Parameters Influencing The Luminescence Of Sodium-iodide.

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PARAMETERS INFLUENCING THE LUMINESCENCE OF NaI

by

Peter V. Meyers

A Dissertation
Presented to the Graduate Committee
of Lehigh University
in Candidacy for the Degree of
Doctor of Philosophy
in
Physics

Lehigh University
1978

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

January 9, 1978
(date)

W Van Sciver
Professor in Charge

Accepted January 9, 1978
(date)

Special committee directing the doctoral work of Peter V. Meyers.

W Van Sciver
Chairman

W. Beall Fowler

S R Butler

Dedication

To my family,

Carole, Gregory and Peter

Acknowledgements

The author is indebted to Professor Wesley Van Sciver for introducing him to the field of solid state physics and for the guidance, encouragement and support which he provided. Without his help this work could not have been completed.

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Table of Contents

List of Tables

List of Figures

Abstract

A series of relatively independent experiments were performed in an attempt to determine the parameters which cause the quenching of luminescence in the surface region of NaI. This region is called the dead layer. External electric fields temporarily increase or decrease luminescence excited with energy greater than the band gap. This effect depends upon temperature and field direction. A qualitative model is given. External fields on the order of 10^6 V/m decrease the relative probability of radiative decay of the self-trapped exciton, but naturally occurring fields in the surface region were not detected. Crystals were cleaved at liquid nitrogen temperature in vacuums as low as 3×10^{-7} torr and in N_2, He, and $N_2 + O_2$ atmospheres in order to determine whether adsorbed gas is the principal cause of the dead layer. Adsorbed gas does decrease the observed luminescence, but is not the principal source of luminescence quenching. Exposure of NaI to I_2 gas at 500°C did not affect the dead layer. Exciton diffusion with surface annihilation is not responsible for the luminescence quenching. Flash lamp experiments showed that the luminescence quantum efficiency of a freshly cleaved crystal initially increases with uv exposure and that thereafter the quantum efficiency is influenced by the intensity of the uv light to which the crystal had previously been exposed. A measurement of the

Dember effect determined an upper limit of 9×10^3 V/m for the photo-induced field strength.

Using a technique in which recombination luminescence is stimulated with red/infrared light in a crystal which has been exposed to ultraviolet light, evidence is found that copper impurity $\lesssim 10^{-7}$ molar fraction acts as a "catalyst" for producing intrinsic luminescence upon excitation in the low energy tail of the exciton absorption peak, and possibly at higher energies. This is explained with a model in which a hole is ionized from a Cu^+ center with an energy ~0.25 eV less than that necessary to create a V_k center in the perfect crystal. It is also shown that at least some of the copper luminescence at 370 nm excited in the low energy tail of the exciton absorption peak is due to recombination of an electron with a hole at a copper center. The stimulated intrinsic and impurity luminescences in crystals with detectable copper concentrations exhibit a peak in intensity after pre-exposure in the low energy tail of the exciton absorption peak. The energy of this peak is found to be a function of the absorption coefficient and to shift with temperature in accordance with Urbach's rule. A simple model for this behavior is given. No stimulated luminescence is observed after pre-exposure in the copper absorption band at 4.85 eV or in the thallium "A" or "D" bands. Stimulated luminescence is observed after pre-exposure in the thallium "C" band.

1.0 Preface

1.1 Motivation For These Investigations

During the summer of 1973 the author worked under the direction of Dr. W. J. Van Sciver and Dr. W. L. Emkey in an investigation of the non-luminescent "dead layer" in NaI. The "dead layer" is a region beneath the crystal surface which does not luminesce in the same way as the rest of the crystal. The "dead layer" concept was well established[1-7] at this time, and by the end of that summer we had succeeded in making a quantitative measurement of the dead layer depth in NaI.[8] Having demonstrated the existence of this layer, the obvious question arose, what causes the dead layer?

There was no shortage of possible mechanisms. Surface electric fields, adsorbed gases, exciton diffusion, impurity effects and photo-induced effects all seemed to be viable alternatives. Thus the author began his investigations in hopes of determining the primary cause of the dead layer.

1.2 Organization

The first section is designed to acquaint the reader with the luminescence processes which occur in NaI. Also included in this section is a discussion of the mechanisms by which a dead layer could be created.

The following six sections are relatively independent investigations of the various possible dead layer mechanisms presented generally in the order in which they were performed. In some cases, such as in the electric field and flash lamp experiments, interesting effects were observed. Other experiments, such as the adsorption, excess I_2 and Dember measurements, as well as the exciton diffusion calculation, led to largely null results, but are included for completeness.

The stimulated luminescence experiments were initially conceived as an extension of the Dember measurements. Once initiated, however, it became clear that these experiments could be used to explain some of the results of the electric field and flash lamp experiments, as well as providing some insight into the luminescence processes of NaI.

The final section is a summary of the results of all the experiments with a few suggestions for further research.

2.0 Background

2.1 Luminescence In NaI

In order to understand the results which follow, it is necessary to review the well-known luminescence processes which occur in NaI.[9-11]

2.1.1 Intrinsic Luminescence

NaI is a face-centered cubic crystal with the NaCl structure. Figure 1 is a graph of the optical density of NaI in the uv region at liquid nitrogen temperature (LNT). The energy gap between the top of the valence band and the bottom of the conduction band is 5.8 electron volts.[12] Light of energy equal to or greater than this value removes an electron from the valence band, which is made up of 5p orbitals of the iodine ions, and places it in the conduction band, the lower edge of which is made up from the 3s orbitals of the sodium ions.

The electron is free to move throughout the crystal, but the hole quickly becomes self-trapped and forms a V_k center. The V_k center is essentially an I_2^- molecular ion which is distorted by the crystal field.[13] Two nearest neighbor iodine ions are drawn toward one another along one of the <110> directions as shown in Figure 2. The V_k center is <u>not</u> associated with any crystaline defect, such as a vacancy, and is probably formed within a few lattice vabration periods after the electron is removed, i.e. $\sim 10^{-13}$ seconds. It is certainly created in less than 10^{-11} s.[14]

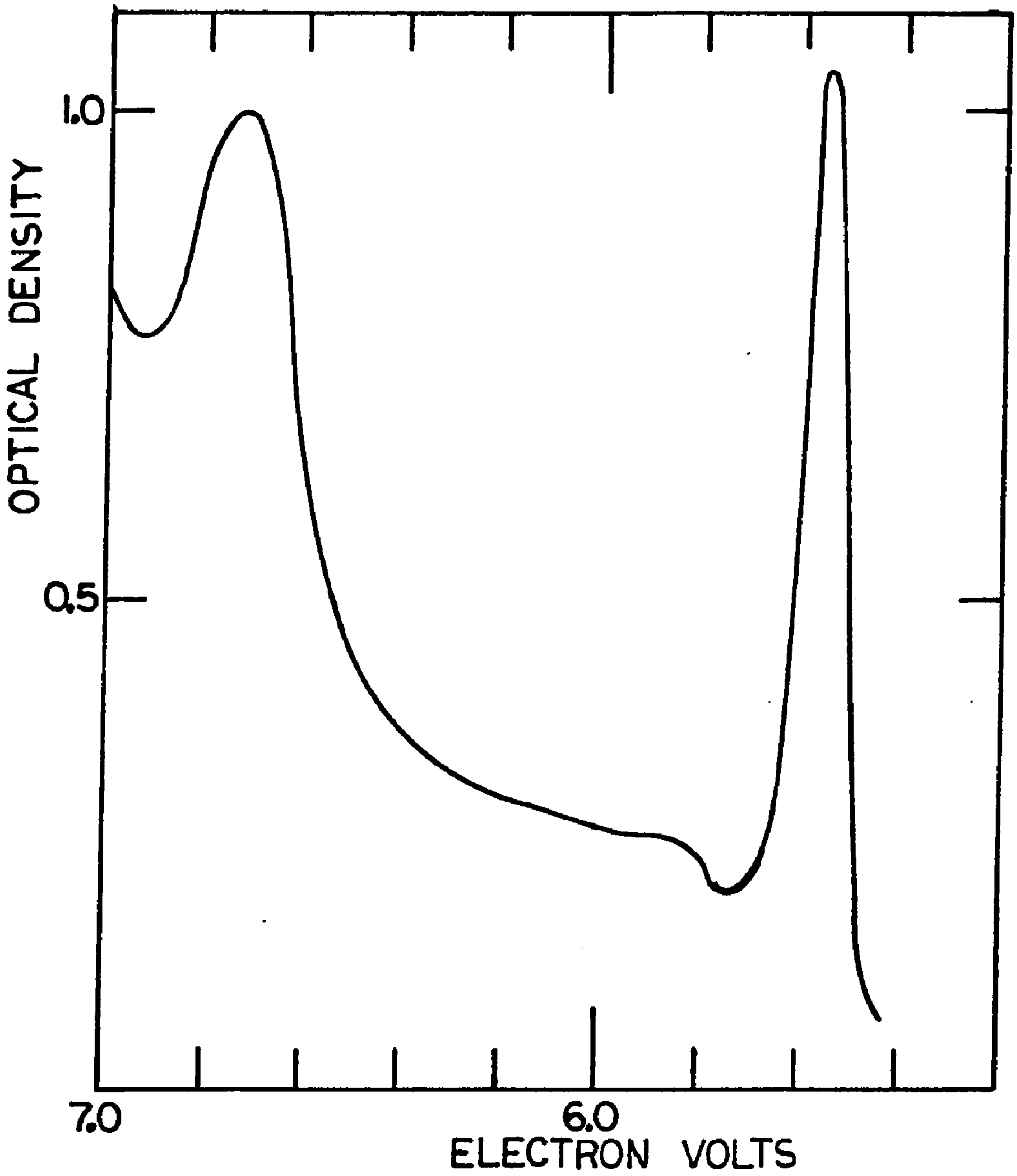

Figure 1. Optical Density of NaI. Data were recorded on a thin film (~ 900 Å) at LNT. Optical density is defined as $\log_{10}\left[\frac{\text{incident light intensity}}{\text{transmitted light intensity}}\right]$. Adapted from reference 12.

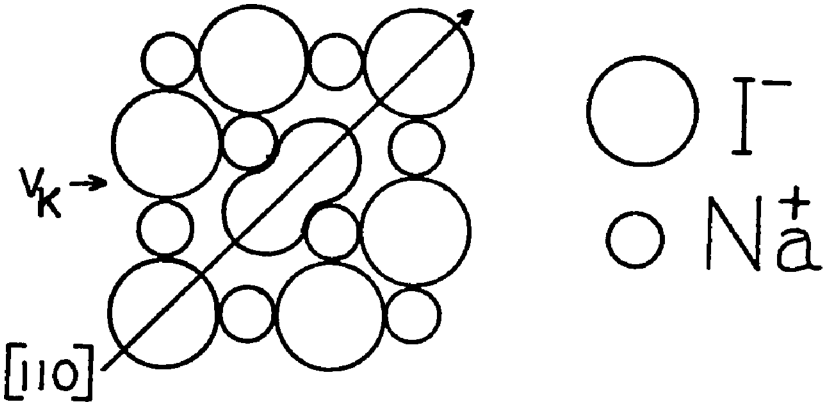

Figure 2. The V_k Center.

Below 58 K[10] the V_k center is frozen into its original orientation, but above this temperature it can reorient by activation over a barrier of 0.18 eV.[15] When a V_k center reorients, at least one iodine ion in the V_k center is replaced by another at a different lattice site. By this process the V_k center migrates through the crystal. Its diffusion coefficient, D, is given by Popp and Murray[15] $D \geq \frac{a^2}{12} K_{110}$ where a is one half the lattice constant of NaI, about 3.237 Å and K_{110} is the reorientation frequency. One may estimate from their data that the best straight line fit to the graph of ln (K_{110}) versus 1/T is $K_{110} \approx 2.18 \times 10^{13} \exp\left(\frac{-0.163 \text{ eV}}{kT}\right) s^{-1}$ over the temperature range 44-50 K. The electron and the V_k center have a coulombic attraction, modified by the crystal lattice, and an electron captured by a V_k center creates a V_k + e center. This center may or may not be mobile on the order of the V_k center, but it certainly cannot diffuse far within its lifetime, $\lesssim$ 110 nanoseconds.[16] Below ~ 60 K the V_k + e center decays with the emission of a 4.2 eV photon. Above ~ 60 K the V_k + e center may collapse nonradiatively to the perfect lattice with an activation energy of about 0.07 eV.[16]

Light of energy just below the band gap is also strongly absorbed. In this case the electron is not given enough energy to escape from the hole and the electron and the hole remain bound together. This excited state is called an exciton. The exciton in this state is very mobile and therefore is probably not associated with much, if any, distortion of the lattice. The exciton may travel through the crystal until it collides with an impurity and transfers its energy to the impurity.[17, 18] If the impurity decays radiatively the luminescence of the impurity can be observed. This is called host sensitized luminescence and will be discussed below.

The proper exciton may also decay by thermal activation over an 0.015 eV barrier to form the V_k + e center. For this reason, the V_k + e center is sometimes referred to as a self-trapped exciton (STE).[19] The STE thus formed decays by the same routes as stated above.[16]

2.1.2 Luminescence Due To Impurities

The large band gap in NaI means that the crystal is nearly transparent to light over the energy range from a few tenths of an electron volt (infrared) to about 5.5 electron volts (near ultraviolet). This property allows us to study the absorption and luminescence of many types of impurity centers within the crystal, especially when both the light absorbed by the impurity center and the light emitted by it are transmitted by the host crystal. Two such "color centers" are formed by thallium and copper ions.

A. Thallium Luminescence

Thallium is the better known impurity center because NaI(Tl) is useful as a detector of high energy radiation.[20, 21]

Thallium in NaI exists as Tl^+ and is substitutional for Na^+ in the lattice. The electronic configuration of the ground state is $^1S_0$. The first excited state is formed by exciting an electron from the 6s to one of the 6p orbitals (see Figure 3).

Transitions between the $^1S_0$ and the $^3P_2$ and $^3P_0$ states are dipole forbidden. The transition to the $^1P_1$ state is allowed and results in an absorption called the "C" band. There is also an "A" band absorption due to the $^1S_0$ to $^3P_1$ transition, which is allowed because of spin-orbit coupling. A weak absorption due to the transition from $^1S_0$ to $^3P_2$ is observed because of interaction with lattice vibrations. This temperature sensitive absorption is labeled the "B" band. In NaI at LHeT (liquid helium temperature) the "A", "B" and "C" bands are at 4.25, 5.0 and 5.3 eV, respectively.[22]

Although there are several transitions allowed in absorption,[22, 23] there is only one principal emission above LNT. This emission is at 425 nm and is attributed to a diffuse excitonic state localized near a thallium ion. At lower temperatures a second emission at 325 nm is also observed. The latter emission is attributed to the transition $^3P_1 \longrightarrow {}^1S_0$.[24] In order to decay to the $^1S_0$ state from the $^3P_2$ or $^3P_0$ state the Tl^+ ion must absorb or emit a phonon from the NaI host lattice. The $^3P_0$ and $^3P_2$ states act as electron traps at low temperatures.[25] For a more complete analysis of the thallium ion in the alkali halides, see

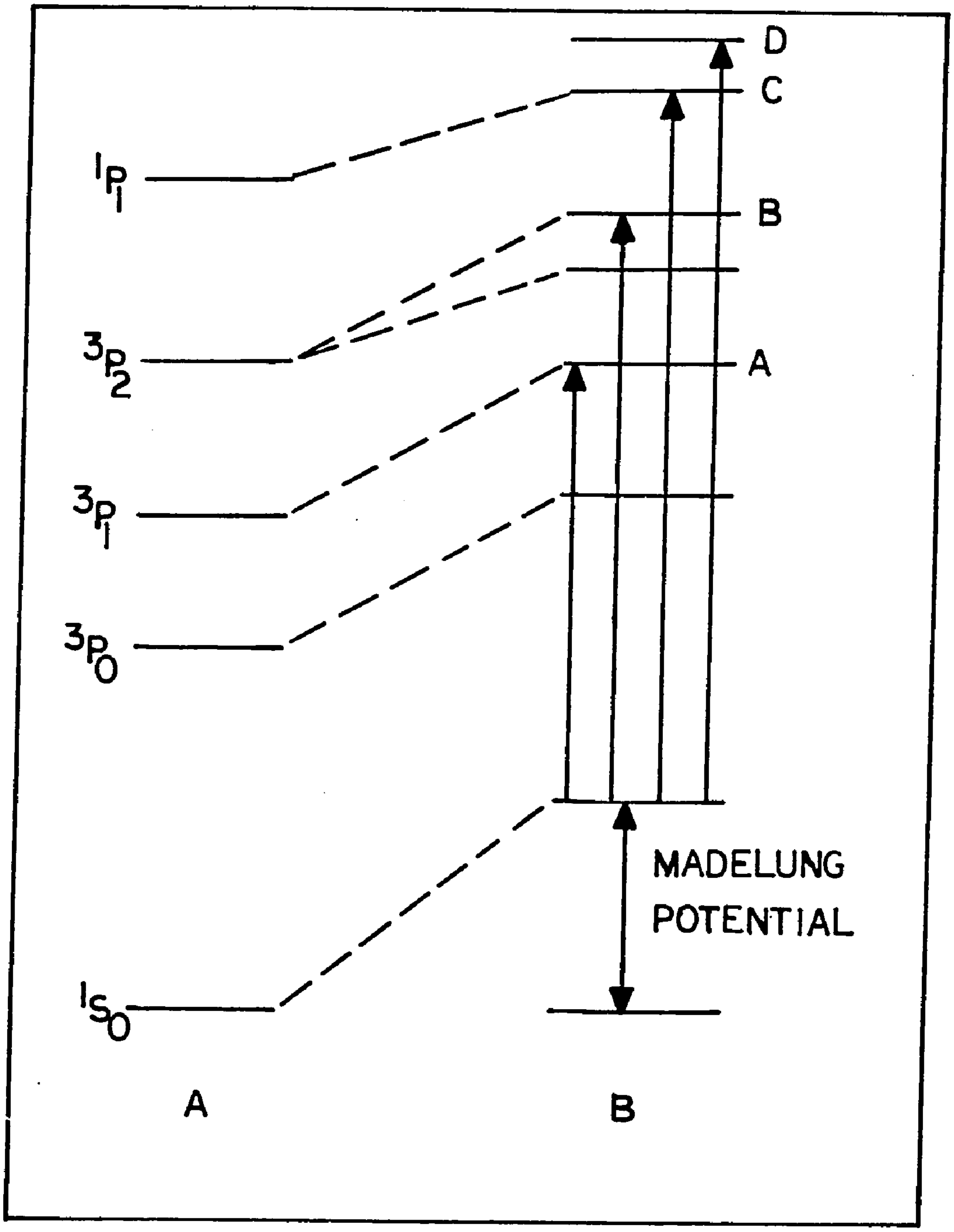

Figure 3. Energy Scheme of the Positive Thallium Ion. A - free ion; B - ion in the crystal field. The transitions producing the principal absorption bands are indicated. Adapted from reference 21.

references 26 and 27.

B. Copper Luminescence

The situation is similar with the copper impurity. The copper is believed to be substitutional for Na^+ and to exist as Cu^+. The Cu^+ center absorbs light which excites the ion from a $3d^{10}$ to a $3d^94s$ state.[28] At LNT this absorption occurs at 4.85 eV. The emission is due to the reverse transition and occurs at 3.30 eV. As is the case with the Tl^+ impurity, the absorption and emission are modified by the host lattice.

2.1.3 Host Sensitized Luminescence

Under this heading will be included emissions which are due to the presence of impurities, but in which the absorption is not by the impurity itself. The host lattice absorbs energy and transfers this energy to a defect or impurity by any of several mechanisms.

A. Perturbed Excitons

There is an additional absorption band in NaI(Tl) which is called the "D" band. This occurs at an energy near the low energy tail of the exciton absorption band and is thought to be due to an exciton formed next to a Tl^+ impurity, i.e. a perturbed exciton.[23, 29, 30] The perturbed exciton model explains the location of the α and β absorption bands in the alkali halides.[29] These are due to excitons created next to anion vacancies and F-centers, respectively, and their locations can be predicted using the charge transfer model.[31, 32] This model as it pertains to NaI(Tl) is made plausible by the following argument. An exciton can be considered as an electron transferred from an iodine ion to six nearest neighbor sodium ions.[33-35] If one of the nearest neighbor Na^+ ions were replaced by a Tl^+ ion, this transfer would be easier because the electron affinity of Tl^+ (ionization potential of Tl^o) (6.108 eV) is greater than that of Na^+ (5.139 eV). Thus the transfer might take place at a lower energy.

The copper luminescence is also excited in the low energy tail of the exciton absorption. Here also this may be the result of a perturbed exciton, an exciton created near a copper impurity. The ionization potential of Cu (7.726 eV) is 2.587 eV greater than that of Na, so that this "copper exciton" should be formed at lower energy than the "thallium exciton".

B. Recombination Luminescence

When free electrons and holes are created in a crystal and they are mobile, some of them will be captured at defects (impurities). When a defect captures both an electron and a hole, this may produce luminescence. The best example of this phenomenon was studied by Dietrich and Murray[36] in the alkali iodides. Thallium, which normally exists in the crystal as Tl^+, acts as both an electron trap, becoming Tl^o, and as a hole trap, becoming Tl^{++}. Luminescence occurs when a V_k center diffuses to a Tl^o (this diffusion limited process is relatively slow and is sometimes called the inertial[37] component of the luminescence) and also when an electron is captured by a Tl^{++} (called the instantaneous component, $<10^{-6}$ s).

C. Exciton Diffusion

a. The Proper Exciton

A second method of energy transfer is via mobile excitons. Strictly speaking, an exciton may exist only in a perfect crystal, where it moves like a polarization wave with momentum and direction specified by a wave vector and effective mass. We call this the proper exciton. It has been estimated that an exciton may travel distances up to 10^{-4} cm and visit 10^7 lattice sites before decaying with a lifetime of 10^{-8} s.[38, 39] Exciton diffusion has been invoked in order to explain several phenomena. Apker and Taft[3] explained a peak in the photoemission spectrum at the exciton absorption energy in RbI with a model in which excitons diffused through the crystal and ionized F-centers. Sydor[40] determined a diffusion length of 3×10^{-5} cm for excitons at room temperature using the results of photoconductivity measurements on a thin film of RbI. The excitons contributed to the photoconductivity by dissociating at the surface. Wolkenstein et al.[41] attributed the quenching of exciton luminescence in Cu_2O by adsorbed gases to the excitons diffusing to the surface where the adsorbates act as recombination centers. Emkey and Van Sciver[18] explained the presence of a peak in the photoconductivity spectrum of NaI with a model based upon work by DeVore.[42] In this case diffusing excitons free electrons from shallow traps in the crystal.

As mentioned earlier, the exciton as formed in NaI is highly mobile and travels easily through the crystal.[17, 43] In this case the "proper" or "hot" exciton is moving and energy transfer occurs before the exciton self-traps. (Redfield[44] notes that excitons will be polarized by the electric field, F, of charged defects and thus will be attracted toward the defect by a force equal to αF where α is the polarizability of the exciton. This increases the efficiency of energy transfer.) This phenomenon has been observed in many of the alkali halides involving transfer to heavy metal impurities[45, 46] as well as to halogen impurities.[47] In this case the lifetime of the intrinsic luminescence is not affected because energy transfer occurs prior to self-trapping. The quantum efficiency, of course, depends upon impurity concentration and temperature.

Rosenstock[48] has examined the quantum efficiency of luminescence in a crystal with mobile excitons. While his solutions were not exact, he showed that the quantum efficiency depends upon the ratio of the probability of luminescence or self-trapping at any one step $1/t_1$ to the probability of moving to another site, $1/t_2$ and upon the impurity concentration. t_1 is the lifetime of the excited state in the absence of impurities, while the diffusion coefficient is proportional to $1/t_2$.

Nishimura and Tomura[45] state that the diffusion coefficient, D, for excitons in a pure crystal, where the scattering is due to phonons, is given by

$$\frac{1}{D} = \frac{1}{D_{ac}} + \frac{1}{D_{op}}$$

where D_{ac} varies as $T^{-1/2}$ and reflects scattering by acoustical phonons (dominant at low temperatures) and D_{op} is $\beta T^{1/2}(\exp(\hbar\omega_{LO}/kT) - 1)$ where ω_{LO} is the frequency of the longitudinal optical phonon. D_{op} reflects the effects of scattering by optical phonons and dominates at higher temperatures.

b. The Relaxed Exciton

Even after an exciton becomes self-trapped, it is not entirely immobile. In order to move, however, it must overcome the energy barrier created when the lattice distorts during the self-trapping process. In this case the diffusion coefficient will vary as $\exp(-E_d/kT)$ where E_d is the energy of the barrier to diffusion. In this same temperature range, however, the probability of thermal decay of the excited state varies as $\exp(-E_t/kT)$ where E_t is the energy of the barrier to thermal decay. Thus the distance which the exciton is likely to move is $\sqrt{2\,Dt}$, where t is the lifetime of the excited state, ~ $\exp(-(E_d - E_t)/2kT)$. Thus if $E_d > E_t$ there will be an increase in the host sensitized luminescence as the temperature is raised.

