common use are indicated. However, the standard practice of using the atomic symmetries will be followed.

In alkali halides doped with thallium four absorption bands are observed in general. These are labelled A, B, C and D bands in order of increasing energy. The work of Vaidanich (1966) showed the position of these bands to be at 292 nm, 248 nm, 234 nm and ~230 nm respectively in NaI. Transitions from $^1S_0$ to $^3P_1$ and to $^1P_1$ are allowed. Transitions to $^3P_2$ are forbidden in the free ion but Seitz suggested that interaction with lattice vibrations might make them weakly allowed. The strong temperature dependence of the B band (Yuster and Delbecq, 1953) is evidence in favour of this hypothesis. Thus, as illustrated in Fig. 1-1, the transitions $^1S_0 \rightarrow {}^3P_1$, $^1S_0 \rightarrow {}^3P_2$ and $^1S_0 \rightarrow {}^1P_1$ are responsible for the A, B, and C absorption bands respectively. The D band is difficult to fit into the Seitz model and is explained by Knox (1959) as excitation of a halogen-ion electron into a final state in which the electron is on the Tl^+ ion. This is analogous to the β band which is a similar excitation with an F-centre (Delbecq, Pringsheim and Yuster, 1951, 1952).

The emission spectra observed due to Tl^+ ions are more complicated than the absorption spectra. The work of Edgerton and Teegarden (1963, 1964) on KI(Tl) provided a coherent picture and their model is now referred to as the Seitz-Edgerton-

Figure 1-1

Energy levels of Tl^+ ion


Energy (eV)
10
5
0
$^1P_1$
$^3P_2$
$^3P_1$
$^3P_0$
$^1S_0$
$^1\Gamma_4^-$ $^1T_{1u}$
$^3\Gamma_3^-$ ^3E_u
$^3\Gamma_5^-$ $^3T_{2u}$
$^3\Gamma_4^-$ $^3T_{1u}$
$^3\Gamma_1^-$ $^3A_{1u}$
$^1\Gamma_1^+$ $^1A_{1g}$
Madelung Potential
A
B
C
D
Free Ion
Cubic Field
Absorption Bands

Teegarden (SET) model. In KI(Tl), they found five separate emission bands for the temperature range 12°K to 300°K. These bands were assigned to the transitions $^3P_0 \rightarrow {}^1S_0$, $^3P_1 \rightarrow {}^1S_0$, $^3P_2(^3T_{2u}) \rightarrow {}^1S_0$, $^3P_2(^3Eu) \rightarrow {}^1S_0$ (the $^3P_2$ level is assumed to be split by the crystal field as shown in Fig. 1-1) and $^1P_1 \rightarrow {}^1S_0$. The work of Illingworth (1964) and Trinkler and Plyavin (1965) indicated that the SET model needed to be altered and Fowler (1968) indicates a proposed model due to Edgerton in better agreement with the data. This modified the SET model by introducing a metastable level between the $^3P_0$ and $^3P_1$ levels and allowing the $^3P_1$ level to be split. Further data appear to be required to clarify the situation. However, as pointed out by Illingworth (1964), the transition $^3P_0 \rightarrow {}^1S_0$ is normally forbidden and yet this transition is included in the SET model. In fact the single emission band observed at room temperature is assigned to this transition. At low temperatures this band is excited strongly by absorption in the D band. Consequently Illingworth (1964) suggests that this may be associated with a charge-transfer transition that is analogous to that proposed to explain the D absorption band. Experimental evidence in favour of this explanation has been found by Hadley et al. (1966) in KI(Tl) and by Delbecq et al. (1966) in KCl(Tl).

The work of Hadley et al. (1966) also gives an indication of the possible processes that produce radioluminescence in thallium doped alkali halides. It seems likely that electrons and holes are generated by the ionizing radiation and these must somehow recombine at a thallium centre. They assume that most holes are produced as V_K centres which can normally move around freely above a certain temperature. ($58^\circ K$ in NaI according to Murray and Keller (1967)) These holes are then trapped at a thallium centre as indicated by the process

$$I_2^- + Tl^+ \rightarrow 2I^- + Tl^{++} \qquad (1.2)$$

Kaufman and Hadley (1967) indicate that this process is extremely efficient. An electron then recombines at the Tl^{++} centre producing an excited Tl^+ ion which then emits its characteristic radiation.

$$e^- + Tl^{++} \rightarrow (Tl^+)^* \rightarrow Tl^+ + h\nu \qquad (1.3)$$

This process can proceed in the reverse order

$$e^- + Tl^+ \rightarrow Tl^0 \qquad (1.4)$$

$$I_2^- + Tl^0 \rightarrow 2I^- + (Tl^+)^* \rightarrow 2I^- + Tl^+ + h\nu \qquad (1.5)$$

The Tl^0 centre produced in process (1.4) is only stable below a certain temperature and thermal excitation can produce the reverse process

$$Tl^0 \rightarrow Tl^+ + e^- \qquad (1.6)$$

These electrons can then recombine via process (1.3). The intrinsic recombination process is also possible

$$e^- + I_2^- \rightarrow (V_{Ke})^* \rightarrow 2I^- + h\nu \qquad (1.7)$$

where the emitted light is characteristic of the pure lattice but this process is observed only for extremely low thallium concentrations. Normally only emission characteristic of the thallium centres is observed. Concerning the nature of the low energy emission band, associated with the transition $^3P_0 \rightarrow {}^1S_0$ in the SET model, Van Sciver (1966) has proposed that a loosely bound electron with the Tl^+ centre may behave like process (1.3). The ground state of the system Tl^{++} plus electron may be different from the normal Tl^+ system, resulting in a lower energy emission band. At present the exact nature of this transition is not understood.

Theoretical treatments of the absorption and emission spectra were made initially by Williams (1951, 1953). He used a semi-empirical method and computed configuration-coordinate curves. This provides a model for the interaction of the electrons with the lattice in terms of vibronic coupling with an effective mode coordinate. Interpretations based on this model have been presented by Dexter (1958) and Fowler and Dexter (1962, 1965). In Williams' model the single effective mode was chosen to be the "breathing mode" (Γ_1^+) having the full cubic symmetry of the point defect. The results obtained with this theory for KCl(Tl) compared favourably with experimental results, but serious objections to the theory have been raised (Knox and Dexter, 1956). Two major faults lie in the simple wavefunctions employed in the calculation and the fact that recent work (Henry and Slichter, 1968; Bimberg et al. 1969) has shown that other modes can be important in the broadening of absorption and emission bands. At present theoretical treatments of the F-centre absorption and emission bands are based on the method of moments, which was developed mainly by Henry et al. (1965). A recent calculation by Hübner (1969) for the F-centre in KBr indicates that three vibrational modes are necessary to fit the experimental data. Such calculations will probably be extended to include the Tl^+ centre but the problem of appropriate wavefunctions still remains.

In the case of Tl^+ ions in NaI, three emission bands are observed that are attributed to the thallium centre. These occur at 430 nm, 330 nm and 280 nm (Vaidanich, 1966) and can be explained qualitatively on the SET model as the transitions $^3P_0 \rightarrow {}^1S_0$ (or charge transfer), $^3P_1 \rightarrow {}^1S_0$ and $^3P_2 \rightarrow {}^1S_0$ respectively. At temperatures between 70°K and 300°K only the 430 nm emission is observed while all three are seen at 12°K. The crystals used in our investigations were heavily doped with thallium so that additional absorption and emission bands were observed and attributed to pairs of thallium ions known as dimer centres. These produce absorption bands on the lower energy side of the normal absorption bands and a single emission band is observed at 325 nm (Van Sciver, 1960). Recent work of Herb et al. (1968) indicates that the dimer centres are oriented along the <100> directions. This indicates that an iodine ion site lies between the two thallium ions but no evidence is presented as to what, if anything, occupies this site.

Sodium iodide crystals often contain other impurities that contribute to the absorption and emission spectra. Van Sciver (1960) observed an emission band at 375 nm that he attributed to excess iodine. Recent observations (Van Sciver and Fontana, 1968) suggest that the centre responsible for this might be associated with a cation vacancy but the exact centre configuration is still unknown. The work of Lyskovich and Chornii (1967) showed that the radioluminescence spectrum could include bands at 445 nm and 475 nm besides those already described. These bands they attribute to the inclusion of oxygen-containing impurities in the crystal lattice. No detailed study of these bands has been made but they have been observed by other workers (Teegarden, 1966) in pure sodium iodide crystals.

In conclusion it should be pointed out that NaI(Tl) is an extremely efficient scintillator both at room temperature and liquid nitrogen temperatures while pure NaI is an efficient scintillator at liquid nitrogen temperature. Consequently such crystals are extremely useful in the study of processes involving the production of electrons and holes in crystal. For this reason it is felt these are ideal crystals for the study of electroluminescence.

1-3 Electroluminescence

Application of an electric field to a solid produces a wide range of phenomena. The present discussion will be limited to solids that are classed as insulators and semiconductors and to effects related to the production of light by the solids other than producing incandescent emission.

The original observation of a field effect can be classified as electrophotoluminescence. Gudden and Pohl (1920) observed an enhancement of the phosphorescence of ZnS upon application of an electric field. This effect was shown to be due to the liberation of electrons from traps either by lowering the barrier or by tunnelling. A theoretical study of this effect has been given by Haering (1959). Quenching effects due to an electric field were observed by Déchêne (1935, 1938). The quenching mechanism is not as well understood as the Gudden-Pohl effect but recent work in the alkali halides by Denks and Leiman (1968) has suggested a possible explanation. This will be discussed in a later section.

The initial observation of electroluminescence in solids is attributed to Lossew (1923) in silicon carbide and Destriau (1936, 1937) in zinc sulphide. Since that time considerable time and effort has gone into perfecting electroluminescent systems. There exists a large amount of material on the subject and the reader is referred to reviews by Piper and Williams (1958), Henisch (1962), Ivey (1963) and Thornton (1967) for a complete survey of the work on electroluminescent materials. In the present discussion we will consider the possible mechanisms that can produce light by application of an electric field. This process can be divided into three separate steps.

First the crystal must be excited by the applied field to an energy state at least several electron volts above its ground state. Next this energy may have to be transported to a region where de-excitation can occur. Finally radiative de-excitation must occur. The basic emission processes in alkali halides have been discussed in the proceeding section and so no further comment will be made about the latter step.

The initial process of exciting the crystal can take place in several ways. Three basic processes will be considered.

(a) Minority carrier injection. An ordinary conduction state of a crystal, a free electron in the conduction band or a free hole in the valence band, is an excited state of the crystal and the energy required to produce this state is supplied by the electric field. Such a state is produced by the injection of minority carriers into a semiconductor.

(b) Field ionization of impurities or the valence band. The removal of an electron from the ground state of an impurity centre or from the valence band produces an excited state of the crystal. In this process the action of the field increases the probability that electron tunnelling will occur from the impurity centre or the valence band into the conduction band.

(c) Impact ionization. In this process electrons that are already in the conduction band are accelerated by the applied field to an energy that is high enough to excite or ionize impurity centres and the lattice by inelastic collisions. These inelastic collisions provide the excited states from which the emission is observed.

Minority carrier injection in a semiconductor may occur either near a surface which is in contact with an electrode or at a p-n junction. These types of junctions have been discussed extensively by Shockley (1950) and Henisch (1957). The light that is emitted due to this mechanism is observed for direct current flow, persisting as long as current flows, and the intensity of the emitted light is proportional to the current. It is important to note that this process occurs when the junction is forward biased. The current-voltage relation for a simple p-n junction was shown by Shockley (1950) to be

$$j = j_s \left[\exp(eV/kT) - 1 \right] \qquad (1.8)$$

where j is the current flowing, j_s the reverse saturation current and V is the voltage applied across the junction. The observed junction electroluminescence intensity obeys a similar relationship. The characteristic emission depends upon the semiconductor used and may be intrinsic or dependent upon impurities (extrinsic). The statistics of the recombination process were considered by Hall (1952) and Shockley and Read (1952), now known as Shockley-Read-Hall statistics. Gershenzon (1966) has recently reviewed the materials exhibiting electroluminescence at p-n junctions. The injection mechanism has recently acquired importance since carrier injection at a p-n junction can lead to the population inversion required for laser action. Initial observations of laser emission were made in GaAs by Hall et al. (1962), Nathan et al. (1962) and Quist et al. (1962).

Field ionization of impurities and the valence band was first considered by Zener (1934) in connection with dielectric breakdown. McAfee et al. (1951) and Franz (1952) modified Zener's calculation and showed that the probability that an electron will tunnel from the valence band to the conduction band in unit time is given by

$$P_b = \frac{ea}{h} E \exp\left[- \frac{\pi^2 (2m^*)^{\frac{1}{2}}}{2he} \frac{\Delta e_b^{3/2}}{E} \right] \qquad (1.9)$$

where a is the unit cell dimension, m* the effective mass of the electron, Δe_b the band gap and E the local electric field intensity. A similar relationship was derived for the probability of field ionizing an impurity by using the formula of Oppenheimer (1928) for field ionization of atomic hydrogen. Piper and Williams (1955) showed that the probability is

$$P_i = 17 \times 10^{12} \left(\frac{m^*}{m}\right)^{\frac{1}{2}} \left(\frac{E}{K}\right)^{\frac{1}{4}} \exp\left[- 7 \times 10^7 \frac{m^*}{m}{}^{\frac{1}{2}} \frac{\Delta e_i^{3/4}}{E}\right] (1.10)$$

where K is the dielectric constant, Δe_i is the energy in eV required to ionize the impurity and E is the field strength expressed in V/cm. The exponential factor in equation (1.9) is similar to that in equation (1.10) but the numerical factor is 4×10^7. A similar expression to equation (1.10) was obtained by Franz (1952) and Franz and Tewordt (1956) assuming a square-well potential model for the impurity. Piper and

Williams (1959) showed that in ZnS for these two processes to be effective, fields in excess of those which produce dielectric breakdown were required. They used the breakdown strength of alkali halides in lieu of that for ZnS and so the same conclusion is reached for the alkali halides as for ZnS, particularly since the band gap in alkali halides is larger than that in ZnS. (Note that Von Hippel (1937) measured the breakdown field of NaI to be 7.1 x 10^5 volts/cm at room temperature.) The above mechanism is expected to be effective only for impurities which have a state that is close to the conduction band. Field ionization of the excited state of F-centres in alkali halides has been reported by Lüty (1958) and Spinolo and Fowler (1965). The excited state of the F-centre normally lies 0.1 to 0.2 eV below the conduction band.

There exists two other mechanisms that can be classed as being due to field ionization. One is a suggestion of Piper and Williams (1955) that a sufficiently intense electric field may perturb the impurity states sufficiently to make it probable for the system to go into the excited state. In a rough calculation they showed that field strengths of the order of 10^8 V/cm were required, hence breakdown and other mechanisms would occur before this. Franz (1956) considered the possibility of electron tunnelling from a metal electrode into a crystal. He calculated that such a mechanism gave a current density of

$$J = K_1 \frac{E^2}{\Delta e} \exp\left[- K_2 m^{*\frac{1}{2}} \frac{\Delta e^{3/2}}{E}\right] \qquad (1.11)$$

where K_1 and K_2 are constants, Δe is the height of the potential barrier between the metal and the crystal and E is the applied field. Holes can also be introduced into the crystal by this mechanism (Fischer, 1966). This mechanism was proposed as a source of electrons by Piper and Williams (1955) and experiments on the electroluminescence properties of ZnS by Tyagi and Garlick (1966) favour this explanation.

The impact ionization process is complicated by the fact that four separate steps are involved:- (i) Electrons must be in the conduction band in order that they can be accelerated. (The mobility of holes in the valence band is usually considered to be too low to allow holes to be accelerated.) (ii) These electrons are then accelerated by the field. (iii) Inelastic collisions cause excitation or ionization of centres or the lattice. (iv) Recombination produces emission. The light intensity observed due to this process can be described by the equation (Curie, 1960)

$$B(E) = n(E).f(E).p.\eta \qquad (1.12)$$

where B(E) is the observed light intensity, E is the field strength, n(E) is the number of accelerated electrons, f(E) is the fraction of electrons with sufficient energy to excite a centre, p is the probability that the energy lost during an inelastic collision is transmitted to an emission centre and η is the luminescence efficiency of the excited centre. From such a relationship the dependence of the emission intensity on the applied field lies in the functions n(E) and f(E).

Electrons can be introduced into the conduction band by several mechanisms. They may be thermally released from traps, they can be field ionized from shallow traps or they can tunnel in from an electrode. The field dependence of the latter two effects was discussed in relation to the field ionization mechanism. The thermal release of electrons from traps may be aided by the application of an electric field. Such a field produces an effective lowering of the potential barrier, the process being known as the Schottky effect and was discussed by Frenkel (1938). Euwema and Smoluchowski (1964) made calculations for the Schottky effect and field ionization by tunnelling for the excited state of the F-centre in alkali halides. These calculations indicated that these effects are observable for trap depths less than 0.5 eV with fields below the breakdown field strength. Haering (1959) considered field ionization and found a maximum trap depth of 0.4 eV.

Once there is a supply of electrons in the conduction band these can then be accelerated by the field. This mechanism operates when the device is reverse biased in the sense of a normal semiconductor junction. A few carriers are accelerated in this reverse biased region and multiplication occurs due to impact ionization which is close to a breakdown mechanism. During this process there are three processes that cause the electrons to lose energy. Initially there are lattice and impurity scattering effects that can be thought of as the creation of phonons and finally there is the loss due to ionization of an impurity or the lattice by an inelastic collision. Consequently in order for this process to operate, the rate at which the electrons gain energy from the field must be greater than the rate of loss of energy due to the creation of phonons. Theoretically the electron distribution in energy must be determined together with the probability of ionization. The various theories of this process have been summarized by Baraff (1962). Basically two theories are included in that of Baraff (1962). At low fields a theory due to Shockley (1961) seems applicable and this predicts the probability of causing an ionizing collision to be

$$P_{ic} = \text{const} \exp\left[\frac{-\Delta e}{eE\bar{x}}\right] \qquad (1.13)$$

where Δe is the energy required for ionization, E is the applied field and $\bar{x}$ is the mean free path of the electrons. The intensity of light emitted is proportional to this expression. Baraff (1962) shows that this expression is valid if

$$eE\bar{x} \lesssim \hbar\omega \qquad (1.14)$$

where $\hbar\omega$ is the phonon energy created which is normally taken to be that of the longitudinal optical phonon energy. At high fields this expression is not valid and a theory developed by Wolff (1954) is followed. This predicts the probability of ionization to be

$$P_{ic} = \text{const} \exp\left[-\frac{K}{E^2}\right] \qquad (1.15)$$

where K is a constant and E the applied field. As pointed out by Thornton (1967) both theories, which are due to different electron distributions, are encompassed by the actual electron distribution.

The various mechanisms must now be considered with the possibility of explaining the electroluminescence process in alkali halides. Since the alkali halides cannot be classed as semiconductors and due to the small concentration of free carriers (Georgiobiani and Golubeva, 1962) it is possible to eliminate the minority carrier injection mechanism. Direct field ionization of the lattice and impurity centres requires fields greater than those required for breakdown and can also be eliminated. This leaves electron and hole tunnelling from electrodes and impact ionization as possible mechanisms.

For these mechanisms the dependence of the light intensity on the applied field can be written as

$$B(E) = K_1\ E^n \exp\left[-\frac{K_2}{E^m}\right] \qquad (1.16)$$

where K_1 and K_2 are constants, n is an index between 0 and 2 and m is an index which is equal to 1 or 2. In such a relation the exponential term dominates and it is usual to take n to be zero. However the most successful equation describing the relationship between the light intensity and the applied voltage V is

$$B(V) = K_1\ V^n \exp\left[-\frac{K_2}{V^{\frac{1}{2}}}\right] \qquad (1.17)$$

which was first proposed by Alfrey and Taylor (1955) and it will be referred to as the Alfrey-Taylor relation. Often the relationship due to Déstriau (1940, 1947)

$$B(V) = K_1 \, V^n \exp\left[- \frac{K}{V}\right] \qquad (1.18)$$

can be used over a limited voltage range. The results of Antonov-Romanovsky (1959) for ZnS powders indicated that equation (1.17) is valid at low voltages and equation (1.18) applies at high voltages in his experiments.

To explain the apparent discrepancy between the observed dependence of intensity on voltage, equation (1.17), and the theoretical relationships involving the applied field, equation (1.16), it is usual to postulate that some form of localized field enhancement occurs. This means that most of the voltage drops across a small region of the crystal while the remainder of the crystal experiences a reduced field. The normal assumption is that a high field region exists at the surface and is known as a Schottky or Mott-Schottky barrier. Henisch (1957) discusses the various properties of Mott-Schottky barriers. In such a barrier region both the field and the thickness are proportional to the square root of the applied voltage which makes equation (1.16) compatible with equations (1.17) and (1.18). If equation (1.17) is obeyed for an electroluminescent system it is still difficult to decide which is the controlling mechanism giving such a relation. Usually it is taken to imply an impact ionization mechanism but Tyagi and Garlick (1966) showed that this relation could apply to the number of electrons tunnelling in from an electrode, equation (1.11), through a Mott-Schottky barrier region.

Another possible explanation for the observation of the Alfrey-Taylor relation was given by Lehmann (1960). He showed that a superposition of many functions having the form of equation (1.18), but with different values of the constants involved, would produce the Alfrey-Taylor relation, equation (1.17). The work of Fischer (1962) showed that the emission in ZnS powders came from localized regions and the intensity from individual regions followed equation (1.18) while for the whole system the Alfrey-Taylor relation was observed.

Finally, in this section, consideration must be given to the materials used in studies of electroluminescence. Thornton (1967) lists materials in which electroluminescence has been observed. Attention has been focussed in two areas, namely electroluminescence due to p-n junctions (Gershenzon, 1966) and electroluminescence in II-VI compounds (Fisher, 1966). The latter study has also been divided into the study of powders suspended in dielectrics and single crystals. According to Thornton (1967) electroluminescence was observed in NaCl by Torbin (1960). The theoretical considerations of Georgobiani (1962) indicate that the most likely alkali halides in which electroluminescence should be observed were those with the largest amount of covalent bonding. A consideration of the tabulation of the bonding in alkali halides by Pauling (1960) shows that the alkali iodides possess the largest fractions of covalent bonding. This prediction was confirmed by the observation of electroluminescence in thin films of CsI(Tl) by Georgobiani and Golubeva (1962) and in single crystals of pure KI by Unger and Teegarden (1967). Onaka et al. (1967) have observed emission from NaCl(Ag) at 400^oK that they attribute to electroluminescent processes. The alkali halides are also interesting materials since a moving electron must be considered as a polaron. Electroluminescence may provide a means of testing the various polaron theories (Kuper and Whitefield, (1963)). Thus in order to further study electroluminescence in the alkali halides the present experiments were performed on single crystals of pure sodium iodide and thallium doped sodium iodide.

1-4 Thermoluminescence and Isothermal Decays

In the mechanisms responsible for electroluminescence the release of electrons and holes from various traps can be important. Consequently a knowledge of the existence and depth of these traps is often necessary. These measurements can be made by two methods. One method is to observe the emission that results when a crystal is warmed up from a low temperature where the crystal was excited so that all traps were populated. This is known as thermoluminescence and the peaks that are observed at various temperatures are known as "glow peaks".

Another method is to observe the decay constant of the phosphorescence, which is produced at a constant temperature after the excitation has been removed. The variation of this decay constant with temperature allows one to calculate the trap depths. These two processes are intimately linked and will be discussed together.

Both thermoluminescence and decay curves depend on the kinetics involved in transferring the charge from the trap to the recombination centre that produces the emission. If there is no retrapping once the charge has left the trap and it goes directly to the recombination centre then first-order kinetics determine the shapes of the glow curve and the decay curve. This is known as the monomolecular mechanism. For the case that involves retrapping then the situation is more complicated and the kinetics are usually referred to as second-order or bimolecular.

Consider an electron in a trap where a thermal activation energy Δe is required to liberate the electron. Δe is known as the trap depth and the probability of liberating the trapped electron in unit time is

$$P = s \exp\left[-\frac{\Delta e}{kT}\right] \qquad (1.19)$$

where s is a frequency factor. The mean lifetime τ of the electron in this trap is just the reciprocal of P. Now if every electron that is released from this trap goes to a recombination centre then the number of electrons decreases according to the equation

$$\frac{dn}{n} = - Pdt \tag{1.20}$$

which is a first-order rate equation where n is the number of electrons in the trap. This has the solution

$$n = n_0 \exp \left[- Pt \right] \tag{1.21}$$

where n_0 is the initial number of electrons trapped and t is the time. Now the luminescence intensity is equal to the negative of the rate of loss of electrons from the traps so that

$$I = - \frac{dn}{dt} = Pn = n_0 P \exp (-Pt) \tag{1.22}$$

This is normally written including the mean lifetime of the trap as

$$I = \frac{n_0}{\tau} \exp \left[- \frac{t}{\tau} \right] = I_0 \exp \left[- \frac{t}{\tau} \right] \tag{1.23}$$

where I_0 is the initial intensity. This is the decay observed at a constant temperature for the nomomolecular mechanism. If the temperature is varied at a rate $\beta = dT/dt$ then equation (1.20) can be rewritten as

$$\frac{dn}{n} = - \frac{P}{\beta} dT \tag{1.24}$$

and the number of electrons remaining in a trap at a temperature T is

$$n(T) = n_0 \exp \left[- \int_{T_0}^{T} \frac{s \exp(-u)}{\beta} dT \right] \tag{1.25}$$

where T_0 is the temperature at which the crystal was originally excited and $u = \Delta e/kT$. The emission intensity at a temperature T is then given by

$$I(T) = n(T)P = n_0 S \exp(-u) \exp\left[-\int_{T_0}^{T} \frac{s \exp(-u)}{\beta} \, dT\right] \quad (1.26)$$

This equation was first developed by Randall and Wilkins (1945). For a linear heating rate there is no explicit solution for the shape of the glow curve and various approximate solutions have been applied. The major problem is the evaluation of the frequency factor s since knowing s the activation energy can be determined from the temperature T* at which maximum emission occurs. This temperature can be deduced by requiring the intensity, as defined in equation (1.26), to be a maximum. Thus

$$T^{*2} \exp\left[-\frac{\Delta e}{kT^*}\right] = \frac{\Delta e \beta}{ks} \quad (1.27)$$

and a knowledge of s allows Δe to be calculated. A summary of the various approximations has been given by Nicholas and Woods (1964). A recent analysis by Kelly and Laubitz (1967) utilised the fact that explicit solutions could be obtained if the heating rate is proportional to the square of the absolute temperature. Numerical calculations of equation (1.26) have been made by Fleming (1968) using a computer and presented in tabular form using the notation of Kelly and Laubitz (1967).