Also note that in this case the lifetime of the STE luminescence will decrease as the concentration of impurities is increased. This is because the rate of destruction of STEs is increased by this mechanism. This is the principal factor in determining the intrinsic luminescence lifetime (110 ns in NaI).[16] In the case of transfer by proper excitons the luminescence lifetime is not affected because the time required for self-trapping is short (≤ 5 ns in NaI at LHeT)[17] and energy transfer by this mechanism stops after exciton relaxation.

Relaxed exciton diffusion contributes to the host sensitized luminescence in CsBr(In), CsBr(Tl),[46] and NaCl(Ag).[49] Calculations suggest that the activation energy for STE migration is somewhat less than for the diffusion of V_k centers. For example, in NaCl(Ag) the activation energy of the STE diffusion is 0.21 eV while that of hole diffusion is 0.44 eV.

D. Resonance Transfer

Another mechanism for energy transfer from the host lattice to an impurity center is resonance transfer.[50] This may occur when the emission band of the intrinsic luminescence overlaps with the absorption band of the impurity. In this case the dipole transition in the excited host induces an excitation of a dipole transition in the impurity center via a van der Waals interaction without the emission of a photon. Higher order transfers, e.g. dipole - quadrupole, may also occur, although their efficiencies are much lower. Since the energy is transferred from the luminescing state, both the quantum efficiency and lifetime of the intrinsic luminescence are reduced as the impurity concentration is increased.

Emission from the proper exciton has recently been reported;[51] however there are no known cases of resonance transfer from this state. There are several examples of resonance transfer from the STE[46, 52] in the alkali halides. Among those listed by Lushchik _et al._[46] is NaI(Tl). This, however, is not consistent with earlier work of Fontana _et al._[16] which does _not_ show a decreased lifetime for the intrinsic luminescence excited in NaI(Tl) compared to that of the pure crystal.

E. Emission With Reabsorption

Another possible means of transferring energy from the lattice to an impurity which occurs when the absorption band of the impurity overlaps with the emission band of the intrinsic luminescence is emission followed by reabsorption. In this case the photon is emitted and its probability of absorption depends upon the energy of the specific photon as well as the geometry of the crystal. Dexter[50] notes that the host sensitized luminescence due to this process would be greater for a cylindrical crystal than for a thin film of equal mass and impurity concentration. This is because the probability of transfer depends upon the total cross section for absorption as viewed from the point of emission. This is not the case for resonance transfer. Another difference is that the maximum transfer efficiency is limited by the overlap of the impurity absorption and intrinsic emission bands. Thus, for example, if the absorption band of the impurity overlapped one third of the area of the host emission band, the maximum energy transfer would be one third of the energy absorbed by the host, independent of the impurity concentration. For resonance transfer the efficiency would approach one for high impurity concentrations with the same overlap. A third difference is that while emission followed by reabsorption would affect the observed quantum efficiency of the host luminescence, it would not affect the lifetime. This process occurs in NaI(Tl) in which absorption in the "A" band of Tl produces a dip in the intrinsic emission band at 288 nm.[10]

2.1.4 Stimulated Luminescence

In addition to the methods described above, there are other means of producing luminescence in NaI. A crystal which has previously been exposed to gamma, x-ray or ultraviolet radiation can store energy in the form of trapped electrons and holes. The stored energy is released when the electrons or holes escape from their traps and are allowed to recombine. This phenomenon has been studied in many of the alkali halides.[53-57]

This process may be explained as follows. Thallium in NaI has three charge states; Tl^{+}, the normal state; Tl^{++}, which may be considered as a hole trapped at a Tl^{+}; and Tl^{0}, an electron trapped at a Tl^{+}. Luminescence may occur when a free electron is captured by a Tl^{++} creating Tl^{+*}. The Tl^{+*} may then luminesce. Likewise if a free hole is captured by a Tl^{o} this produces Tl^{+*} which may in turn luminesce.[36]

High energy radiation produces all of these species in addition to V_k centers (self-trapped holes). At sufficiently low temperatures the V_k centers are immobile and the Tl^{o} and Tl^{++} are stable. If the temperature is raised above ~ 60 K, the V_k centers become mobile[15] and may migrate to Tl^{o} centers, producing Tl^{+*} followed by the characteristic Tl luminescence.[58] At still higher temperatures ~ 105 K, the Tl^{o} will be thermally ionized to produce Tl^{+} and free electrons. These free electrons may recombine with Tl^{++} to produce the characteristic Tl luminescence. These processes in general are described as thermal luminescence.

Stimulated luminescence in NaI(Tl) occurs when the crystal is irradiated with low energy light of sufficient energy to activate the diffusion of V_k centers or to ionize the Tl^{o}. In the former case, the characteristic thallium luminescence occurs. In the latter case both the thallium and the intrinsic luminescence would occur as freed electrons would recombine with both Tl^{++} and V_k centers. In the above discussion, Tl^{+} served as an electron trap, but other impurities may serve as well. Crystal stress, as well as doping, has been shown to increase the efficiency of this process.[54]

Unger and Teegarden[59] observed electroluminescence in KI at

77 K. The effect was attributed to electrons being injected into the crystal from the electrodes, and was only observed with AC (500 Hz) fields. If blocking electrodes were used, no luminescence was observed implying that valence band electrons were not ionized at this field strength (50 KV/cm).

2.2 The Dead Layer

It had been suspected for some time that the surface region of NaI, and other alkali halides, does not luminesce in the same way as does the bulk of the crystal. The "dead layer" concept has been used by several scientists to explain the results of experiments. Fano[1] postulated that the lower symmetry of a crystal in the surface region as compared to the bulk of the crystal increased the probability of an exciton losing energy by means other than luminescence (e.g. heat or secondary electron emission). Using a model based upon the mobility of excitons and their high probability of non-radiative destruction at the surface, he produced a theory which agreed with observed cathodoluminescence in willemite in the range of 200 to 1400 volts. Apker and Taft[3] observed that the photoemission spectrum of RbI showed a dip at the energy of the exciton absorption maximum and that the photoemission decreased with increasing absorption coefficient for values of absorption coefficient above 10^6 cm^{-1}. Hebb[2] used a model which assumed exciton destruction in a region within 115 Å of the surface to explain Apker and Taft's results. Teegarden[4] noted that the dip in the excitation spectrum of the intrinsic luminescence of KI coincided with the peak in the optical absorption. Ramamurti and Teegarden[6] noted this effect in the excitation spectra of RbI and KI and attributed it to some modification of the surface region. They used this phenomenon to predict an exciton absorption for the n=3 Wannier exciton based upon a dip in the excitation spectrum. The fact that absorption and reflection maxima are closely related and almost coincident in energy suggested that the dips in the excitation spectra could be due to a reduced number of photons entering the crystal. This was shown not to be the whole cause for these minima when Van Sciver[60] measured the reflected light and quantitatively corrected the excitation spectrum of NaI for reflection losses.

2.2.1 Measurement Of Dead Layer Thickness

The first quantitative measurement of the dead layer depths in the alkali halides was made by Emkey, Meyers and Van Sciver.[8] Their model assumed that there could be no luminescence within a distance d from the surface, and that at greater depths the luminescence is proportional to the energy absorbed. The luminescence is assumed to be isotropic when it is created within the crystal, however some of the light is reflected at the crystal surface. The reflected light and the direct luminescence are phase coherent so that an interference pattern is created and the observed luminescence is anisotropic. The light intensity was measured as a function of angle for various excitation energies, and these angular spectra were compared with theoretical curves for various values of absorption coefficient and dead layer. The results suggested that the dead layer in NaI is approximately 100 Å deep in the region of the exciton absorption maximum and 300 Å for greater energies. This suggests that the mechanism for luminescence quenching may also be different for excitation in the two energy ranges.

2.2.2 Mechanism For The Dead Layer

The analysis by Emkey et al.[8] was completely empirical and made no attempt to explain why a dead layer existed. Having established its existence, the question arises; what causes the dead layer? Several models were considered.

A. Exciton Overlap With The Surface

The simplest model is to assume that the luminescing center interacts physically with the surface. The accepted model for the exciton in NaI[61] suggests that the exciton involves only an iodine ion and its nearest neighbor sodium ions. Polarizability[62] measurements made by electroabsorption can be interpreted to give an effective Bohr radius of about 10 Å. Based upon these facts, it seems unlikely that there can be any overlap of the exciton wave function with the surface at depths greater than 20 or 30 Å.

B. Distortion Of An Ideal Surface

The symmetry of the surface is necessarily lower than in the crystal bulk. This means that the relative positions of the ions in the surface region are different from those deeper inside the crystal and other properties must change also. It is entirely possible that neither the proper exciton nor the STE can exist in the region immediately adjacent to the surface. Benson et al.[63] made some calculations on the ionic positions at the surface of NaCl and their findings suggest that significant distortion, i.e. greater than 0.02 times the lattice constant, occurs at least in the first five ionic layers beneath the surface. The magnitude of the distortion decreased rapidly with depth and although they do not make the calculation for more than five layers, their results suggest that the surface has minimal effect on the ionic displacements at distances of say 50 Å (15 ionic layers) under the surface.

C. Optical Interference Effects

It is an established experimental fact that the lifetime of an excited molecule which emits luminescence is influenced by the presence of a reflecting surface. Experiments by Drexhage[64] and others and calculations by Morawitz,[65] using as a model a classical dipole oscillator as well as a quantum mechanical two level system, demonstrate that the lifetime of the excited state may be increased or decreased, depending upon its distance, in the region within about one wavelength, from the reflecting surface. The initial prediction was that as the distance from the surface approached zero, the lifetime of the excited state could increase by a factor as great as 9.31 (for an excited molecule placed directly on an interface between a material with an index of refraction of 2.00 and air). Experiments showed, however, that the lifetime of the excited state decreased rapidly as the luminescing center approached the surface. This discrepancy was attributed to energy transfer to the reflecting surface and to approximations used in the calculations. In fact, subsequent calculations by Kuhn,[66] who allowed for phase shifts upon reflection (other than zero or π) and absorption by the reflecting surface, and by Chance *et al.*[67] who used antenna radiation theory and included near field effects, both predicted the observed decrease in the radiative lifetime near the surface ($nd/\lambda \leq 0.1$, or $d \leq 150$ Å for NaI, where n is the index of refraction of the material at the wavelength of emission λ).

Kuhn also notes that the quantum efficiency goes to zero as the luminescent center approaches the surface. This is because the probability of radiative emission decreases in this region even though the rate of decay increases. Although this process must occur in NaI, its effect would be greatly reduced because of the relatively low reflectivity of the NaI - N_2 gas interface compared to that of the metal mirrors used by Drexhage.

Kuhn extends these ideas to the case of a luminescent center near a weakly absorbing layer. In this case, also, he shows that the quantum efficiency is decreased as

$$\frac{q}{q_d} = 1 + (d_o/d)^4 + \beta\ (d_o/d)^2$$

where q_d and q are the quantum efficiencies at a distance d from the surface and far from the surface, respectively, d_o is a constant which depends upon the wavelength of the emitted light, λ, index of refraction of the medium, n, and the absorption per unit area of the absorbing layer, A, as well as the value of q. β depends only on A and q.

$$d_o = \gamma\ (\frac{\lambda}{n})\ (Aq)^{\frac{1}{4}} \qquad \beta = \frac{\sqrt{2}}{4}\ (Aq)^{\frac{1}{2}} \qquad \gamma = \frac{1}{4\pi}\ (\frac{q}{2})^{\frac{1}{4}}$$

For NaI λ = 295 nm, n = 1.95 and q ≈ 1 the value of d_o increases from 9.8 Å to 98.6 Å as A increases from 10^{-5} to 10^{-1}.

The surface of a "clean", freshly cleaved crystal may act as an absorbing layer due either to the deformation discussed by Benson <u>et</u> <u>al</u>.[63] or because adsorbed gases absorb some light. In the latter case, we might expect to see an increase in the depth of the dead layer as a freshly cleaved surface is exposed to adsorbing gas.

D. Image Forces

A closely related phenomenon is considered by Deigen and Glinchuk[68] who calculate the self-energy of an exciton near a surface due to its interaction with its reflected image. For the case of equal effective masses of the electron and hole, which may approximate the situation for the proper exciton in NaI, the exciton should be ionized at a distance of 1.5 Bohr radii from the surface. In addition to this the exciton feels a repulsive force in the surface region leading to the conclusion that there is a "dead layer" near the surface of 4-5 Bohr radii where the exciton is unlikely to remain. For NaI this distance would be 40-50 Å.

Deigen and Glinchuk also treat the problem of an electron trapped at a positive impurity, called a localized electron center, in the surface region. The analysis also applies to the STE in NaI in which the effective mass of the hole, V_k center, is very large. In this case they conclude that a "region of enhanced dissociation" exists, although the localized electron center does not become ionized. They calculated that the depth of this region in NaCl is 16.4 Å. It seems reasonable to take this as an order of magnitude value for NaI.

E. Index Of Refraction Near The Surface

Another effect which produces an intrinsic dead layer in the region of the exciton absorption peak is discussed by Hopfield and Thomas.[5] These authors point out that if one considers the wave vector, as well as the frequency, dependence of the dielectric constant then it becomes necessary to apply boundary conditions at the surface in addition to the classical Maxwell conditions. These additional restrictions are placed upon the polarization. Although the actual boundary conditions are complicated, Hopfield and Thomas suggest that these can be approximated by taking the polarization to be zero at some depth d beneath the surface. This depth is essentially determined by the repulsive force exerted by the surface on the excitons and should be on the order of 2 Bohr radii. They further propose that one method of testing this model is to analyze the reflectivity spectrum in the region of the exciton absorption peak in terms of a three layer model of air (a vacuum), a layer of thickness d with an index of refraction which does not include the effects of the exciton, and a region in which the index of refraction includes the effects of the exciton. This model is used to explain some of the features of the reflectivity spectrum of CdS and ZnTe.

Evangelisti et al.[7] used the Hopfield and Thomas model in a study of the dead layer in CdS. They concluded that an intrinsic dead layer existed for each Wannier exciton and that the ratio of the exciton size to the dead layer thickness, d, is on the order of 1.5. Exciton size is defined as $3n^2r_B$ where n is the orbital quantum number and r_B is the Bohr radius of the exciton. They further found that by heating their samples in a vacuum they could change d by producing a dead layer of extrinsic origin. The extrinsic dead layer is attributed to surface damage and to the production of a surface field which ionizes the excitons. This latter conclusion is supported by the fact that crystals treated in the same way show a peak in the photoconductivity at the exciton absorption peak while those with "good" surfaces show a dip at the same energy. (In NaI a dip in the photoconductivity occurs at the exciton absorption peak.[18])

F. Electric Fields

a. Natural

The surfaces and dislocations in ionic crystals are usually charged.[e.g. 69, 70] This is due to the difference in the formation energies of the cation and anion vacanies.[71] The potential difference between the crystal bulk and surface for large crystals is equal to the difference in formation energies divided by the charge of the ion. For pure alkali halides the surface should be positive. When there are divalent cationic impurities in alkali halides on the order of 1 ppm (the usual case), then at low temperatures $\lesssim 500$ K, Kliewer and Koehler[72, 73] showed that the surface ought to be negative. This prediction is supported by data demonstrating that the photoemission threshold for thin films (which can not build up the same potential difference between the bulk and the surface as larger crystals) is reduced.[74] This assumes that the electron is excited from beneath a dipole layer on the surface through which it must pass before it can leave the crystal.

b. Effects On Absorption

Electric fields broaden the absorption bands of solids.[75] Thus in fields which are externally applied or are due to defects or charged surfaces, photons of lower energy than the fundamental absorption are absorbed.[76, 77] (Redfield[44] used this fact to postulate that excitons formed at the surface could emit photons, with no Stokes shift, which could travel large distances in the crystal bulk because of the different absorption coefficient. These photons might then be reabsorbed at surfaces or defects providing a means of energy transfer over large distances.) Duke and Alferieff[78] calculate the effects of a field on absorption due to excitons and likewise find a broadening and lowering of the exciton peak. These effects were studied in the alkali iodides by Menes.[62]

c. Electric Field Experiments

i) F Center In KCl

The effects of field ionization may reduce the lifetime and luminescence quantum efficiency of the excited states either by tunneling or via a Schottky jump over the field-lowered energy barrier. Spinolo and Fowler[79] studied these effects for the F center in KCl. For the Schottky experiment the height of the energy barrier is reduced by an amount proportional to the square root of the applied field. This effect was found to dominate at high temperatures, > 60 K, and the experimental points agreed well with the theory. It was also noted in these experments that the probability of radiative decay decreased with field strength, but was not affected by changes in temperature over the range 57-93 K. At LHeT (liquid helium temperature) tunneling effects dominate. In this case also the probability of radiative decay decreased with field strength as did the luminescence quantum efficiency and lifetime of the excited state. In this case the field dependence is not simple, and agreement between experiment and theory was not as good. The binding energy of an exciton[80] in NaI is greater than that of the F center and the radius of the exciton is probably less than that of an excited F center.[26] This suggests that electric field effects will not be as great as those observed by Spinolo and Fowler for similar field strength (~ 10^5 V/cm).

ii) CdS

In CdS an external electric field can change the quantum efficiency of certain emission bands after excitation in the band to band region.[81] The amount and direction of the change is dependent upon the strength and direction of the field. In fact adsorbed gases reduce the quantum efficiency of luminescence at the same excitation energy, and this is attributed to the electric field produced near the surface by the adsorbates[82] which act as acceptors.

iii) Alkali Halides (Thallium)

Some work has also been done in the alkali iodides, particularly KI, doped with thallium impurity. Denks[83] reported on the spectral effect of applying an electric field on the thallium luminescence in the alkali iodides. He did not study the effects of changing the polarity. He found almost no effect upon excitation in the thallium absorption bands, but a large transitory decrease in intensity after excitation in the energy region greater than the band gap. In KI(Tl) and RbI(Tl) there was no effect in the region of the exciton absorption, but NaI(Tl) and CsI(Tl) showed the same large effect in this energy region as in the band to band region. These measurements were made at room temperature and at 120 K. Denks attributed the effect to separation of electrons and holes by the field prior to build up of a polarization field. In the exciton absorption region the large effect in NaI(Tl) and CsI(Tl) was explained as due to self-ionization of the exciton via indirect interband edges. Thermal ionization and ionization at defects were considered to be less likely explanations.

Hayashi et al.[84] studied the effects of an external field applied at room temperature on the thallium luminescence of KI(Tl). As did Denks, they found a large effect in the band to band region, and no effect in the "A", "B" or "C" absorption bands. Hayashi did see a small effect in the region of the exciton absorption and a large effect in the low energy exciton tail. This was explained as being due to an overlap of the low energy exciton tail with the "D" band of KI(Tl). The field produced a response because some electrons were thermally released from the D state. Hayashi et al. also noted that the integral of the intensity of the response is independent of the intensity of the incident light, but that the time for recovery of normal luminescence intensity after application of the field increased as the light intensity decreased. If the front electrode was positive, the luminescence decreased. If the front electrode was negative, the intensity increased.

Nouailhat et al.[85] explored the effects of an external field <40 KV/cm on thermoluminescence due to the Tl after the crystal had been exposed to α or β rays at 77 and 200 K. They concluded that the applied field ionized the Tl^+ excited state, thus decreasing the capture cross section for electrons at Tl^{++} ions and V_k centers because the initial capture takes place from a hydrogenic state. This is not the case for neutral defects, e.g. Tl^+. The electric field had no effect on V_k center migration.

Grigor'ev et al.[86] studied the effect of an external field on CsI luminescence excited with α radiation. They observed luminescence quenching which they attributed to a field effect upon the luminescent center as opposed to prevention of recombination. They found that the field reduced the thermal activation energy necessary for radiationless decay as well as reducing the lifetime of the luminescence.

G. Adsorbed Gases And Band Bending

Other causes of luminescence quenching in the surface region are adsorbed gases acting as radiationless recombination centers and band bending. As mentioned earlier, the first method has been invoked to explain quenching of luminescence in Cu_2O.[41] In this case, the energy transfer was assumed to take place via exciton diffusion, but it seems that any means of energy transfer to such a recombination center would produce quenching. In any event, some energy transfer must occur in order for this mechanism to be effective over an appreciable region.

Band bending assumes that the band gap at the surface is not as great as in the bulk. Sydor[87] analyzed the transmission and scattering spectra of thin films of RbI using a model in which the energy bands were bent at the surface. He assumed that the band gap was reduced by 0.2 eV in the exciton absorption region and 0.4 eV in the band to band region. The effect of this band bending decreased as $\exp(-x/D)$ where D was chosen to be 150 Å. Sydor further assumed that excitons excited on the low energy side of the exciton absorption peak became trapped in this surface region and contributed to the scattering. These trapped excitons do not become ionized.

H. Photo-induced Effects

It is possible that the dead layer is produced by the light that excites the luminescence. There are two mechanisms by which light can produce an electric field within the crystal. This field may quench the luminescence, as mentioned earlier.

a. Dember EMF

The Dember EMF is a field produced when free electrons and holes are created non-uniformly within a crystal. This occurs because the charge carriers tend to diffuse toward regions of lower concentration according to Fick's law. When one charge carrier is more mobile than the other, and therefore diffuses more rapidly, space charge builds up in such a way as to reduce further diffusion. The electric field of this space charge is called the Dember EMF. This effect has been observed in several materials.[88-90] The criteria for observation of this effect are apparently present when light energy greater than the band gap is incident on NaI. The charge carriers are created non-uniformly because of the high absorption coefficient, and the mobility of the electrons (~ 100 $cm^2/(V \cdot s)$ in KI at 77 K)[91] is probably several orders of magnitude greater than that of the holes, which become self-trapped as V_k centers (~ 2.9×10^{-5} $cm^2/(V \cdot s)$ calculated for NaI from data on the V_k center reorientation rate[15]). The rate at which electrons move, however, is affected by the concentration of electron traps in the crystal. Bube[92] defines the drift mobility of an electron

$$m_d = \frac{n}{n + n_t} m_e$$

where m_d is the drift mobility, n is the concentration of electrons in the conduction band, n_t is the concentration of electrons in traps, and m_e is the mobility of an electron in the conduction band. Since the drift mobility is the observed mobility, the ratio of the electron to hole mobilities will be reduced.

b. Photoemission

Taft[3, 93, 94] and co-workers observed photoemission from the alkali halides in the energy region of the exciton absorption peak and attributed this photoemission to the ionization of F centers by excitons. It seems highly probable that there are other shallow electron traps in the surface region which could be ionized in the same manner. If this is the case, then the crystal surface will tend to build up a positive potential which would prevent continued photoemission. Note that in this case, as well as that of the Dember effect, the surface would become positive with respect to the bulk.

2.3 Complexity Of the Exciton

In concluding this section it should be noted that the exciton is not as simple an entity as has been tacitly assumed thus far. For example, defects can be created in the alkali halides using ultraviolet light, and this is attributed to non-radiative recombination of some excited states of the exciton.[14, 95]

Several investigators have noted that the properties of the exciton are very different in KI depending upon whether it is excited on the high or low side of the exciton absorption peak.[45, 96-98] There have been some theoretical[99, 100] and experimental[14, 80] studies of the different excitonic states, but the picture is still not completely clear. It may be that the diffusion coefficient, efficiency of defect production, and other energy transfer processes are sensitive to the state of the exciton. The reflection spectrum of NaI shows some structure[60, 101] in the region of the exciton peak. A small peak on the high energy side of the main exciton peak can be resolved. Its oscillator strength is 0.1 of the main peak and it has been attributed to a phonon interaction[101] because the separation between the two peaks, 0.041 eV, is comparable to the vibrational energy of the free I_2 molecule, 0.036 eV.

3.0 Electric Field Experiments

3.1 Background

The first experiment performed was to study the effects on the intrinsic luminescence of NaI when an external electric field is applied. As mentioned in Section 2.2.2.F, electric fields are known to produce changes in the luminescence of various solids. Several mechanisms have been proposed to explain this:

1. separation of charge carriers, thus reducing the probability of recombination;
2. ionization of the luminescence center;
3. reduction of the probability of radiative decay of the luminescence center;
4. increasing the probability of non-radiative decay of the luminescence center.

In the electric field experiments we hoped to counteract or enhance the effectiveness of the dead layer by application of external electric fields which were antiparallel or parallel, respectively, to the naturally occurring fields. The parallel field should decrease the observed luminescence while the antiparallel field should increase it.

3.2 Equipment

The experiment was performed with a crystal of "pure" NaI from the Harshaw Chemical Company. It was cleaved in a dry box to a size of 1 x 1 x 0.092 cm and placed between two 200 mesh stainless steel screens to which a high voltage could be applied. The sample was transferred into an Andonian exchange gas cryostat where it was cooled in N_2 gas. The temperature was monitored with copper-constantan thermocouple soldered to the sample holder.

The uv light source was a deuterium lamp, the light from which passed through a half meter monochromator with a band pass of either 1 or 2 nm. There was also a tungsten halogen lamp which shone through Corning filter 7-69 onto the crystal. This filter has a peak transmission at about 850 nm and a half width of 250 nm. This light was used to bleach the crystal by emptying shallow electron traps. Light from either source could be blocked by use of shutters.

The luminescence was monitored with an EMI 6256S photomultiplier tube after passing through a Bausch and Lomb grating monochromator with a band pass of 30 nm. The signal from the photomultiplier tube was measured with a Keithly 640 vibrating reed electrometer and recorded on a Varian G-14 strip chart recorder.

3.3 Procedures And Results

The response of the intrinsic luminescence to externally applied fields was found to be sensitive to several variables.

1. Excitation energy - When a field was applied while exciting in the low energy tail of the exciton absorption peak, the luminescence decreased at all temperatures and for both field directions. This effect was permanent, or at

least the recovery time was $\gg$ 120 seconds. See Figure 4. For energies above the exciton absorption peak, the response was transient and the luminescence reached a steady level within about 60 seconds. See Figure 5.

2. Field Direction - The response for energies greater than the exciton absorption peak at LNT was opposite for the different field polarities. Applying a positive field decreased the luminescence and shorting this field increased the luminescence. See Figure 5. In contrast a shorted negative field decreased the luminescence but if a negative field was then applied, the luminescence increased above its normal value.

3. History - The response due to the negative field at LNT depended upon the fields which had been applied previously. The first time a negative field was turned on, the luminescence decreased. Shorting this field again produced a decrease, but when the negative field was applied for the second and subsequent times the luminescence increased. Bleaching the crystal with infrared light "recycled" this sequence so that the next time that a negative field was applied the luminescence would decrease.

4. Temperature - The responses at LNT have been described above, but for temperatures greater than about 83 K all changes in the applied field decreased the luminescence

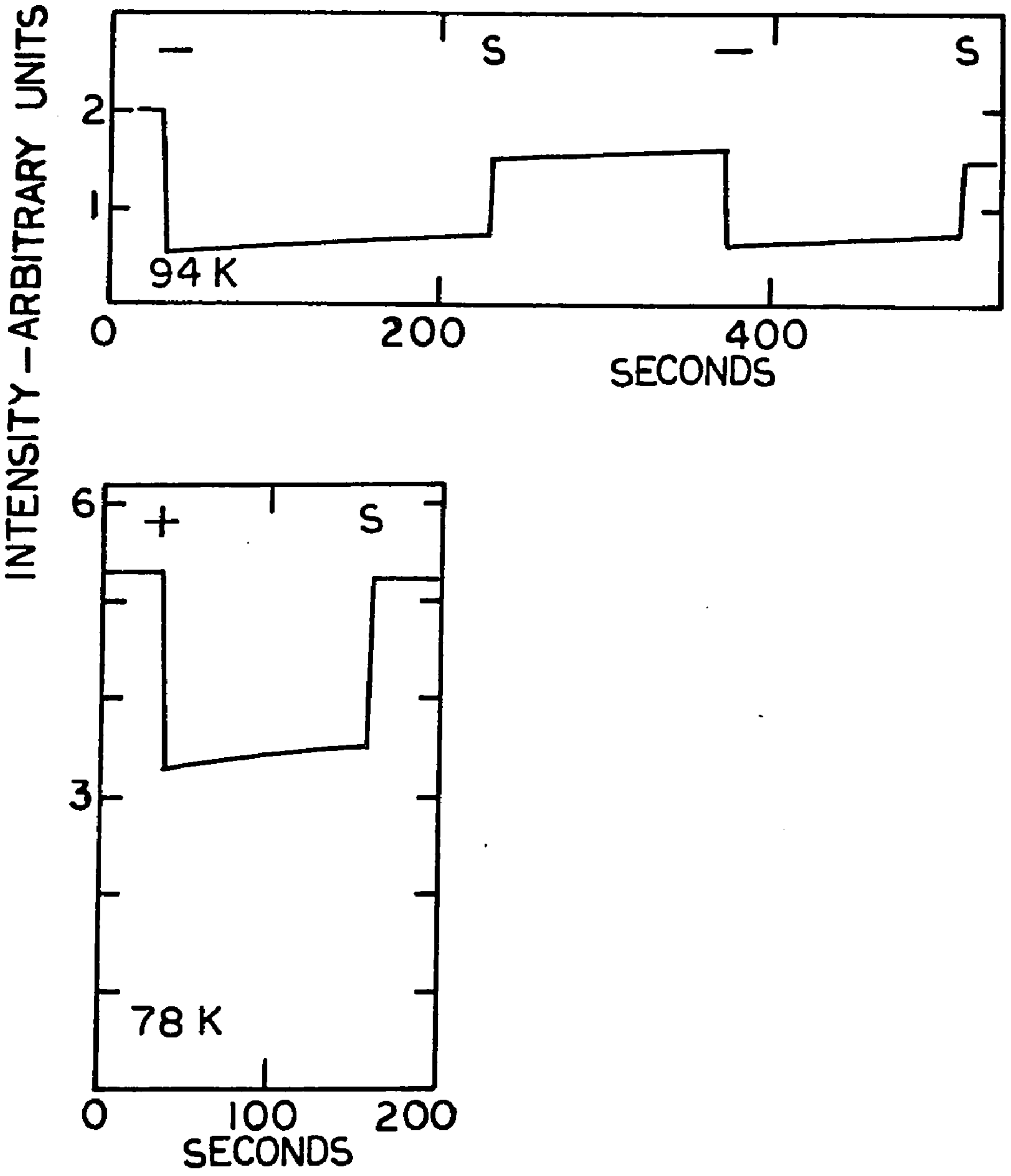

Figure 4. Electric Field Data - Low Energy Tail of the Exciton Absorption Peak. This is a tracing of data showing the effect of an electric field on the intrinsic luminescence excited in the low energy tail of the exciton absorption peak, at 78 K and 94 K. + - apply +4 KV to front screen, — - apply -5 KV to front screen, S - short the applied field.

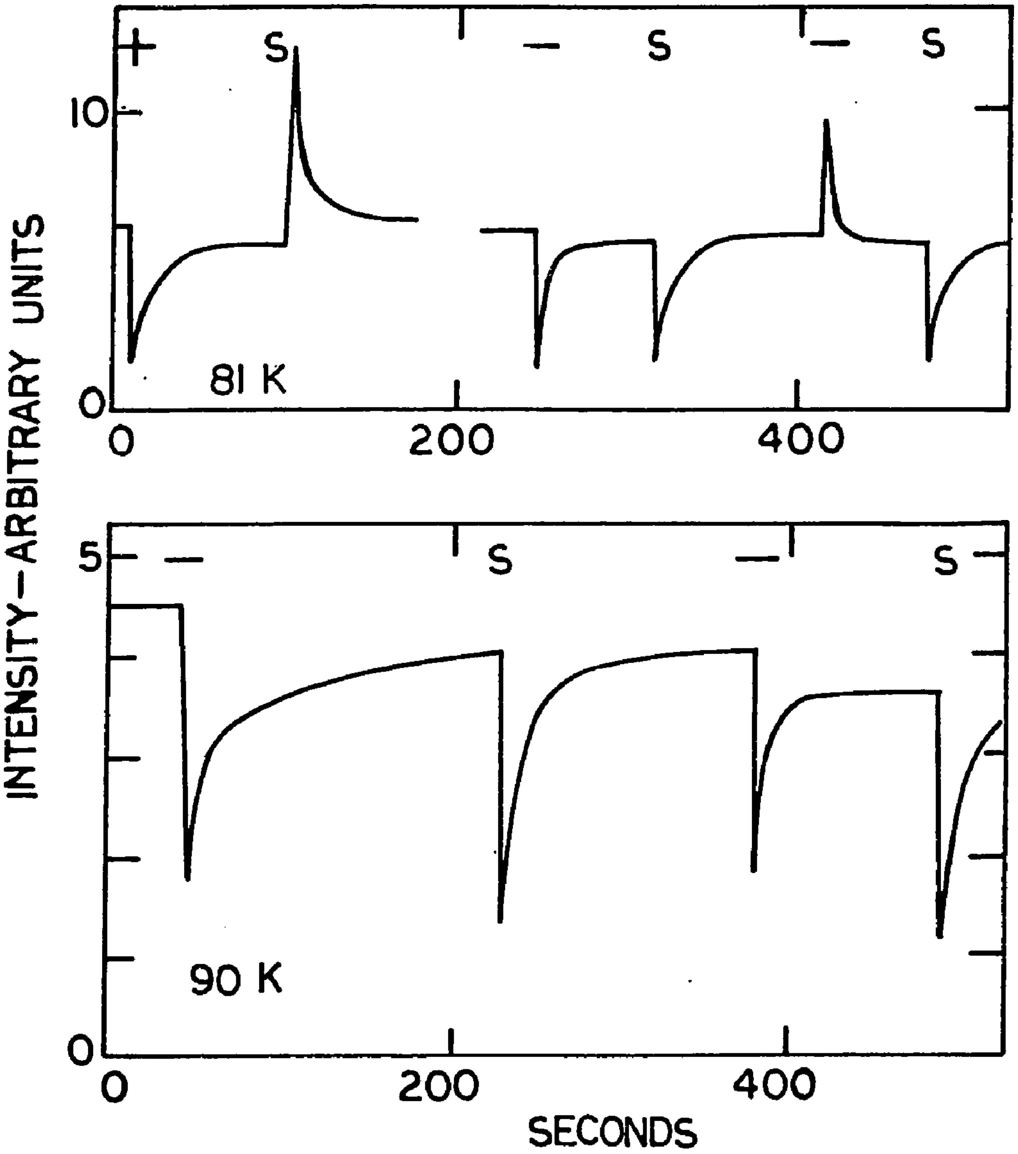

Figure 5. Electric Field Data - Band to Band Excitation. This is a tracing of data showing the effect of an electric field on the intrinsic luminescence excited in the band to band region, at 81 K and 90 K. + - apply +5 KV to front screen, — - apply -5 KV to front screen, S - short the applied field.

excited with energies greater than the exciton absorption peak. See Figure 5. The response in the low energy tail of the exciton absorption peak was not affected.

With these effects in mind, data were collected as follows. The spectral response was recorded using the sequence:

1. With no field applied, expose the crystal to light of desired energy, 1 nm band pass on the monochromator.
2. Apply 5,000 volts to the front screen and allow the luminescence to reach a steady value.
3. Short the applied field and allow the luminescence to reach a steady value.

The procedure for collecting data with a negative field was the same except that the excitation wavelength was changed while the negative field was applied. The peak of the transitory response was recorded in each case. This data is plotted for two temperatures in Figures 6-9.

One feature to be noted in these results is the similarity between the effects of shorting a positive field and applying a negative field for the second time. Also note the difference in the response above and below the exciton absorption peak (5.6 eV). Perhaps the most dramatic effect is the drastic change produced by increasing the temperature from 78 K to 88 K.

The temperature dependence of the response due to shorting a positive field and to applying a negative field was investi-

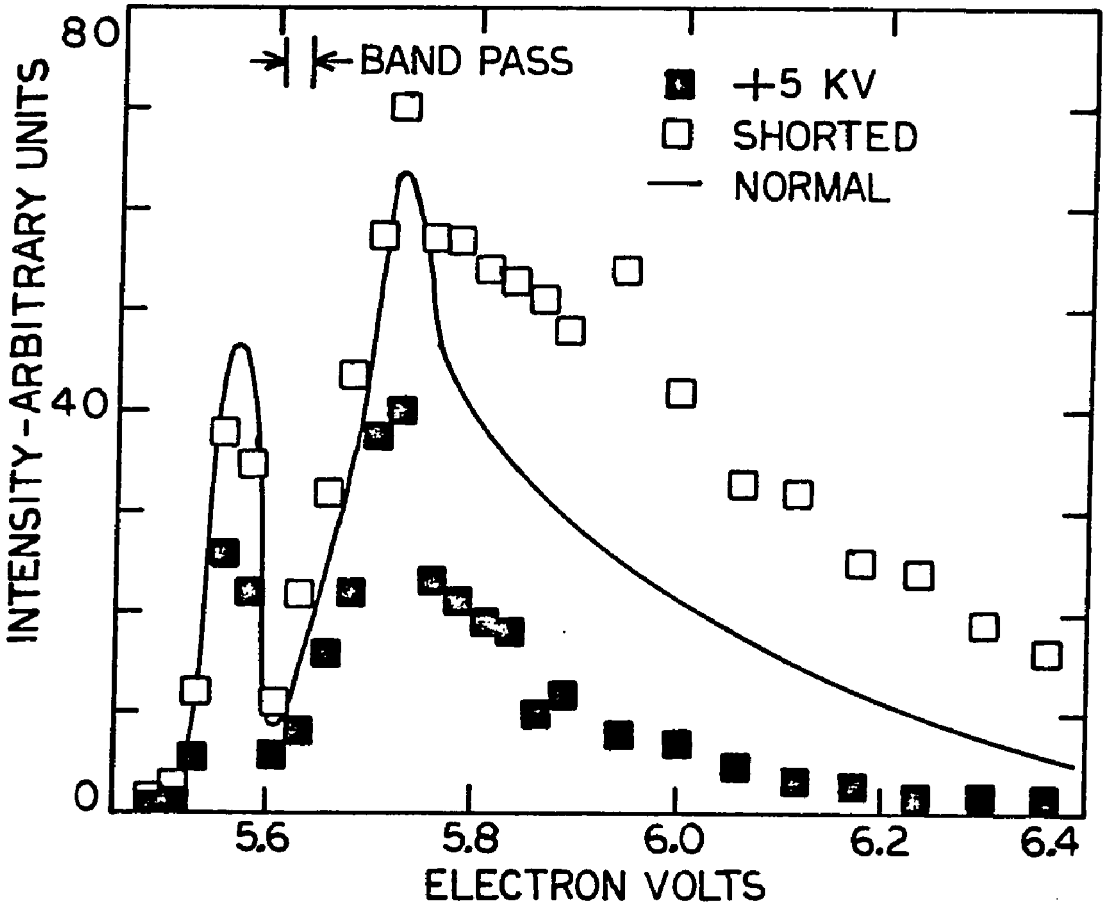

Figure 6. Spectral Response to Positive Electric Field at 78 K. These data show the instantaneous effect on the intrinsic luminescence of applying +5 KV to the front screen, plotted as a function of the uv excitation energy.

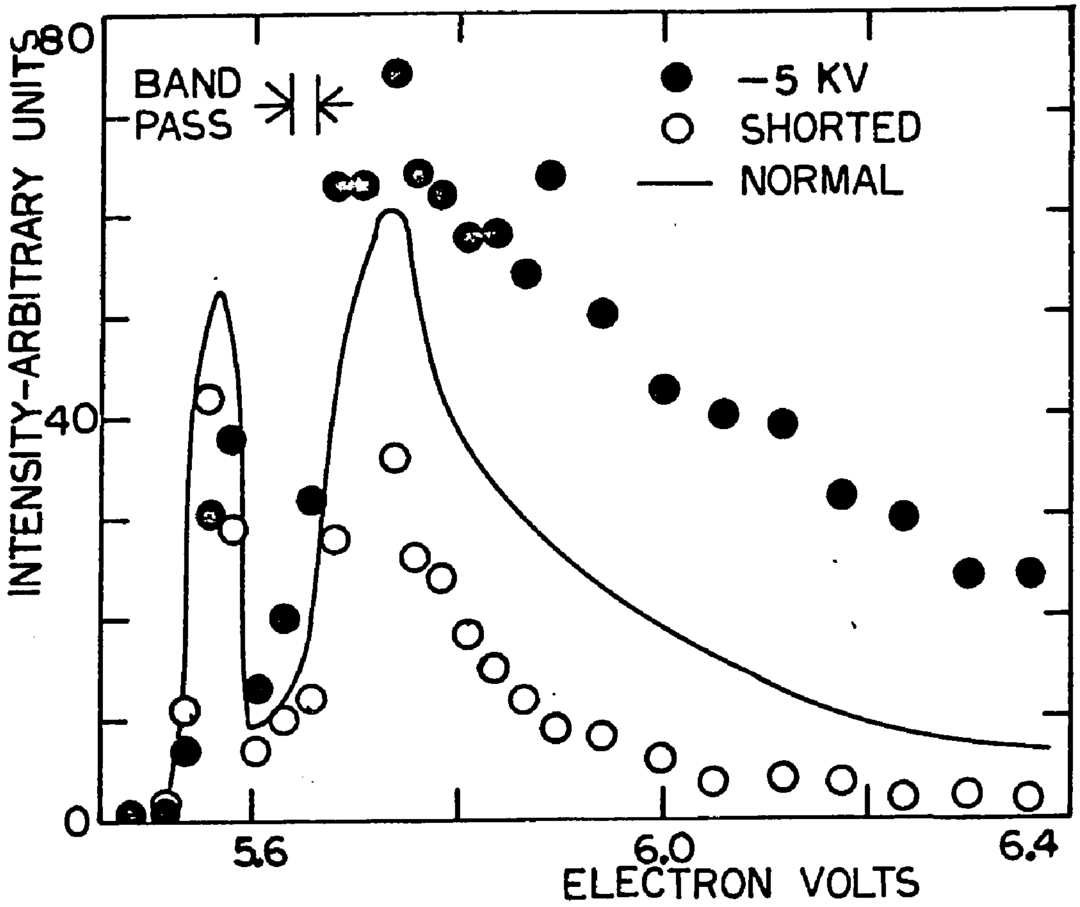

Figure 7. Spectral Response to Negative Electric Field at 78 K. These data show the instantaneous effect on the intrinsic luminescence of applying -5 KV to the front screen, plotted as a function of the uv excitation energy.

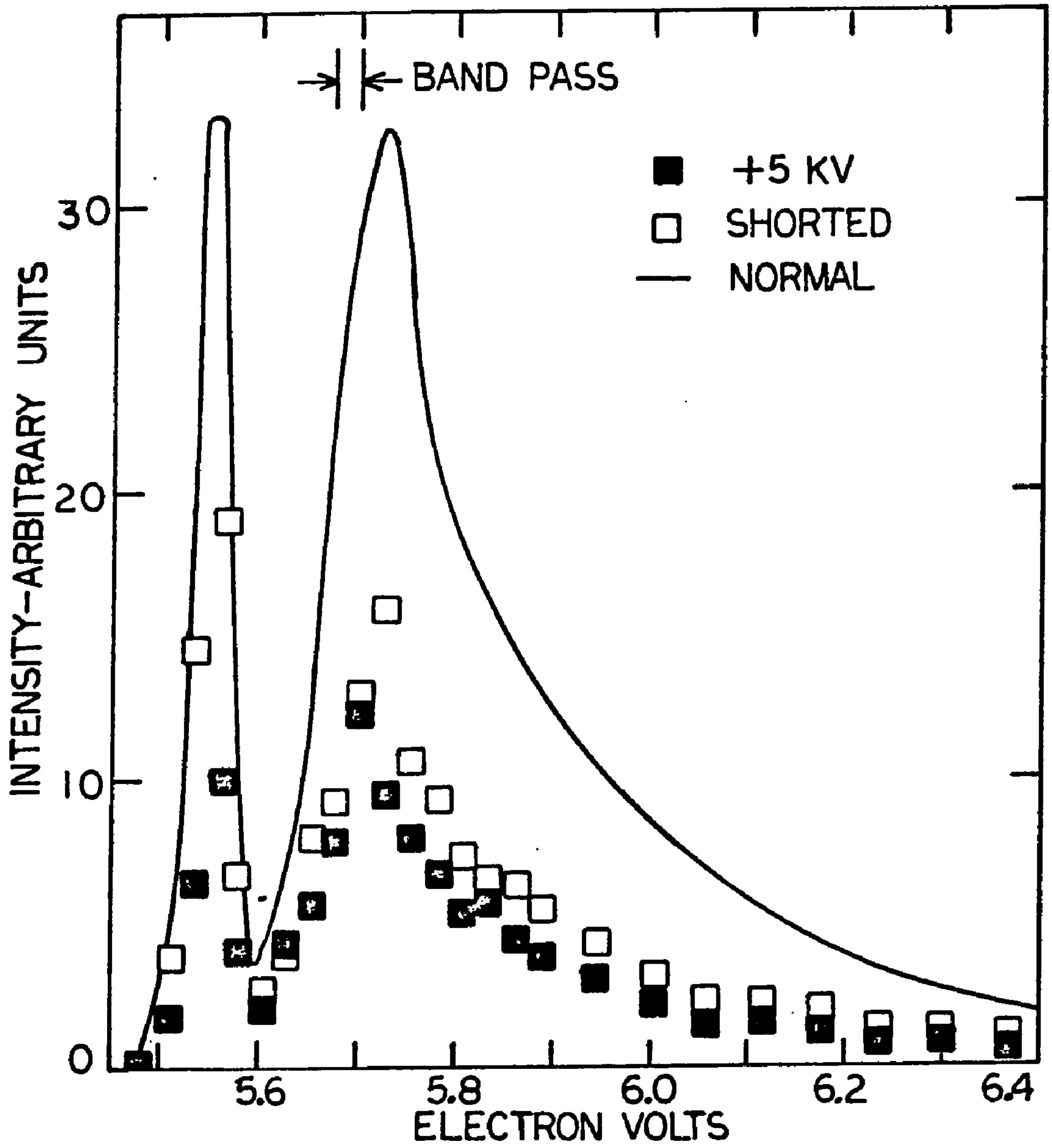

Figure 8. Spectral Response to Positive Electric Field at 88 K. These data show the instantaneous effect on the intrinsic luminescence of applying +5 KV to the front screen, plotted as a function of the uv excitation energy.

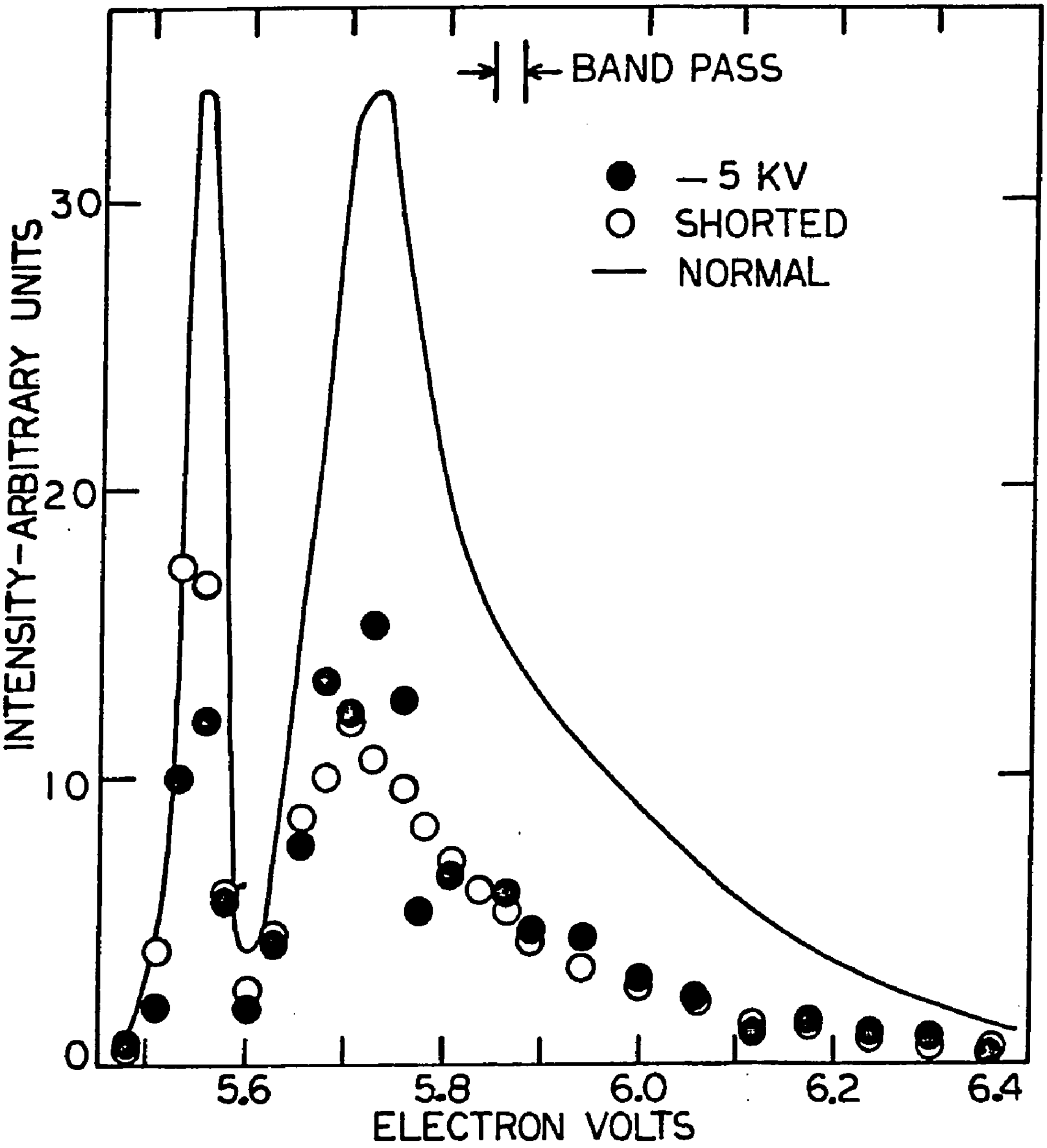

Figure 9. Spectral Response to Negative Electric Field at 88 K. These data show the instantaneous effect on the intrinsic luminescence of applying -5 KV to the front screen, plotted as a function of the uv excitation energy.

gated. The results are shown in Figure 10. Although there is some scatter in the data, it appears that the transition temperature from one type of behavior to the other occurs at about 83 K.