A similar analysis can be performed for the case of second order kinetics. Here equation (1.20) becomes

$$\frac{dn}{n} = - Pndt \qquad (1.28)$$

since the probability of recombination is proportional to the number of available centres. This has a solution

$$n = \frac{n_0}{(1 + n_0 Pt)} \qquad (1.29)$$

and the decay intensity is

$$I = - \frac{dn}{dt} = Pn^2 = \frac{Pn_0{}^2}{(1 + n_0 Pt)^2} \qquad (1.30)$$

which is usually written as

$$I = \frac{I_0}{(1 + at)^2} \qquad (1.31)$$

where $I_0 = Pn_0{}^2$ and $a = Pn_0$. However, as shown by Curie (1960), this analysis is only correct if the probabilities of reaching a centre or an empty trap are equal. Otherwise the index in the denominator of equation (1.31) can be different from 2.

Glow curves can again be analysed with bimolecular kinetics assuming equal capture cross-sections for centres and traps as initially assumed by Garlick and Gibson (1948). The equation for the intensity as a function of temperature becomes

$$I(T) = \frac{n_0{}^2 \, s \, \exp(-u)}{n_t \left[1 + \frac{n_0}{n_t} \int_{T_0}^{T} \frac{s \, \exp(-u)}{\beta} \, dT \right]} \qquad (1.32)$$

where n_t is the total number of traps and n_0 is the number initially filled. The analysis of Kelly and Laubitz (1967) shows that the glow curve in the bimolecular case is symmetrical whereas the monomolecular case gives unsymmetrical curves. Also the expression for the temperature of the peak maximum is much more complicated. Kemmey et al. (1967) performed an interesting analysis of glow curves in which they performed a computer simulation of glow curve shapes. This allowed them to remove the restriction of only considering equal trapping probabilities. By altering the number of centres and the number of traps they could generate whole families of glow curves with the same activation energy Δe and frequency factor s. Their method seems particularly useful for well resolved glow curves once an initial estimate of the perameters has been made by another method. In another paper (Townsend et al., 1967) the same authors compare various methods on their data on thermoluminescence in LiF. They use an analysis due to Hoogenstraaten (1958) which requires the determination of the peak temperatures T* for various heating rates β. These are related by

$$\ln(T^{*2}/\beta) = \Delta e/kT^{*} + \text{constant} \tag{1.33}$$

and Δe can be determined. Another method is to consider the leading edge of the glow curve where the rate of loss of electrons from traps is slow. Then the integrals in equations (1.26) and (1.32) are approximately zero and the intensity is given by

$$I(T) \approx n_0 s \exp(-u) \tag{1.34}$$

Thus, as has been shown, the determination of the parameters relating to traps in phosphors can be complex. The measurement of iso-thermal decay curves is satisfactory if monomolecular recombination occurs and if the various time constants, i.e. activation energies, do not overlap too much. Decays are usually analysed in terms of monomolecular decays only. Glow curves can give all the parameters, provided the curves do not overlap too much. In our present experiments a rough knowledge of any traps that might relate to the electroluminescent process is required.

CHAPTER II

EXPERIMENTAL APPARATUS

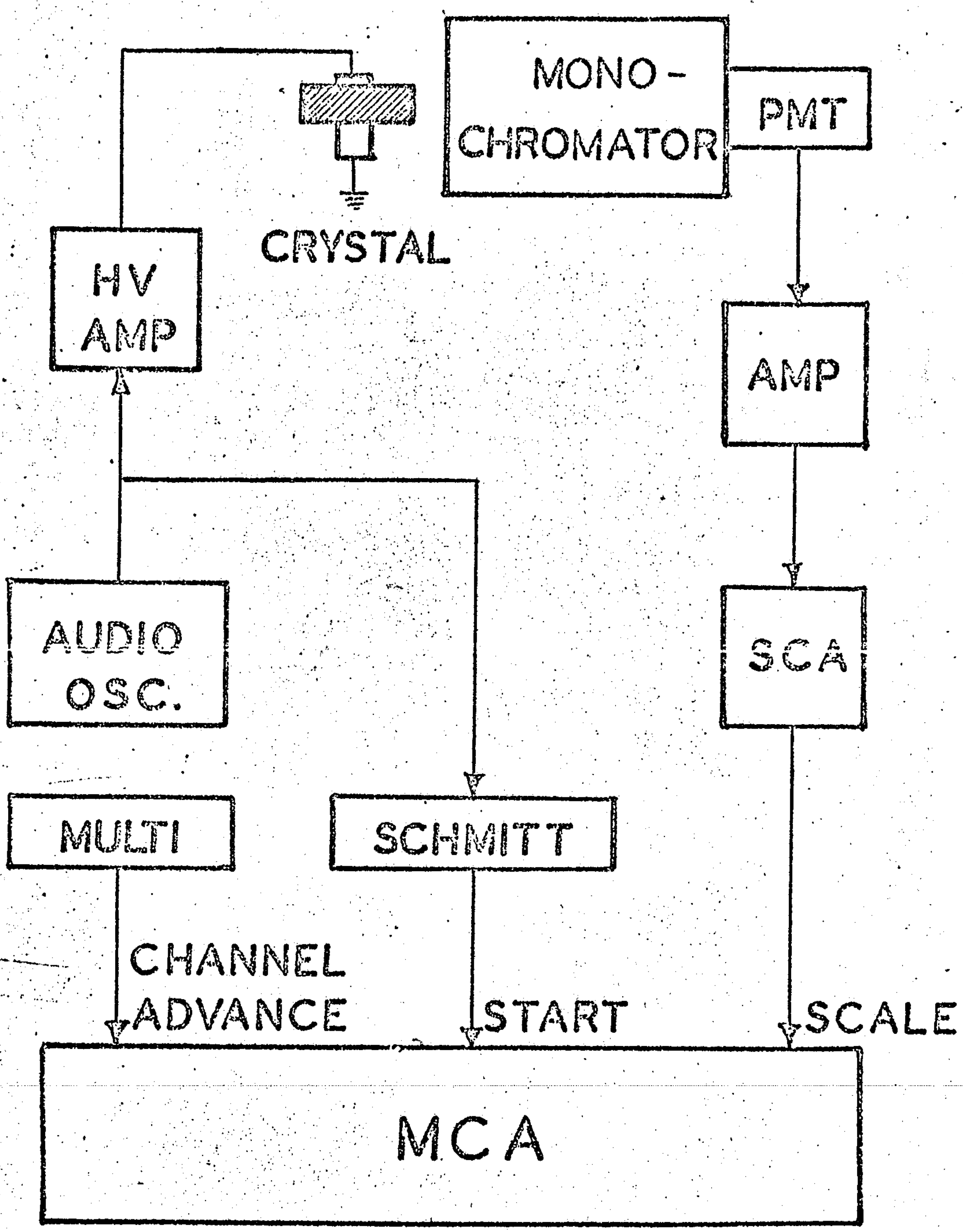
The basic apparatus used in the present experiments was essentially similar to that described by Palser (1969), with the addition of a new crystal holder and high voltage leads necessary to apply A.C. or D.C. fields to the crystals. This consisted of a liquid nitrogen cryostat constructed such that access to the cryostat cold finger was through a dry box since sodium iodide crystals are hygroscopic. The crystals were cleaved in the dry box and mounted into a crystal holder which was bolted into the cold finger of the cryostat. Optical access was provided by quartz windows on the remaining three sides of the cryostat.

A schematic representation of the apparatus including the associated electronics, isshown in Fig. 2-1. A high voltage electric field was applied across the crystal which was mounted in the liquid nitrogen cryostat (not shown). The ground electrical contact provided a thermal contact between the crystal and the cryostat. A thermocouple mounted on this ground electrode was used to measure the crystal temperature. The high voltage field was supplied either by a D.C. high voltage power supply via a reversing switch (not shown) or from a variable frequency audio oscillator. The output from this oscillator was current amplified by a push-pull transistor

Figure 2-1

Schematic Diagram of the Apparatus

Fig 2-1


MONO-CHROMATOR
PMT
CRYSTAL
HV AMP
AMP
AUDIO OSC.
SCA
MULTI
SCHMITT
CHANNEL ADVANCE
START
SCALE
MCA

amplifier and then voltage amplified by a step-up transformer. This is shown in Fig. 2-1 as the high voltage amplifier. Normally this system was operated on a sinusoidal waveform and a measurement of the high voltage waveform indicated approximately 5% harmonic content. The oscillator would also generate a square wave but the high voltage waveform was distorted considerably. A typical alternating voltage required to observe electroluminescence was several kilovolts applied across crystals 0.1 to 0.2 cm thick. Fields of this order could be supplied in the frequency range 50 to 2000 Hz by this equipment.

The measurement of this alternating voltage proved to be quite a problem. Since the emitted intensity is so strongly dependent upon the applied field it is necessary to control the field to within ±0.1%. Another problem was providing a voltage measurement that was independent of the frequency. Both these problems were solved by construction of a diode-clamp circuit together with a rectifier circuit. This gave a direct voltage that was equal to the peak to peak voltage. Also this circuit proved to be independent of the frequency over the range of frequencies used. The use of a digital voltmeter to measure this voltage provided the required precision.

The light emitted from the crystals was observed through a Bausch and Lomb 500 mm monochromator and detected by an EMI 6256 photomultiplier tube. The photomultiplier tube was normally operated with its cathode at -2000 V, which was supplied by a Keithley Model 242 high voltage supply. The photomultiplier was operated as a photon counter and the output pulses were amplified by a linear amplifier (Sturrup Model 101). A single channel analyser (SCA) (Sturrup Model 501) was then used to select only the pulses due to a single photoelectron emitted from the photocathode. This effectively removed background events due to thermal emission from the dynodes and high energy cosmic ray events in the photocathode. The pulses from the SCA were then counted in a multichannel analyser (MCA) (Victoreen Model ST400M) operating in the multichannel scaling mode. The data collected in this way were normally punched onto paper tape (Tally Model 420) for later computer processing. An interface unit was constructed of DEC modules (Digital Equipment of Canada Ltd.) which performed a parallel to serial conversion between the MCA and the punch unit. Additional outputs were provided by a Hewlett Packard parallel printer (Model 562A) or an analogue output that drove a strip chart recorder (Leeds and Northrop Speedomax G).

In order to measure the emission spectra of the crystals the monochromator was scanned over the wavelength range of interest by a synchronous motor. The control system was provided by a system of microswitches, two of which were limit switches for the scanning motor each one causing the motor to reverse its direction. Two other microswitches were set to mark the wavelength range required and these controlled a logic system, again built from DEC modules. A start signal was manually given to the MCA at the start of a scan and at the start of the required wavelength range the microswitch started a clock in the logic system. The pulses from this clock were used to channel advance the MCA and their frequency was chosen to provide either 100 or 200 channels over the region of interest before the final microswitch put the system into the readout mode. In this system the effective band pass of the spectrum is determined by the monochromator slits and the wavelength range covered in a single channel i.e. the time between clock pulses multiplied by the scanning speed. The data from the MCA were corrected for the response function of the monochromator-photomultiplier system as described by Palser (1969). (The author is indebted to Dr. R. Palser for supplying the correction data and programs.) The data were normally presented on a linear wavelength scale after correction but provision was made to present the data on a linear energy scale. In this latter case, a computer program developed by Putnam et al. (1965) was used to fit the emission peaks with Gaussians (Palser, 1965).

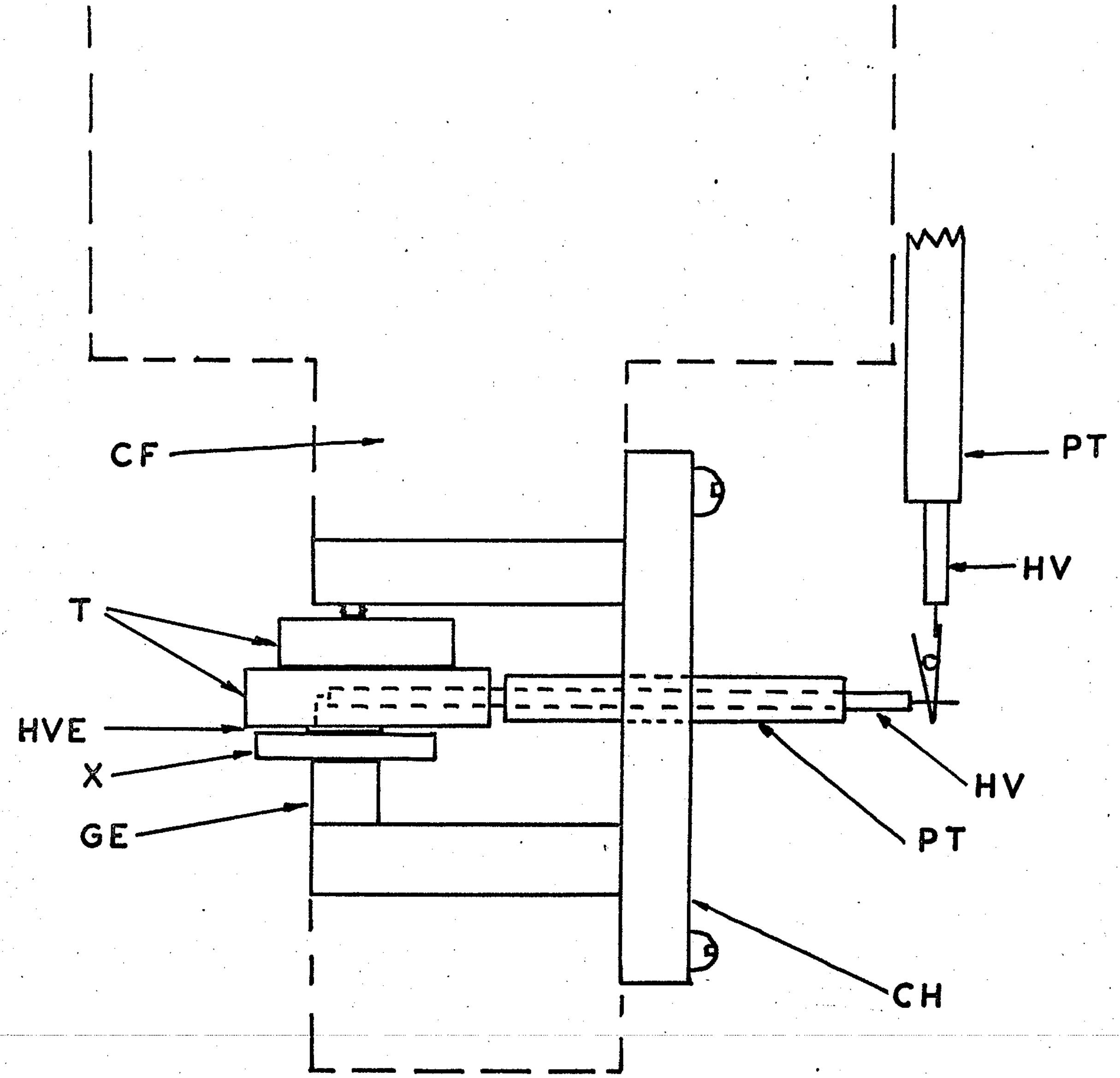
Data were collected in the MCA for other experimental configurations. In the study of isothermal decay curves from various crystals the monochromator was set at a particular wavelength and the intensity of the emission after removal of the excitation was studied by channel advancing the MCA with pulses derived by scaling down the 60 Hz mains frequency. The same arrangement was used to collect the glow curve data. An important experiment was the study of the intensity of the emission from the crystal as a function of the phase of the applied alternating voltage. The electronics involved are shown schematically in Fig. 2-1. In this the alternating signal from the audio oscillator was fed into a Schmitt trigger which provided an output pulse as the voltage crossed a certain value, usually adjusted to be close to the zero cross. This pulse went to the start gate of the analyser and started it scaling in channel 1. A multivibrator operating at a frequency that was a multiple (usually 30) of the applied voltage frequency provided the channel advance pulses. Thus photons detected by the photomultiplier were scaled in a channel that was related to phase of the applied voltage at the time the photons were emitted. A similar method to this has been used to study optical and radio emissions from pulsars (Taubman, 1969). Calibration of this system was accomplished by scaling the multivibrator output and using the Schmitt output pulse to channel advance the MCA. A fine adjustment on the timing circuit of the multivibrator allowed an accurate setting of the number of channels for each voltage cycle. A final calibration was to display the high voltage signal and the start pulses simultaneously on a double-beam oscilloscope to determine the channels equivalent to the voltage zero crosses and the voltage peaks. This was particularly important due to the slight distortion in the applied waveform.

Special care was taken in an effort to try and reduce the likelihood of an electric discharge within the cryostat. The cryostat was evacuated with an oil diffusion pump with its own liquid nitrogen cold trap. This maintained the system at a pressure of approximately 10^{-5} mm of mercury. The high voltage lead was taken into the cryostat through a Kovar seal and it was found necessary to use a high voltage insulated lead within a polyethylene tube in the sections where the lead was likely to come close to the metal cryostat. If such insulation was not used application of a high voltage alternating field resulted in corona discharge between the leads and the metal cryostat. This was observed by the detection of Trichel pulses with an oscilloscope (Trichel, 1939). These pulses result from corona discharge through insulators and are discussed by Loeb (1965). Similar precautions were taken in the construction of the crystal holder as indicated in Fig. 2-2. The high voltage lead was encased in polyethylene tubing where it entered the brass crystal holder. This lead was then taken into a block of teflon. The wire protruded from this teflon block and was soldered onto a thin piece of brass 0.5 cm square. This was usually coated with indium, which was just pressed on, and served as the high voltage electrode. A cube of brass 0.5 cm in length connected permanently to the crystal holder served as the ground electrode. Again a thin layer of indium was usually

Figure 2-2

Crystal Holder

CF - cold finger
T - teflon blocks
HVE - high voltage electrode
X - crystal
GE - ground electrode
CH - brass crystal holder
HV - high voltage insulated wire
PT - polyethylene tubing


CF
T
HVE
X
GE
PT
HV
HV
PT
CH

pressed onto this electrode. Crystals used in the investigation were usually 1.0 cm square and between 0.1 cm and 0.2 cm thick. With this electrode configuration it was felt that there would be no possibility of an electric discharge around the crystal. The complete system was checked to ensure that no Trichel pulses could be detected and electroluminescence was observed in the absence of such pulses.

CHAPTER III

EXPERIMENTAL RESULTS

3-1 Electroluminescence

The crystals used in this investigation were nominally pure sodium iodide and sodium iodide containing 0.1 mole % thallium obtained from the Harshaw Chemical Company. Crystals of nominally pure sodium iodide grown in this laboratory were also used. As described, the crystals were placed between two plane, parallel electrodes that were normally made of indium. Application of an alternating electric field of approximately 10^4 V/cm at a temperature of 100°K produced the emission of light characteristic of the intrinsic crystal lattice and also light characteristic of impurities in the crystals. In the following discussion the results refer in general to excitation by an alternating field of frequency 500 Hz and at a temperature of approximately 100°K, except for the results concerning the variation of these parameters.

Since there is always a practical interest in materials exhibiting electroluminescence, it was of interest to visually observe the emission. At a voltage that was approximately four times that needed to initially detect emission with a photomultiplier tube it was possible to see the emission from the crystal. The intensity was such that it was not necessary to 'dark adapt' the eye. However the intensity of this level of emission tended to be erratic. A photograph of a NaI(Tl) crystal during such a visual experiment is shown in Plate 1(a) while the crystal and crystal holder are shown illuminated from the side in Plate 1(b). This view of the crystal is through the cryostat window normally used by the monochromator. The emission is observed through the side of the crystal but, as shown in Plate 1(a), the light leaves the crystal through the edges and surface imperfections. This effect is probably because the light tends to be internally reflected from smooth surfaces. Such an effect makes it impossible to decide whether the light comes from a particular region within the crystal. Unger and Teegarden (1967) claim that in pure KI they observe that the light is emitted from regions close to the electrodes. Assuming that KI behaves similarly to NaI, it is felt that their results can be interpreted as the observation of light leaving the crystal at the edges.

Emission Spectra

The electroluminescent emission spectra from "pure" NaI can be classified into two types. Fig. 3-1 shows the emission spectrum of Type 1 NaI. This spectrum was taken at 100°K and shows emission bands at 295 nm, 375 nm, 440 nm and approximately 530 nm. Fig. 3-2 shows an emission spectrum from Type 2 NaI which consists of bands at 295 nm, 375 nm and approximately 430 nm. Both types of crystals were obtained from the Harshaw Chemical Company but in separate batches bought at different

Plate 1

(a) NaI(Tl) crystal excited by an alternating field at 100°K

(b) Crystal and crystal holder with external illumination

44a

Figure 3-1

Electroluminescence spectrum of Type 1 NaI at 100°K

(The spectrum has been corrected for instrument response and the intensity is in arbitrary units)