The field strength dependence was studied for excitation in the low energy tail of the exciton absorption peak (Figure 11) and in the band to band region (Figure 12). In both cases the crystal was bleached prior to application of a new field strength for the first time. At 5.51 eV the response, which is independent of field direction, was always negative and varies linearly with field strength. The instantaneous effect in the band to band region is roughly proportional to the applied field also, at least for low field strengths. Again, we see the similarity between shorting a positive field and applying a negative field for the second time. Also the response due to the first application of a negative field is similar to that of a positive field of equal strength. For higher field strengths the transitory response in the band to band region increases more slowly with field strength and may approach some saturation value.

3.4 Analysis Of Electric Field Effects

We found that the electric field affected the excitation spectrum quite dramatically. In the band to band region the response was transitory and decreased, probably as space charges developed which counteracted the applied fields. Both increases and decreases were observed, and the response depended upon the

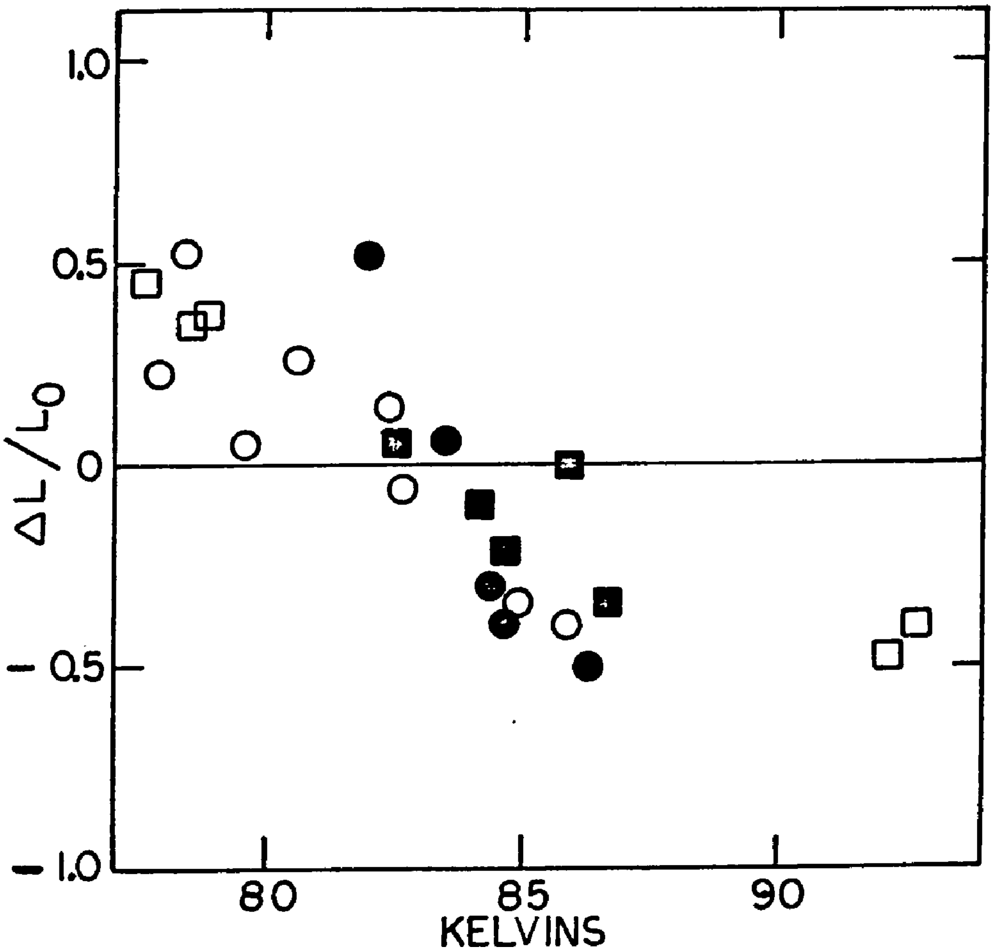

Figure 10. Temperature Dependence of Electric Field Effect. These data show the temperature dependence of the electric field effect on the intrinsic luminescence excited on the high energy side of the exciton absorption peak and in the band to band region. The ordinate is the relative change in the luminescence (L - L_0)/L_0 where L is the instantaneous luminescence intensity and L_0 is the normal value. □ - +5 KV shorted, exciting with 5.71 eV light; ○ - -5 KV, the second time applied, exciting with 5.71 eV light; ■ - +5 KV shorted, exciting with 5.92 eV light; and ● - -5 KV, the second time applied, exciting with 5.92 eV light.

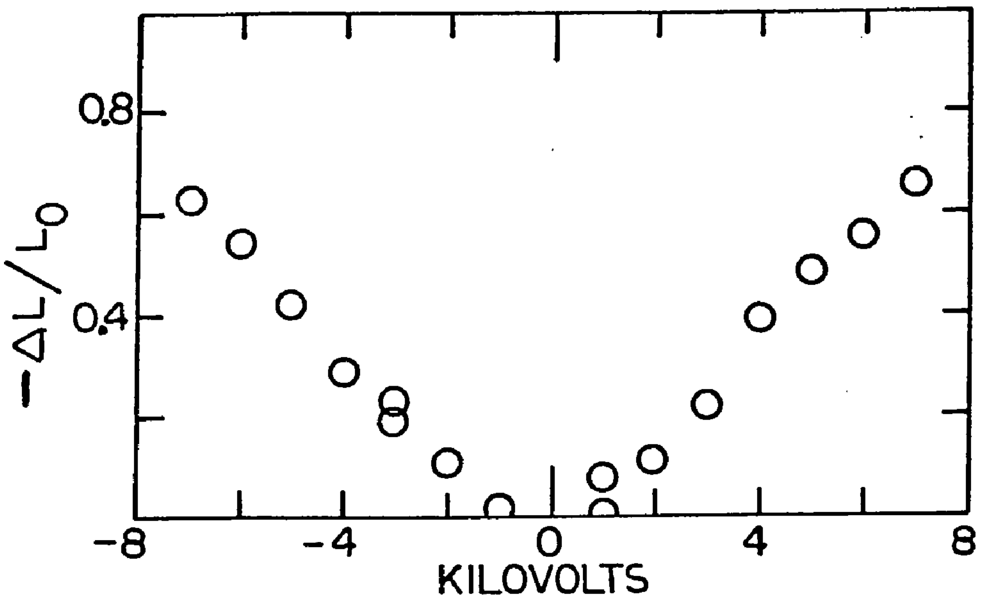

Figure 11. Field Strength Dependence - Low Energy Tail of the Exciton Absorption Peak. These data show the dependence on the applied voltage of the electric field effect observed when exciting in the low energy tail of the exciton absorption peak. The ordinate is the relative change in intensity $(L - L_0)/L_0$ where L is the instantaneous luminescence intensity and L_0 is the normal value. The temperature was 78 K.

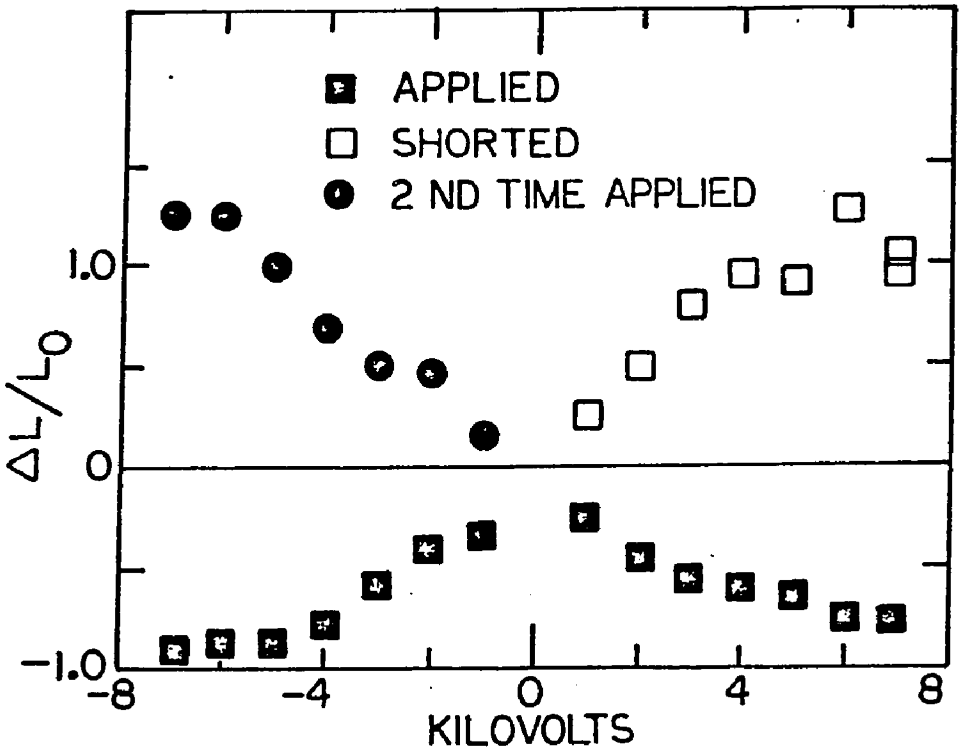

Figure 12. Field Strength Dependence - Band to Band Excitation. These data show the dependence on the applied voltage of the electric field effect observed when exciting in the band to band region. The ordinate is the relative change in intensity $(L - L_0)/L_0$ where L is the instantaneous luminescence intensity and L_0 is the normal value. The temperature was 78 K.

direction of the field. In the exciton region the effect was permanent, negative, and independent of field direction. The response in the band to band region was very sensitive to temperature.

Although these results are very similar to those for which we looked, they are not sufficient to explain the dead layer. Since there is no field polarity, excitation energy or temperature for which the application of a field for the first time increases the luminescence, it is difficult to argue that any of the observed effects are due to the increase or decrease of naturally occurring surface fields. On the other hand, the external fields do have a large effect; can we understand what is going on inside the crystal? We must review the steps in the luminescence process and consider how they might be altered by an external field.

3.4.1 Absorption

First an incident photon is absorbed by the crystal to create either a proper exciton or a free electron and a free hole, depending upon the energy of the photon. Since the absorption coefficient is proportional to the probability of the photon creating either or these excited states, we would expect that if this step were altered by the electric field, we should see some change in the absorption coefficient. Menes[62] studied the changes in the absorption spectrum of NaI at 90 K in an electric field.

With a field strength of 2 x 10^5 V/cm the changes were less than 2%. This is more than twice the field strength employed in these experiments, and yet we observed changes in luminescence greater than 60%. On this basis we will ignore the effects of the electric field on the probability of either free electron-hole production or creation of proper excitons.

3.4.2 Exciton Relaxation

Once the proper exciton has been created we must consider whether the electric field reduces the probability of relaxation to the STE state. The proper exciton is very mobile at low temperatures[17, 43] and is therefore probably associated with little or no lattice distortion. Also it readily decays to the STE state via thermal activation over an energy barrier of 0.015 eV. Thus it is hard to see how an electric field which polarizes the lattice and lowers the symmetry could extend the life of the proper exciton. On the other hand, it is doubtful that the field ionizes the proper exciton because this should result in electric currents which would produce space charges and reduce the effect of the field. This is not observed. For these reasons, we will assume that the proper exciton decays normally to the STE state.

The above arguments apply to proper excitons excited in the low energy tail of the exciton absorption maximum. For energies greater than this, it appears that space charges do develop, and the changes in luminescence are transitory. It is not clear whether this is due to a low energy tail of the band edge in this region or to ionization of higher excited states of the exciton. In either case, the subsequent behavior will be treated in our model as a band to band transition.

3.4.3 Recombination Of Electrons With Holes

The electric field may affect the recombination of free electrons and holes in at least two ways. The first is by tending to separate the electrons from the holes by pushing them in opposite directions. The second process is by ionizing some of the higher excited states of the STE. This model assumes that the electron is first captured in a high, hydrogenic state by the coulomb attraction of the V_k center. This state may be easily ionized before it can decay to the STE state. This latter model was used by Nouailhat et al.[85] to explain the results of their thermoluminescence experiments in KI(Tl).

3.4.4 Probability Of Radiative Decay

It also seems plausible that the electric field could reduce the probability of radiative decay of the STE. It was noted by Spinolo and Fowler[79] that an electric field had this effect on the F center luminescence in KCl.

3.4.5 Model

Thus our model will assume that the electric field reduces the quantum efficiency by inhibiting electron-hole recombination and by reducing the probability of radiative decay of the STE.

We will also assume that there are large concentrations of electron and hole traps in the crystal, and that the electrons can be ejected from their traps with infrared light. Also, we will use the fact that it has been shown that there is no luminescence within a few hundred angstroms of the surface.[8] It is known that the mobility of V_k centers increases approximately exponentially with temperature. Combining these ideas we can reconstruct the sequence of events under various conditions.

A. Low Energy Tail Of Exciton Absorption Peak

In this energy region the field affects only the probability of luminescence of the STE. The decrease in luminescence is permanent as long as the field is applied and does not depend on the direction of the field. The magnitude of the decrease varies linearly with the field strength, but the detailed effects on the luminescence process are unknown. This response occurs at all temperatures investigated.

B. Low Temperature - Band To Band Region

At LNT the V_k centers are considered to be immobile. Thus they are unaffected by the applied field, while the electrons are able to respond. The observed electron mobility is not the mobility of a free electron, however, but is the drift mobility[42] $m_d = \frac{n}{n+n_t} m_e$ where n is the concentration of free electrons, n_t is the concentration of electrons in shallow traps and m_e is the true mobility of a free electron in the absence of traps.

When a positive field is applied to the crystal the electrons move toward the illuminated surface. Thus the luminescence decreases for two reasons: First, the electric field reduces the probability of emission of the STE; second, the electrons are physically separated from the V_k centers, thus reducing the number of STEs created. Within a few tens of seconds a negative space charge of trapped electrons builds up in the surface region reducing the electric field in the luminescing region, and therefore the luminescence increases to a steady value which is near its original value.

When the field is shorted, we are left with a dipole layer consisting of a layer of trapped electrons just beneath the surface and beneath that a broader layer of positive charge due to the V_k centers. Since the combined charge in the two layers is zero, the electric field must be zero at the surface and in the crystal bulk. There will be a strong field directed toward the surface, however, in the surface and luminescence regions. Inspite of the fact that the surface region does not luminesce, many electrons are freed in this region by the incident light, and these will be accelerated toward the region of positive charge. This results in a high concentration of electron-hole pairs and thus a high probability of forming STEs in the luminescing region. Therefore, the luminescence increases, even though the STEs are initially in a high field region, because the concentration of

STEs increases. As electrons leave the surface region, equilibrium is established.

When a negative field is applied, the luminescence is decreased because of the effect on STEs and because the electrons move deeper into the crystal, away from the self-trapped V_k centers. As in the case above, this effect diminishes as space charges build up, reducing the field in the luminescence region. When the negative applied field is shorted, there will be a strong positive field in the surface regions due to the positive V_k centers near the surface and the electrons trapped beneath the luminescence region. As before, the luminescence decreases partially due to the field effect on the STE, but also because electrons freed in the luminescence region are accelerated toward the surface where they either become trapped or recombine non-radiatively. The difference between this case and that observed when shorting a positive field is that there is no flow of electrons from the negatively charged region. This is because the electrons responsible for this space charge are trapped, and no electrons are freed in this region because almost no light penetrates this far into the crystal. Thus the new space charge which builds up will be due to electrons freed in the luminescing region and trapped near the surface thus reducing the field in the luminescence region.

When the negative field is applied the second time, the situation is similar to that observed when a positive field is shorted. Thus the electrons freed by the incident light in the surface region are accelerated toward the luminescence region. The field in this region is much smaller than it was the first time the field was applied, however, due to the high concentration of trapped electrons beneath the luminescence region. Thus the concentration of STEs, and the luminescence, increase.

C. Higher Temperatures - Band To Band Region

As the temperature increases, so does the mobility of the V_k center. This has two effects on the observed luminescence changes.

The first effect is that the V_k center moves around during the time that these other processes are occurring until it becomes trapped at some defect. For example, Tl^+ can trap a V_k center forming stable Tl^{++}. Electron recombination with a hole trapped at such a center does not lead to intrinsic luminescence, but rather to luminescence characteristic of the defect or none at all. Thus, even though all the sequences described above may occur, the positive space charge is no longer due to V_k centers but is due to positively charged defects. The observed decrease is due to the effect of the electric field on the STEs and to the separation of V_k centers from electrons by the field, but this is not compensated for by high V_k and electron recombination because the V_k concentration is reduced by the V_k diffusion.

A second, but less important cause of the change in the electric field effect at higher temperatures is that, since the V_k centers are more mobile, the region over which the positive charge is distributed is greater. This may be significant when a positive field is applied and the holes are driven deeper into the crystal. The reason this should increase the magnitude of the decrease in luminescence is that while the field due to the space charges must be equal and opposite to the applied field in the regions of high conductivity, it must also go to zero at the outer edges of the space charge regions. If the space charge regions are pushed apart by the increased mobility of the holes, then the fringing effect will be reduced in the luminescence region, i.e. a larger fraction of this region will coincide with the high field region when the screens are shorted.

3.4.6 Summary

From these experiments we have learned that electric fields do affect the luminescence, and that at least part of this effect is to reduce the relative probability of radiative decay of the STE. This implies that an electric field in the surface region could produce a dead layer in NaI.

On ther other hand, the lack of any observed increase in the luminescence on a "recycled" crystal due to an electric field suggests that we were not merely increasing or decreasing a naturally occurring field. The fact is that we were able to explain the observed increases and decreases, at least qualitatively, on the basis of redistribution of space charges with a model which assumed a dead layer of unknown origin. Thus although we found evidence that an electric field would be able to create a dead layer, we failed to produce any evidence that there is such a field which does produce the dead layer.

4.0 Crystal Cleaves At LNT

4.1 Background

4.1.1 Surface Electric Fields Due To Vacancy Diffusion

If there is an electric field in the surface region of NaI due to the diffusion of vacancies as described by Kliewer and Koehler,[72, 73] and Lehovic,[71] then the rate at which the space charge is built up should depend upon the diffusion coefficient of the vacancies involved. From the data of Chan and Van Sciver[102] one may calculate the time required for a vacancy to migrate 10 Å (about three ionic layers) from the surface. At 300 K the vacancy requires ~ 185 seconds. At 80 K the time needed is ~ 8.0×10^{30} seconds. Of course this calculation extrapolates the data beyond its probable range of validity, but this should be correct to within a few orders of magnitude.

It is true that the act of cleaving the crystal may cause a rise in the temperature in the surface region. Benson et al.[63] estimate that the energy released by allowing the ions in the first five ionic layers to move to new equilibrium positions is 107.4 ergs/cm^2 for NaCl. If we take the Debye expression for the specific heat[103] with the Debye temperature of NaI, 164 K,[104] then at 80 K the specific heat is 2.05×10^8 ergs/(mole·degree). Assuming that the contribution to the surface energy for NaI is close to that calculated for NaCl, and that upon cleaving, all this energy is distributed within the five ionic layers which are allowed to relax in Benson's model, we calculate that the temperature should rise 132 K, producing a local temperature of 212 K. In this case the diffusion time for a distance of 10 Å is 3.9×10^6 seconds.

As the above calculation may be an underestimate of the energy released during cleaving, an upper limit was calculated by considering the energy of a single ion in a normal lattice position next to a cubic crystal with 1.3×10^5 ions. The Coulomb energy of such an ion is -0.469 eV, or 716 ergs/cm^2 of surface. If we assume that this much energy must be supplied in order to create a new surface, and that once created, the new surface absorbs this energy while relaxing to the configuration predicted by Benson et al., then the crystal surface would be given an energy of 823 ergs/cm^2. Under these circumstances the time required for a Na^+ vacancy to diffuse 30 Å is only 1.5 seconds (when all the energy is distributed within this distance from the surface). In order to obtain diffusion over 100 Å, however, requires 4×10^9 seconds, where now the energy is distributed over a greater volume. Thus, even under these assumptions, it is not possible to obtain a 100 Å dead layer due to an electric field built up via the Lehovic, Kliewer and Koehler model in a crystal cleaved at LNT.

4.1.2 Adsorption Of Gases

By cleaving the crystal inside the sample chamber at LNT, we can observe the luminescence immediately, as adsorption proceeds. It can be shown that if every gas molecule which strikes the surface sticks there, then it takes approximately one second to form a monolayer at a pressure of 10^{-6} torr. The time needed to form a monolayer is proportional to the pressure, thus in order to be certain that the surface is clean, we would need a vacuum on the order of 10^{-9} torr.

In order to determine whether the dead layer is affected by adsorbed gases, we can study the change in the excitation spectrum immediately after the crystal is cleaved and later as adsorption proceeds. We do this because the shape of the excitation spectrum is affected by the thickness of the dead layer. Consider a luminescing crystal which has no surface quenching. For small values of the absorption coefficient most of the incident light will be transmitted and the luminescence will be small. As the absorption coefficient increases, the luminescence will increase until essentially all the exciting light is absorbed. Further increases in absorption coefficient would not measurably increase the luminescence.

In the absence of surface quenching and after correction for the reflection of part of the incident light, we would expect the excitation spectrum to increase with absorption coefficient in the low energy tail of the exciton absorption peak, and to reach some constant value which is independent of further increases in the absorption coefficient. This is not observed in NaI[60] and the excitation spectrum can be explained using the dead layer model.[8] This model predicts that further increases in the absorption coefficient, beyond that at which all the incident light is absorbed, will result in a decrease in the luminescence. This is because for high values of the absorption coefficient the fraction of the light absorbed in the non-luminescing surface region increases.

The simple model employed by Emkey *et al.*[8] in which the quantum efficiency is zero between the surface and some distance d beneath the surface, and is one for greater depths, predicts that the total quantum efficiency for large values of α will be exp $(-\alpha d)$ where α is the absorption coefficient. In any case, we expect the effect of an increasing dead layer to be most evident where the absorption coefficient is large. Specifically, the region of the exciton absorption peak should be most sensitive to changes in the dead layer.

These experiments were of an exploratory nature. Crystals were cleaved in various degrees of vacuum and in various atmospheres at about LNT. The principal effect which we looked for was a decrease in the depth of the luminescence dip at the exciton absorption peak, because this is the most striking effect of the dead layer. As the shape of the excitation spectrum is very sensitive to the angle of observation, the experiments were performed by watching the shape of this spectrum with time after the crystal was cleaved.

4.2 Equipment And Procedures

In all cases, the crystal was excited by light from a deuterium lamp which passed through a half meter monochromator with a band pass half width of about 2 nm and was focused on the cleaved surface. The luminescence was viewed at 90° from the direction of the exciting light and from slightly behind the illuminated surface. The emitted light was detected by an EMI 6256S photomultiplier tube after passing through either an interference filter or an Engis monochromator. The interference filter has a peak transmission of 21% at 293 nm and a band pass half width of about 17 nm, but the wavelengths at which the transmission is 0.1% are 274 and 330 nm. The band pass of the Engis monochromator was about 8 nm. The crystals were nominally pure NaI purchased from the Harshaw Chemical Company.