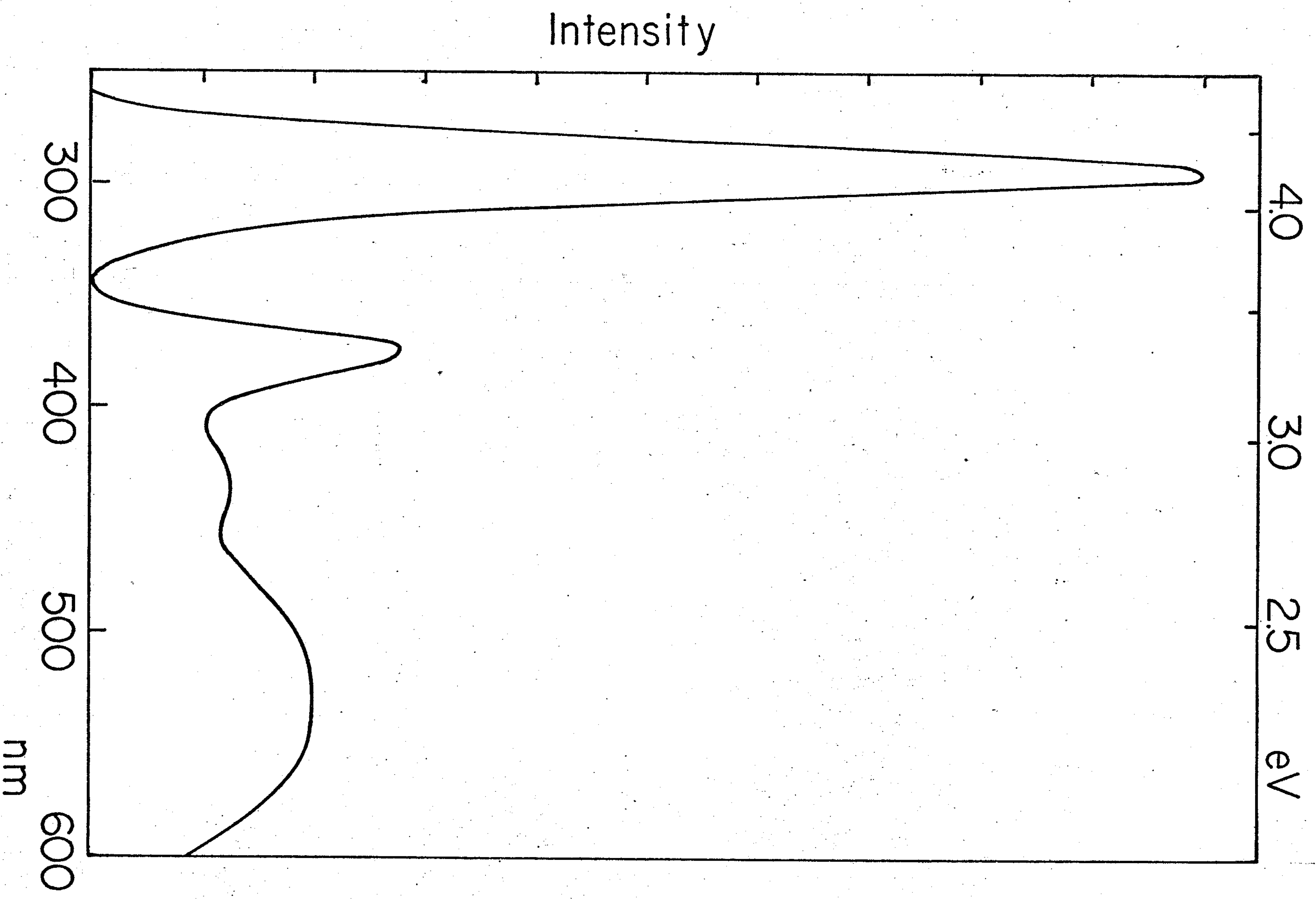
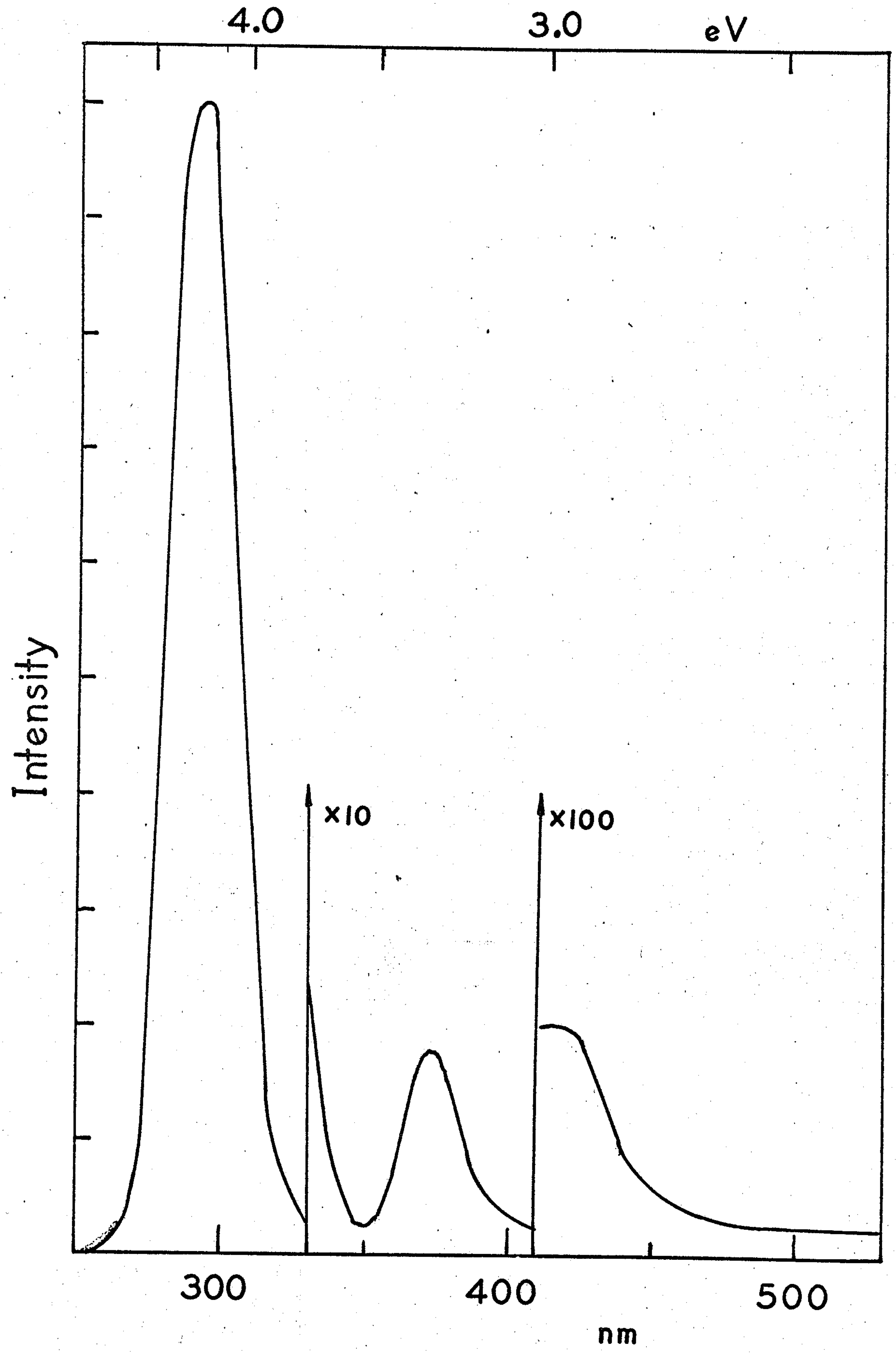

Intensity
300
400
500
600
nm
4.0
3.0
2.5
eV

Figure 3-2

Electroluminescence spectrum of Type 2 NaI at 100°K

(The spectrum has been corrected for instrument response and the intensity is in arbitrary units)

456



times. Crystals grown in our laboratory exhibited Type 1 emission spectra. The difference between these two types of pure NaI seemed to be that Type 2 contained more excess iodine which is responsible for the 375 nm emission band according to Van Sciver (1960). Scintillation spectra from two similar crystals of each type showed that in Type 2 crystals the 375 nm band was approximately 10 times as intense as in Type 1 crystals. It was also noted that the surface of Type 2 crystals remained clear while the Type 1 crystals quickly became cloudy on their outer surfaces even in the dry box. It is felt that such contamination of the crystals probably is responsible for the 530 nm emission band. The experiments of Lyskovich and Chornii (1965) show that heating pure NaI in air can produce emission bands at 445 nm and 475 nm. It is possible to identify the 530 nm band shown in Fig. 3-1 with the 475 nm band quoted by Lyskovich and Chornii (1965) since their results had not been corrected for the response of their detection system. Indeed, before our data were corrected this band appeared to lie at approximately 500 nm. Thus the 440 nm and 530 nm bands are attributed to oxygen-containing impurities in pure NaI from the work of Lyskovich and Chornii. The 375 nm band has been attributed to the presence of excess iodine by Van Sciver (1960) while the 295 nm band is the intrinsic luminescence of NaI which was shown by Murray and Keller (1967) to be due to recombination of electrons at V_K centres. Thus the electroluminescence process excites the same centres seen in photoluminescence and radioluminescence experiments.

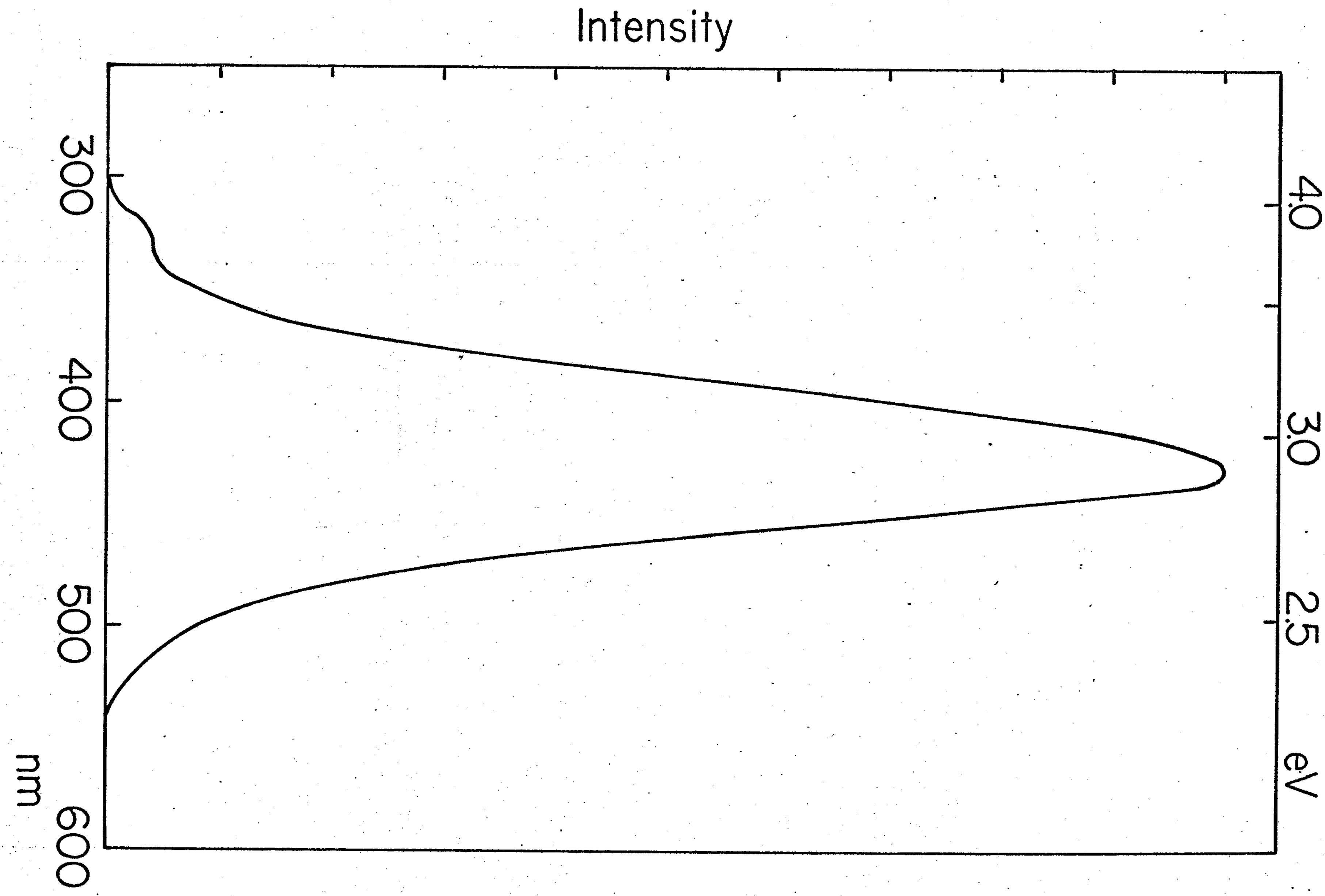
The emission spectrum of a NaI(Tl) crystal at 100°K for 500 Hz excitation is shown in Fig. 3-3. This shows the 430 nm band that is attributed to emission from thallium monomer centres and a small band at 325 nm that is due to emission from thallium dimer centres. This spectrum is identical to that observed with gamma-excitation and shows the same bands observed in photo-excitation, although in the latter case the relative intensity of the bands can be varied by selective excitation. Consequently the electroluminescence process does not provide a selective excitation but behaves exactly like gamma ray excitation.

Raising the temperature of all the crystals studied results in a decrease in the electroluminescent intensity. This effect appears to be two-fold. First there is the normal decrease in efficiency of luminescent centres due to the increase in temperature making non-radiative transitions from the excited state to the ground state more probable. The dependence of this effect was indicated in equation (1.1). This is particularly noticeable for the intrinsic emission of pure NaI whose intensity decreases by a factor of 11 in warming from 70°K to 273°K (Van Sciver and Bogart, 1958; Murray and Keller, 1967). As shown in Fig. 3-4, at room temperature the intrinsic emission is not detected in the electroluminescence spectrum. The long

Figure 3-3

Electroluminescence spectrum of NaI(Tl) at 100°K

(The spectrum has been corrected for instrument response and the intensity is in arbitrary units)

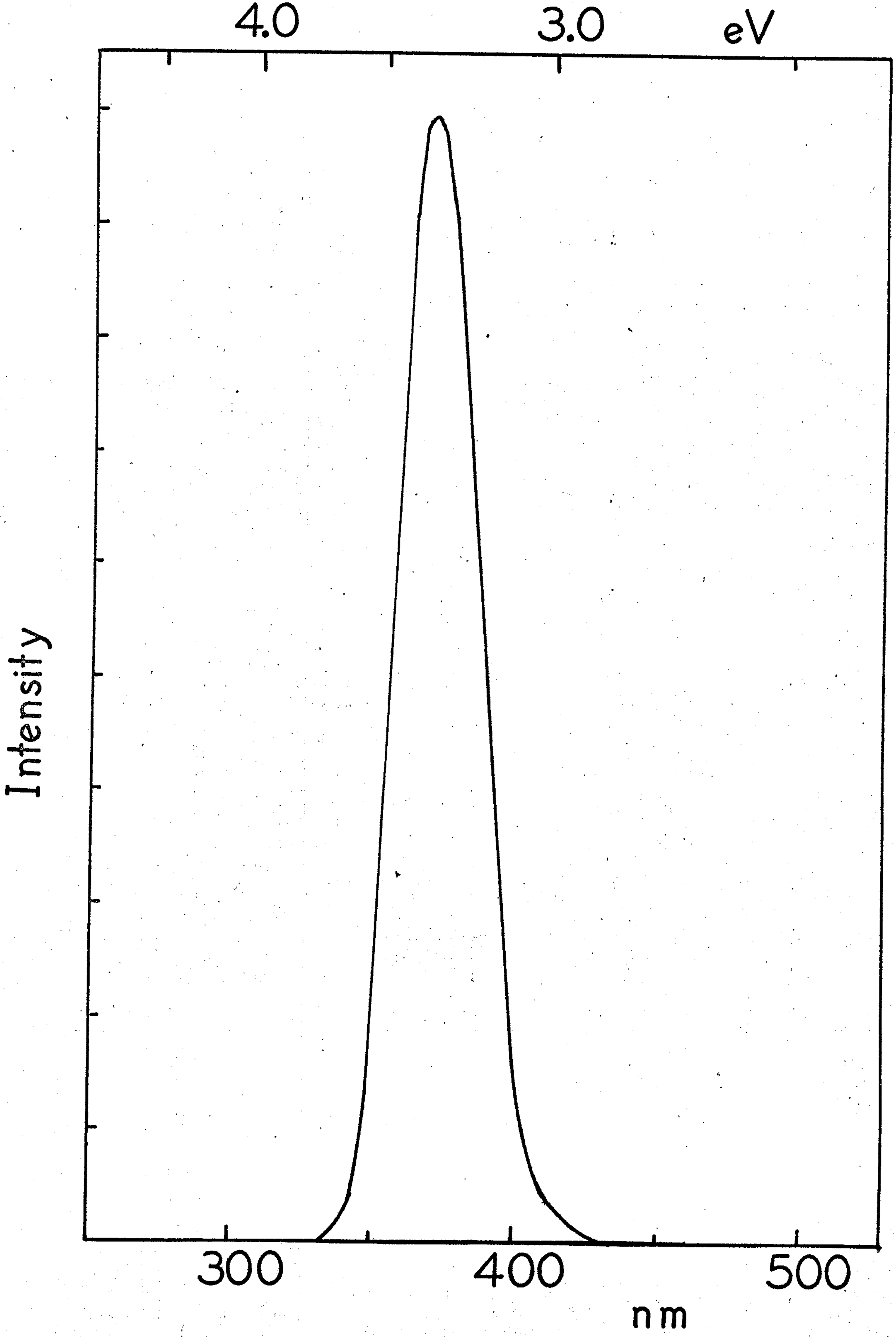


Intensity
300
400
500
600
nm
4.0
3.0
2.5
eV

Figure 3-4

Electroluminescence spectrum of NaI at room temperature

(The spectrum has been corrected for instrument response and the intensity is in arbitrary units)


4.0
3.0
eV
Intensity
300
400
500
nm

wavelength bands are also not visible and the spectrum consists only of the 375 nm band. For NaI(Tl) the intensity is again reduced at room temperature. Fig. 3-5 shows a room temperature electroluminescence spectrum in which both monomer and dimer emission bands are observed. As in the radioluminescence spectrum the dimer band is more prominent at room temperature than at 100°K.

In all these systems raising the temperature has the second effect of reducing the efficiency of the electroluminescence process. Indeed, at the voltages used to observe electroluminescence at 100°K, there is insufficient emission at room temperature and the voltage has to be increased considerably. This makes it difficult to obtain an accurate measure of the decrease in efficiency. Experiments were possible with only the 375 nm emission in pure NaI. For a constant voltage the intensity of this band decreased by a factor of approximately 80 from 100°K to 300°K, while a subsidiary experiment indicated that the normal reduction in intensity due to non-radiative transitions was by a factor of 3. This implies that the electroluminescence process exciting this emission is approximately 25 times more efficient at 100°K than at 300°K. A similar decrease in emission is observed for emission at 430 nm in NaI(Tl). Fig. 3-6 shows a plot of the logarithm of the intensity, corrected for the decrease in efficiency due to non-radiative transitions, against the reciprocal of the absolute

Figure 3-5

Electroluminescence spectrum of NaI(Tl) at room temperature

(The spectrum has been corrected for instrument response and the intensity is in arbitrary units)

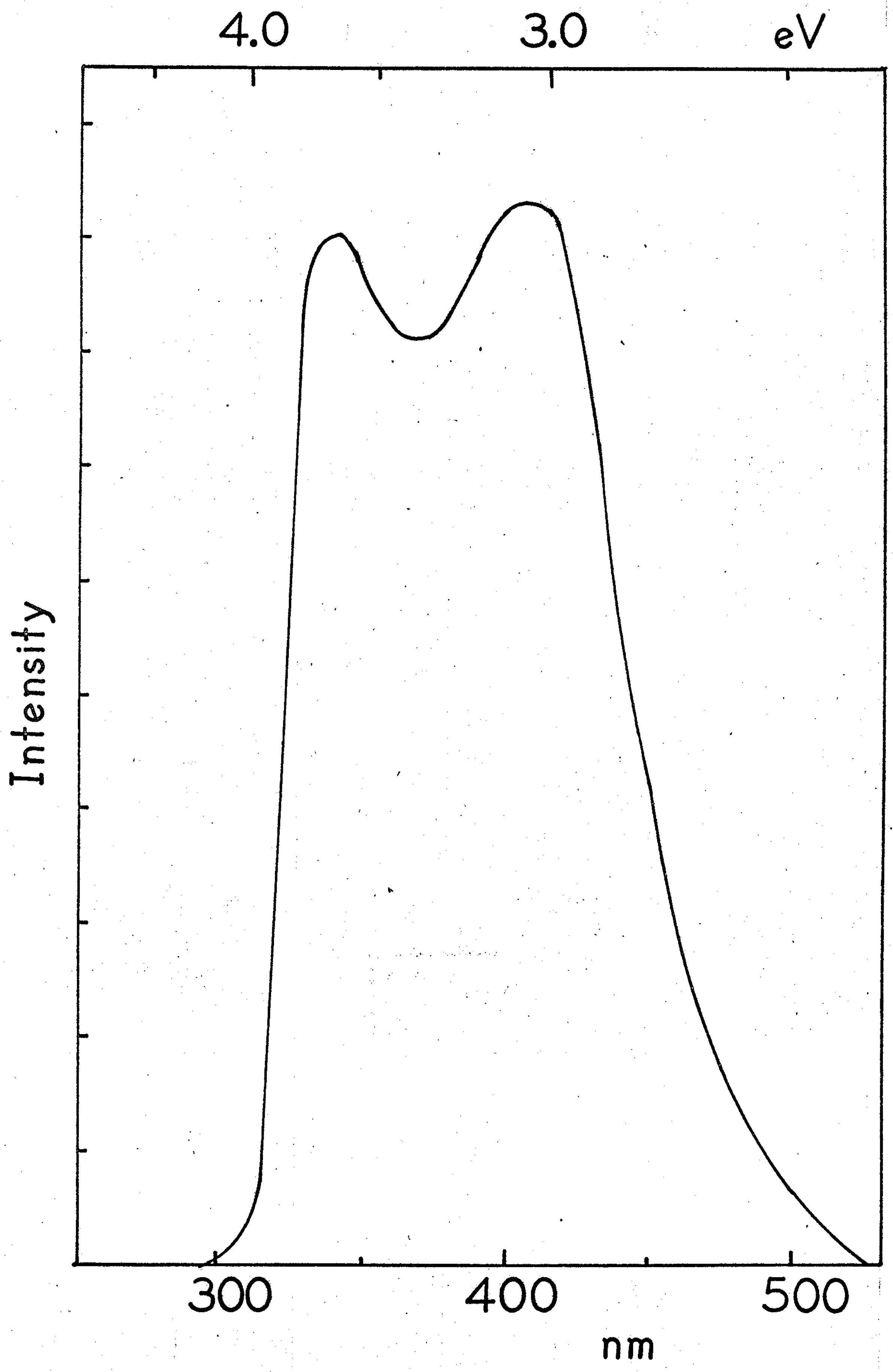
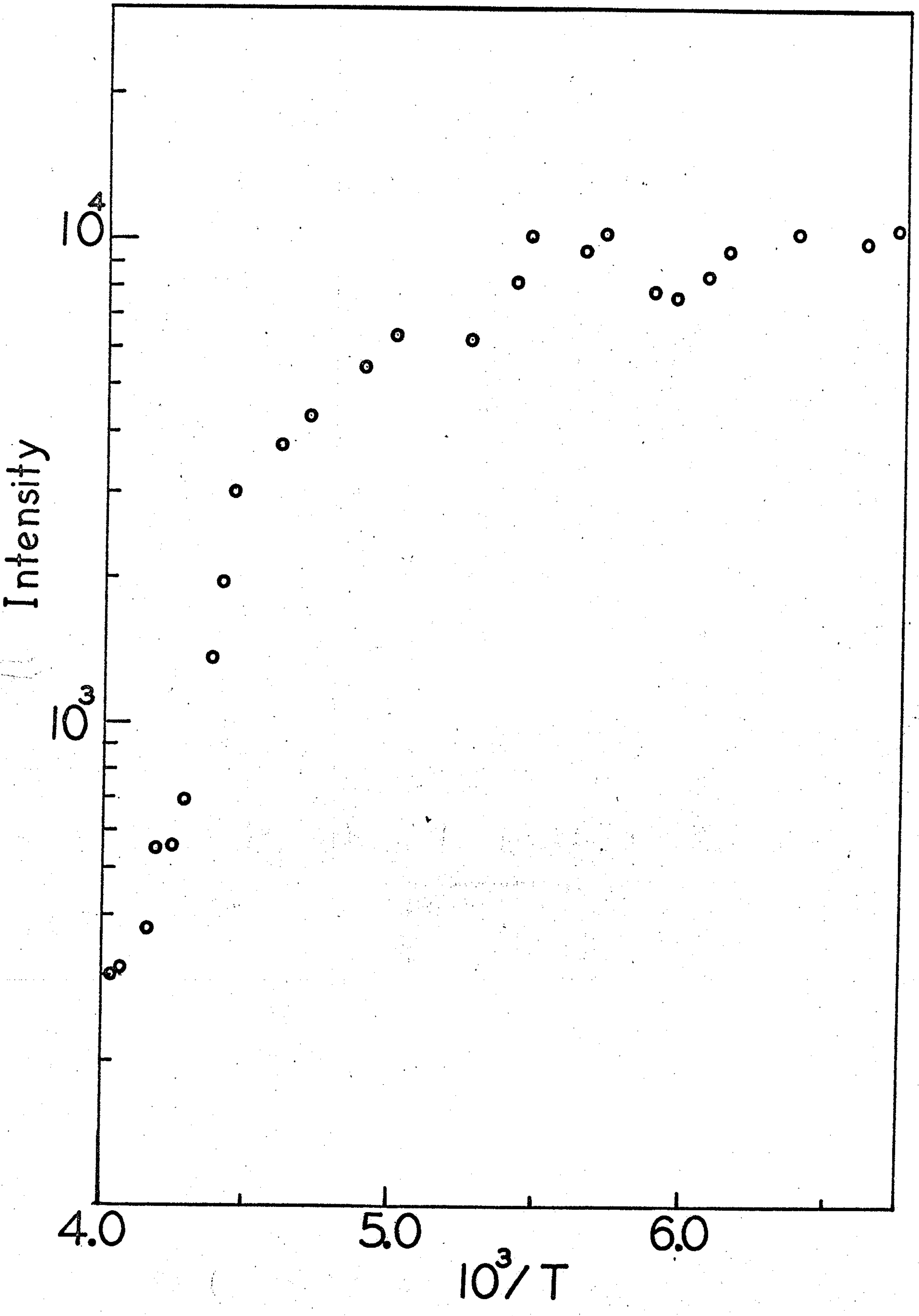

4.0
3.0
eV
Intensity
300
400
500
nm

Figure 3-6

Temperature variation of the electroluminescence of NaI(Tl) at 430 nm



Intensity
10^4
10^3
4.0
5.0
6.0
10^3/T

temperature. This shows that in NaI(Tl) the electroluminescent intensity of the 430 nm band decreases by a factor of approximately 20 between 150°K and 273°K and is approximately constant below 170°K. These data appear to obey an equation similar to equation (1.1) with an activation energy of 0.3 ± 0.1 eV. However this activation energy cannot be interpreted as a thermal quenching due to non-radiative processes in the centre since the data have been corrected for this effect. This quenching must affect the electroluminescence process itself.

Measurements of the mobility of electrons in alkali halides, at low fields, by Brown and Inchauspé (1961) and Ahrenkiel and Brown (1964) show a temperature dependence similar to that indicated in Fig. 3-6. The observed curves of the mobility were interpreted as containing three scattering mechanisms and the total mobility μ is given by

$$\frac{1}{\mu} = \frac{1}{\mu_{op}} + \frac{1}{\mu_{ac}} + \frac{1}{\mu_{i}} \qquad (3.1)$$

where μ_{op} represents optical mode scattering, μ_{ac} represents acoustic mode scattering and μ_i is from scattering at impurities. For optical mode scattering the temperature variation is given by

$$\mu_{op} = \text{constant}[\exp(\Theta/T)-1] \qquad (3.2)$$

where Θ is the Debye temperature which equals $\hbar\omega_{LO}/k$ where ω_{LO} is the longitudinal optical mode frequency. (See the book edited by Kuper and Whitfield (1963)) Acoustical mode scattering has a temperature dependence of (Seitz, 1948)

$$\mu_{ac} = \text{constant } T^{-3/2} \qquad (3.3)$$

while the mobility due to impurity scattering μ_i is constant and predominates at low temperatures. Now, provided the mobility is the controlling effect, these mechanisms may provide the temperature variation. Measurements by Woods, Brockhouse and Cowley (1963) on NaI gave $\omega_{LO} = 3.25 \times 10^{13}$ sec^{-1} which gives a Debye temperature of 248°K. Using this value in equation (3.2) shows the mobility varies by a factor of 2.2 over the temperature range 273°K to 170°K. The intensities of Fig. 3-6 could be fitted to a $T^{-3/2}$ dependence between 273°K and 170°K and are approximately constant at lower temperatures. Thus a possible explanation of the temperature dependence is that acoustical mode scattering governs the mobility of electrons between 273°K and 170°K while a constant mobility at lower temperature applies due to only impurity scattering.

A further possibility is that some electron or hole trap with thermal activation energy 0.35± 0.10 eV plays a vital role in the electroluminescence process. This trap must behave in such a way that while the trap is filled it assists the process. This is the reverse of the normal role of traps whereby they are required to release their charge carriers. A possible explanation is that this trap is necessary to form a barrier region near the surface and may indeed have the form of a surface state. In a later section the relative merits of these explanations will be discussed.

Phase Dependence

For alternating field excitation of electroluminescent materials it is always of interest to observe the phase dependence of the emitted light with respect to the applied voltage. This is usually referred to in the literature as the study of "brightness waves". The normal technique is to display both light signal and applied voltage on a double beam oscilloscope. As described previously the present results were obtained using a multichannel analyser that was controlled by the applied voltage.

Typical results for excitation with a 500 Hz sinusoidal waveform are shown in Fig. 3-7. Curve (a) represents the emission from the 295 nm band in pure NaI, curve (b) represents the emission from the 430 nm band in NaI(Tl) while curve (c) represents the 500 Hz applied voltage. These curves show that the emission from the crystal begins at the voltage cross-over point, rises rapidly to a peak before the voltage peak and then decays away through the remainder of the half cycle. This is then repeated over the other half-cycle. If a square wave is applied to the crystal through the high voltage amplifier considerable distortion of the waveform occurs. However, it is still possible to excite the crystal as is shown in Fig. 3-8. This illustrates very clearly that the light emission from

Figure 3-7

Phase dependence for sinusoidal applied fields

(a) Emission from 295 nm band in NaI

(b) Emission from 430 nm band in NaI(Tl)

(c) Applied voltage

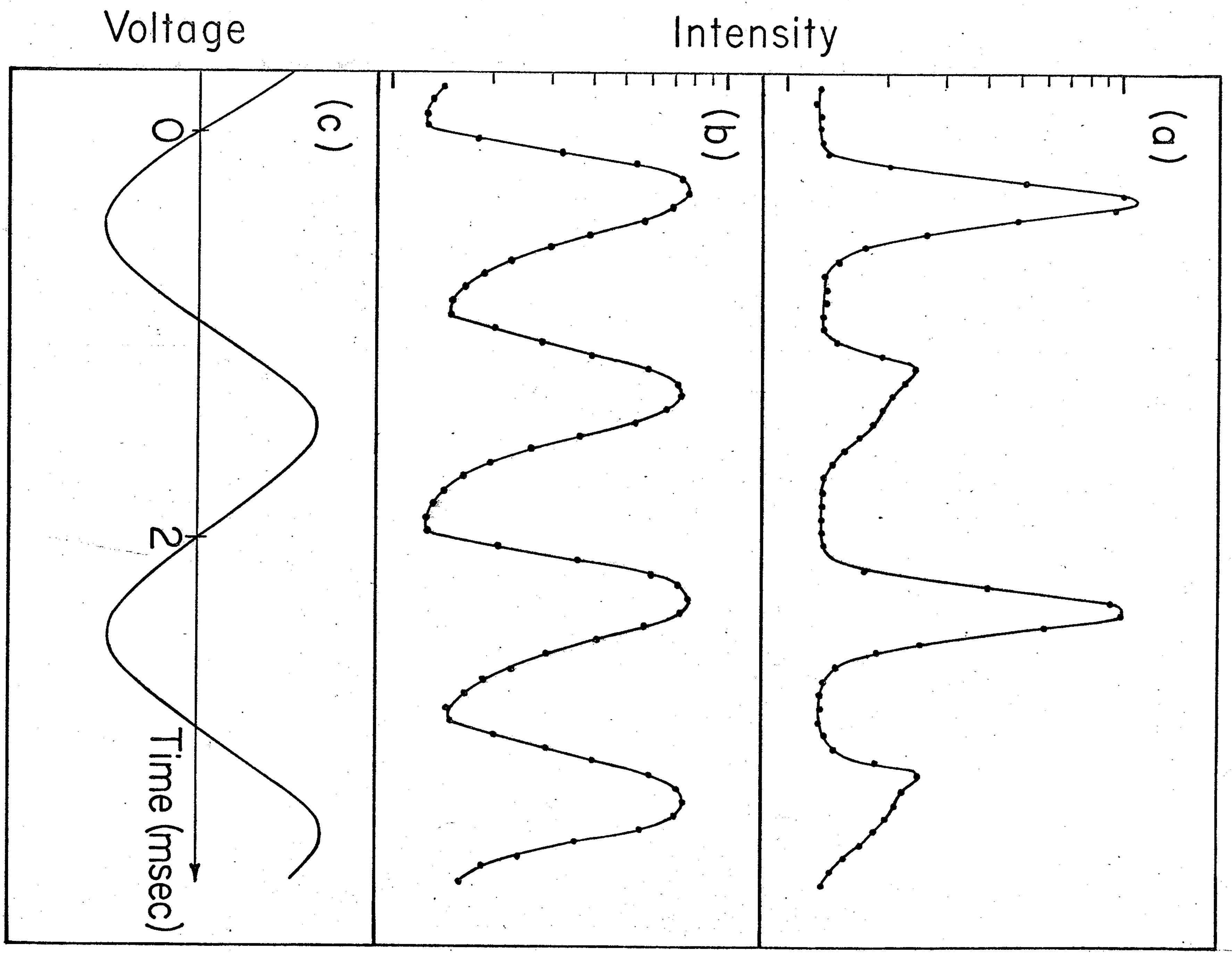
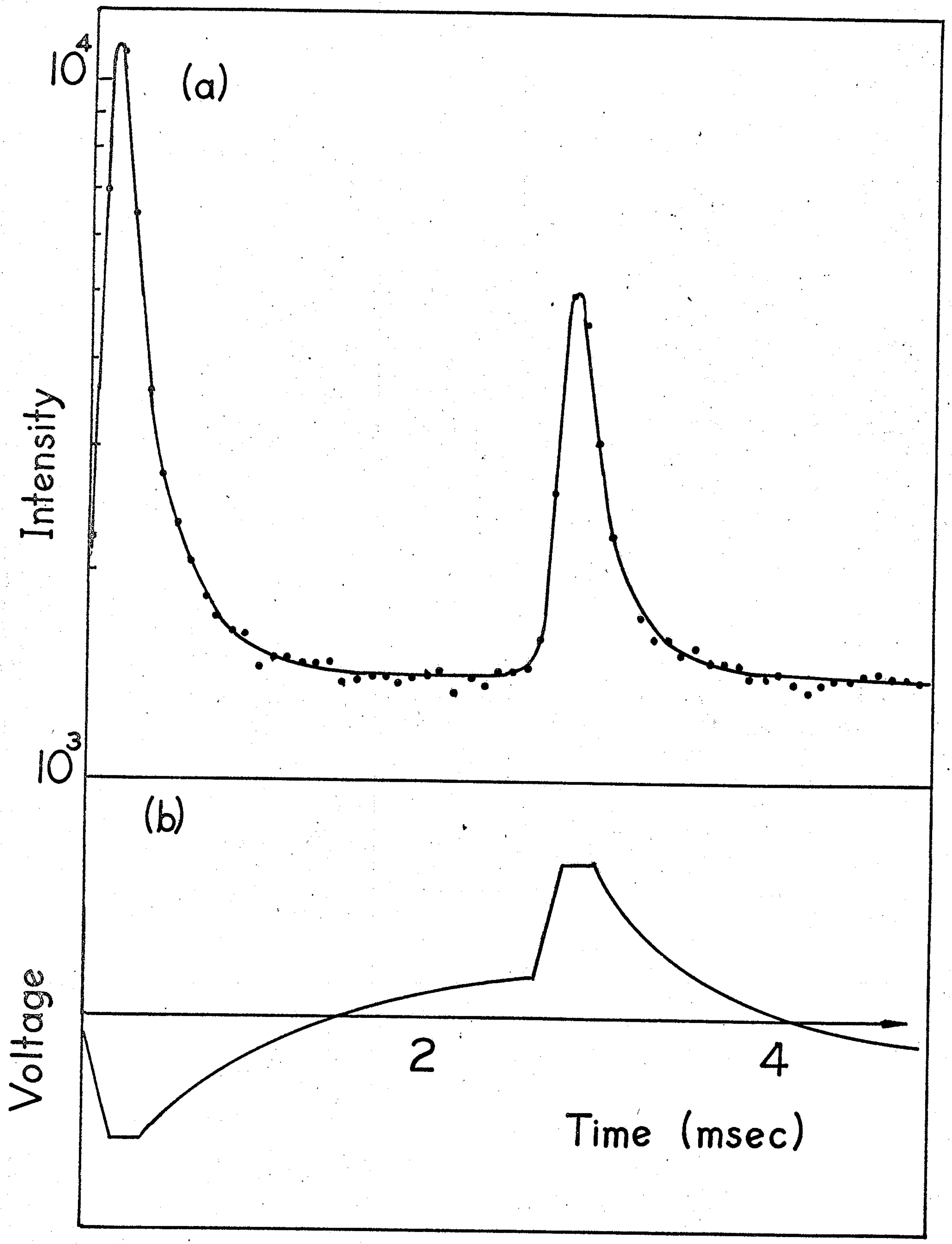

Voltage
Intensity
(a)
(b)
(c)
0
2
Time (msec)

Figure 3-8

Phase dependence for 'square wave' applied field

(a) Emission from 430 nm band in NaI(Tl)

(b) Applied voltage



10^4
(a)
Intensity
10^3
(b)
Voltage
2
4
Time (msec)

NaI(Tl), curve (a), occurs after the zero cross and on the rising edge of the applied voltage waveform, curve (b). In Fig. 3-8 the frequency of the applied voltage was 200 Hz. A study of the possible frequencies that the multichannel analyser would respond to indicated that light was always emitted as the voltage was increasing from zero and peaked before the voltage peaked.

Fig. 3-9 shows the various curves obtained as the applied voltage is increased. This shows that at low voltages the intensity does fall to the background level during the latter half of the negative half cycle. As the voltage increases the intensity rises faster and the emission does not fall to zero before it increases again on the next half cycle. This emission at zero voltage is probably due to energy being released from meta-stable levels or trapping centres. Evidence for the existence of such states will be presented in a later section.

From a study of the curves of the phase dependence of the emission, it is obvious that there can be asymmetries in the intensity of light emitted on each half cycle of the applied voltage. The asymmetries varied with each crystal studied. It was even found that the so-called "brightness waves" varied with the wavelength of light accepted by the detection system. Fig. 3-10 shows the phase dependence of the emission with the detection monochromator set on the four emission bands observed

Figure 3-9

Phase dependence of 430 nm emission from NaI(Tl) at various voltages

______ 8.6 kV/cm

- . - 7.1 kV/cm

----- 5.7 kV/cm

..... Background

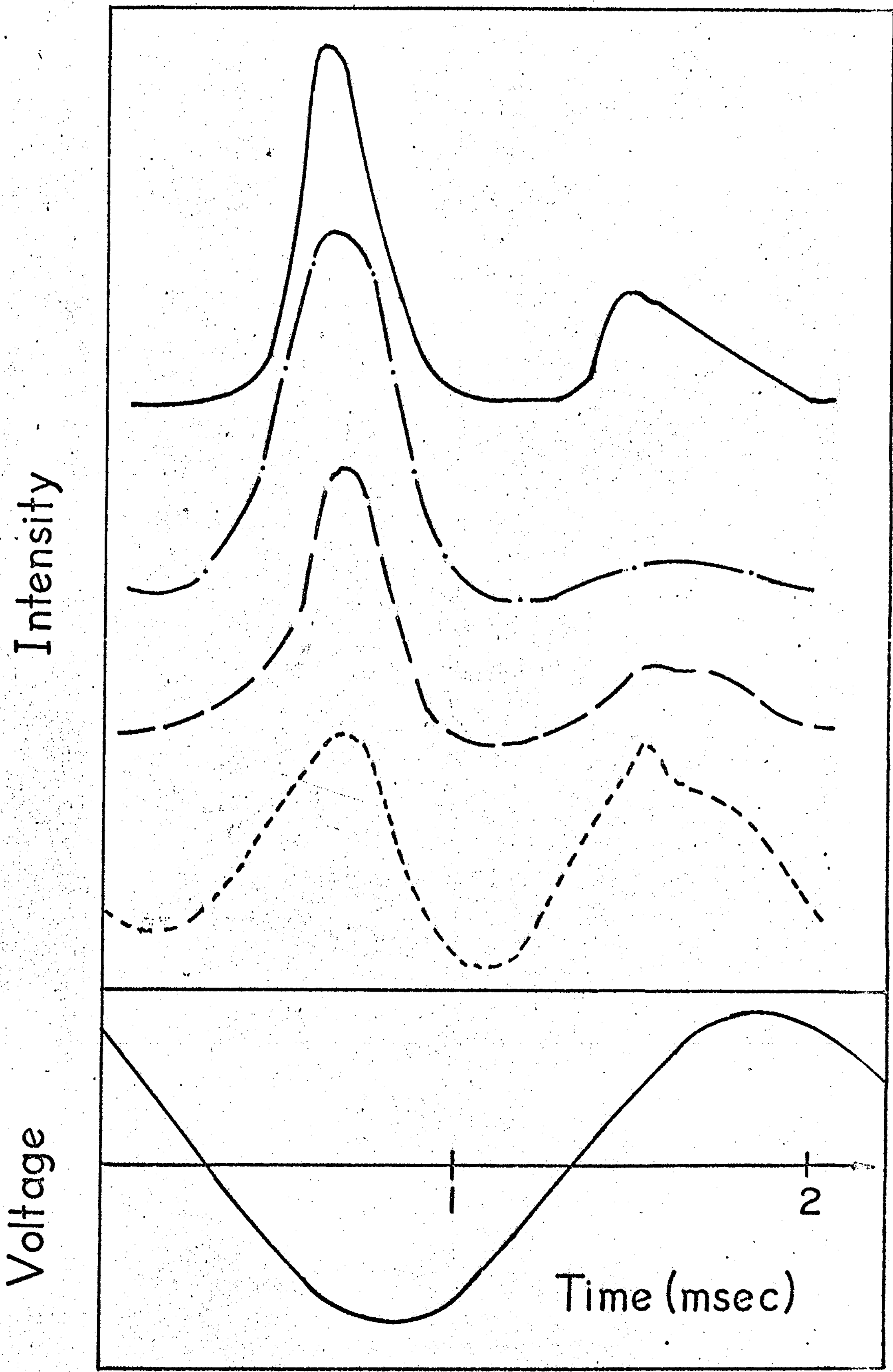

Intensity
Voltage
1
2
Time (msec)

Figure 3-10

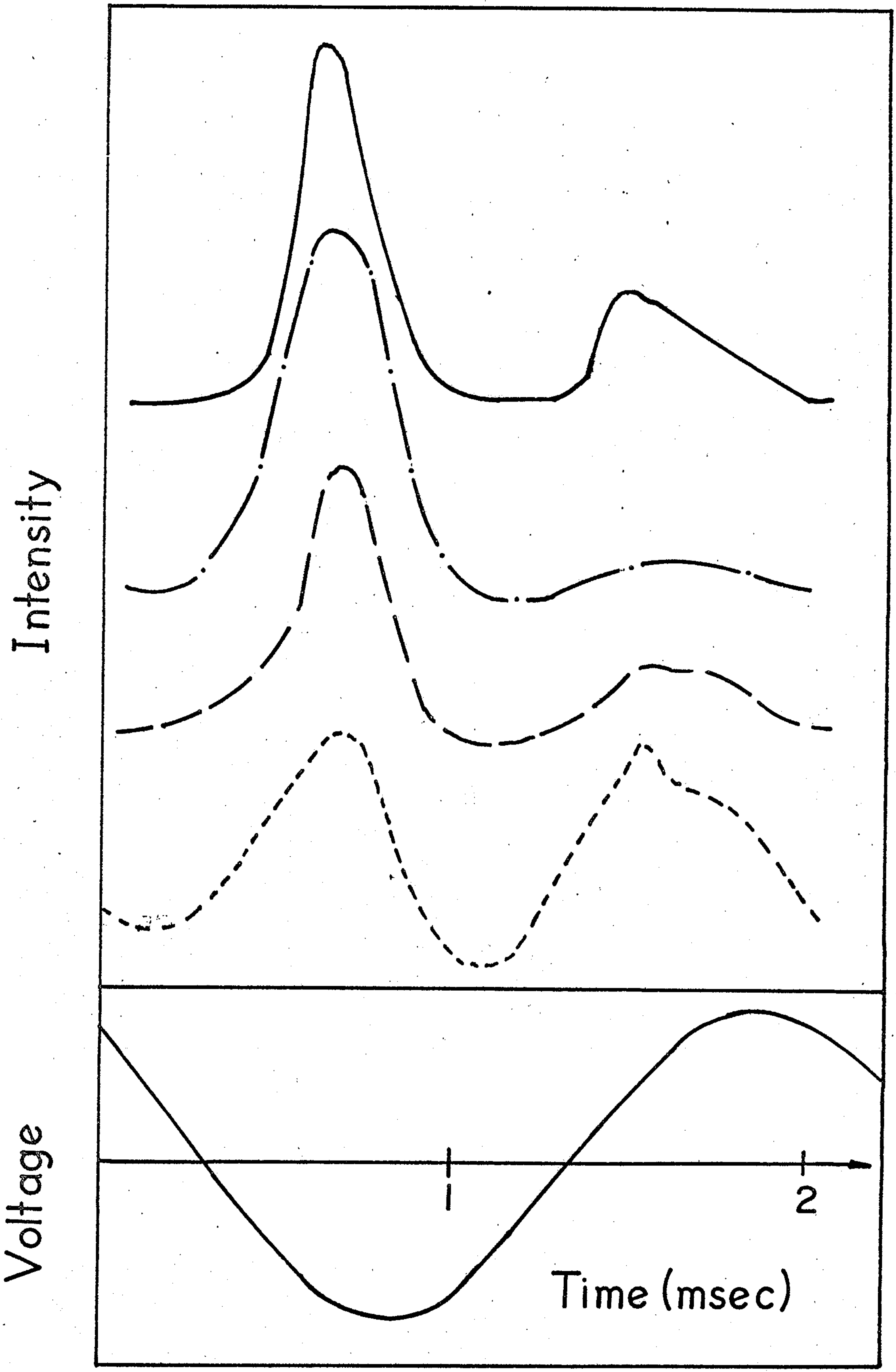
Phase dependence for the various emission bands in pure NaI

______ 295 nm

_ . _ 375 nm

_ _ _ 440 nm

------ 530 nm


Intensity
Voltage
1
2
Time (msec)

from Type 1 NaI. These curves indicate a considerable variation and it is difficult to propose a mechanism to explain such variations. Results from other electroluminescent systems also show asymmetries (Henisch, 1962) which are usually attributed to system geometry. This undoubtedly can produce asymmetries if it is assumed that light emitted during one half cycle comes from a different position than light emitted during the other half cycle. However as described previously visual observation of the crystals at high voltages indicates that the light leaves the crystal through surface cracks and at the edges. Light emitted from the crystal in this manner can undoubtedly show asymmetries but makes it very difficult to draw any conclusion from the observed asymmetries.

Finally it was observed with certain samples that application of a higher than normal voltage resulted in emission that was mainly in phase with the applied voltage and usually occuring on only one of the voltage half cycles. This effect was observed together with the typical phase dependence but the in-phase component predominated at high voltages. It was felt that this was due to a different process from the normal emission process, perhaps due to the establishment of a higher conductance path through the crystal. The emission observed under these conditions was very erratic and consequently most experiments were performed in voltage regions showing the normal phase dependence.

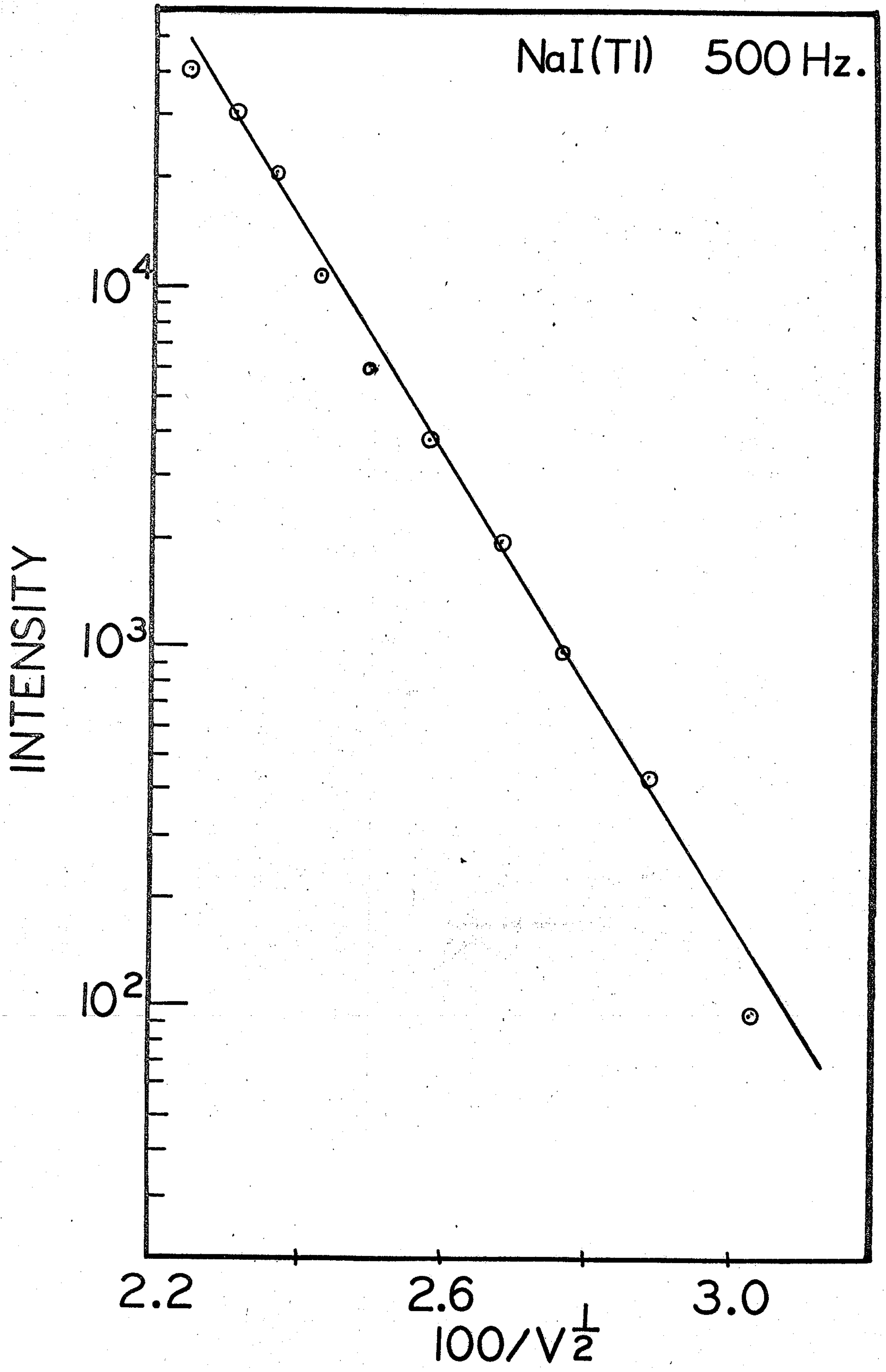
Thus the process involved in producing emission starts as the applied voltage crosses zero but is quenched before the voltage reaches its peak, the emission decaying over the remainder of the half cycle. This phase dependence appears to be in disagreement with the results of Unger and Teegarden (1967) for electroluminescence in pure KI. They observe electroluminescence under application of an alternating field of frequency 500 Hz that was detected at 1000 Hz using a phase-sensitive detector. This signal they observe to be "90° out of phase with the reference frequency". This is interpreted as meaning that the light peak occurs on the zero cross of the applied voltage, in contrast to our results. It must be pointed out that their description is somewhat ambiguous and the use of a phase-sensitive detector may not give the accuracy of our results. As a result of this their results may be in agreement with ours and our present results are undoubtedly similar to those observed in other electroluminescent materials. (Ivey, 1963).

Voltage Dependence

The voltage dependence of the emission from NaI(Tl) and pure NaI was studied at 100°K. At room temperature the emission was too low to make any accurate measurements as to the voltage dependence. Fig. 3-11 shows a typical curve for the 430 nm emission in NaI(Tl) when excited by an applied field of frequency 500 Hz. The line drawn through the data points represents a

Figure 3-11

Voltage dependence of the 430 nm emission from NaI(Tl) at a frequency of 500 Hz


NaI(Tl) 500 Hz.
INTENSITY
10^4
10^3
10^2
2.2
2.6
3.0
$100/V^{\frac{1}{2}}$

least squares fit to the equation

$$B(V) = B_0 \exp(-C/V^{\frac{1}{2}}) \qquad (3.3)$$

where B(V) is the observed intensity, V is the applied R.M.S. voltage and B_0 and C are constants. This is equivalent to equation (1.17) (Alfrey and Taylor, 1954) with the index n=0. This relationship is the one that fits the data best in most electroluminescent materials and has been observed in KI by Unger and Teegarden (1967) and in CsI(Tl) by Georgobiani and Solodovnikova (1968). Attempts were made to fit the voltage dependence with equation (1.18) but it was found that equation (3.3) provided a better representation of the data.