In the initial experiment, the crystal was mounted on a cold finger and no attempt was made to measure the temperature. Mechanical access to the vacuum space was by a brass rod passing through an "o" ring seal. This rod was threaded at the end to fit into another brass fitting which held a razor blade used for cleaving the crystal. The blade, which moved along a track, could be retracted after the cleave. Although the crystal was cooled for six hours prior to cleaving, it never became really cold, probably because of heat conduction through the brass rod. From the size of the luminescence signal, the temperature was estimated to be ~ 100 K. The pressure as measured with a thermocouple gauge was ~ 10^{-3} torr.

The second and third experiments were performed in a Sulfrian cryostat. The cold finger could be cooled with either liquid nitrogen or helium. The temperature was measured with a constantan-chromel thermocouple soldered to the nickel plated copper crystal holder. Mechanical access was via a steel rod inside a piece of flexible stainless steel tubing. In this case the cleaving razor was mounted on the sample holder, but there was no contact between the sample holder and the mechanical access rod except during the actual cleaving. No attempt was made to retract the blade after cleaving and thus approximately 10% of the crystal face was shielded from the incident light. The vacuum was produced by a series combination of a liquid nitrogen cold trap, a diffusion pump and a mechanical fore pump. The pressure in this case was estimated to be ~ 10^{-5} torr.

For the third run, the pressure was monitored with a vac-ion gauge capable of measuring pressures down to 10^{-8} torr. The cryostat, which had been thoroughly leak checked, was sealed when the pressure was $< 10^{-5}$ and liquid helium was put into the inner reservior of the cryostat. The pressure immediately dropped below 10^{-8} torr (zero on our gauge), but by the time the crystal had cooled, the pressure had risen to ~ 3.3 x 10^{-7} torr. This pressure is attributed to helium gas diffusing through the Viton A "o" rings. The temperature at the time of the cleave was ~ 64 K, but rose slowly to 72 K within one hour.

The other low temperature cleaves were done in an Andonian exchange gas cryostat. The crystal temperature was measured with a copper-constantan thermocouple screwed onto the sample holder. The razor blade was mounted on the sample holder beneath the crystal, and cleaving was accomplished by tapping the sample holder against the bottom of the sample chamber.

This experiment was performed in N_2 gas at 79 K, in $N_2 + O_2$ gas at 91 K (in order to insure that there would be a high partial pressure of oxygen) and in He gas at 82 K. This experiment has also been done in liquid N_2. The purity of the gases, for example the amount of water vapor present, is unknown.

4.3 Results

The data is tabulated in Appendix I. The trend of the changes was an increase in the emission intensity in the low energy exciton region and a decrease in the region of the exciton absorption peak, the high energy side of the exciton peak and in the band to band region. Only the crystals cleaved in He and N_2 plus O_2 showed any increase in any of the latter regions. The spectrum of the crystal cleaved in He was the only curve in which the low energy exciton peak did not increase relative to the rest of the spectrum.

Only the crystal cleaved in LN_2 decreased in emission intensity over the entire spectrum. Of the crystals cleaved in vacuums, that cleaved at ~ 10^{-3} torr changed the most dramatically, while that cleaved at 3.3×10^{-7} torr decreased the least in intensity over the long run. Of all the curves, those from the crystals cleaved in N_2 gas and He changed the least. Figure 13 shows how the spectrum changed for the crystal cleaved at ~ 10^{-3} torr.

4.4 Analysis

In no case was there an appreciable change in the depth of the luminescence minimum, but there were changes in the shape of the spectrum which were consistent throughout this series of experiments and are therefore real effects. The fact that the crystals behave qualitatively in such a similar manner, as well as the lack of more quantitative knowledge of the partial pressure of the various gases, makes it impossible to identify any specific adsorbed gas as responsible for the observed changes in the spectra.

There are differences, however, which suggest that adsorbed gases do play a role. If we accept the idea that decreases in emission intensity are related to a deterioration (i.e. a change from the initial condition) of the surface, then it appears that the deterioration is accelerated by a poor vacuum, but inhibited by an N_2 atmosphere. On the other hand, the liquid nitrogen is apparently not as effective at inhibiting surface deterioration. This suggests that the effects of adsorption may be due to some

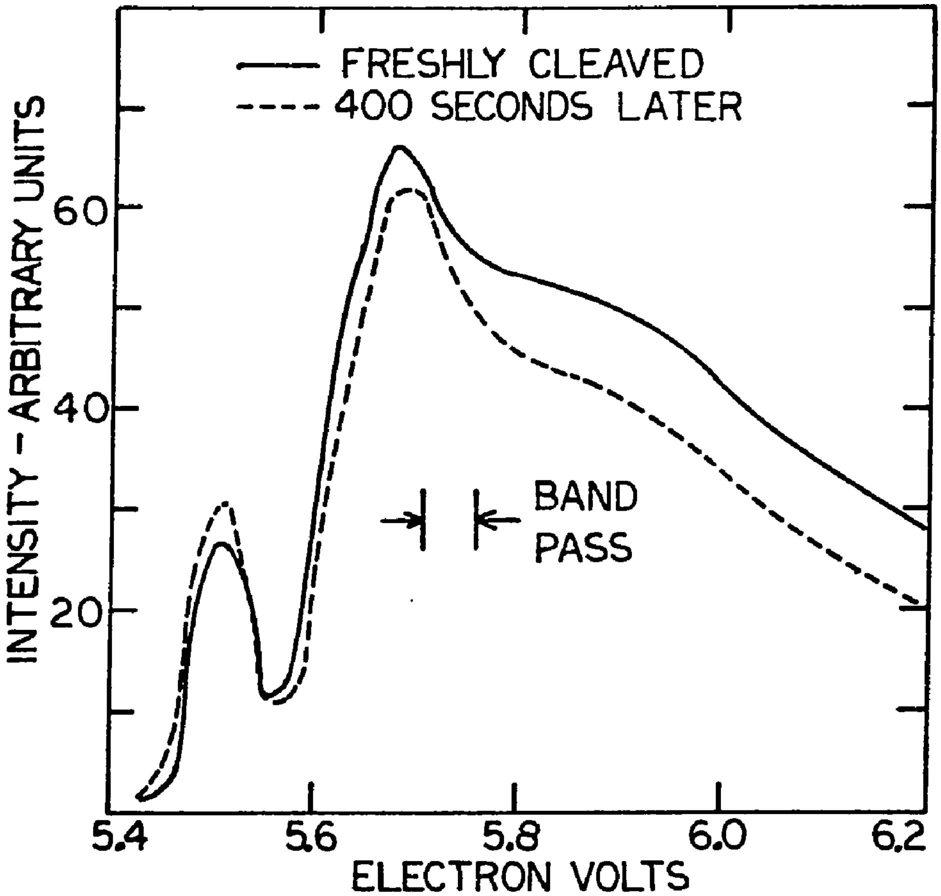

Figure 13. Change in the Excitation Spectrum of a Freshly Cleaved Crystal. This is a comparison of the excitation spectra of a NaI crystal freshly cleaved and after 400 seconds at 100 K in a vacuum of ~ 10^{-3} torr.

gas which was not controlled, for example H_2O.

In any case, the goal of these experiments was to determine whether the dead layer could be attributed to the presence of adsorbed gas. The conclusion is, that although the atmosphere in which the crystal is cleaved does have some effect on the shape of the excitation spectrum, adsorbed gas is not the principal cause of the dead layer.

5.0 Effects On NaI Of Heating In An I_2 Atmosphere

5.1 Background

Van Sciver[60] studied NaI crystals heated to 500°C while exposed to I_2 gas at a pressure of 1.4 atmospheres. One effect of this treatment was an enhancement of the quantum efficiency in the band to band region of the excitation spectrum. Since we had observed that we could produce a similar increase, at least temporarily, by applying a negative electric field, we decided to duplicate the earlier experiments and further study this phenomenon.

5.2 Equipment

5.2.1 Optical Apparatus

The crystal was excited by light from a deuterium lamp which passed through a half meter monochromator which was evacuated and had a band pass half width of about 2 nm. The luminescence was monitored with an EMI 6256S photomultiplier tube behind either an Engis monochromator or an interference filter. The band pass half width of the Engis monochromator was about 8 nm. The interference filter had a peak transmission of 21% at 293 nm and a band pass half width of 17 nm, but the transmission was 0.1% at 274 and 330 nm.

5.2.2 Sample Preparation

The preparation of the sample was as follows:

1. Two fused quartz tubes, sealed at one end, were cleaned

with water, then filled with HF and allowed to stand for about one minute. The tubes were rinsed five times with distilled water and once in ethyl alcohol to dry them. They were evacuated using a mechanical pump and torched to a glowing red for about five minutes. The evacuated tubes were transferred to the dry box and backfilled with dry air.

2. Two crystals of pure NaI from the Harshaw Chemical Company were cleaved on six surfaces. One crystal was placed in each tube.

3. About two grams of crystalline I_2 were placed in one of the tubes. This tube was then evacuated with a mechanical pump and sealed with a torch.

4. The tube containing the control sample was also evacuated with the mechanical pump, but was then backfilled with dry N_2 gas to a pressure of ~ 300 torr. The purpose of the N_2 gas was to inhibit sublimation. This tube was also sealed with a torch.

5. Both samples were placed in a tube furnace preheated to 500°C in the center. (See Figure 14.) The temperature of the cool end of the excess I_2 sample tube was monitored with a thermocouple and kept at 250°C. This produces a vapor pressure of about 1500 torr of I_2.

6. Both crystals remained in the furnace 92 hours. After

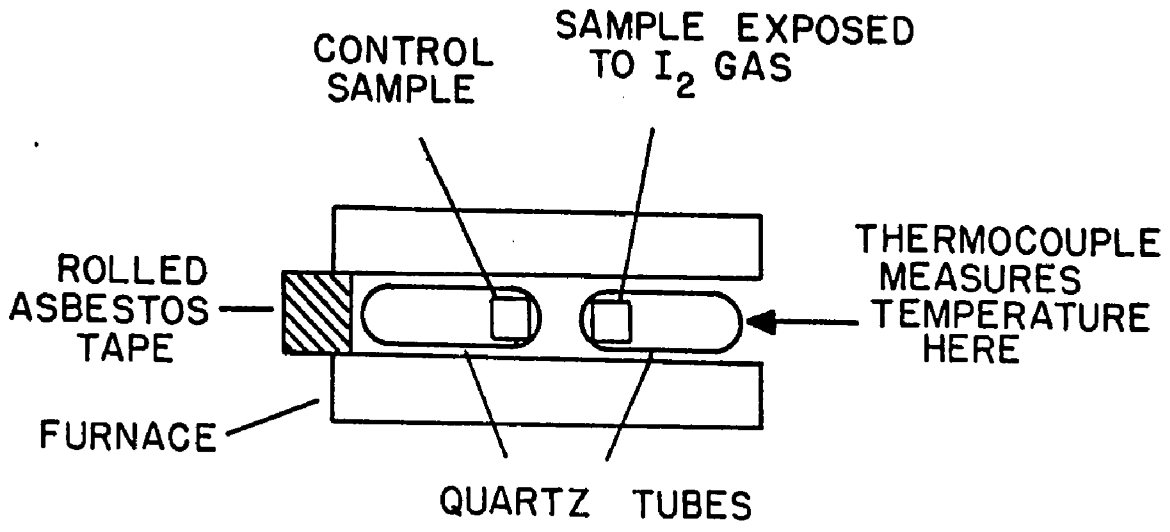

Figure 14. Apparatus for Heating NaI in I_2 Gas.

this time the furnace was turned off and the tubes cooled to ~ 80°C before they were placed in the dry box.

7. A tube was broken open inside the dry box and the crystal mounted onto the sample holder without further cleaving. The sample dimensions were 10 x 10 x 9 mm. The sample holder was constructed so that crystals could be cleaved in the sample chamber.

8. The crystal was transferred to the Andonian exchange gas cryostat.

Other crystals were prepared in an atmosphere of H_2 + I_2. This was done by placing the samples with I_2 crystal in a quartz tube, cleaned as above, through which a steady flow of H_2 was maintained (see Figure 15). The center of the tube, with the NaI samples, was at 500°C while the ends of the tube were at about 95°C, which would produce a vapor pressure of I_2 gas of ~ 60 torr. In practice, the I_2 sublimated from the upstream side of the tube and deposited on the downstream side. The tube was turned around twice in order to increase the exposure to I_2 gas. The treatment lasted 40 hours.

5.2.3 Data Recorded

Excitation spectra were recorded both before and after cleaving. After the crystal had been cleaved, its front face was no longer at the same angle relative to the detector. Since the shape of the excitation spectrum is known to be sensitive to the

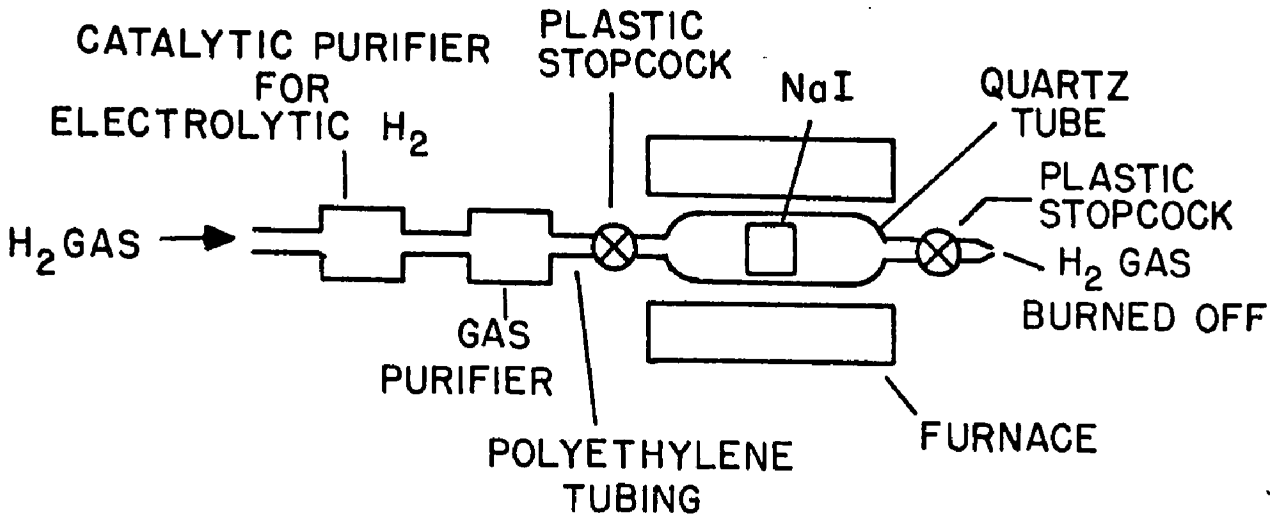

Figure 15. Apparatus for Exposing NaI to $I_2 + H_2$ Gas. The H_2 gas passes through a Deoxo hydrogen purifier made by Engelhard and a Model 460 gas purifier made by the Matheson Company before passing over the NaI at 500°C.

angle of observation, spectra were recorded after maximizing the observed signal at specific excitation wavelengths. This method was adopted in order to adjust the crystal so that the relative angles between the surface and the emitted light would be as much the same as possible.

5.3 Results

The data on the effect of excess I_2 on the luminescence quantum efficiency in the band to band region is summarized in Appendix II. Although there is some scatter in the data, no consistent pattern emerged. Specifically, the quantum efficiency in the band to band region of the excitation spectrum was not enhanced by exposure to the I_2 gas.

Another phenomenon observed was the appearance of two emission bands excited at 5.4 eV. These bands peak at 314 and 331 nm, and appeared in every heat-treated crystal, whether or not exposed to I_2 gas. The emission spectrum at LNT for excitation at 5.4 eV is given in Figure 16, for a crystal exposed to H_2 + I_2 gas. This curve shows four peaks. The peak at 295 nm is due to intrinsic luminescence. The two peaks at 314 and 331 are of unknown origin. The peak at 371 nm is due to copper impurity. The excitation spectrum for the 314 nm emission is given in Figure 17. This spectrum is dominated by a peak that is fairly symmetric about 5.45 eV but which shows a strong dip at the exciton absorption peak. This dip causes the observed peak to appear at 5.36 eV.

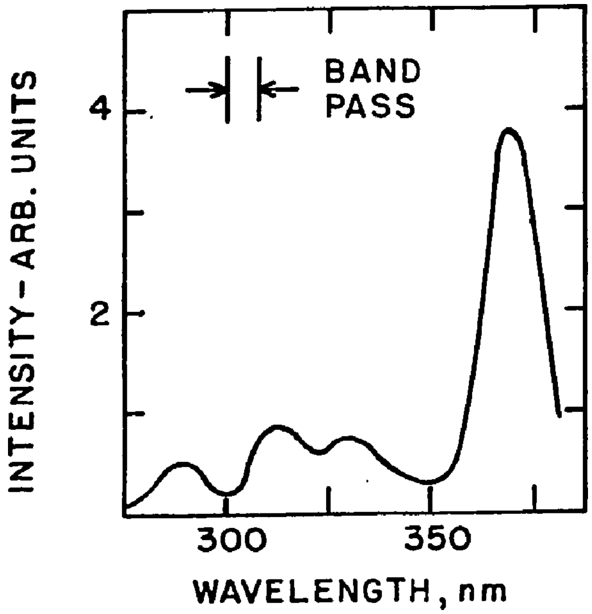

Figure 16. Emission Spectrum of Heat Treated NaI. The NaI crystal was exposed to H_2 plus I_2 gas at 500°C. The excitation energy was 5.3 eV and the temperature was 78 K. The peaks at 331 and 314 nm appeared only in the heat treated samples.

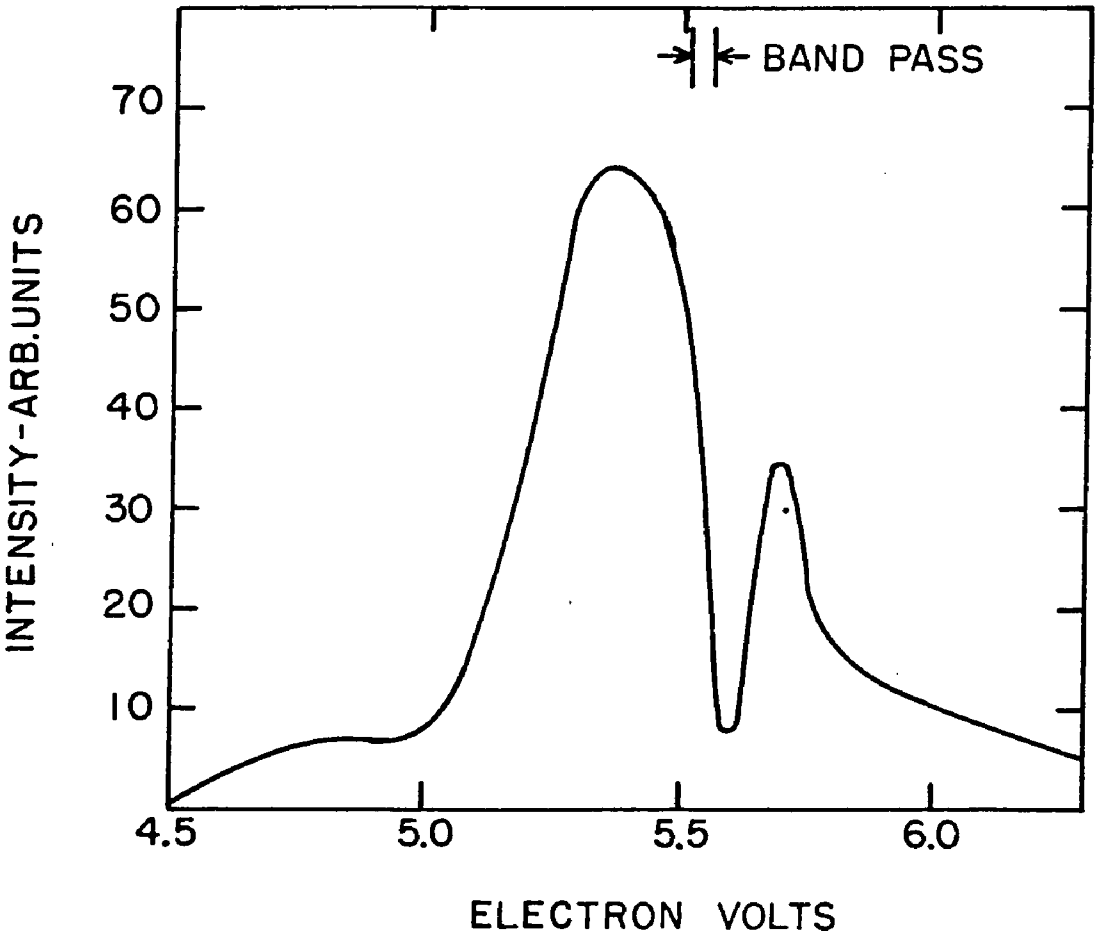

Figure 17. Excitation Spectrum for the 314 nm Emission at 78 K.

There is also a shoulder at around 4.8 eV.

5.4 Analysis

The expected increase in the quantum efficiency in the band to band region of the crystals exposed to I_2 gas at 500°C was not observed. The effect observed by Van Sciver[60] was quite dramatic and should have been evident even without quantitative comparison. Thus we must conclude that some step in our method of exposing NaI to I_2 differed in some subtle manner from that of Van Sciver, or that our crystals differed from his in some way that led us to obtain different results. Since an emission band at 375 nm excited at 4.85 eV, which is now known to be caused by copper impurity, was also attributed to the I_2 treatment, it may be that the other effect was also due to copper added during the excess I_2 treatment.

The emission bands at 314 and 331 nm were apparently produced, or at least enhanced, by the heat treatment, as they appeared in all of the crystals that were heated, but have not been observed in any other crystal. They may be due to an impurity which was inadvertantly put into the crystal, or to a center created at high temperature, such as an anion or cation vacancy, or to a complex created at the high temperature, such as a copper atom next to an anion vacancy. Although these effects are interesting, they do not appear to be related to the present investigations, and they were not studied further.

6.0 Flash Lamp Experiments

6.1 Background

As mentioned earlier, we considered the possibility of photo-induced effects producing the dead layer. For example, mobile charges could become trapped at the surface to create electric fields in the surface region. Other possibilities are that electric fields could be built up via the Dember effect, or from the positive charge resulting from photoemission from shallow electron traps. In any case, if one of these mechanisms is operative, then there must be a finite amount of light which strikes the crystal before a "dead layer" is created. Thus, especially in a freshly cleaved crystal, we expect to see some change in the quantum efficiency as the crystal is illuminated.

In these experiments, light was shone onto the crystal in flashes of ~ 25 ns duration. By monitoring the intensity of luminescence excited by each flash, one could see the effects of the history of the crystal on the luminescence quantum efficiency.

6.2 Equipment

The light source was a free running flash lamp which discharged in N_2 gas. The flash duration was about 25 ns. The firing rate could be controlled from a low rate of 4 or 18 Hz to a high rate of 70 or 100 Hz (depending upon how the spark gap was adjusted and whether there was a flow of N_2 gas over the electrodes), by changing the applied voltage to the input. The light could be blocked at this point, otherwise it was focused onto the entrance slit of a half meter monochromator with a band pass of 5 nm. The light from the monochromator was focused onto a crystal of "pure" NaI, obtained from the Harshaw Chemical Company, inside an Andonian exchange gas cryostat. The temperature of the crystal was determined by a thermocouple fastened to the sample holder. (See Figure 18)

The luminescence was monitored with an EMI 9594QUB photomultiplier tube after passing through Corning filter 7-54. It was necessary to use this filter rather than the interference filter in order to obtain a satisfactory signal. This has the disadvantage of passing a significant portion of the impurity luminescence as well as the intrinsic luminescence. The signal from this photomultiplier tube went to a Tektronix 7903 oscilloscope. The oscilloscope trace was triggered with the signal from an 1P28 photomultiplier tube which looked directly at the flash lamp. The output of the oscilloscope was connected to a Monsanto 1008 counter-timer and to a Tullamore, Scippy 400, multichannel scaler (MCS). The rate of firing was monitored with the counter-timer, while the pulse height distribution could be recorded in any one of four channels of the MCS. This pulse height distribution could be displayed and photographed using a Dumont Camera, type 297.