Fig. 3-12 shows that the same relation is observed for the intrinsic emission band in pure NaI at 100°K. The impurity emission bands also followed this relation. Curve (a) is for excitation with an applied voltage of frequency 100 Hz while for curve (b) the frequency was 1500 Hz. This indicates that the slope of the curves, i.e. C in equation (3.3), appears to be approximately independent of frequency. Alfrey and Taylor (1955) found the slope to be slightly dependent upon the frequency in ZnS crystals.

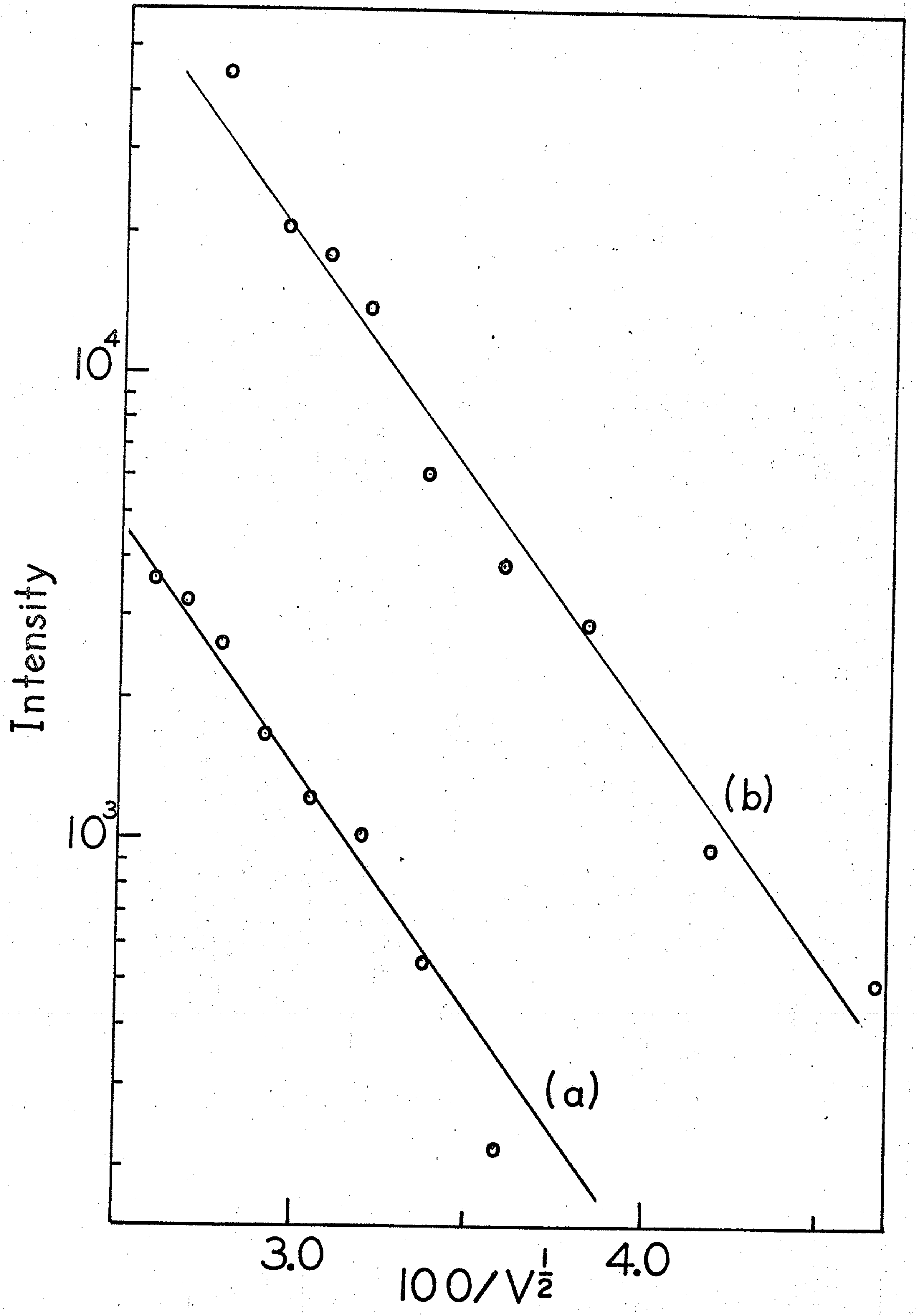
In the present experiments there is some ambiguity as to the field applied to the crystal because the electrodes are smaller than the crystal. Thus parts of the crystal are in a non-uniform field. The voltage dependence experiments were checked with an electrode system that was larger than the

Figure 3-12

Voltage dependence of the 295 nm emission from NaI

(a) 100 Hz

(b) 1500 Hz

10^4
10^3
Intensity
(b)
(a)
3.0
4.0
100/V^½

crystal so that all the crystal experienced a uniform field. With this system the same voltage dependence was observed.

Frequency Dependence

With the present experimental arrangement it was possible to vary the frequency of the applied field from 50 to 2000 Hz while maintaining a constant voltage on the crystal. The dependence of the electroluminescent intensity upon frequency for NaI(Tl) at 100°K is shown in Fig. 3-13. This indicates that the intensity appears to increase linearly with frequency. There was no change in the spectral distribution of the emission over the exciting frequency range. A linear relationship is to be expected if the intensity emitted during each cycle is constant.

For crystals of pure NaI the frequency dependence of the emitted light is more complicated. Fig. 3-14 shows the frequency dependence of the emission from the 295 nm and 375 nm bands. The 295 nm emission shows a linear dependence on frequency while the 375 nm emission shows a saturation effect at higher frequencies. Observation of the emission from this crystal with the monochromator set at zero order also showed a saturation effect.

These results are comparable with results on other electroluminescent materials. Buller and Waymouth (1955) find a frequency dependence of the blue and green emission bands that is very similar to that we observe in pure NaI. Henisch

Figure 3-13

Frequency dependence of the 430 nm emission from NaI(Tl)

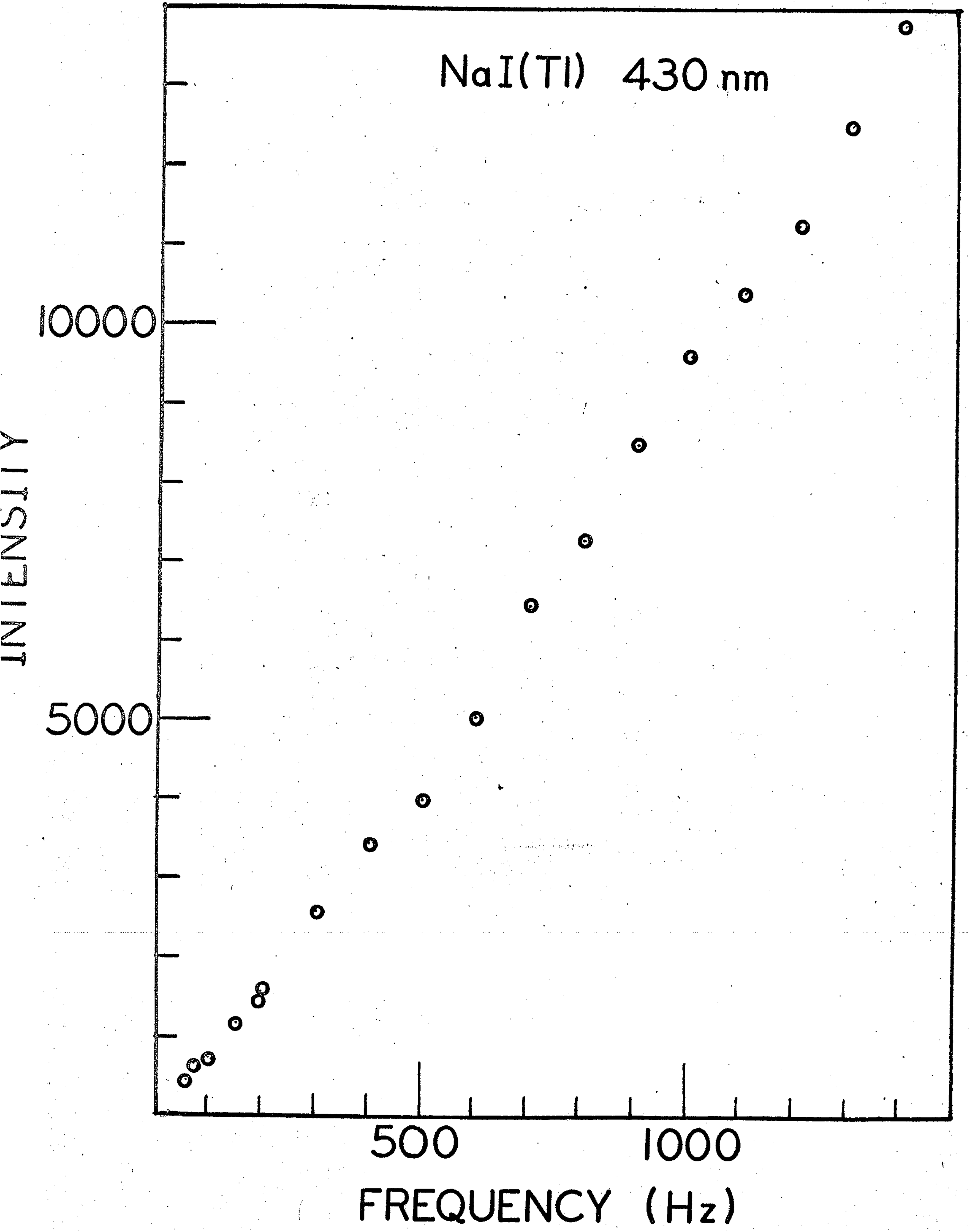

NaI(Tl) 430 nm
10000
5000
INTENSITY
500
1000
FREQUENCY (Hz)

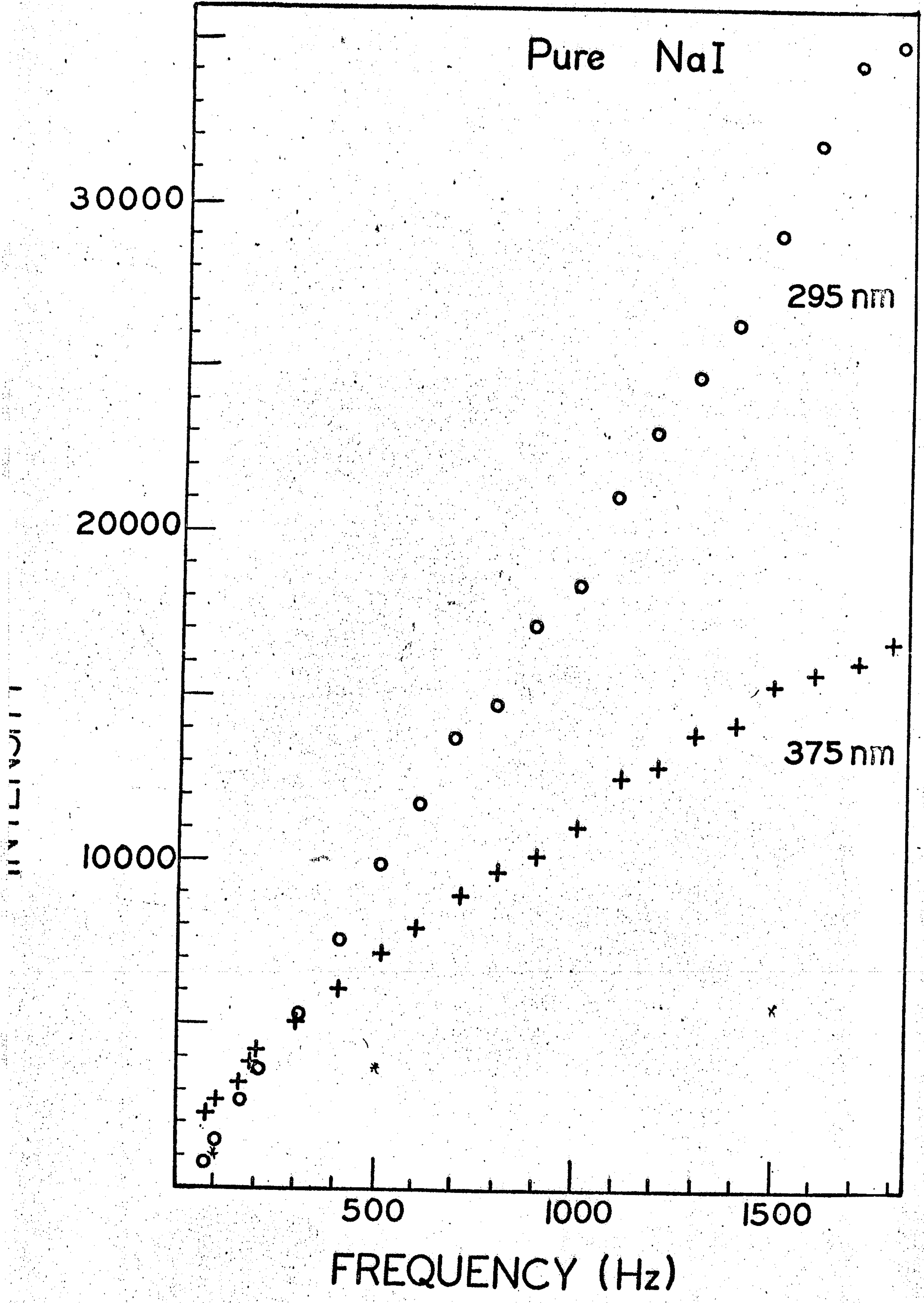
Figure 3-14

Frequency dependence of the emission from NaI

0 295 nm

+ 375 nm

Fig. 3-14


Pure NaI
295 nm
375 nm
30000
20000
10000
500
1000
1500
FREQUENCY (Hz)

(1962) indicates that single emission bands usually show a linear frequency dependence while for two or more bands an increase in frequency alters the spectral composition towards the shorter wavelengths. Fig. 3-15 shows emission spectra for pure NaI at various frequencies. This indicates that the 295 nm band is linearly increasing while both 375 nm and 440 nm bands are showing saturation effects. The spectra in Fig. 3-15 have not been corrected for the efficiency of the detection system.

Electrode Dependence

As discussed earlier the crystals were held between a high voltage electrode and a ground electrode by a simple pressure arrangement. The ground electrode provided thermal contact between the crystal and the cryostat. Various materials were tried as electrodes including brass, indium, silver and aluminum. In all cases electroluminescence was observed and no noticeable differences were observed except that indium made a more consistent contact due to its malleability. As a result the normal configuration used was with brass electrodes that had a thin piece of indium pressed onto them.

Experiments were also performed to determine if the electrodes had to be in direct contact with the crystal surface. Thin pieces of various insulators were inserted between one or both electrodes and the crystal. The results of these experiments indicated that there was still electroluminescent

Figure 3-15

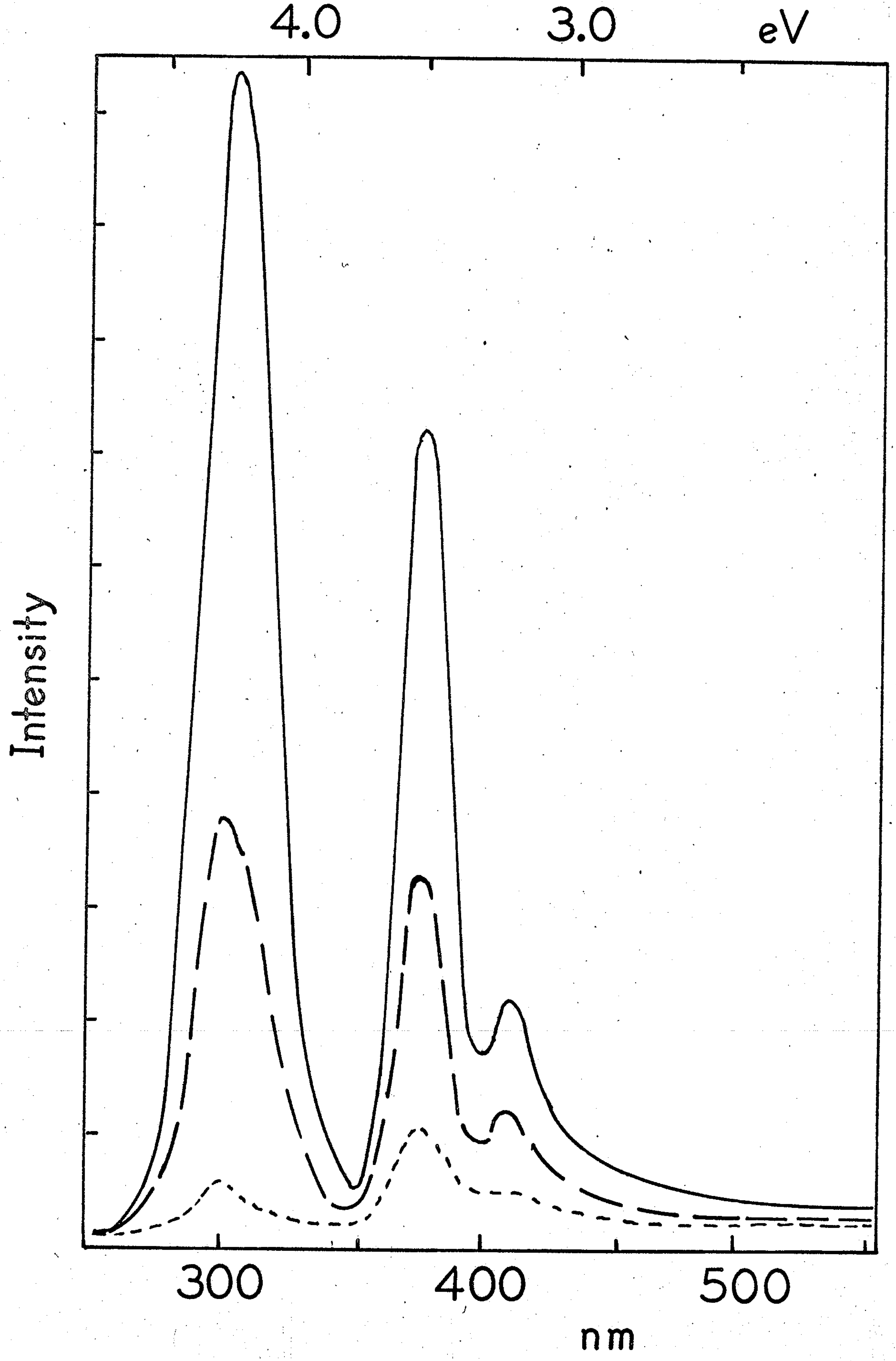
Electroluminescence spectra of NaI at various frequencies

______ 1500 Hz

— — 500 Hz

------ 100 Hz

(The spectra are shown uncorrected)


4.0
3.0
eV
Intensity
300
400
500
nm

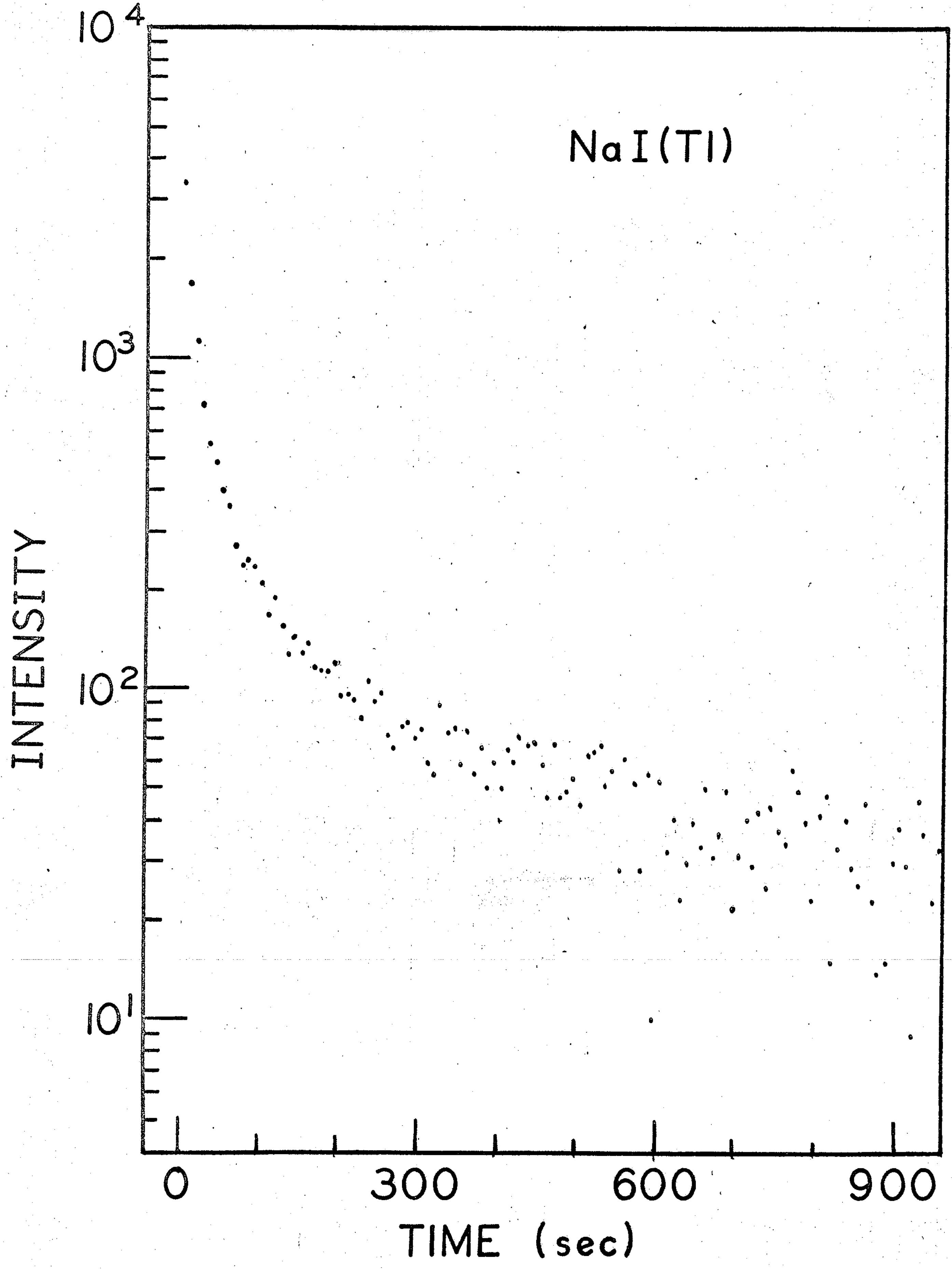
emission with insulators between the crystal and the electrodes. However, the intensity observed was extremely low and identification of the emission was not possible although it was consistent with emission from the crystal. Such emission only occurred with the application of fields that were larger than those required to produce electroluminescence without any insulators between the crystals and the electrodes and the intensity fluctuated considerable. These results tend to show that direct contact between the electrodes and the crystal is not required but a definitive result requires identification of the emission.

Experiments with D.C. Fields

Application of D.C. fields of up to 3×10^4 V/cm did not, in general, cause any electroluminescence as also observed by Unger and Teegarden (1967). Occasionally some form of emission was observed that was usually erratic and at a low level. This emission was possibly correlated with the observation of the 'in phase' emission observed with large alternating fields and because the effect was not reproducible it was not studied. However if the polarity of the applied voltage was reversed by means of a mechanical reversing switch then a large burst of light was observed. The initial intensity greatly exceeded the normal light level due to alternating fields. This emission then slowly decayed, with the field on or off, as indicated in Fig. 3-16 which is a logarithmic plot of the

Figure 3-16

Decay curve of NaI(Tl) emission at 100°K


NaI(Tl)
INTENSITY
10^4
10^3
10^2
10^1
0
300
600
900
TIME (sec)

intensity as a function of time after the voltage reversal. An estimate of the current flowing during such a reversal was made by limiting the current supplied by the power supply. This indicated that an instantaneous current of the order of 1 mA was involved.

A study of the spectral distribution of the light during the decay period showed that it was identical to the impurity emission of the crystals. The intrinsic emission was not detected. This indicates that the voltage reversal causes many centres to be ionized and also it populates trapping centres. The release of charge carriers from these traps and their recombination at emission centres produces the observed decay. As a further indication that many trapping centres are filled, if a thermoluminescence experiment is performed after a single voltage reversal then several glow peaks are observed. These glow peaks will be discussed in a later section. Excitation of the crystal at 100°K with gamma rays produces the same glow curves on warming.

This voltage reversal effect is possibly related to the alternating field case since it was found that a voltage reversal was necessary, no emission being observed when the voltages were applied and removed. To explain the initial high level of emitted light two possibilities exist. One is that the voltage is applied for a much longer time before the reversal occurs and the other possibility is that the rate of change of the voltage as the reverse voltage is applied is much larger than for the alternating fields used.

Discussion

The results quoted in this section represent the first observations of electroluminescence in sodium iodide single crystals. In an effort to explain the electroluminescence process the following experimental results must be explained:-

(a) There is no selective excitation of emission centres within the crystal as is the situation for radioluminescence.

(b) The emission, in general, is observed only with some form of alternating field and the emission maximum occurs before the voltage maximum for sinusoidal fields.

(c) The voltage dependence of the emission intensity appears to follow the usual Alfrey-Taylor relation.

(d) A temperature dependence for which the excitation is more effective at low temperatures.

(e) A linear frequency dependence observed for the main emission centres (thallium emission in NaI(Tl) and the intrinsic emission in pure NaI) while there are saturation effects for some emission centres.

The processes that were shown to be probable in alkali halides must now be considered in relation to the above experimental observations. Electron tunnelling from the electrodes, as considered by Franz (1956), is possible with the fields used provided the barrier between the metal and the crystal is not too high. If such a mechanism was operative a supply of holes would also be required without having to infer impact ionization. These could be provided by tunnelling from the opposite electrode. Such a mechanism has been proposed by Fischer (1963) for II-VI compounds and was suggested also by Unger and Teegarden (1967) for electroluminescence in KI. Emission results from this process when the voltage is reversed and the electrons tunnelling in recombine with trapped holes. This mechanism was rejected by Unger and Teegarden (1967) since they postulated that this process would give emission in phase with the applied voltage, in contrast to their observations. However it is worthwhile reexamining this mechanism in the light of our observed phase dependence.

From the model of Fischer (1963), as the voltage is increased electrons and holes tunnel into the crystal from opposite electrodes. The mobility of holes in alkali halides is small and they are trapped at a variety of centres. Thus the holes trap in the vicinity of the electrode. These trapped holes form a polarization field that limits the tunnelling of holes into the crystal, and hence also limits electron tunnelling since equal numbers of electrons and holes will tunnel in. As the applied field reverses then electrons tunnel into the region containing trapped holes and the space charge due to these holes enhances the electron tunnelling. Recombination of electrons and holes produces emission. Hole tunnelling from the opposite electrode also occurs and the process is limited again by a polarization field. Therefore in an alternating field it is more likely for emission to occur as the voltage is increasing from zero in agreement with the present results.

The voltage dependence of such a tunnelling mechanism follows the basic form of equation (1.18) provided the internal field is proportional to the applied voltage. However due to the space charge enhancement effect the internal field may be modified. Assuming a Mott-Schottky modification, then the observed voltage dependence can be derived. This model assumes that the holes are trapped. The temperature dependence can be explained on the assumption that at a certain temperature the holes are free to move and decrease the probability of recombination. The present measurements indicate an activation energy of 0.3 ± 0.1 eV for this process. The results of Unger and Teegarden (1967) also indicate that the electroluminescence decreases as V_K centres, which are trapped holes, become mobile in pure KI. In pure NaI some other hole trap would have to be responsible since V_K centres are mobile at 58^{o}K according to Murray and Keller (1967). The fact that intrinsic emission is observed in the pure NaI electroluminescence experiment is then difficult to explain on this model. For NaI(Tl) a hole trap is provided by the Tl^{+} centre becoming a Tl^{++} centre. The observed activation energy could be that required to free a hole from a Tl^{++} centre. The linear frequency dependence requires that an equal number of electrons and holes tunnel in during each voltage cycle. Since the process is limited by the polarization field it is the maximum applied voltage and not the length of time the voltage is applied that limits the number of carriers tunnelling. Thus a linear frequency dependence would be expected. Saturation effects can be accounted for by noting that the time for recombination to take place is decreased at high frequency. Consequently for centres that have a low density in the electrode region the higher frequencies will allow less recombination at these centres. Also the higher frequencies may reduce the region of excitation because the carriers cannot move as far. This will decrease the light output from low density centres while for the major centres an increased density of excited centres will result. With this model it is difficult to explain the large amount of light observed upon reversal of the polarity of a D.C. field. Since the intensity of emission is dependent on the number of holes which tunnel in and that this depends upon the maximum applied field, the intensity observed during a polarity reversal should be the same as the amount of light emitted during a half cycle of an alternating field. Consequently some other mechanism must be involved in this process.

Thus it is possible to explain most of the experimental data with the electron and hole tunnelling model. A major problem lies in determining whether the electrode system will allow electrons and holes to tunnel into the alkali halide from opposite electrodes, or are electrons removed through one electrode. Fischer (1966) has shown that the former mechanism can be achieved but only with special electrode systems. It is interesting to comment that the electron and hole tunnelling mechanism is the one that at present explains the electroluminescence of ZnS powders suspended in a dielectric medium (Fischer, 1963). In such systems electroluminescence is observed only under alternating field excitation. The model assumes that there are inclusions of Cu_2S in the ZnS particles which have been doped with copper. The field around these conducting regions is enhanced and electron and hole tunnelling into the ZnS occurs on opposite cycles of the alternating field. Light is emitted when electrons and holes recombine at activator centres. A similar mechanism involving silver inclusions in pure AgCl has been suggested for the electroluminescence observed by Meczynska and Oczkowski (1968). However, it is difficult to suggest possible inclusions that may occur in alkali halide crystals, in particular the pure crystals.

The other mechanism that can be applied to alkali halide crystals is that of impact ionization. This mechanism is the one used by Unger and Teegarden (1967) and Georgiobiani and Solodivnikova (1968) to explain the electroluminescence observed in pure KI and CsI(Tl) respectively. In both cases such a mechanism was infered from the voltage dependence of the emitted intensity and a Mott-Schottky barrier region was assumed. Furthermore Unger and Teegarden (1967) assumed that the electrons which are accelerated are produced by a tunnelling process from the metal electrodes.

It is perhaps worthwhile at this time to summarise the results of these two papers which stand as the only other quantitative measurements of electroluminescence in alkali halides. Both observed the same voltage dependence reported here. Unger and Teegarden (1967) reported that electroluminescence was not observed with insulating layers between the crystal and the electrodes while Georgiobiani and Solodovnikova (1968) actually had a dielectric between the crystal film and one electrode. Georgiobiani and Solodovnikova (1968) observed the intensity to be independent of the frequency between 1 kHz and 100 kHz although their results do indicate that the intensity was decreasing as the frequency was decreased from 2 kHz. Measurements were not made below approximately 900 Hz. Unger and Teegarden (1967) observed that electroluminescence became undetectable as the temperature was raised past the temperature at which V_K centres became mobile and also they indicated that the light was emitted from a region close to the electrodes.

The main reason for attributing the electroluminescence to impact ionization is because such a process can occur in lower average fields than most other processes. However, the model is complicated by the requirement of some mechanism to supply the accelerated electrons. Normally thermal emptying of shallow traps is proposed but such a mechanism would not account for our observed temperature dependence. The suggestion of Unger and Teegarden (1967) was that these electrons tunnel in from the electrodes. This mechanism itself depends upon the field as E^{-1} in the exponential argument and so makes it difficult to identify which is the dominant process. The observed voltage dependence is obtained from either process by the assumption of a Mott-Schottky barrier region.

In the impact ionization model it is assumed that the electrons in the conduction band are accelerated to optical energies where they can excite or ionize impurities and the lattice. Since the impurity excitation process will have a smaller cross section than either of the ionization processes the latter will predominate. Furthermore, since the impurity centres have ground states close to the top of the valence band, the most likely process is simply that of ionization of centres having the highest density, so that lattice ionization will be the most important kind of excitation in the impact ionization process. Thus this mechanism will produce a supply of electrons in the conduction band and holes in the valence band. These holes will then be captured at various centres as in the radioluminescence process and recombination with electrons gives the emission. In this way the emission spectrum observed would be similar to the radioluminescence spectrum.

To explain why an alternating field is necessary to support this mechanism some form of polarization must be produced that limits the flow of charge carriers. Polarization effects due to the movement of charge carriers are observed in mobility measurements in alkali halides (e.g. Hirth and Tödheide-Haupt, 1969). The application of an alternating field will remove any slow polarization that does occur. The observed phase dependence is compatible with the idea that there is some process limiting excitation since the intensity peaks before the voltage peak, and it is possible that a polarization mechanism is responsible. Experiments with D.C. fields would allow a substantial internal polarization to build up which would be removed on reversal of the voltage polarity, giving a large amount of excitation probably due to impact ionization.

The observed temperature dependence on this model must be due to increased scattering of the electrons at higher temperatures. As was discussed earlier, experiments on electron mobility in alkali halides show three types of scattering, namely longitudinal optical mode scattering, acoustic mode scattering and impurity scattering. Seitz (1949) has shown that acoustic mode scattering will predominate over longitudinal mode scattering at higher electron energies. Thus, as already indicated, the decrease in efficiency can be fitted with a $T^{-3/2}$ dependence characteristic of acoustic mode scattering (Seitz, 1948). The level region of the temperature dependence can be attributed to impurity scattering of the accelerated electrons. Longitudinal optical mode scattering is probably too weak to contribute. The observed frequency dependence must be explained as in the tunnelling model, that an equal number of electrons must be accelerated for each voltage cycle, regardless of the rate of change of the voltage cycle. In this model the internal polarization could limit the number of electrons that are accelerated.

Thus, as has been indicated, there appear to be two mechanisms capable of explaining the observed electroluminescence. However, to obtain the observed voltage dependence the models must be coupled with the postulate that excitation occurs as a result of a locally enhanced field at a Mott-Schottky barrier. The work of Lehmann (1960) in ZnS showed that the Alfrey-Taylor relation could be obtained from a superposition of various Destriau relations, equation (1.18). This removes the restriction of a locally enhanced field but is difficult to justify for alkali halide single crystals.

With regard to the possibility of a uniform field throughout the crystal or an enhanced one at the electrodes it is worthwhile considering experiments on the mobility of electrons in alkali halides (e.g. Brown and Inchauspé, 1961; Ahrenkiel and Brown, 1964). These experiments were performed with crystals where the field was maintained between plane parallel electrodes that were usually considered to be blocking electrodes, that is non-ohmic. Low voltages were used such that the electrodes behaved as if they were ohmic and a uniform field was maintained across the crystal. Photocurrents produced by electrons released from F-centres obey Ohm's Law at low voltages. Experiments performed with higher fields in AgCl by Masumi (1963) and in KBr by Mikkor and Brown (1967) showed deviations from Ohm's Law such that the photocurrents were proportional to $E^{0.5}$ in AgCl and to $E^{0.6}$ in KBr. This behaviour was explained by the authors in terms of 'hot electron' effects using the approach introduced by Schockley (1951). This theory is the same theory that was used to treat impact ionization, giving the voltage dependence of equation (1.13). This observation points to the possibility of impact ionization occuring at higher fields. In these experiments care was always taken to work with small photocurrents. This indicates the possibility of polarization and space charge effects if higher currents are involved. Also since the electrodes in our experiments can be considered as blocking electrodes in our high field experiments it is likely that some form of barrier region occurs.

Thus, in conclusion, it has been shown that two possible models can be inferred from the present data. Reference to mobility experiments indicates that impact ionization is a likely process in alkali halides, while there is no collaborating evidence in favour of the electron and hole tunnelling model. Further experiments at lower temperatures may increase our knowledge of the system and measurements of the mobility of electrons in these crystals should provide insight into the possibility of impact ionization.

3-2 Electrophotoluminescence

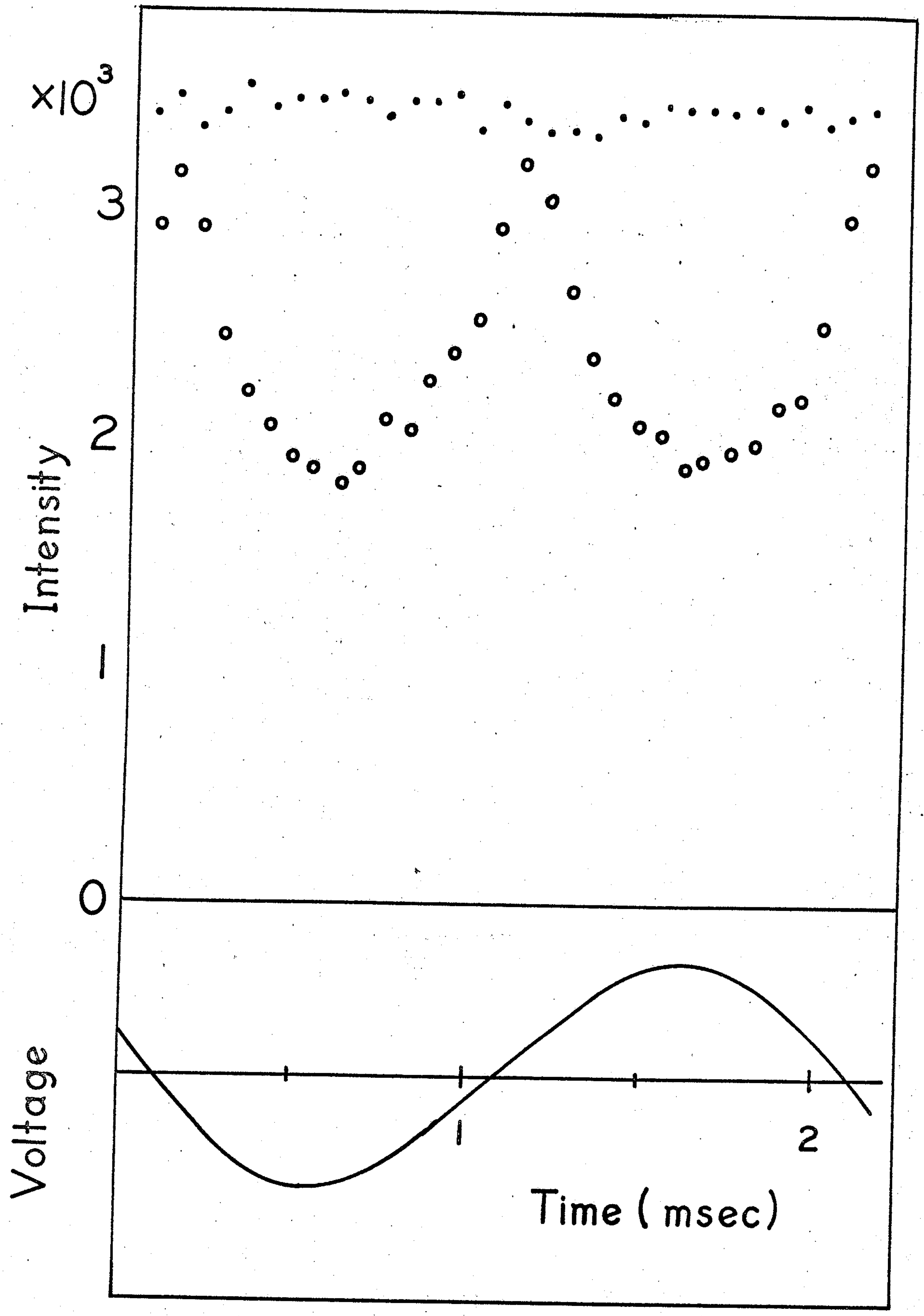
In an attempt to elucidate possible effects of electric fields in sodium iodide crystals experiments were performed with crystals excited by γ-rays. For these experiments the crystals were in the same configurations as for the electroluminescence experiments but a source of γ-rays was placed either in the crystal holder or beside one of the windows of the cryostat that was not in use. It was observed that a voltage applied to the crystals usually resulted in a decrease in light output from the various emission bands. This is illustrated in Figure 3-17 which shows a modulation of the light output from a crystal under the application of a small alternating field at room temperature. These results were taken for the 375 nm emission band in pure sodium iodide using the same experimental set up as for the observation of brightness waves. Modulation with an alternating field was only possible at room temperature and with voltages low enough not to cause observable electroluminescence. Such observations were not possible at liquid nitrogen temperatures where the electroluminescenc mechanism is more efficient. Consequently field effects were observed with only D.C. applied voltages at liquid nitrogen temperatures while both A.C. and D.C. fields were used at room

Figure 3-17

Voltage modulation of the 375 nm emission from NaI at room temperature, excited by gamma rays

..... no applied voltage

ooooo with a 500 Hz applied voltage


×10³
3
2
Intensity
1
0
Voltage
1
2
Time (msec)

temperature.

Pure Sodium Iodide

The largest effects of an applied field were seen in the case of pure sodium iodide. Figure 3-18 shows the emission spectra of a pure sodium iodide crystal when excited by γ-rays at room temperature. Curve (a) is with no applied field, curve (b) is for 2.0 KVDC applied field and curve (c) for 0.6 KVAC. This shows no observable variation in the 295 nm band but the 375 nm emission shows a large decrease when electric fields are applied to the crystal. The small peak at 440 nm shows a small increase with applied field. These spectra also indicate that an alternating field is more efficient in the quenching process. This is probably due to a polarization effect reducing the bulk field in the case of a D.C. applied voltage. Fig. 3-19 indicates the change in peak height of the 375 nm and 440 nm bands with increasing alternating field. The 375 nm band shows a linear decrease with increasing voltage while the 440 nm band shows a linear increase in peak height with applied voltage.

The emission spectrum for pure crystals at liquid nitrogen temperature is shown in Fig. 3-20(a). Here the 295 nm emission band is comparable with the 375 nm band. With the application of a D.C. voltage to the crystal a reduction in intensity of the 295 nm and 375 nm bands is observed, Fig. 3-20(b), while the 440 nm band shows no observable variation. The variation of peak height with applied voltage for the 295 nm and 375 nm bands is shown in Fig. 3-21 and again a linear decrease with increasing

Figure 3-18

Emission spectra of NaI at room temperature, excited by gamma rays

(a) _____ no applied voltage

(b) _ . _ 2.0 KVDC applied

(c) ------ 0.6 KVAC applied

(The spectra are shown uncorrected)