The intensity of a flash from the lamp was measured by placing

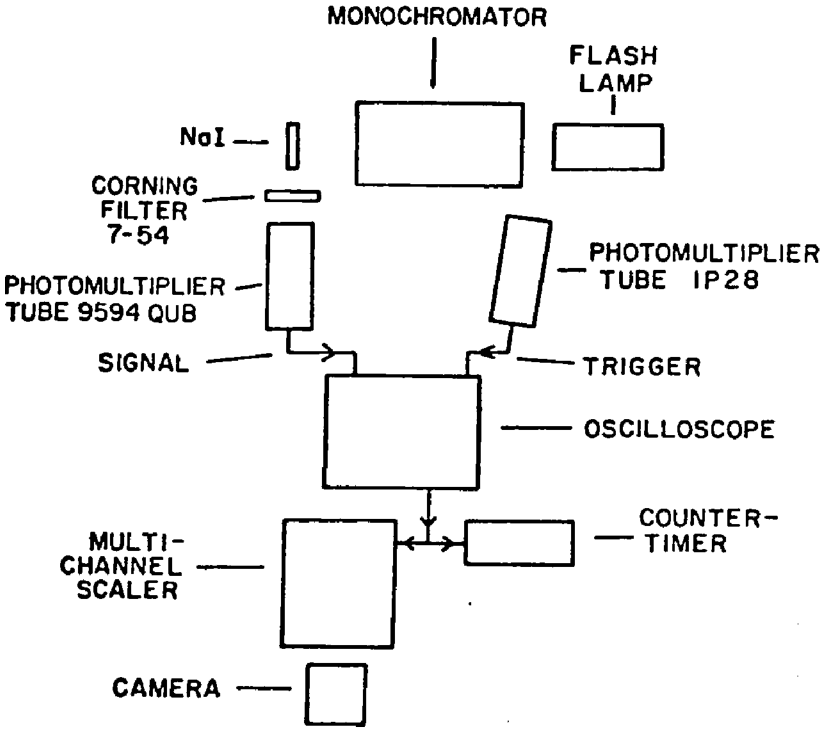

Figure 18. Apparatus for the Flash Lamp Experiments.

the EMI 9594QUB PMT at the exit port of the half meter monochromator. Stainless steel screening with a measured transmission of 0.045 was used as a neutral density filter. The cathode was connected to ground through $10^{10}\Omega$ impedance head of a Keithly 640 vibrating reed electrometer, and the first dynode held at 100 volts. The flash lamp firing rate was set at 100 flashes per second and the cathode current measured. The resulting current was divided by the product of the transmission of the screen, the number of photo-electrons per incident photon emitted from the S-13 photocathode, the charge per electron, and the number of flashes per second. This gave a result 2.3×10^{7} photons/flash at 5.77 eV. A similar measurement using the Gates deuterium lamp resulted in a value of 4.3×10^{11} photons/second.

6.3 Results

The most dramatic effects were observed on the freshly cleaved surface. The experiment was performed twice in which a crystal, freshly cleaved at LNT in the sample chamber, was exposed to about 50 flashes of light at a low rate, then to several thousand flashes at a high rate, followed by flashes at the lower rate. In one case the excitation energy was 6.05 eV and the temperature was 79 K. The low rate was ~ 4 Hz and the fast rate ~ 70 Hz. After exposure to 5,000 high speed flashes, the luminescence increased by 100%. In the second attempt the crystal was exposed to 5.92 eV light at 78 K. The low flash rate was 18 Hz and the fast rate was 100 Hz. In this case the increase was 43% after exposure to 7,000 high speed flashes.

After exposure to the high flash rate, the enhanced quantum efficiency would decrease toward its original value, the rate of decrease depending upon the low flash rate. If the crystal was left in the dark before being exposed to the light, the increased quantum efficiency decayed to half its original value in ~ 15 seconds at 79 K. Even after half an hour in the dark, however, the quantum efficiency of the recently cleaved crystal was 20% greater than when first cleaved. In fact the original large effect was not observed, even in a crystal left in the dark overnight.

In order to determine the spectral response, the following experiment was performed. The crystal was left in the dark for two minutes, then exposed to about 50 low speed counts, followed by 7,000 high speed counts. Then the count rate was reduced and another fifty pulse heights recorded. These data were recorded for various wavelengths at 78 K. The data are displayed in Figure 19.

This experiment was also performed exciting with 6.05 eV light at temperatures of 60-70 K at a pressure of a few hundred torr. Under these conditions the effect was reduced from an increase of 15% to an increase of 8%. In this case the quantum efficiency apparently did not decrease as rapidly as had occurred at higher temperatures, thus reducing the effect of further exposure to light.

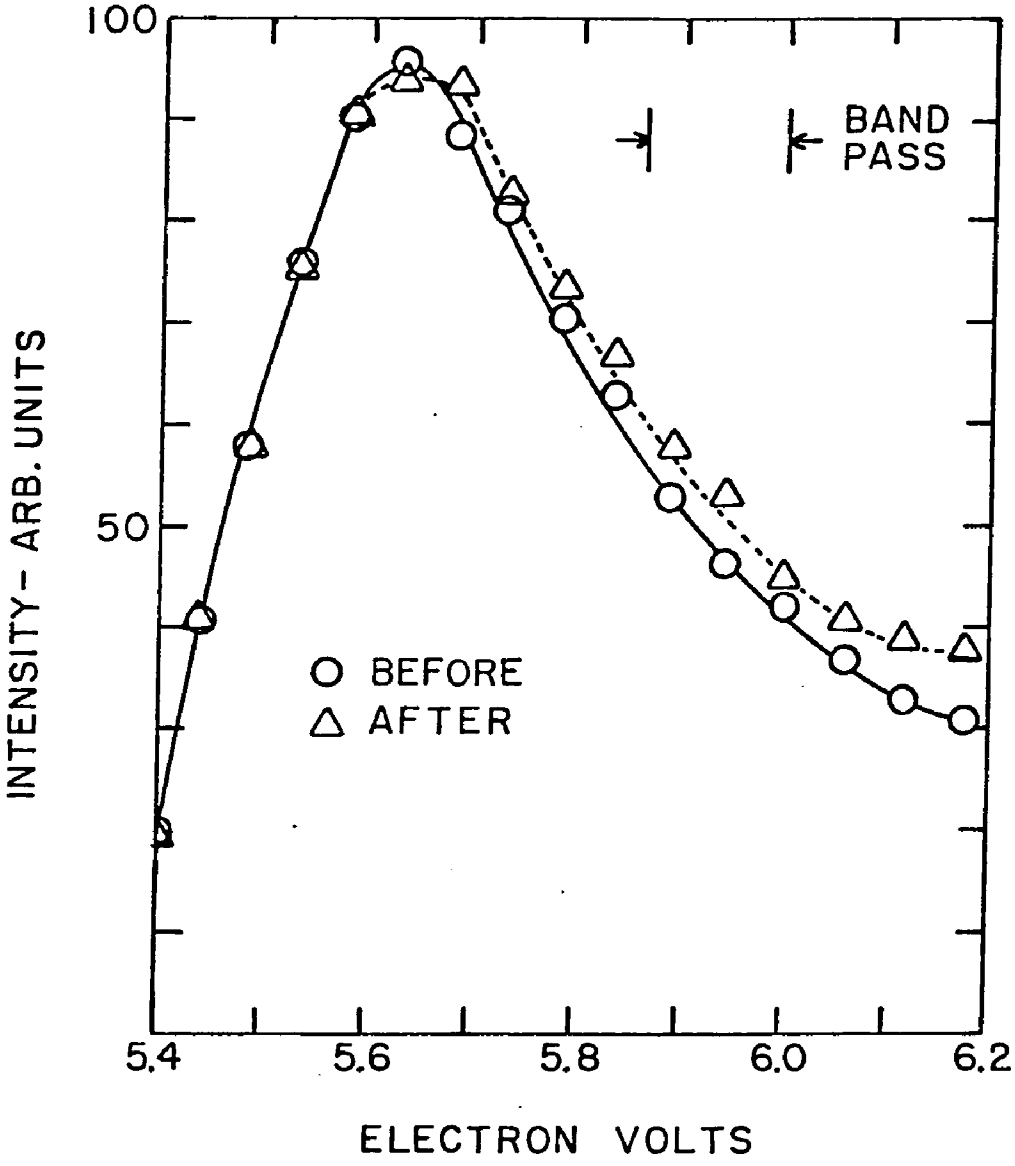

Figure 19. Spectral Response of Flash Lamp Experiments. These data show the intensity of luminescence excited with a flash rate of 4 Hz. The crystal was in the dark for two minutes prior to the "before" measurement. The "after" data were recorded after the crystal had been exposed to ~ 7,000 flashes at ~ 70 Hz. The temperature was 78 K.

An attempt was made to determine whether the quantum efficiency could be further increased by exposing the crystal to the high flash rate for a longer period of time. It was found that exposure to more than ~ 5,000 light pulses had no apparent effect. A crystal exposed to a flash rate of ~ 22 Hz after having been in the dark for fifteen minutes increased its quantum efficiency by ~ 10% with exposure, but this effect saturated after 1,500 flashes.

6.4 Analysis

The results of these experiments can be understood if one realizes that there are many shallow electron traps even in "pure" NaI. This means that some electrons excited into the conduction band during the light flash will not recombine with holes, but will become shallowly trapped. Thus when the flash is over, some holes will remain "self-trapped" as V_k centers. These leftover V_k centers are not immobile, however, and during the time between flashes they will diffuse slowly and some will recombine with trapped electrons or find other hole traps. The greater the time between flashes, the fewer V_k centers will remain. When the next light flash occurs the remaining V_k centers will be available for recombination with the newly freed electrons and thus contribute to the observed luminescence. The more V_k centers that are left, the greater the quantum efficiency of the incident light flash will be.

These ideas are put in a more quantitative form in the following model. In this model a photon flux of I_0 photons $\cdot s^{-1} \cdot cm^{-2}$ is incident on a crystal with absorption coefficient α cm^{-1}. The crystal contains a concentration N cm^{-3} of electron traps. The traps have only two states, full or empty. The probability of capture (volume recombination rate) for an electron in an empty trap is λ $cm^3 \cdot s^{-1}$ and the capture cross section for ionization of a full trap by a photon is β cm^2. The concentration of full traps is n_i cm^{-3}, the concentration of free electrons is n cm^{-3} and the concentration of holes is p cm^{-3}. The holes are also mobile and the volume recombination rate for a hole with a full trap is γ $cm^3 \cdot s^{-1}$. For simplicity we assume that the volume recombination rate for free electrons and holes is also λ. With these assumptions the general rate equation can be written:

$$(1) \quad \frac{dp}{dt} = \alpha I_0 \exp(-(\alpha + \beta n_i)x) - \lambda np - \gamma n_i p$$

$$(2) \quad \frac{dn}{dt} = (\alpha + \beta n_i) I_0 \exp(-(\alpha + \beta n_i)x) - \lambda np - \lambda n(N - n_i)$$

$$(3) \quad \frac{dn_i}{dt} = -\beta n_i I_0 \exp(-(\alpha + \beta n_i)x) + \lambda n(N - n_i) - \gamma n_i p$$

$$(4) \quad p = n + n_i$$

where formula (4) is the condition for electrical neutrality and makes one of equations (1) - (3) redundant. Since in the energy region of interest the absorption due to impurities is much less than that due to the host, we neglect the dependence of the absorbed light on n_i and write $I \equiv I_0 \exp(-(\alpha + \beta n_i)x)$.

In the first step, we assume for simplicity that the crystal is illuminated with a flash of light of such short duration t_f that no recombination occurs during the light flash. At this time the concentrations are $n = (\alpha + \beta n_i)It_f \equiv n_0 \approx$ constant, $p = p_r + \alpha It_f \equiv p_0$, $n_i = n_{ir} - \beta n_{ir}It_f \equiv n_{i0}$, p_r and n_{ir} are the residual concentrations of holes and trapped electrons, i.e. those holes and trapped electrons existing before the flash. We assume that at the time of the flash there are no free electrons, as will be discussed below, and that changes in βn_i are negligible compared to α so that n_o is a constant.

After the flash the crystal is in the dark and our equations for step two become:

$$(1) \quad \frac{dp}{dt} = - \lambda np - \gamma n_i p$$

$$(2) \quad \frac{dn}{dt} = - \lambda np - \lambda n(N - n_i)$$

$$(3) \quad \frac{dn_i}{dt} = \lambda n(N - n_i) - \gamma n_i p$$

$$(4) \quad p = n + n_i$$

Since the volume recombination rates are roughly proportional to the diffusion coefficients of the reactants,[105] we can neglect γ relative to λ for NaI because the hole mobility is much less than that of the free electron. These equations can be solved, giving

$$n = \frac{Nn_0}{(N + n_0)\exp(\lambda Nt) - n_0}$$

$$p = p_0\left(\frac{N}{N + n_0} \right)\left(1 - \left(\frac{n_0}{N + n_0} \right)\exp(- \lambda Nt)\right)^{-1}$$

$$n_i = N \cdot \frac{p_0 - n_0 \exp(-\lambda N t)}{N + n_0(1 - \exp(-\lambda N t))}$$

For large times the free electron concentration goes to zero and the trapped electron concentration becomes equal to the hole concentration. Since the lifetime of the intrinsic luminescence is 110 ns in NaI, we are safe in assuming that the electron concentration has gone to zero by 10^{-6}s. At this time we have $n = 0$ and $n_i = p = p_0 \cdot \frac{N}{N + n_0}$. In step three the crystal is in the dark and there are no free electrons. The only term left in our equation is $\frac{dp}{dt} = -\gamma n_i p = -\gamma p^2$. This has the solution

$$p = n_i = 1/(\gamma t + (\frac{N + n_0}{p_0 N})).$$

The hole concentration decreases toward zero until the next flash of light occurs at time T_0. T_0 is the period of the flash lamp and is ~ 10^{-2}s. At this time p is defined to be p_r. Thus, for a given flash period T_0, substituting for p_0,

$p_r = 1/(\gamma T_0 + (\frac{N + n_0}{N(p_r + \alpha I t_f)}))$. This can be solved for p_r.

$$p_r = \frac{1}{2} (\alpha I t_f + \frac{n_0}{\gamma T_0 N})((1 + \frac{4\alpha I t_f}{\gamma T_0 (\alpha I t_f + \frac{n_0}{\gamma T_0 N})^2})^{\frac{1}{2}} - 1)$$

We see that for small values of T_0, the residual value of p is very large, but as T_0 increases p_r approaches zero.

This model is sufficient to explain the observed results. The traps in the freshly cleaved crystal are empty before illumination and there are no free holes. Thus the luminescence, which is proportional to λnp, is initially low but rises as the hole concentration reaches its equilibrium value. When the flash rate is high the residual concentration of holes increases so that the quantum efficiency at the low pulse rate, after exposure to the higher rate, is initially high. Recall that the crystal left in the dark also lost some of its enhanced quantum efficiency (as the hole concentration decreased).

As stated in Section 2.1.1, the holes are immobile below 58 K; thus when the temperature was reduced, the magnitude of the increase in luminescence after exposure to the high flash rate decreased. This is because γ, which is proportional to the hole diffusion coefficient, is reduced. In this case the dependence of the residual value of p on T_0 is also reduced.

This model does not explain why the crystal failed to return to its original low quantum efficiency when left in the dark overnight. The reason for this is probably that some holes become trapped at centers which are initially neutral, for example Tl^{++} is known to be stable, although Tl^{+} is the normal state.[56] Since the filter used on the emission could not discriminate against some of this impurity luminescence, this may have been the source of the apparently higher quantum efficiency. This phenomenon was further studied with an experimental arrangement which allowed more careful spectral measurements (see Section 9).

7.0 Dember Measurements

7.1 Background

As mentioned in Section 2.2.2.H, the Dember effect occurs when light is absorbed non-uniformly within a photoconducting crystal. In the case of NaI excited in the band to band region the non-uniform absorption is due to the high absorption coefficient, ~ 10^5 cm^{-1}. Since the holes become self-trapped almost immediately,[14] their mobility is very small,[15] and the current is carried by the electrons, whose mobility is larger.[91] In the absence of an electric field the free electrons created by band to band transitions diffuse at random in the crystal until they either become trapped at some defect, or find a hole and recombine. Since the concentration of free electrons is greatest near the illuminated surface, the electrons will tend to move deeper into the crystal. As this happens, space charges build up which inhibit this migration. For a homogeneous crystal, we expect that the surface will become positive with respect to the bulk.

In these experiments the crystal was placed between the plates of a capacitor, at least one of which was transparent. It was expected that when the crystal was exposed to the light, the front plate would become positive and a transitory current could be detected as charge flowed from this plate.

7.2 Equipment

The basic experimental setup was very simple; see Figure 20.

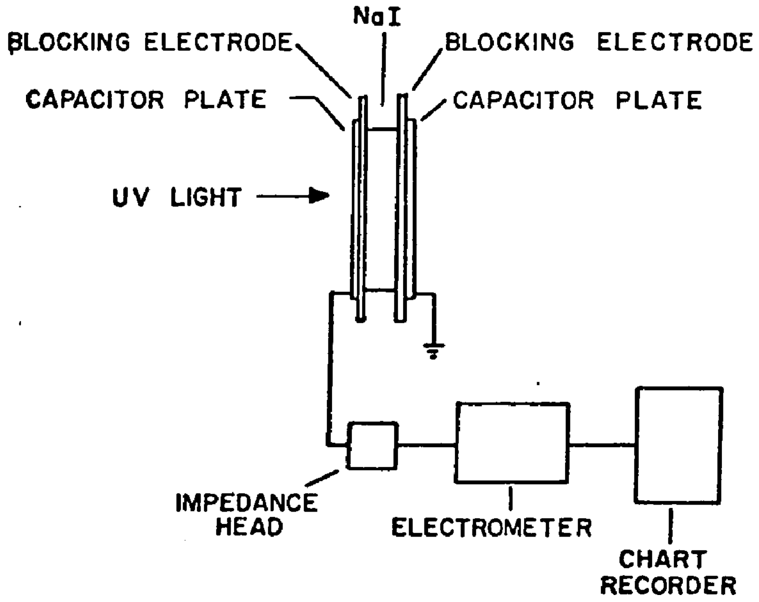

Figure 20. Apparatus for the Dember Measurements.

A crystal, freshly cleaved on the front and rear surfaces, was placed in the sample holder. The sample holder was a sandwich consisting of a transparent electrode on the front, a piece of fused silica, and an electrode which is grounded. The front electrode is connected to the impedance head of a Keithly 640 vibrating reed electrometer. The current from the front electrode was the voltage measured with the electrometer divided by the impedance of the impedance head.

The light source was a deuterium lamp. The light was filtered using Corning filters. Also a tungsten bulb was used as a source of visible light. The temperature of the sample was estimated from the temperature of the sample chamber, which was measured with a copper-constantan thermocouple.

Two designs were used for the sample holder, all of which used Teflon for the principal structure. In the first design, the front electrode was made of stainless steel screen which transmitted 26% of the light, and the back electrode was a copper plate. The blocking electrodes were 0.1 mm thick fused silica. The second design used stainless steel screen for both plates.

In one experiment performed at 82 K, -45 volts was applied across the crystal for five minutes while visible light shone on the crystal. The light was turned off and the voltage removed. Then the response to uv and white light was recorded.

7.3 Results

There was a response to uv light. The response was not observed with light passing through a Corning filter 9-54 (0% transmission at 210 nm, 5% transmision at 220 nm, 75% transmission at 260 nm). The uv response was reduced to zero by long exposure, on the order of hours for a new crystal. White light also produced a response that was different from that of the uv. This effect was also reduced by exposure, for times on the order of minutes. Similar effects were observed when NaI was replaced by plexiglass, cardboard, mica, Teflon, or even nothing at all. Although each material produced slightly different results, the response to uv light was of the same order of magnitude. Furthermore, the results were not reproducible from one day to the next. It is believed that photoemission, thermal gradients, contact potentials, and possibly other uncontrolled variables affect the results. It is not at all clear that the signals observed were due to a Dember effect. The largest signal observed was 5×10^{-13} amps and this signal decreased with a time constant on the order of 100 seconds.

In the case of the crystal which had been exposed to white light while a negative field was applied, the response to white light was $\gtrsim -7 \times 10^{-13}$ amps and decreased with a time constant $\sim$ 100 seconds.

7.4 Analysis

Although this experiment has not detected a Dember field, it can place an upper limit on the size of such a field.

The model is that the crystal is an infinite slab of thickness d, with a net charge of zero. The change in potential of the front (illuminated) face of the crystal relative to the back is

$$V(0) - V(d) = \int_0^d E dx = Ex\Big|_0^d - \int_0^d x\frac{dE}{dx}dx = - \int_0^d \frac{x\rho}{\epsilon}dx = - \frac{P}{\epsilon}$$

where we have integrated by parts and used Poisson's equation for $\frac{dE}{dx}$. Since the net chage on the crystal is zero, $E(0) = - E(d) = 0$. ρ is the net charge per unit volume at a distance x from the front surface, ϵ is the static dielectric constant, and P is the dipole moment per unit area[106] which results from the displacement of charges within the crystal.

This change in potential will cause a charge to flow onto the capacitor plates, $Q = C \cdot \delta V$, which will result in a current through the measuring circuit. If we assume that the charge flows on with a characteristic time t_0, then the current in the meter will be $I_m = \frac{Q\exp(-t/t_0)}{t_0}$. Thus the larger t_0 is, the smaller I_m will be. The capacitance for plates of area A is $C = \frac{\epsilon A}{d} = 5.84 \times 10^{-12}$ farads, where $A = 1\ cm^2$, $d = 1$ mm, and $\epsilon / \epsilon_0 = 6.6$ for NaI. Using $I_m = 5 \times 10^{-13}$ amps and $t_0 = 100$ seconds this gives $\delta V = \frac{t_0 I_m}{C} = 8.55$ volts. If the electric field is uniform in the crystal $E = \frac{\delta V}{d} = 8.55 \times 10^3$ volts/meter. In the electric field experiments the applied fields were on the order of 10^6 volts/meter.

The theoretical expression for the electric field due to the Dember effect is[107] $E = \frac{kT}{e}\left(\frac{dn}{dx} - (m_p/m_n)\frac{dp}{dx} \right)/(n + (m_p/m_n)p)$ where n and p are the electron and hole concentrations respectively, m_n and m_p are the electron and hole mobilities, respectively, and the Einstein relation, $\frac{D}{m} = \frac{kT}{e}$ has been used for the ratio of the diffusion coefficient D, to the mobility. If the hole mobility is negligible compared to that of the electron, this reduces to $E = -\frac{kT}{ne}\frac{dn}{dx}$. When the light is first turned on the electron concentration is proportional to $\exp(-\alpha x)$, where α is the absorption coefficient. In order to maintain this electron distribution the electric field would be $E = -\frac{kT}{e}\frac{1}{n}\frac{dn}{dx} = \frac{kT}{e}\alpha = 6.65 \times 10^4$ volts/meter where $T = 77$ K and $\alpha = 10^7\ m^{-1}$. In other words, the electrons would initially behave as though they were in a field of this strength directed outward from the illuminated surface.

There are at least two possible reasons why the Dember field would not be as large as assumed here. The first is that the crystal is undoubtedly filled with shallow traps. This is evidenced by the experiment in which a large charge redistribution was observed when white light was shone onto the crystal which had previously been exposed to white light while an electric field was applied. The white light probably emptied the shallow traps and the electrons moved so as to reduce the "frozen in" field. As mentioned in Section 2.2.2.H, the traps reduce the observed electron mobility by a factor $n/(n + n_t)$ where n_t is the concentration of trapped electrons. Thus the ratio of hole to electron mobilities may not be as small as has been assumed.

The second factor is the spatial distribution of these electron traps. A high concentration of surface traps, for example, would tend to produce a field opposite to that induced by the incident light.

8.0 Exciton Diffusion Calculation

8.1 Background

It has been known for some time that proper excitons in NaI are mobile at low temperatures,[17] and this has recently been reconfirmed.[43] The evidence for this is the relationship between a decrease in observed intrinsic luminescence excited in the exciton band coupled with an increase in the luminescence due to impurities as the temperature is lowered. Since the proper excitons are known to annihilate at impurities, it seems plausible that they may also annihilate at the surface. It was also considered that the self-trapped exciton (STE) might be mobile at higher temperatures and that this could also lead to surface annihilation. This is evidently not the case, as is shown below.

8.2 Model

The model is that an exciton is mobile with a diffusion coefficient D. If the exciton diffuses to a surface, it is annihilated. The crystal is considered to be much thicker than the inverse of the absorption coefficient length, α^{-1}, and is treated as semi-infinite and one dimensional. We want a solution of Fick's law for the concentration of excitons $C = C(x,t)$, $\frac{dC}{dt} = D\frac{d^2C}{dx^2}$ with the boundary conditions $C(x,0) = \alpha\exp(-\alpha x)$, $C(0,t) = C(\infty,t) = 0$. This has the solution

$$C(x,t) = \tfrac{1}{2}\alpha \exp(\alpha^2 Dt)(\exp(-\alpha x)\cdot\mathrm{erfc}(\alpha(Dt)^{\frac{1}{2}} - x/(2(Dt)^{\frac{1}{2}})) - \exp(\alpha x)\cdot\mathrm{erfc}(\alpha(Dt)^{\frac{1}{2}} + x/(2(Dt)^{\frac{1}{2}})))$$

where $\mathrm{erfc}(z) = (2/\pi^{\frac{1}{2}})\int_z^\infty \exp(-x^2)\,dx$ and z is the quantity inside the brackets.