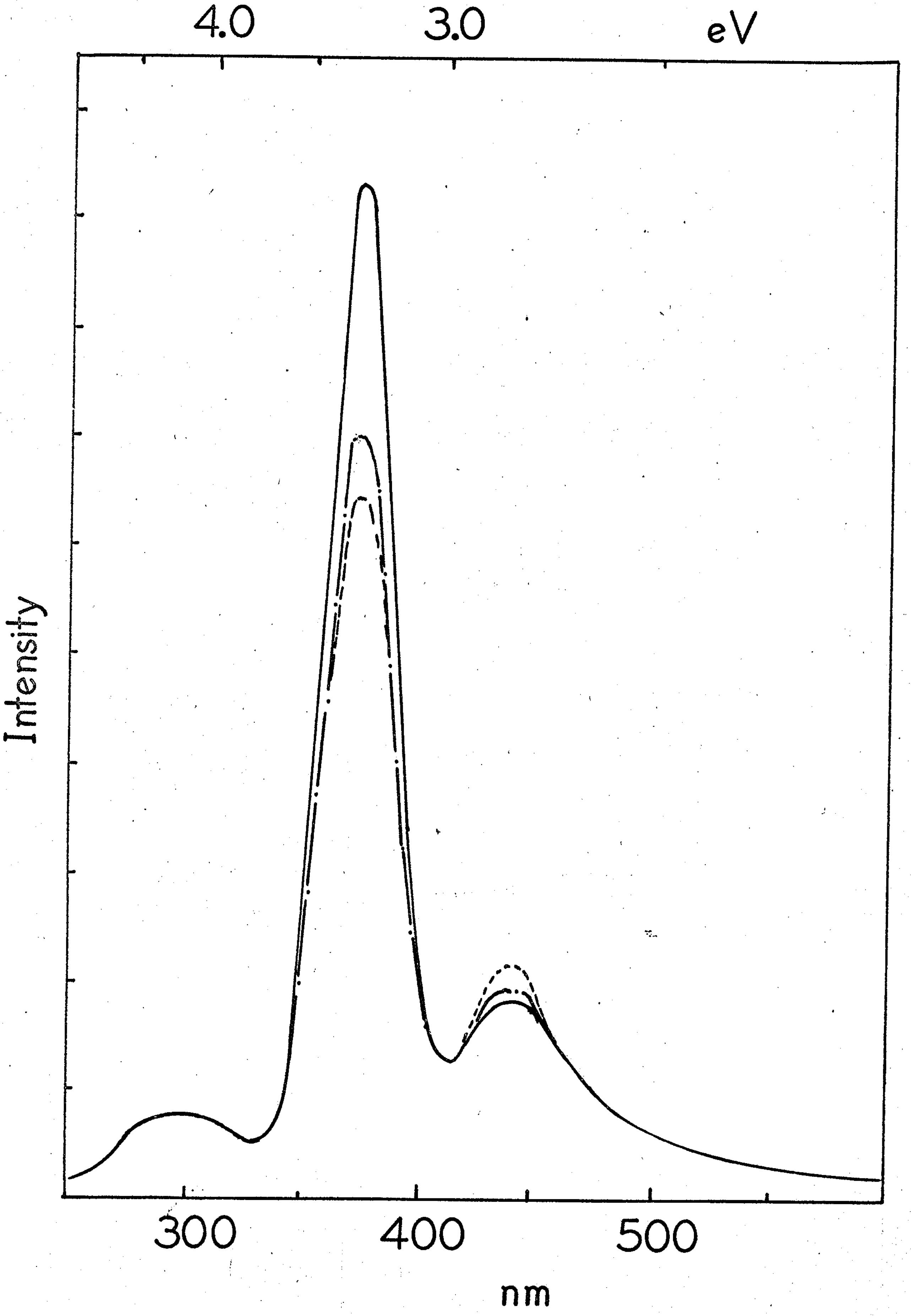

4.0
3.0
eV
Intensity
300
400
500
nm

Figure 3-19

Variation of the emission intensity from NaI at room temperature

+ 440 nm

○ 375 nm

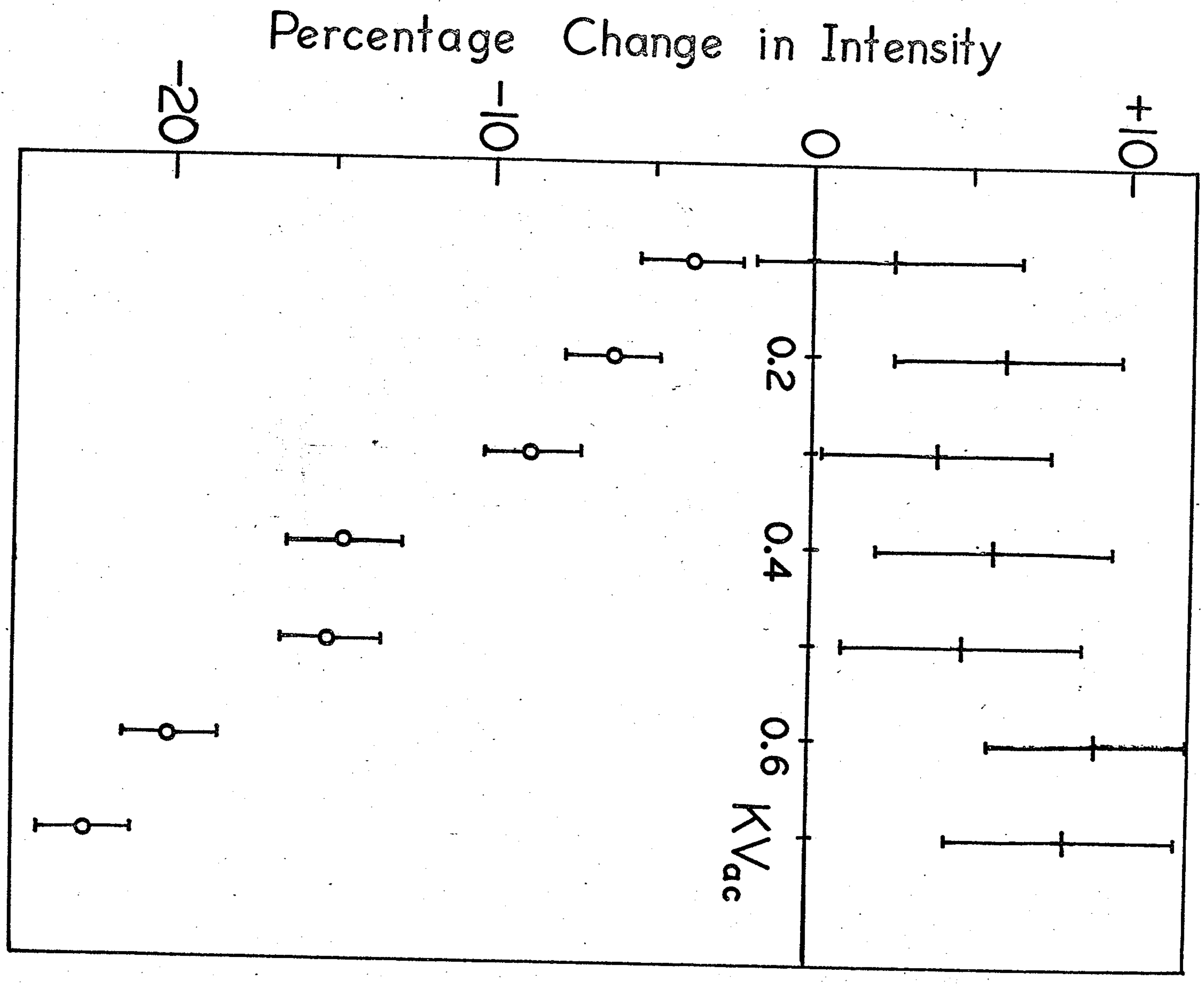

Percentage Change in Intensity
-20
-10
0
+10
0.2
0.4
0.6
KV_{ac}

Figure 3-20

Emission spectra of NaI at 100°K excited by gamma rays

(a) _____ no applied voltage

(b) __.__ D.C. applied voltage

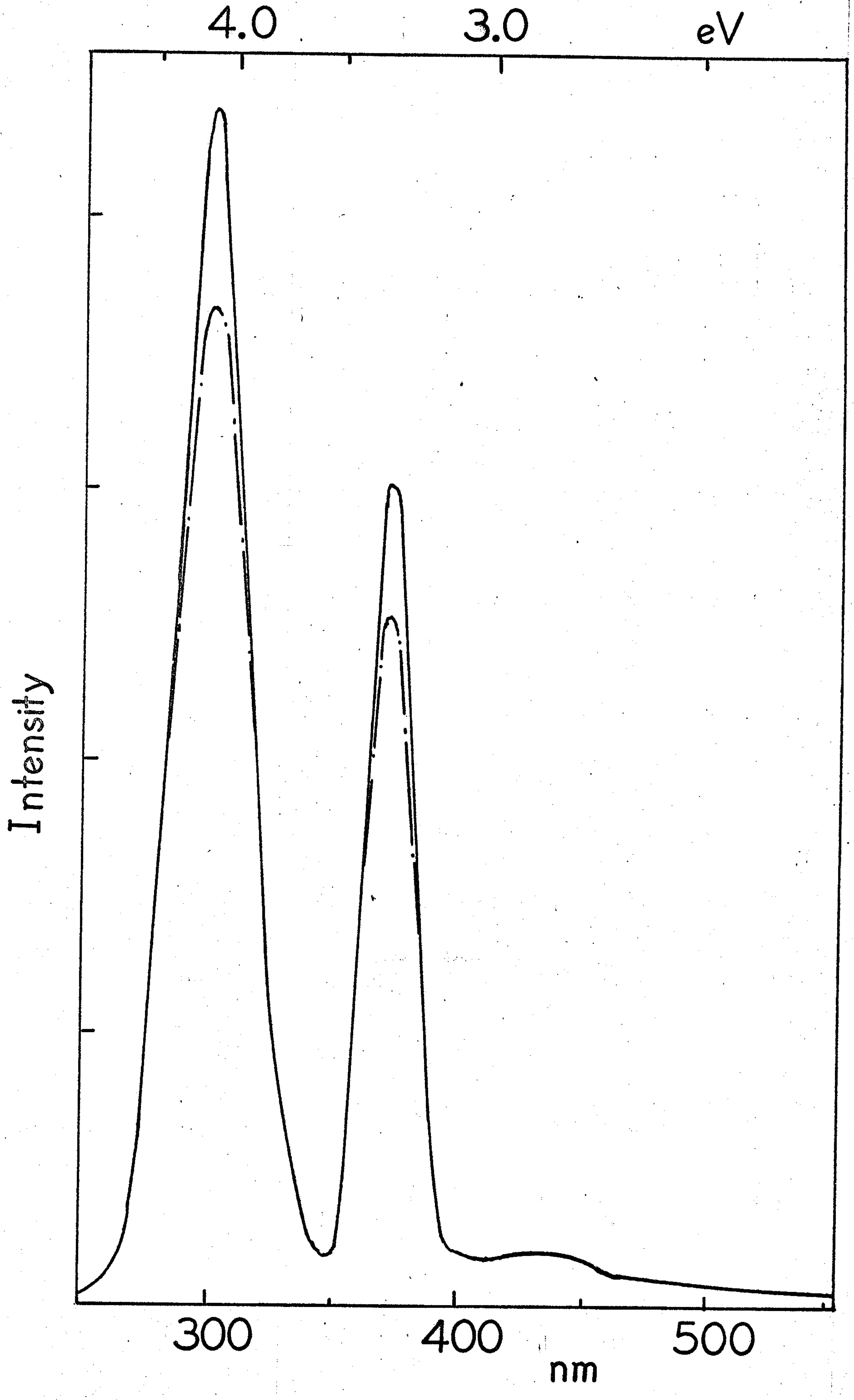
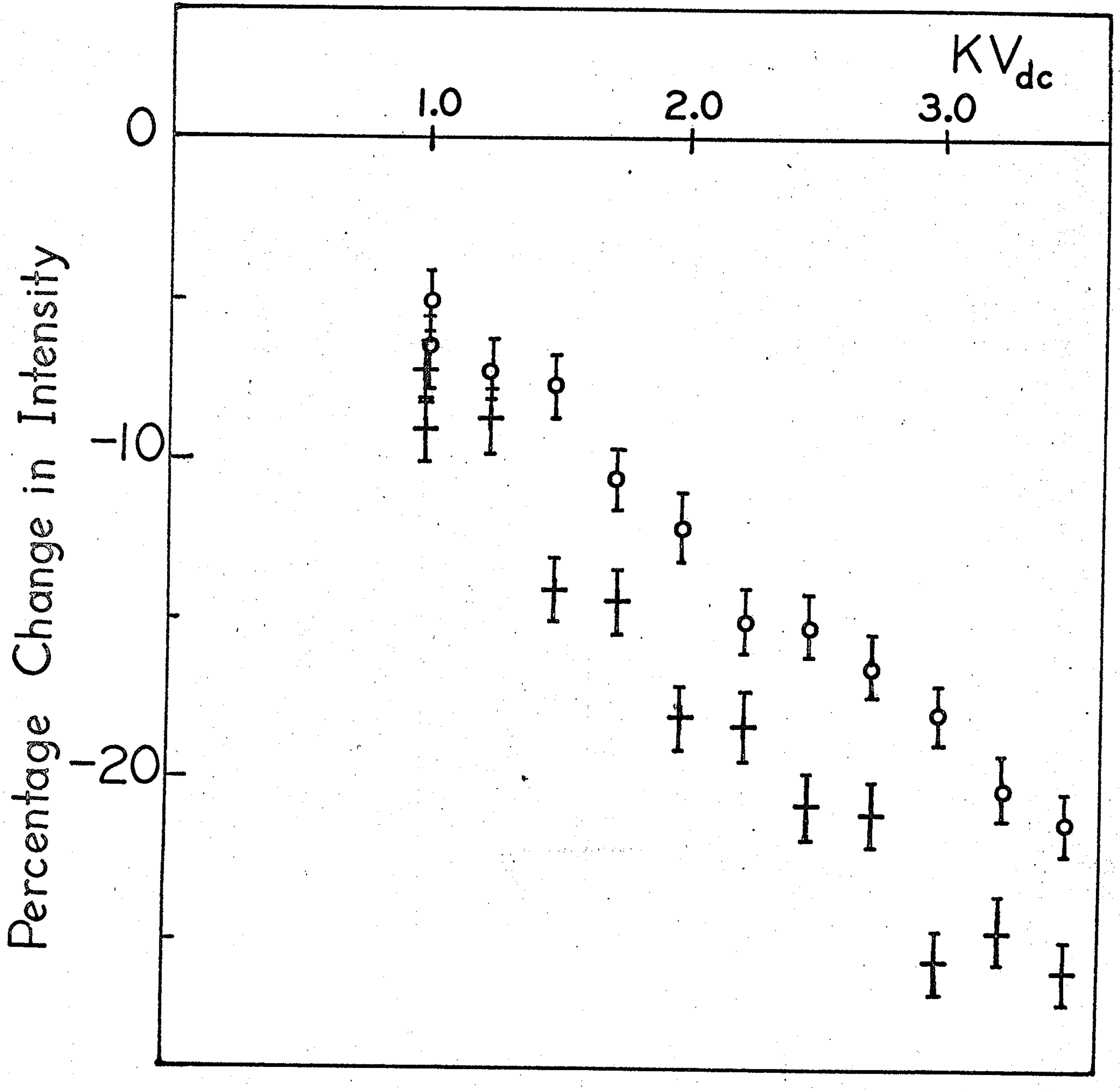

4.0
3.0
eV
Intensity
300
400
500
nm

Figure 3-21

Variation of the emission intensity from NaI at 100°K

○ 295 nm

+ 375 nm


KV$_{dc}$
1.0
2.0
3.0
0
-10
-20
Percentage Change in Intensity

voltage is observed. A detailed analysis of the emission band shapes of the 295 nm and 375 nm bands is shown in Fig. 3-22 and this indicates that there is no variation in the band shapes (first and second moments), just a decrease in area (zeroth moment) indicating a decrease in emission. This observation indicates that the field is not affecting the emission centre itself but is altering the energy transport properties of the crystal during the scintillation process.

Thallium doped Sodium Iodide

The effect of an applied field on the scintillation process in NaI(Tl) was also investigated. Fig. 3-23 shows the room temperature scintillation spectrum with and without an applied D.C. field. Again a decrease in intensity is observed in the main emission band at 430 nm but the decrease in intensity is not as pronounced as in pure NaI. It is not possible to observe whether there is a decrease in the emission from dimer centres at 330 nm. A small decrease in intensity is observed at LNT as shown in Fig. 3-24(a). The dependence of the decrease in peak height on applied voltage is indicated in Fig. 3-24(b). Here the relationship does not appear to be linear but the statistics are not good enough to draw any definite conclusion as to this relationship.

Optical Excitation

As a further investigation of the effect of the electric field in pure and thallium doped sodium iodide, emission and excitation spectra for the crystals were taken with and without

Figure 3-22

Emission spectra of NaI at 100°K on an expanded scale

______ no applied field

_ • _ D.C. applied field

(The spectra are shown uncorrected)

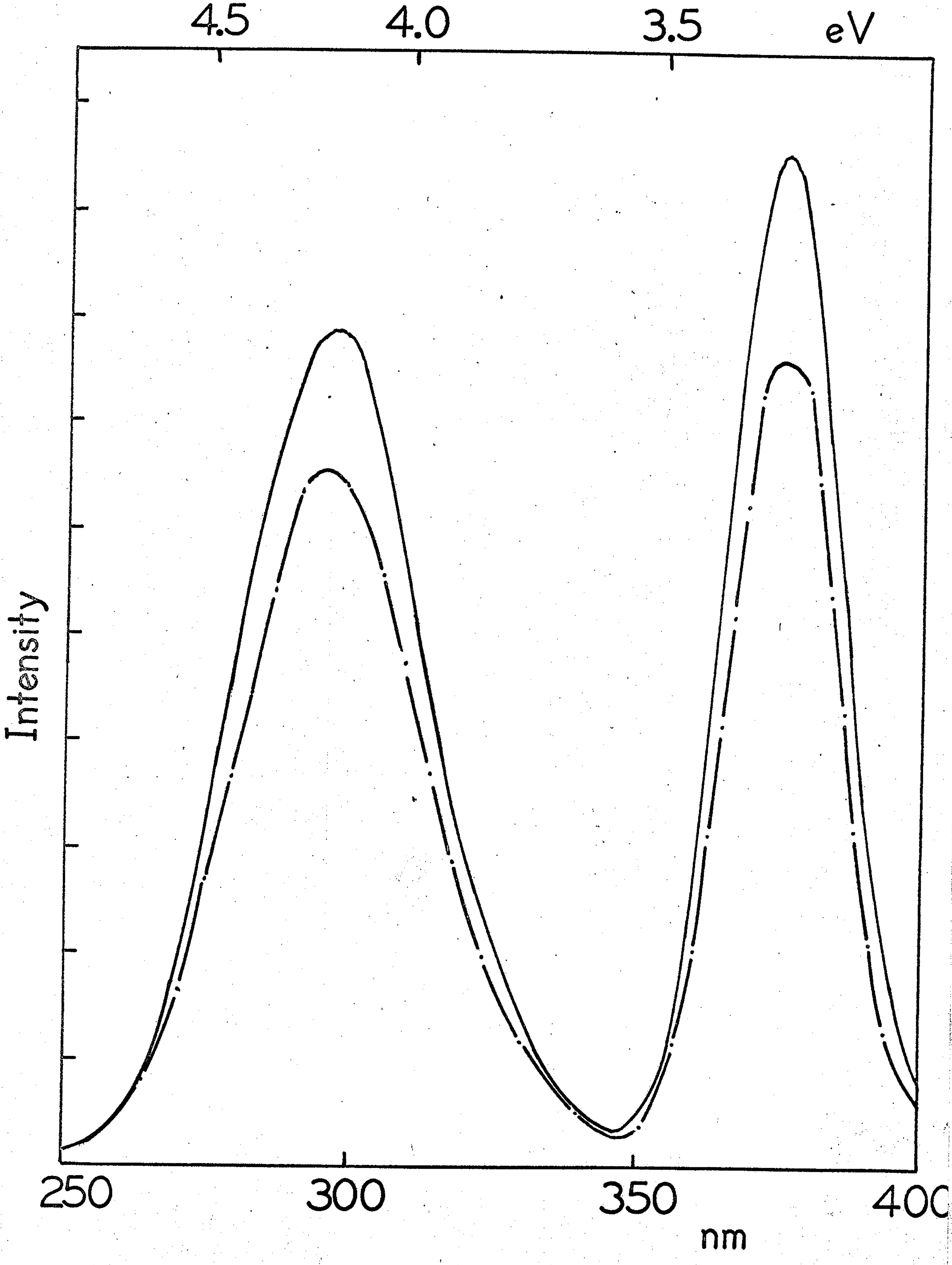

4.5
4.0
3.5
eV
Intensity
250
300
350
400
nm

Figure 3-23

Emission spectra of NaI(Tl) at room temperature, excited by gamma rays

_____ no applied field

_ . _ D.C. applied field

(The spectra are shown uncorrected)

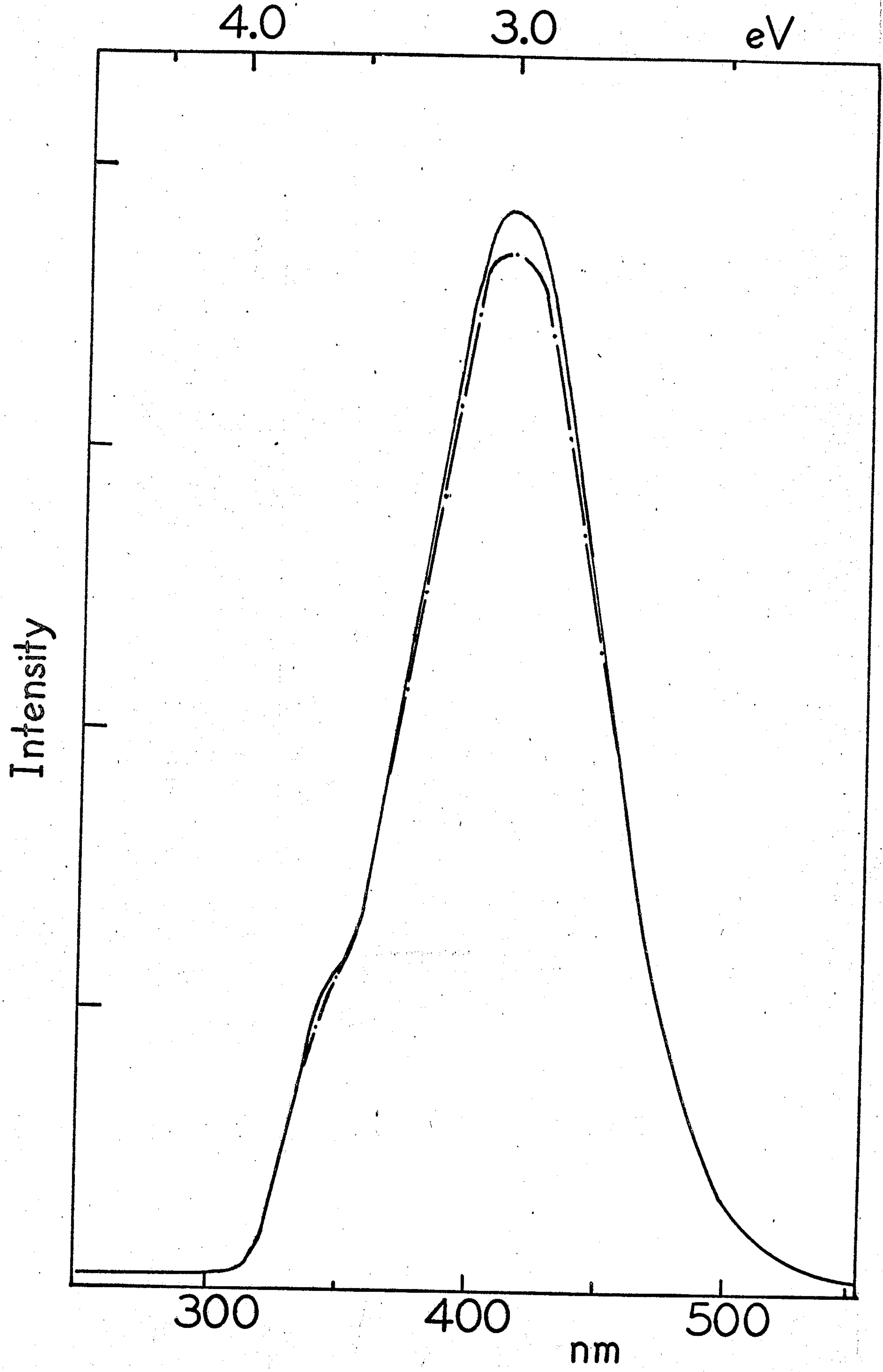

4.0
3.0
eV
Intensity
300
400
500
nm

Figure 3-24

(a) Uncorrected emission spectra from NaI(Tl) at 100°K

_____ **no applied voltage**

_ . _ D.C. **applied voltage**

(b) Variation of the intensity of the 430 nm emission

an applied field. With our present excitation system it was only possible to observe the optical excitation of the 375 nm emission in pure sodium iodide. The emission intensity showed no effect due to the electric field and the excitation spectrum, consisting of bands at 230 nm and 260 nm (Van Sciver and Fontana, 1968), did not alter when a field was applied to the crystal. In NaI(Tl) it was possible to see excitation bands corresponding to the A, B, A' and B' absorption bands and again no noticeable change in intensity was noted in emission or excitation spectra. This is in agreement with the work of Denks (1966) and Denks and Leiman (1968) who showed that a field did not affect the emission from thallium and indium doped alkali halides when excited in A and B bands. However they did observe field effects when exciting with U.V. light in the C band of the thallium and indium doped absorption spectra and when band-to-band transitions were excited.

Discussion

It is pertinent at this point to summarise the results of other workers who have observed electrophotoluminescence in alkali halide crystals. First the work of Zakharko and Triska (1965) showed a decrease in light output from NaI(Tl) when excited by X-rays. They observed a linear decrease with applied field for X-rays striking the crystal through the negative electrode and a more complex relationship when this electrode was made the anode. Also the relative reduction decreased as the X-ray intensity was increased. The work of Denks (1966) showed field effects for

U.V. excitation of the thallium centre in the fundamental absorption region. In these experiments the crystals were excited through a grid electrode and due to the high absorption coefficient of the crystals in the fundamental region only a thin layer of the crystal was excited. Under these conditions application of an electric field showed a transient supression of the emitted intensity. Taking the initial value of the supressed intensity reproducible results were obtained. These showed that in KI(Tl) and RbI(Tl) the emission from the thallium centres was supressed for excitation that produced band-to-band transitions and there was no effect for excitation in the thallium absorption bands or the first exciton peak. For NaI(Tl) and CsI(Tl) a supression was seen for excitation in the first exciton peak as well as for band-to-band transitions but no effect was seen due to the normal thallium absorption bands. In these experiments the effect of an applied field can be explained as altering the movement of electrons and, to a lesser extent, holes formed by band-to-band excitation. These carriers can be removed from the region of excitation, decreasing their concentration in the luminescing region. In KI(Tl) and RbI(Tl) excitation in the first exciton peak does not produce free carriers and hence no field effect is observed, but in NaI(Tl) and CsI(Tl) the excitons formed by absorption in the first exciton peak must be ionized producing free carriers.

Results similar to those of Denks (1965) have been observed for the intrinsic emission in pure KI at liquid nitrogen temperature by Onaka (1966) when the crystals were excited in the band-to-band region. However a study by Onaka et al. (1967) of NaCl(Ag) showed an enhancement of the Ag^+ emission bands excited by band-to-band transitions when an electric field was applied to the crystal. The enhancement is explained by the assumption that the free electrons produced are not only moved by the field but actually accelerated by the field. These accelerated electrons excite centres by collision as envisaged in electroluminescence processes. Further results by Denks and Leiman (1968) show quenching of emission in KBr(Tl), KI(Tl), KBr(In) and KI(In) when excited by band-to-band transitions and also when excited in the C absorption band. This latter effect is explained in the same way as that for band-to-band excitation since excitation in the C band leaves the electron in a $^1P_1$ excited state that can easily be thermally ionized which produces free electrons.

Finally electrophotoluminescence experiments by Stella and Gustinetti (1969) on KCl(KI) showed an enhancement of the 430 nm emission at room temperature. This emission was shown to be due to the capture of a hole by an F-centre by Timusk and Martienssen (1962). The enhancement in this emission seen by Stella and Gustinetti (1969) was found for excitation in the X exciton region. The classification of the peaks in the fundamental absorption region is made from the work of Baldini and Bosacchi (1968) and Roessler and Walker (1968). To explain these results Stella and Gustinetti (1969) proposed that the electric field ionized the X excitons formed leading to an increase in the number of free holes present in the excitation region and hence giving an increase in light observed due to the process of an F-centre capturing a hole.

It is possible to explain the effects of an electric field, with the exception of those of Onaka et al. (1967), by a slight modification of the theory proposed by Denks and Leiman (1968). Here we must consider the possible excitation and recombination processes:-
(1) an exciton is created which then transfers its energy directly to a radiative centre which produces this centre's characteristic emission (2) electron-hole pairs are created during excitation which then diffuse separately to an activator centre. Emission is only observed after a centre has trapped an electron and a hole in any order. An electric field is considered to be able to affect only the motion of separate charge carriers and thus only process (2) is influenced. Now this latter process may be further subdivided. (a) Unimolecular Recombination. This means that a free electron must recombine with the hole created by the same photon at some recombination centre. (b) Dimolecular Recombination. This allows for the possibility of a free electron recombining with a hole from a different electron-hole pair. Competing with these processes is a trapping process for electrons and holes at various trapping centres and such a process may emit light characteristic

of the trapping process. Thus it is possible to summarise the various processes as follows:-

exciton $\rightarrow$ (activator)* $\rightarrow$ activator emission (1)

$$\begin{tikzcd}
\text{electron + hole} \arrow[r] \arrow[dr] & \text{(activator + electron) + hole} \arrow[r] & \text{(activator)*} \arrow[d] \\
& \text{(activator + hole) + electron} \arrow[ur] & \text{activator emission}
\end{tikzcd}$$

(2)

electron $\rightarrow$ electron trap $\rightarrow$ possible emission during trapping (3)

hole $\longrightarrow$ hole trap $\longrightarrow$ possible emission during trapping (4)

When a field is applied it tends to separate the electrons and holes thus increasing the probability of processes (3) and (4) at the expense of process (2). Consequently the experiments which monitor the activator emission see a reduction in intensity while the work of Stella and Gustinetti (1969), observing light emitted via process (4), shows an increase in observed intensity. The experiments of Denks and Leiman (1968) provide good confirmation of the above mechanism. They observed a field effect for excitation in the C-band of Tl^+ and In^+. This produces the system of a hole trapped at the activator centre and an electron that can be freed from the centre. Now it can recombine at the centre or be trapped via process (3). So with the field helping process (3) a decrease in activator emission is observed. As the excitation intensity is increased a reduction of the field effect is observed and is attributed to a transition from unimolecular to dimolecular recombination kinetics. This means that the electron traps become ionized activator centres and process (3) actually becomes identical with process (2).

Our present experimental results are consistent with the model proposed by Denks and Leiman (1968). In the case of NaI(Tl) the effect is smaller than in pure NaI and can be explained in terms of the thallium centres being most efficient in capturing electrons and holes. This is the reason that NaI(Tl) is a very efficient scintillator. In pure NaI at room temperature the centres responsible for the 375 nm emission are the predominant activator centres participating in the scintillation process. Application of a field reduces the intensity of the 375 nm emission but increases the 440 nm emission. This we can interpret by proposing the 375 nm emission occurs through process (2) while the 440 nm emission is due to process (3) or (4). At liquid nitrogen temperatures the 295 nm intrinsic emission is observed besides the 375 nm emission and both show a decrease in intensity upon application of an electric field. Thus both of these emissions are excited via process (2) and application of a field increases the probability of processes (3) and (4). No increase of any emission is observed at liquid nitrogen temperature which means these processes are either radiationless or the emission efficiency is low. A subsidiary experiment on a pure crystal showing an appreciable 440 nm band at room temperature did indicate that the emitted intensity at 440 nm was low at liquid nitrogen temperatures. Consequently the centre producing the 440 nm emission can still be acting through process (3) or (4). One final point is that the work of Denks (1966) indicated that excitation into the first exciton peak in NaI(Tl) still produced a field effect. This complicates the process since the field affects process (1) to break up the exciton giving an electron-hole pair and then process (2) must be involved in recombination. However it is difficult to estimate how much this contributes to the emission process and it may be concluded that the electron-hole process is the most important in the scintillation process.

3-3 Thermoluminescence and Decay Curves

Excitation of the crystals by a sudden reversal of the applied voltage produces a large emission of light that slowly decays (see Fig. 3-16). Also this form of excitation at low temperature populates the trapping states that are thermally stable at that temperature. Consequently, increasing the temperature of crystals excited in this manner produces glow curves. Excitation of the crystals with alternating fields at low temperatures produced weak glow peaks when the crystal's temperature was increased, indicating that trapping did occur.

An analysis of the decay curves gives a measure of the traps that contribute to phosphorescence at that temperature and glow curves give information of traps that are stable at that temperature.

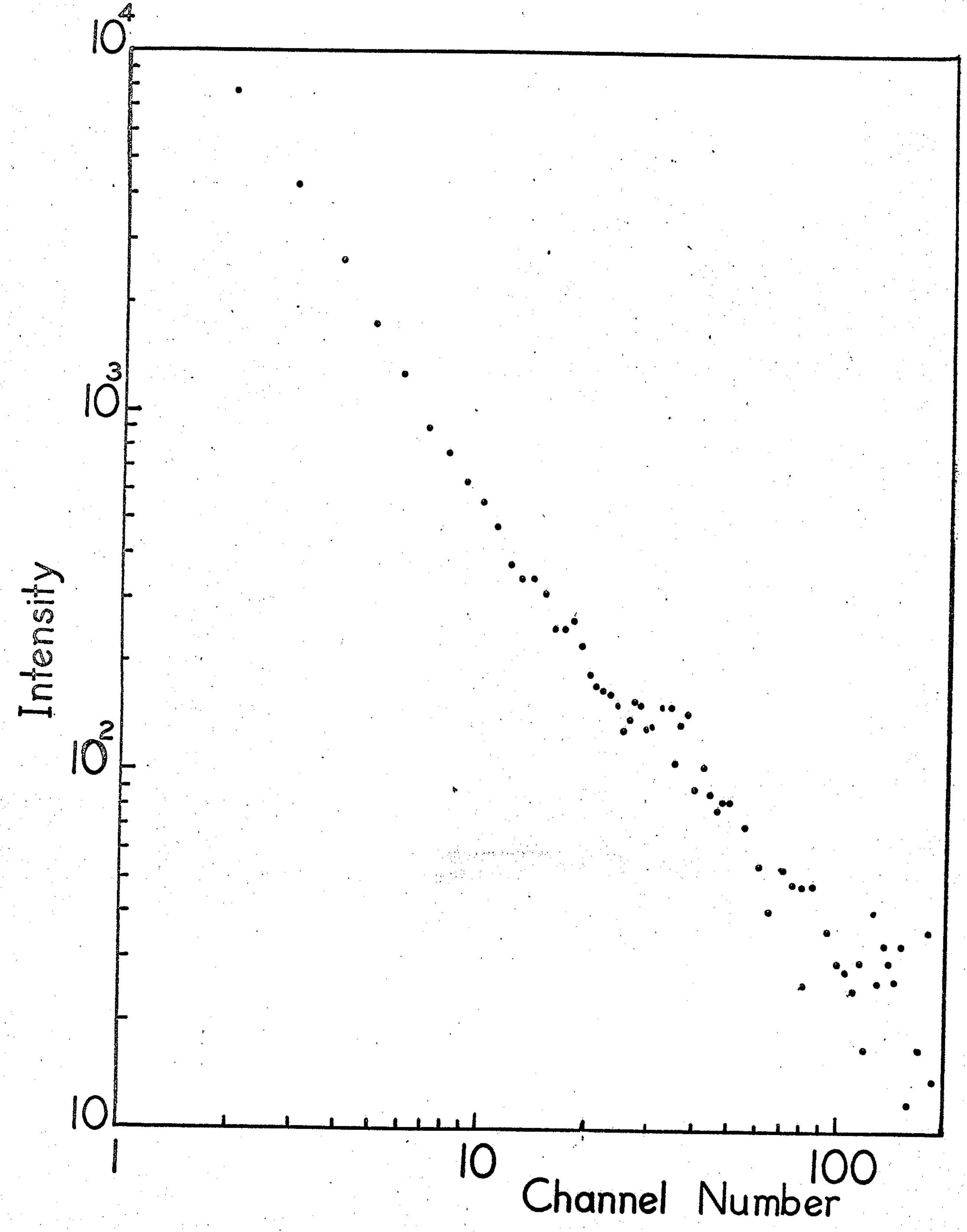
The decay curves were initially analysed assuming that first order kinetics were involved. That is that the decay curves were composed of a sum of exponential decays as given in equation (1.23). In this analysis a least squares fitting program developed by Wall (1968) was used. However difficulties were found with this method of analysis because consistent values of the time constants for the decays involved were not obtained. This situation occurred even though the Chi-squared analysis indicated that the fits were a good representation of the data. Two explanations of this result are possible. First it is possible that because of the mode of excitation considerable Joule heating occurs and thus the decay curves were not taken at a constant temperature. Secondly it may be necessary to invoke second order kinetics to explain the observed decays. In the former case no analysis is possible but the data can be analysed in terms of the latter explanation.

Fig. 3-25 shows a decay curve obtained at $100^{\circ}K$ and is plotted as the logarithm of the intensity versus the logarithm of the time measured from the time of excitation. This indicates that the decay on this type of plot can be represented by a straight line of slope -1.3. As was indicated in the introduction the normal analysis of second order decays usually requires that this slope be equal to -2. However, Curie (1960) has shown that this is only a special solution to the general second order equations and the index in the denominator of equation (1.30),

Figure 3-25

Decay curve of NaI(Tl) at 100°K on a log-log plot

(1 channel = 6.67 sec)



10^4
10^3
10^2
10
Intensity
1
10
100
Channel Number

and thus the negative slope of the line in Fig. 3-25, can differ from 2. Consequently the decay curves observed at 100°K follow second order kinetics or a temperature effect makes it impossible to identify first order decays.. Decay curves obtained between 100°K and 300°K followed this pattern although in some cases a combination of an initial second order decay with a final exponential decay was observed. For the purpose of studying the trapping of charge carriers the analysis of glow curves gave more information.

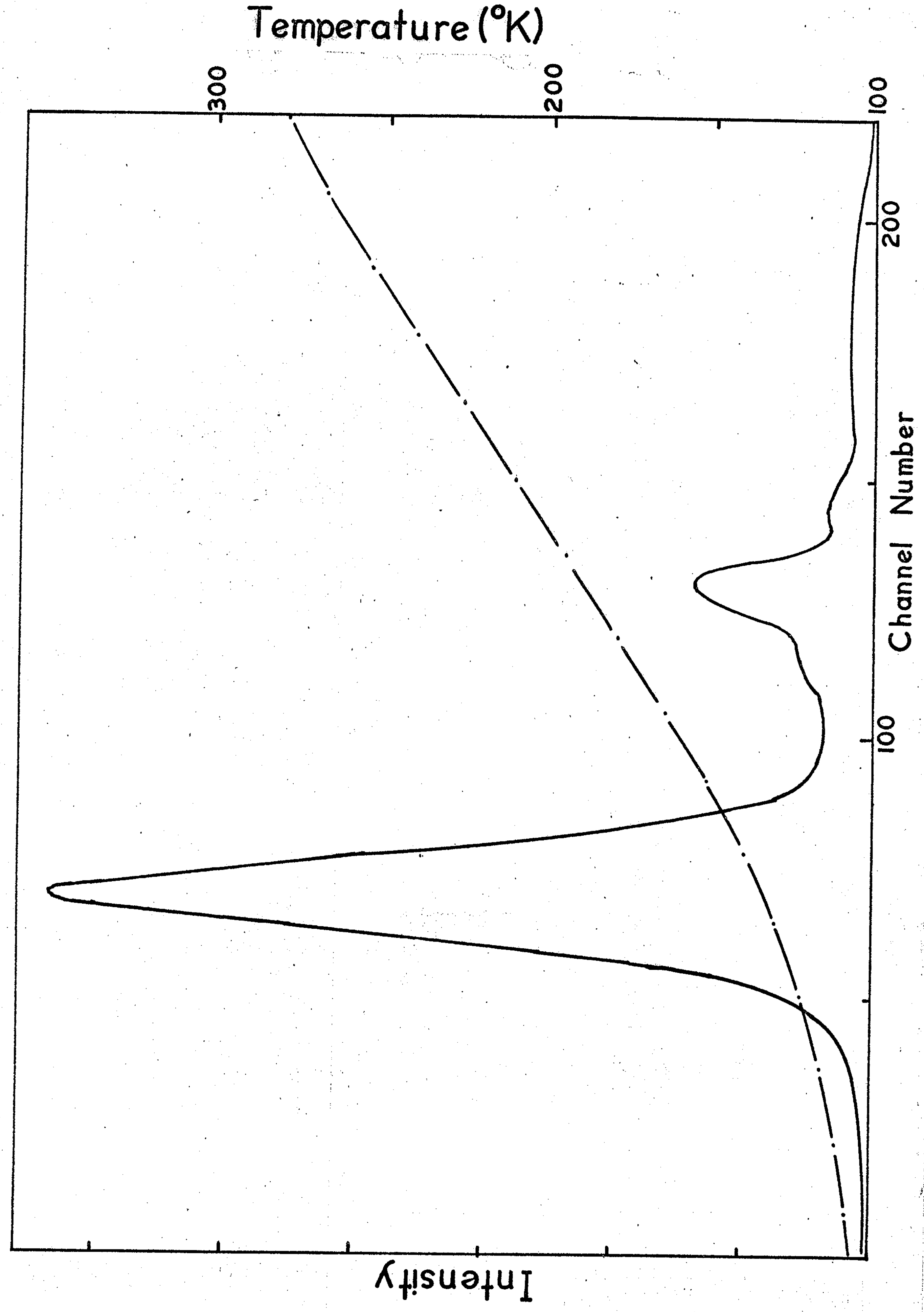
Fig. 3-26 shows a typical glow curve obtained from pure NaI with the monochromator set to look at the 375 nm emission band. This shows that there are two main glow peaks between 105°K and 295°K when the crystals were excited by a field reversal at 100°K. These peaks occur at temperatures of 134°K and 187°K. Other smaller peaks also are detectable at the approximate temperatures of 175°K, 205°K and 245°K but these peaks were too small to allow any analysis. Excitation with gamma rays at low temperatures gives the same glow curves. Experiments with Type 1 crystals with the monochromator set at 500 nm revealed two prominent peaks which again occured at 134°K and 187°K. No glow curves were observed when the monochromator was set to observe the 295 nm intrinsic emission. This is to be expected since V_K centres are mobile at 58°K according to Murray and Keller (1967) and so at temperatures above this they move through the lattice until they remove an

Figure 3-26

Typical glow curve for NaI

_____ emission intensity of 375 nm band

_ . _ temperature


Temperature (°K)
300
200
100
200
100
Channel Number
Intensity

electron from an activator centre, leaving an ionized centre. Kaufman and Hadley (1968) report a glow curve at 59°K which they attribute to this process in NaI(Tl). Thus above this temperature V_K centres do not exist for longer than the time required to diffuse to an activator centre once the source of excitation has been removed. Therefore in pure NaI two main glow peaks are observed which give emission in the impurity emission bands. Consequently these peaks can be assigned to some defects of the pure lattice which supply electrons or holes to impurity centres in the crystal.

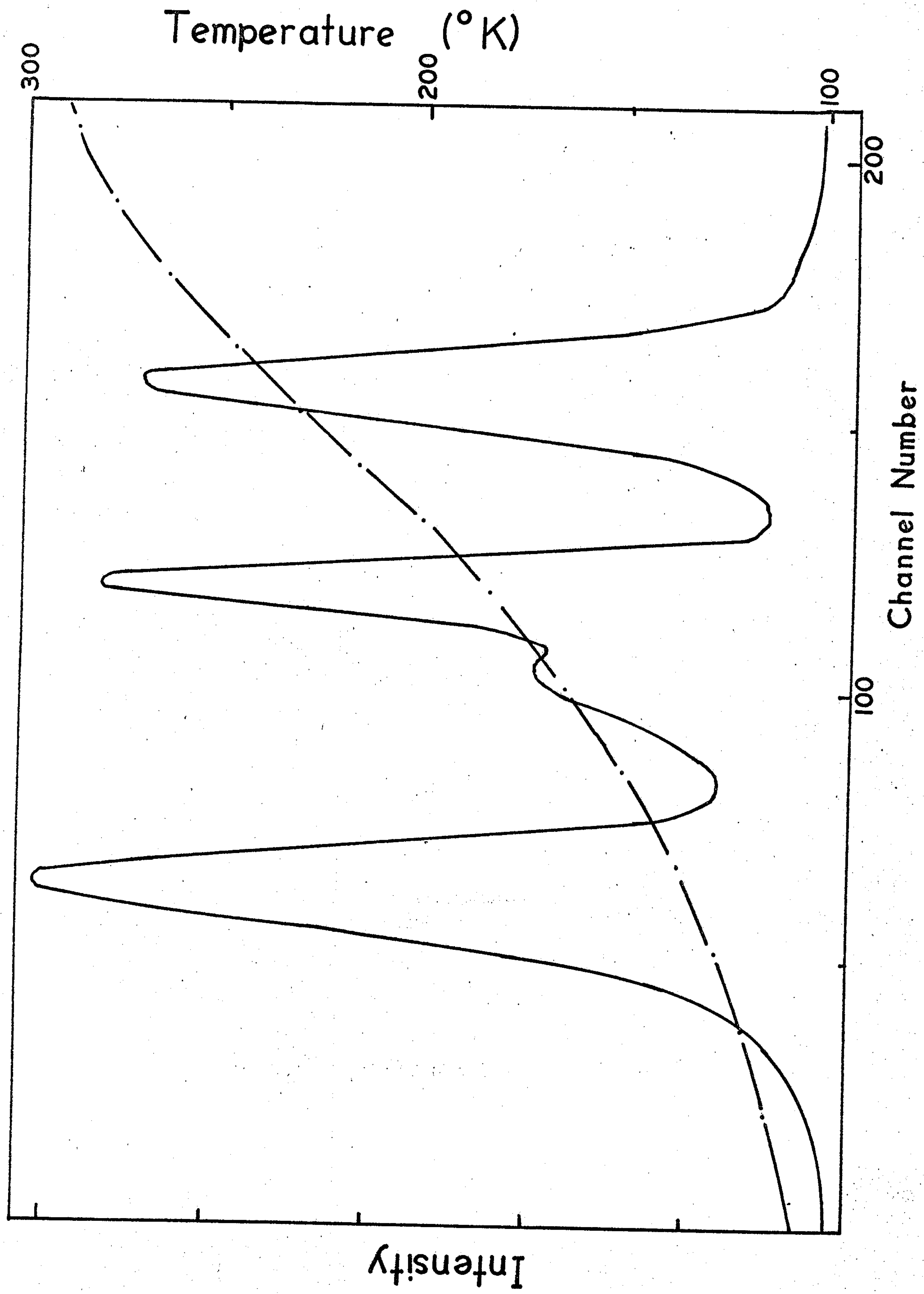
Experiments were also performed on NaI(Tl). Fig. 3-27 shows a typical glow curve for the 430 nm emission in NaI(Tl) between 105°K and 300°K after the crystal had been excited by a field reversal at 100°K. Peaks are observed at 134°K, 166°K, 187°K and 238°K. The same peaks are observed after the crystal has been excited by gamma rays. It is interesting to note that two of these peaks correspond to peaks observed in pure NaI for the impurity emission bands. This strengthens the hypothesis that these peaks result from the release of electrons or holes from defects that are properties of the pure lattice. The glow peak at 166°K may be the same as the small one in the region of 175°K in Fig. 3-26 but the large peak at 238°K must be associated with the addition of thallium to the pure crystal. Possibly the 166°K peak may also be associated with thallium centres. A study of the lifetimes involved in the radioluminescence process by Wall (1968) between 180°K and 300°K

Figure 3-27

Typical glow curve for NaI(Tl)

_____ emission intensity of 430 nm band

_ . _ temperature


Temperature (°K)
300
200
100
Channel Number
100
200
Intensity

indicates three discontinuities in the temperature variation of the lifetimes observed in NaI(Tl) (0.11 mole % thallium which is the same nominal concentration as the crystal used in the present experiments.) These occured at 198°K, 240°K and 273°K. Undoubtedly the discontinuity observed at 240°K can be associated with the glow peak at 238°K, providing further verification that this glow peak is associated with thallium centres in NaI(Tl).

The four peaks observed in the various glow curves were analysed to determine the trap depth Δe and the frequency factor s defined in equation (1.19). The analysis was performed using the leading edge method (Nicholas and Woods, 1964) to determine the activation energy of each peak using equation (1.34). The problem of overlapping peaks was removed by performing an excitation at a temperature just below each peak such that a clean leading edge was obtained. The peak at 167°K appeared to be composed of more than a single peak and the activation energies for this peak were not reproducible. The value of the frequency factor s was determined from equation (1.27) which involves the glow peak position T* and the heating rate. This equation is valid for first order kinetics and so must be regarded as only a rough estimate of the frequency factor which is all that can normally be obtained. The results of the present measurements are presented in Table 3.1 along with results of earlier work in NaI and NaI(Tl).

Table 3-1

Authors	Glow Peak Temperature T^* (^oK)	Δe (eV)	$\log_{10} s$
Present Work	134 166 187 238	0.34 ± 0.03 --- 0.42 ± 0.03 0.44 ± 0.03	10 ± 2 --- 9 ± 2 7 ± 2
Bonanomi and Rossel (1951)	114 138 119 140 150	0.30 0.38 0.37 --- ---	11.9 12,7 13.4 --- ---
Bonanomi and Rossel (1951)	115 138 148	0.35 0.41 0.53	13.4 13.5 16.0
Sharma (1956)	140 170	--- ---	--- ---
Lyskovich Chornii and Guseva (1965)	120 140 160 220 290	--- --- --- --- ---	--- --- --- --- ---
Shamovskii (1966)	145 265 325	--- --- ---	--- --- ---
Lyskovich & Chornii (1967)	120 140	--- ---	--- ---
Kaufman & Hadley (1968)	59 105	--- ---	--- ---

Discussion

As can be seen from Table 3.1 it is difficult to compare the thermoluminescence results of various workers. The main problem in making such a comparison is the different heating rates β used by various workers. As can be seen from equation (1.27) for a given trap the temperature T* corresponding to the maximum of the glow peak is a function of the heating rate β. Therefore only if β is quoted is it possible to compare glow curves. Only the results of Bonanomi and Rossel (1952) include the heating rate and the thermoluminescence peak positions quoted are with a heating rate that is approximately the same as used in the present experiments (approximately 0.06°K/sec). The heating rate used by Kaufman and Hadley (1968) can be estimated from their data to be approximately 0.03°K/sec. Of these results, the glow peaks observed by Kaufman and Hadley (1968) lie outside the range of the present experiments and so only those of Bonanomi and Rossel (1952) can be used to make a comparison. Most likely the glow peak they observe at 138°K is the same as that observed by this author at 134°K. The thermal activation energies for these peaks agree within experimental error but there are discrepancies in the frequency factors. As was mentioned before, the measurement of the frequency factor is difficult to perform with precision. The peak observed at 148°K by Bonanomi and Rossel (1952) is probably hidden in the leading edge of the peak at 166°K which would account for the difficulty in obtaining consistent activation energies for this peak. The traps that produce the peaks at 115°K probably empty even at 100°K and so this peak is not to be expected in the present data. The peak at 115°K observed by Bonanomi and Rossel (1952) probably is the same as that observed at 105°K by Kaufman and Hadley (1968).

In an attempt to explain the various glow peaks that can be observed in NaI that is doped with various impurities, Kaufman and Hadley (1968) have associated the glow peak at 59°K with the temperature at which V_K centres become mobile. Murray and Keller (1967) report that this temperature is 58°K from studies of the reorientation of V_K centres. Light is emitted when the V_K centre, which is essentially a hole trapped in the lattice, moves to a Tl^0 centre, that is a Tl^+ centre that has trapped an electron. This process was described in equations (1.4) and (1.5). The glow peak at 105°K is attributed to the release of electrons from Tl^0 centres and their recombination at Tl^{++} centres as described in equations (1.6) and (1.3). This mechanism would also lead to a decay curve at this temperature that obeyed second order kinetics as was observed. This is because the electron released from the Tl^0 centre must find a Tl^{++} at which to recombine and produce light. There is opportunity for retrapping at a Tl^+ centre as the electron moves through the lattice and so second order kinetics apply to the decay. Shamovskii (1966) indicates that a possible mechanism responsible for the glow peak at 265°K is the release of holes from Tl^{++} centres and their recombination at Tl^{o} centres. Our present results indicate that the glow peak at 235°K is caused by thallium centres and the mechanism suggested by Shamovskii (1966) would be a possible explanation.

To explain the two other main glow peaks observed at 134°K and 187°K a mechanism involving the NaI lattice itself must be considered since these peaks appear in the various types of sodium iodide crystals. The work of Townsend et al. (1967) considered the observable glow peaks in relation to the lattice parameters of alkali halides. They observed correlations between the temperatures of the glow peaks and the lattice parameters of various alkali halides. These correlations indicate peaks in NaI would be expected at approximately 60°K, 130°K and 150°K. These they attribute to H-centres (two halogen ions at the site of a single halogen ion), a hole trapping defect and an electron trapping defect, probably an F'-centre, respectively. However, these assignments are very speculative but they do indicate that intrinsic lattice defects are to be expected to produce glow peaks in the region observed.

Therefore there are four major traps in NaI(Tl) that produce glow peaks between 100°K and 295°K. Only one (235°K) can be directly attributed to thallium centres while the remainder are due to lattice defect centres and these produce glow peaks in nominally pure crystals. The activation energies of three of these traps have been measured.

CHAPTER IV

CONCLUSIONS

4-1 Electrophotoluminescence

The radioluminescence spectrum of nominally pure NaI and thallium doped NaI was observed in relation to an applied electric field. At both 100°K and 300°K the effect of the electric field was to reduce the intensity of the main emission bands while an enhancement of one of the minor bands in pure NaI was also observed. The field effects have been explained using a modification of the mechanism proposed by Denks and Leiman (1968) which assumes that free electrons and holes are created in the scintillation process and the applied field alters the probability that direct recombination of an electron and hole will occur. The field causes the electron to move farther through the lattice giving a greater probability to various trapping processes. These trapping processes may produce light which would account for the increase in one emission band. The reduction in intensity appears to be linear with applied field and this is in agreement with the theory of free electron mobilities where the mean distance an electron moves, or Schubweg, is proportional to the applied field. A study of the time constants in the scintillation process as a function of applied field would provide further insight into this process.

These experiments were originally performed to possibly provide information about the internal fields. Since the scintillation process can be assumed to be a bulk phenomenon the fact that field effects were observed serves to indicate that substantial fields do occur in the bulk and are not completely concentrated in a barrier region. Also these fields do affect the movement of free charge carriers. The observation that an alternating field reduced the emission more than an equivalent D.C. field does indicate the possibility of an internal polarization occurring in the latter case which reduces the field in the bulk of the crystal. This polarization is due to the movement and subsequent trapping of free charge carriers and these charge carriers are probably involved in producing the large amounts of light observed when the polarity is reversed.

4-2 Thermoluminescence

The thermoluminescence experiments served to show that the effect produced by reversing the polarity of a D.C. applied field did populate the trapping centres in NaI that were stable at the temperature of excitation. These trapping states were also populated in the alternating field electroluminescence process indicating a similarity between these processes.

The results indicate that at least three trapping centres exist in pure NaI that are stable at $100^{o}K$ and are characteristic of the pure lattice. A fourth trapping centre that produces a glow peak at 235°K is associated with thallium centres in NaI crystals. A discontinuity in the time constants of the NaI(Tl) radioluminescence at this temperature (Wall, 1968) can be associated with the fact that this trapping centre will be effective below this temperature, consequently removing an energy transfer process.

The thermal activation energies associated with three of the glow peaks were evaluated and are listed in Table 3-1. Comparison with the results of other workers indicated that only one of the peaks had been analysed previously and the values of the activation energy for this peak were in agreement. The present calculations of the frequency factors were roughly in agreement with previous values since the errors involved in these results allowed the frequency factors to vary by up to two orders of magnitude. This is because the analysis of glow peaks is not sensitive to the value of the frequency factor.

4-3 Electroluminescence

The results presented here are the initial observations of electroluminescence in sodium iodide single crystals. This emission was produced by exciting the crystals with a high voltage alternating field. The emission spectra observed from the various sodium iodide crystals studied were remarkably similar to the radioluminescence spectra due to gamma rays. From this it is inferred that similar processes are involved, that is the recombination of free electrons and holes that have been produced by some excitation mechanism. Indeed this statement may be extended to include the same mechanism producing the free electrons and holes, namely impact ionization by high energy electrons. However it is not obvious if the analogy can be extended that far.

In the present work two mechanisms have been discussed with regard to explaining the experimental observations, namely electron and hole tunnelling from the electrodes and excitation by impact ionization. Both of these mechanisms can account for most of the experimental observations. However the observed effects with reversal of the polarity of a D.C. field are compatible with the impact ionization mechanism only. The derivation of the observed voltage dependence of the emission intensity provides a difficulty with both the proposed mechanisms and this problem is unresolved in many electroluminescence systems where the Alfrey-Taylor relation is observed. A Mott-Schottky barrier region is usually proposed to overcome this difficulty. The electrodes used in the present investigations were blocking electrodes and undoubtedly a barrier region does exist between the electrode and the crystal which can be assumed to be similar to a Mott-Schottky barrier. The observed voltage dependence is then explained as due to the number of electrons tunnelling through such a barrier region. In the impact ionization model it is these electrons that are then accelerated to optical energies.

The results of the electrophotoluminescence and the thermoluminescence experiments must also be included in a discussion of the possible electroluminescence mechanisms. From the electrophotoluminescence results it is clear that a substantial field exists throughout the bulk of the crystal and that such a field can influence the motion of charge carriers. There is also evidence of a polarization build up due to the motion of charge carriers when a D.C. field is applied which is necessary to explain the emission observed when the polarity is reversed. These results favour the impact ionization model. Thermoluminescence measurements show that there are several stable trapping centres at low temperatures where the luminescence process is more efficient. However these traps are only populated after some form of excitation has occurred at low temperatures. Thus they are populated by the electroluminescence process and do not supply electrons that are accelerated in the conduction band. The electron and hole tunnelling mechanism depends upon the holes being trapped and so this mechanism would predict a strong temperature dependence in the regions of the various glow peaks. A variation is observed in the region of only one glow peak and taken as a whole this can be considered as evidence against the electron and hole tunnelling mechanism.

Therefore it must be concluded that impact ionization is the most likely mechanism responsible for the observed electroluminescence. This mechanism is in agreement with the experimental observations and also experiments on electron mobilities in high fields do indicate effects that are related to this mechanism. Experiments to study the electron mobility in these crystals are suggested as a promising approach to provide further insight into the luminescence process together with the study of electroluminescence of alkali halides at lower temperatures.

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