If we assume that the lifetime as determined by all other factors is given by t_0, then the probability of exciton destruction due to these other effects will be, for constant irradiation

$P(x) = \alpha(\exp(-\alpha x) - \exp(-x/(Dt_0)^{\frac{1}{2}}))/(1 - \alpha^2 Dt_0)$

This expression is equivalent to that given by Devore,[42] equation (2), when the surface annihilation rate is infinite. The total probability is the integral of this expression, i.e. the ratio of the number of excitons that decay somewhere in the bulk to the number created is $P = 1/(1 + \alpha(Dt_0)^{\frac{1}{2}})$ which is also equivalent to an expression given by Devore under the same conditions.

In addition to these results we can find the rate of decay of luminescence after illumination by a short pulse of light at $t = 0$. The result is $C = \exp(-t/t_0)\cdot\exp(\alpha^2 Dt)\cdot\mathrm{erfc}(\alpha(Dt)^{\frac{1}{2}})$. The main point is that the decay is not exponential, but is faster than exponential. The term $\exp(\alpha^2 Dt)\cdot\mathrm{erfc}(\alpha(Dt)^{\frac{1}{2}})$ is one half its original value in a time slightly less than $\alpha^2/D \equiv t_s$. Under constant irradiation the probability of annihilation at the surface can be shown to be $\alpha(D/t_0)^{\frac{1}{2}}$.

The experimenters who have estimated the distance which an exciton diffuses have done so on the basis of efficiency of energy transfer to impurities rather than to the surface. If x_0 is the most probable distance which an exciton moves from its origin in three dimensional space, then $(Dt_0)^{\frac{1}{2}} = x_0/6^{\frac{1}{2}}$ in our one dimensional model. In terms of this variable, the overall probability of exciton decay by means other than annihilation at the surface becomes $P = (1 + \alpha x_0/6^{\frac{1}{2}})^{-1}$. The characteristic time for decay due to annihilation at the surface is expressed $t_s = 6t_0/(\alpha x_0)^2$ and the probability of annihilation at the surface under constant illumination becomes $\alpha x_0/(6^{\frac{1}{2}}t_0)$.

8.3 Comparison With Experiment

As mentioned above, the proper exciton is mobile and known to annihilate at impurities. In this case the lifetime of the proper exciton is not believed to contribute significantly to luminescence lifetime, so we can see the effect of surface annihilation only through its influence on the quantum efficiency. Blume *et al.*[17] and Nishimura *et al.*[43] both give estimates for the diffusion length x_0 which are on the order of 150 Å at low temperatures. Taking the value of α to be $\sim 10^5$ cm^{-1}, gives $P = 0.94$. This should be an observable effect, and in fact Blume *et al.* did notice a decrease in the total light sum (luminescence of all wavelengths) at lower temperatures. Nishimura *et al.* however, found that the light sum remained constant over the temperature range from 2.4 to 180 K. On the basis of the latter result, one would conclude that the exciton is reflected at the surface. In any case, the theoretical effect on the quantum efficiency is too small to explain the observed dip in the intrinsic excitation spectrum. In order to obtain quantum efficiencies on the order of 0.2, one must assume that the product αx_0 is larger by a factor of 100 than has been suggested.

If the STE is mobile and annihilates at the surface, on the other hand, one expects that the observed lifetime as well as the quantum efficiency would be affected. In fact, however, for small values of αx_0 the effect on luminescence decay should be minimal. In order to have a noticeable effect, αx_0 would have to be at least of order unity. Measurements of the lifetime of the STE luminescence show that it does decay exponentially.[17, 43] This fact, coupled with the lack of reported host sensitized luminescence due to this process, leads us to believe that STE migration with annihilation at the surface is not an important factor in creation of the dead layer.

9.0 Stimulated Luminescence

9.1 Background

Much work has been done in which optically stimulated impurity and intrinsic luminescence in the alkali halides has been excited with low energy visible or infrared light in a crystal which has previously been exposed to high energy radiation.[53-58] This luminescence is generally attributed to the recombination of charged species which had been trapped during the uv, x-ray or high energy particle exposure. In this section the results of experiments on nominally pure NaI pre-exposed to uv light are given. We find evidence that the stimulated luminescence is sensitive to very small concentrations of copper and that the copper acts as a "catalyst" for intrinsic luminescence excited in the low energy exciton tail and possibly at higher energies.

9.2 Experimental Procedure

9.2.1 Samples

Single crystals of "pure" NaI were obtained from Harshaw Chemical Company, Isotopes, Inc. and Bicron Corporation. The impurity concentration of the crystals was determined from absorption measurements at liquid nitrogen temperature using a Cary 118CX spectrophotometer. The thallium concentration was calculated from the optical density of the "A" band at 4.27 eV using Smakula's equation. An oscillator strength of 0.17 was assumed in analogy with the A band of KI(Tl).[29] The copper concentration was determined by the same procedure from an absorption band at 4.85 eV based upon the results of Bateman *et al.*[28] The results of this analysis are listed in Table 1. It should be noted that while thallium could be detected in all three crystals as evidenced by the emission spectra, there was no evidence of copper in the Isotopes crystal.

Manufacturer	Concentration, 10^{-8} Molar Fraction Copper	 Thallium
Isotopes	< 0.2	8 ± 1
Bicron	2 ± 1	< 0.7 (approximate)
Harshaw	8 ± 2	0.2 (approximate)

Table 1. Impurity Concentration of NaI from Three Manufacturers.

The crystal sample was cleaved on all surfaces in a dry box and mounted in a brass sample holder. This was transferred into an Andonian exchange gas dewar where it was cooled by the boil off from liquid nitrogen. The crystal temperature, as monitored with a copper-constantan thermocouple soldered to the brass sample holder, could be controlled to within one Kelvin by adjusting the flow of N_2 gas in the sample chamber.

9.2.2 Optical Apparatus

The uv source was a deuterium lamp, the light from which was focused onto the NaI crystal after passing through a half meter monochromator with a 1200 line·mm^{-1} grating. (See Figure 21) An electrically controlled shutter was placed between the deuterium lamp and the monochromator. The source of visible or infrared

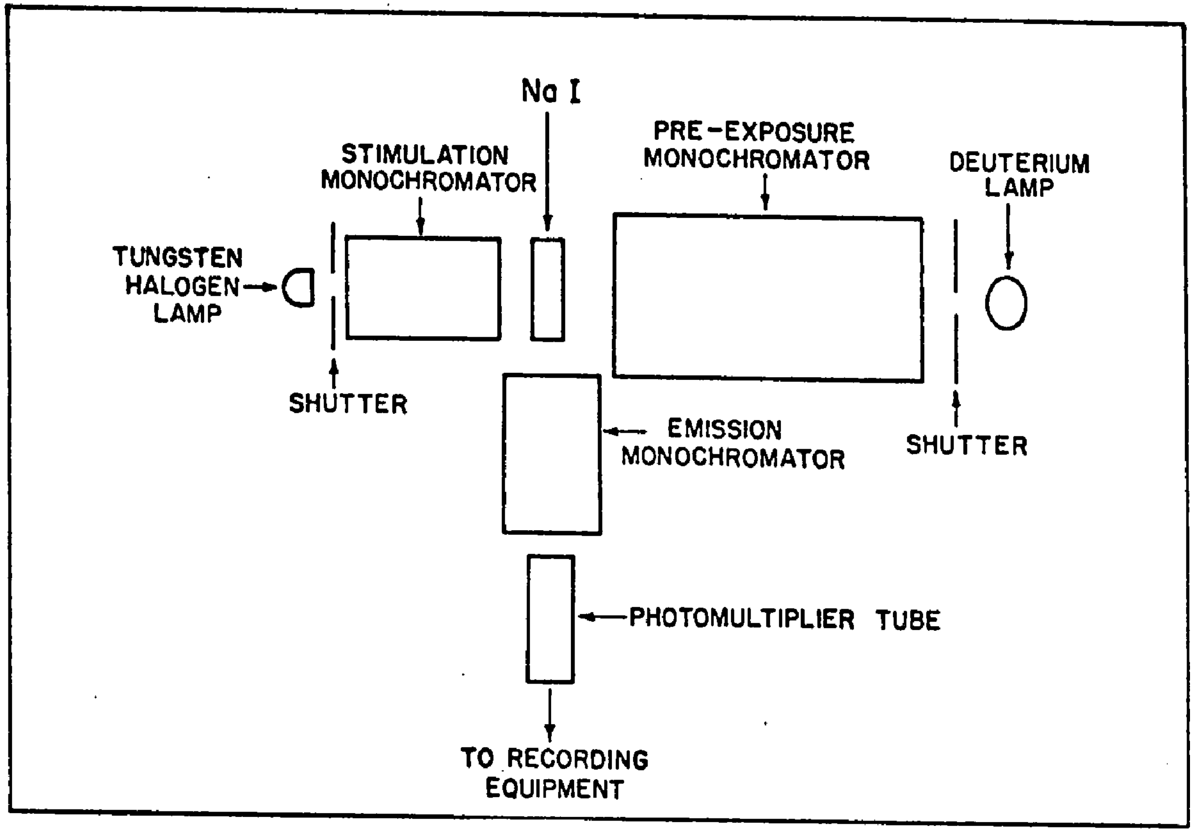

Figure 21. Apparatus for Stimulated Luminescence Experiments. A glass filter was often used in addition to, or instead of, the stimulation monochromator.

light was a tungsten halogen lamp. The light from this lamp passed through a Bausch and Lomb infrared monochromator, catalog No. 33-86-03, and/or through Corning glass filters before being focused onto the NaI at 180° from the uv light. Although this meant that the stimulating light did not strike the same surface as the uv, in practice this makes no difference because the visible and near infrared light is not appreciably attenuated in passing through the crystal. This light could also be blocked with an electrically controlled shutter. The luminescence was viewed at right angles to both the uv and infrared light through another Bausch and Lomb uv-visible monochromator, catalog No. 33-86-07, and detected with an EMI 6256S photomultiplier tube. The signal was amplified using a Keithly 640 vibrating reed electrometer with a remote impedance head, and recorded on a Varian G-14 strip chart recorder.

9.2.3 Data Collection

Data were recorded in the following manner. First the crystal was exposed only to uv light of specified energy for some time, called the pre-exposure time. During this time, free charges could be created, some of which became shallowly trapped. Then the uv shutter was closed and the crystal left in the dark for a "dark time". Luminescence was stimulated with the visible or infrared light by opening the shutter on the tungsten halogen lamp. Shallowly trapped charges were freed and could recombine with oppositely charged species. Luminescence of any wavelength could be monitored continuously. A typical signal is shown in Figure 22. The stimulated luminescence is transitory and goes to zero as the concentration of trapped charges is reduced through recombination. The integral of the stimulated luminescence is insensitive to stimulating light intensity, but the shape of the intensity versus time curve is not. For spectra in which the stimulating light intensity is constant, only the peak value of the stimulated luminescence is recorded. Repeated measurements of a specific point in a spectrum varied ± 15%. Spectra in which the stimulating light intensity varied were normalized using an empirical correction to the lamp intensity. The response time of the recording system was 0.5 seconds. Specific data were recorded on an oscilloscope using an amplifier with a response time of 30 ms. Comparison of these results with those recorded on a chart recorder indicates that the shape of the stimulated luminescence intensity versus time curve is not appreciably affected by the response time of the recording equipment.

Data were recorded by several methods, each varying one step of the above procedure. By varying the energy of the uv light while keeping the pre-exposure time, dark time, stimulating light energy and emission wavelength constant, one obtains a "pre-exposure spectrum". Perhaps the most significant advantage of this method of data collection is that it allows us to study the photon

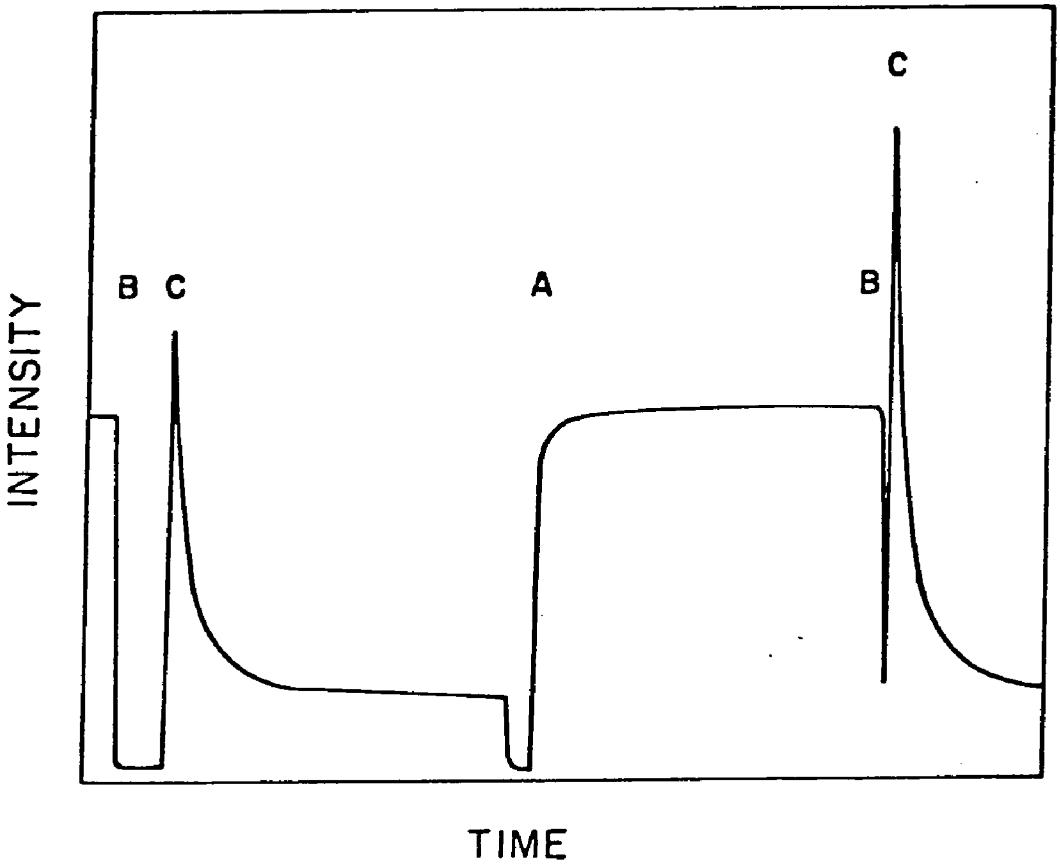

Figure 22. Typical Data from Stimulated Luminescence Experiments. This is a tracing of typical data as recorded with a chart recorder. At time A the uv shutter is opened and we observe the excited luminescence. At time B the uv shutter is closed and the crystal is in the dark until time C when the shutter on the red light is opened. A transitory response is observed which decreases to a constant value due to scattered light. The curve shown is intrinsic luminescence pre-exposed for 1 minute with dark times of 1 and 8 seconds at 85 K.

energy necessary to produce these effects. It is often instructive to compare the pre-exposure spectrum to the excitation spectrum, which is luminescence observed while the uv light is on, as a function of the energy of the uv light.

If we keep the pre-exposure energy constant and change the emission monochromator, we record the "stimulated luminescence spectrum". In addition, the stimulated luminescence spectrum was found to depend dramatically on the dark time. For a given pre-exposure energy, emission and dark time, we could obtain a "stimulation spectrum" by varying the energy of the stimulating light. In addition to the above, we could vary the pre-exposure time and/or the sample temperature. Thus this procedure is a flexible tool for studying the recombination mechanisms involved in the luminescence process.

9.3 Results

Figures 23-25 show a comparison between the excitation and pre-exposure spectra for the intrinsic luminescence at 295 nm taken at liquid nitrogen temperature. The band pass at half maximum of the uv monochromator was 1 nm, or about 0.025 eV at these energies. Since the shape of the excitation spectrum is known to be sensitive to the angle between the illuminated crystal face and the direction of the luminescence detector,[8, 60] excitation and pre-exposure spectra were recorded at the same orientation on the crystal from a given manufacturer. The orientation of the different

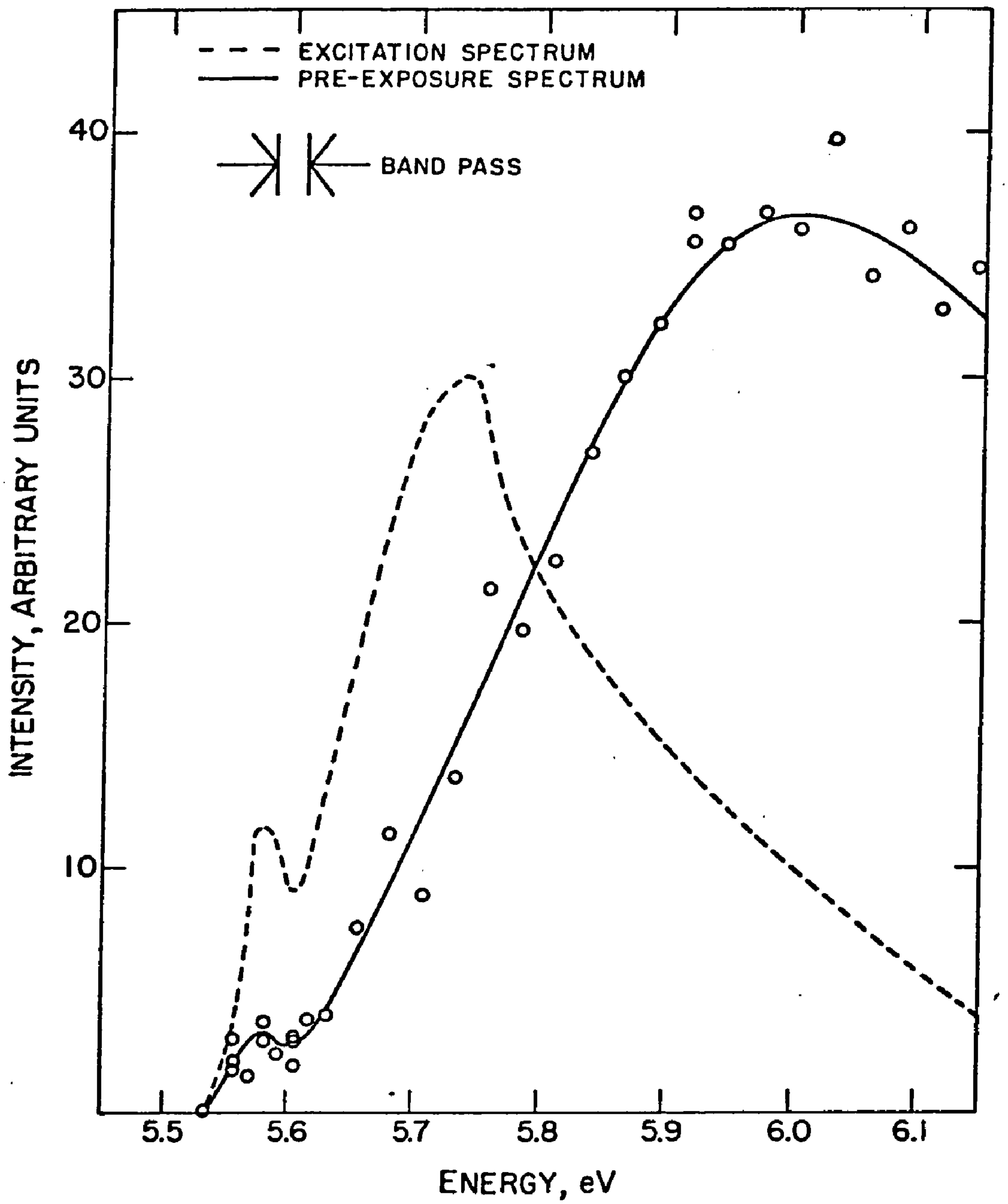

Figure 23. Excitation and Pre-exposure Spectra of Isotopes Crystal. This is a comparison of excitation and pre-exposure spectra for intrinsic luminescence in the Isotopes crystal ($< 2 \times 10^{-9}$ molar fraction copper). The pre-exposure time was two minutes, the dark time was 2 seconds and the temperature was 79 K. The absolute intensity of the excitation spectrum is not directly comparable.

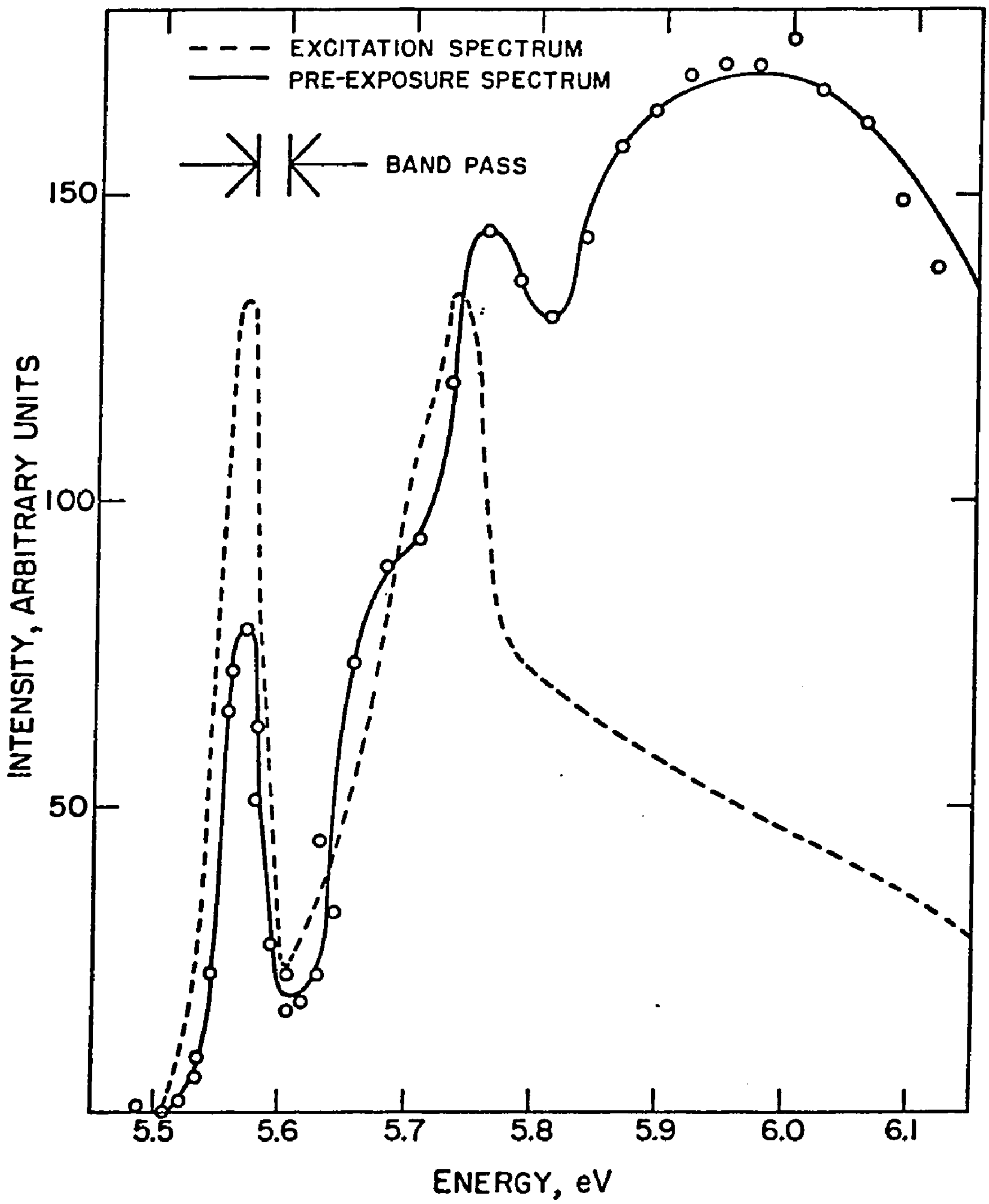

Figure 24. Excitation and Pre-exposure Spectra of Bicron Crystal. This is a comparison of excitation and pre-exposure spectra for intrinsic luminescence in the Bicron crystal (2×10^{-8} molar fraction copper). The pre-exposure time was 2 minutes, the dark time was 2 seconds and the temperature was 79 K. The absolute intensity of the excitation spectrum is not directly comparable.

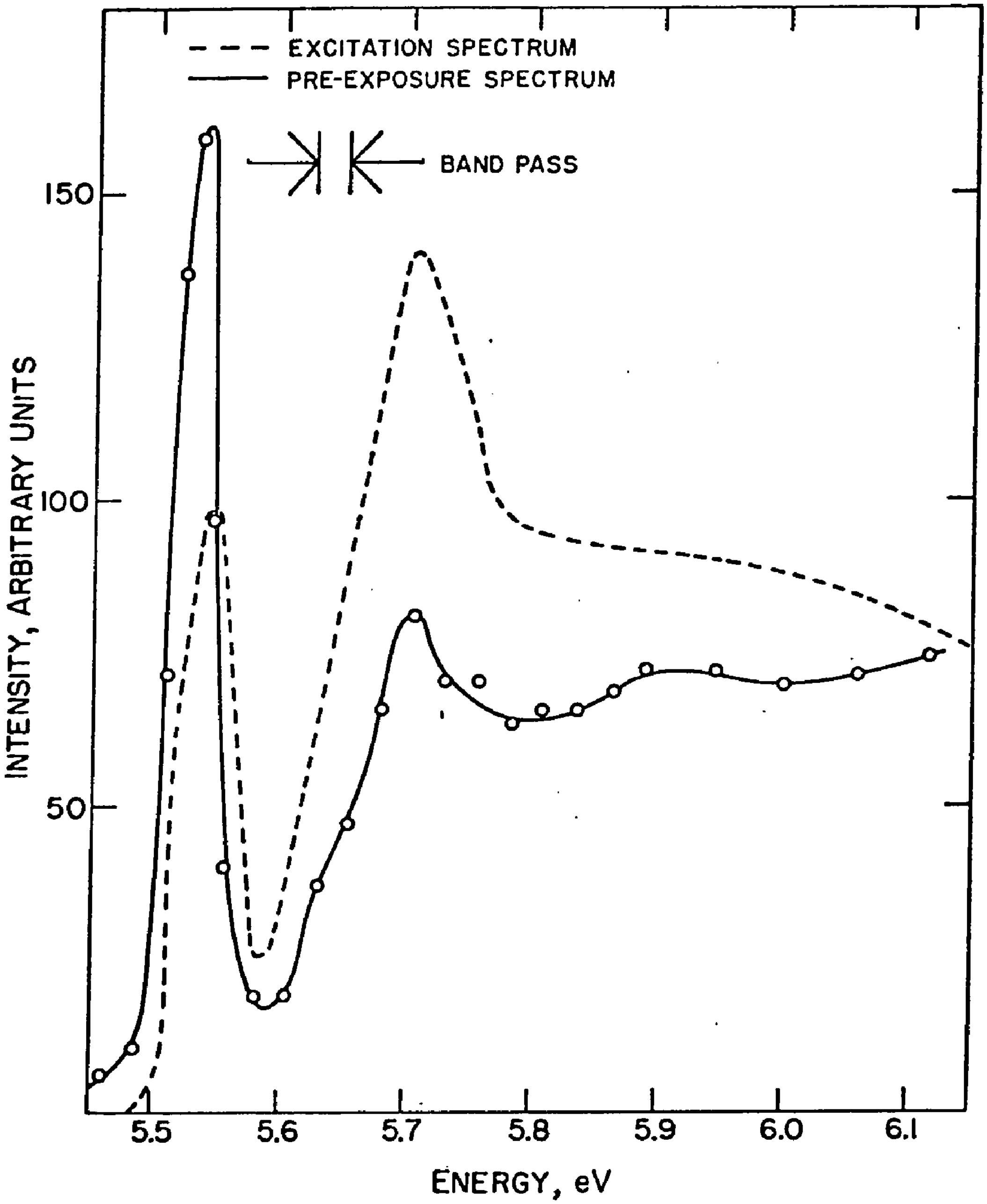

Figure 25. Excitation and Pre-exposure Spectra of Harshaw Crystal. This is a comparison of excitation and pre-exposure spectra for intrinsic luminescence in the Harshaw crystal (8×10^{-8} molar fraction copper). The pre-exposure time was 2 minutes, the dark time was 2 seconds and the temperature was 78 K. The absolute intensity of the excitation spectrum is not directly comparable.

crystals may differ from one another by a few degrees.

The most striking effect was the difference in the pre-exposure spectra in the region around the exciton absorption peak, 5.6 eV. The crystal with the most copper has a very strong peak in the low energy tail of the exciton absorption peak while the crystal with no measurable copper has minimal response in that region compared to that observed above the band edge, 5.8 eV. The crystal with an intermediate copper concentration has an intermediate response in the low energy tail. The ratio, in the pre-exposure spectra, of the intrinsic luminescence at the peak on the low energy side of the exciton absorption to that at 6.0 eV is plotted in Figure 26 as a function of copper concentration.

It should be pointed out that it is somewhat surprising to observe stimulated intrinsic luminescence after pre-exposure in the exciton absorption region because we are not creating electrons and holes by excitation from the valence to conduction band. Since stimulated intrinsic luminescence can be obtained by pre-exposure in this region, it follows that some crystal defect is involved. The data plotted in Figure 26 strongly suggest that copper is responsible for this effect. In addition a study of the excitation spectra of these crystals shows that the low energy tail is moved about 0.02 eV toward lower energy in the crystal with more copper. This effect was confirmed by recording data at several crystal orientations.

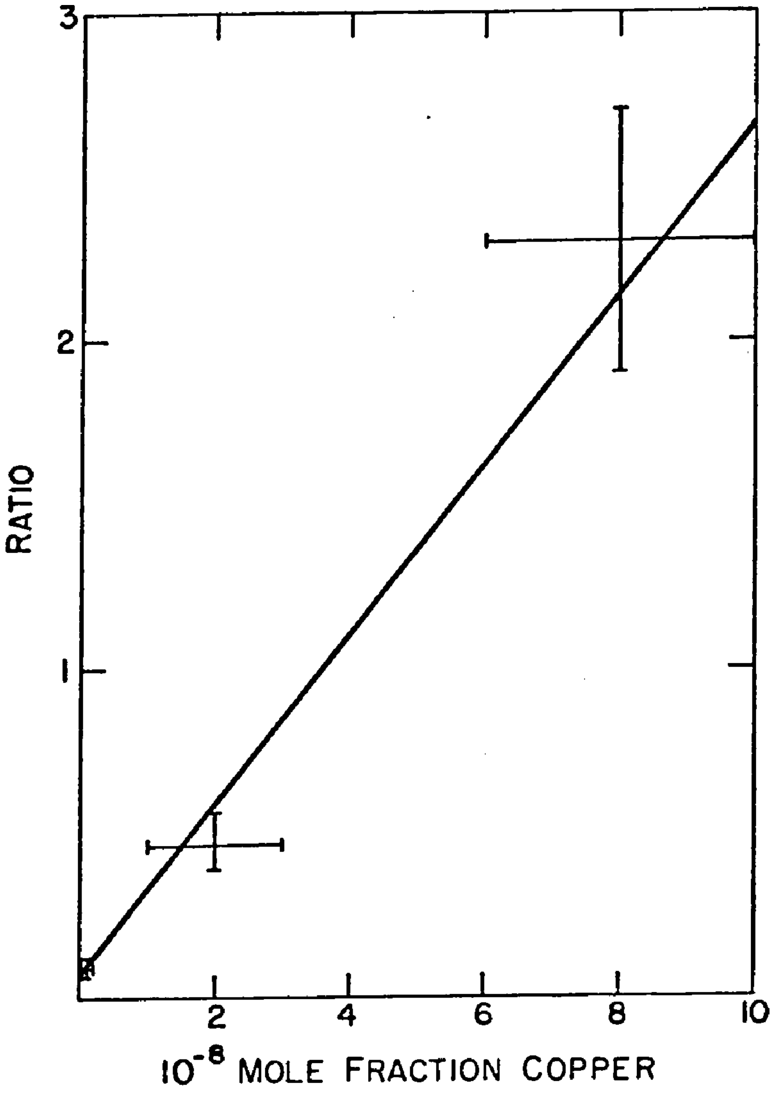

Figure 26. Relative Intensity of Stimulated Luminescence in the Low Energy Tail of the Exciton Absorption Peak as a Function of Copper Concentration. These data show the ratio, in the pre-exposure spectrum of the intrinsic luminescence at LNT of each crystal, of the peak on the low energy side of the exciton absorption peak (5.6 eV) to the signal observed at 6.0 eV, plotted as a function of the copper concentration of the crystal.

Stimulated luminescence could also be observed at 370 nm and 425 nm. Luminescence at these wavelengths has been attributed to copper and thallium impurities, respectively. If the dark time was increased, the stimulated impurity luminescences would increase at the expense of the intrinsic luminescence as shown in Figure 27. This implies that V_k centers, which have a finite mobility at LNT, are diffusing and becoming trapped at copper and thallium impurity centers creating Cu^{++} and Tl^{++}. In Figure 28 the intensity of the stimulated intrinsic luminescence is plotted versus dark time on a semi-logarithmic scale for three temperatures. Note that initially the concentration of V_k centers decreases exponentially with dark time, but this is not true for longer times. It is also apparent that the rate of decrease increases with temperature as is expected for a thermally activated process.

In addition to the intrinsic luminescence, the copper and thallium luminescences also show peaks in the pre-exposure spectra in the low energy tail of the exciton absorption peak. These peaks are very close to that of the intrinsic luminescence, within about 0.01 eV, but appear at slightly lower energy. As the temperature is raised the peaks in the pre-exposure spectra of the intrinsic as well as the impurity luminescences shift toward lower energies. (See Figures 29-31) It is known that the absorption in the exciton absorption tail broadens and moves toward lower energies as the temperature is raised. The shape of the absorption curve has been

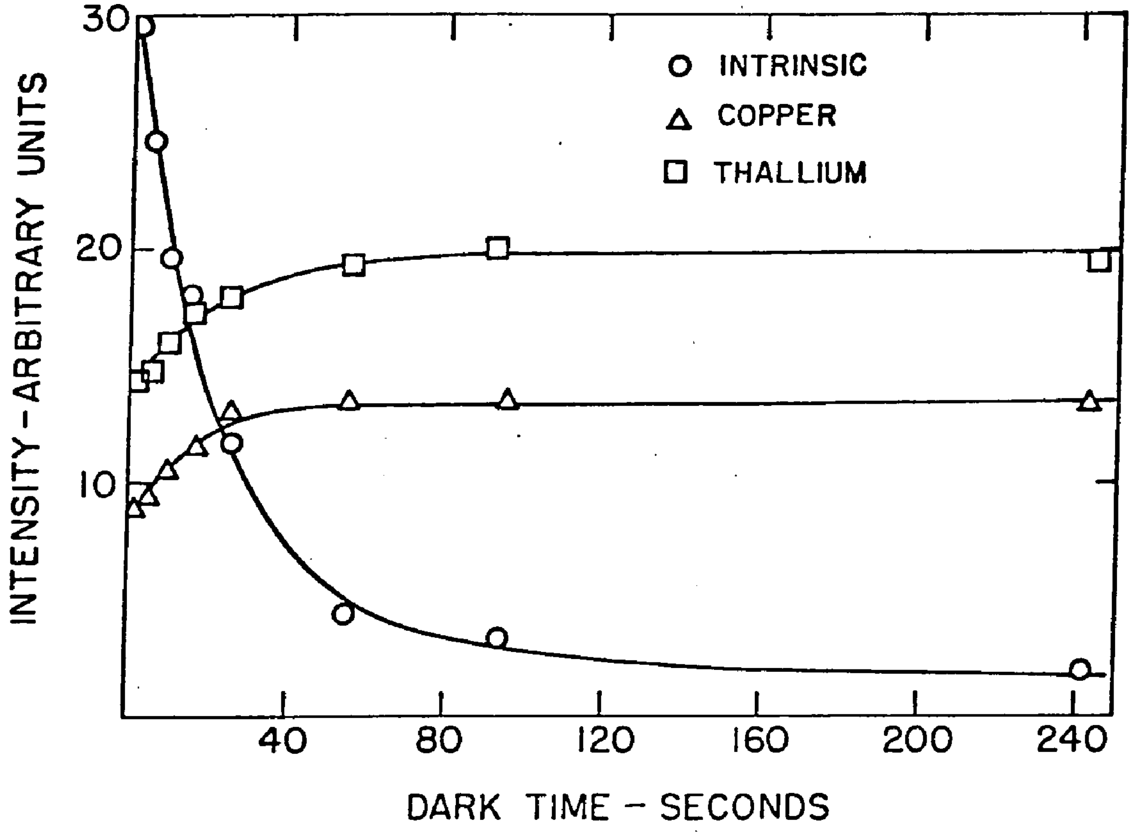

Figure 27. Intensity of Stimulated Luminescence versus Dark Time. These data show the intensity of stimulated luminescence at 295 nm (intrinsic), 370 nm (copper), and 425 nm (thallium) as a function of dark time. Data were recorded on the Harshaw crystal pre-exposing at 5.53 eV for 60 seconds at 86 K.

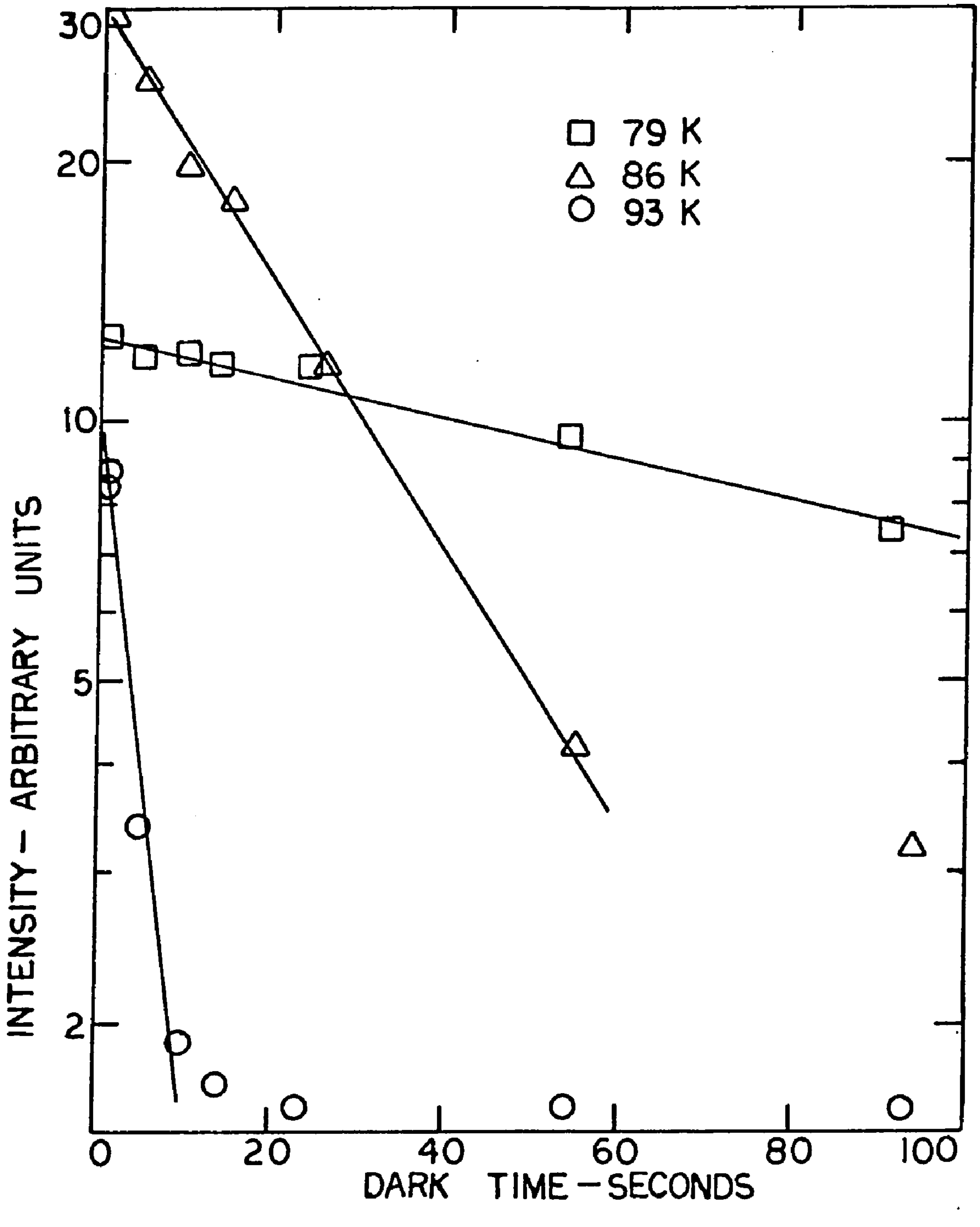

Figure 28. Intensity of Stimulated Intrinsic Luminescence versus Dark Time at Various Temperatures. Data were recorded on the Harshaw crystal pre-exposing at 5.53 eV for 60 seconds.

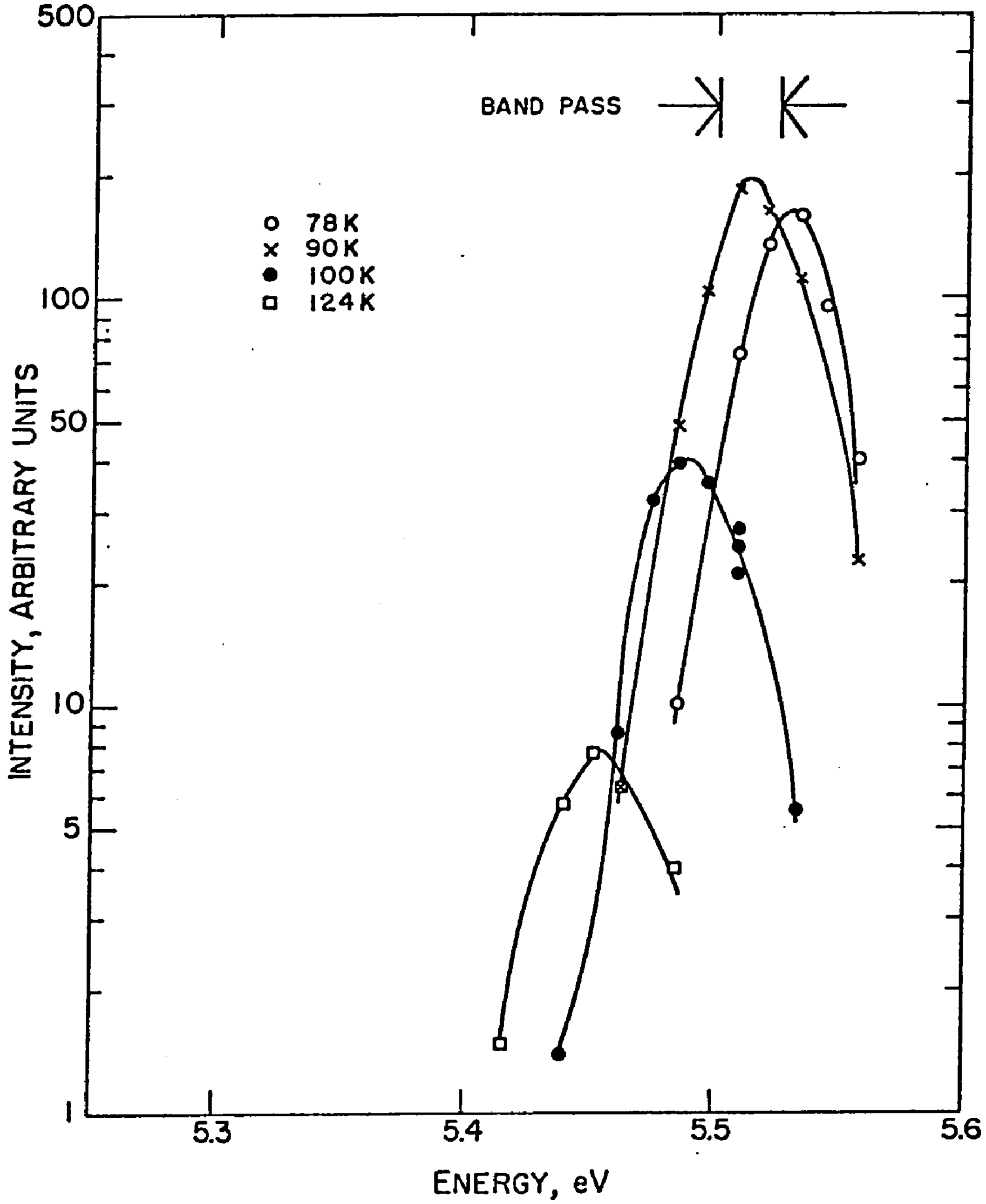

Figure 29. Pre-exposure Spectra of 295 nm Luminescence for Various Temperatures. These data were recorded on the Harshaw crystal. The pre-exposure time was two minutes and the dark time was two seconds.

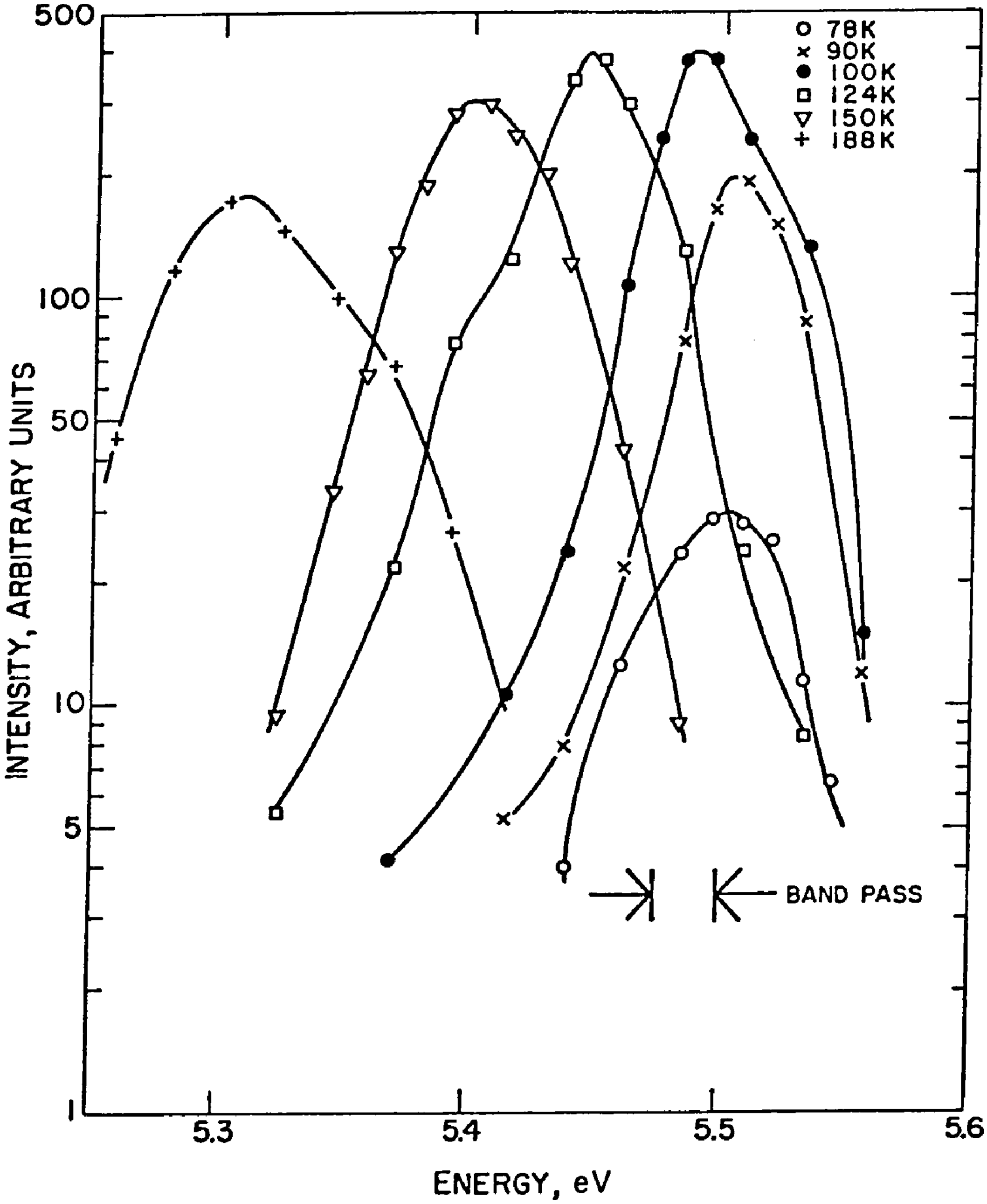

Figure 30. Pre-exposure Spectra of 370 nm Luminescence for Various Temperatures. These data were recorded on the Harshaw crystal. The pre-exposure time was two minutes and the dark time was two seconds.

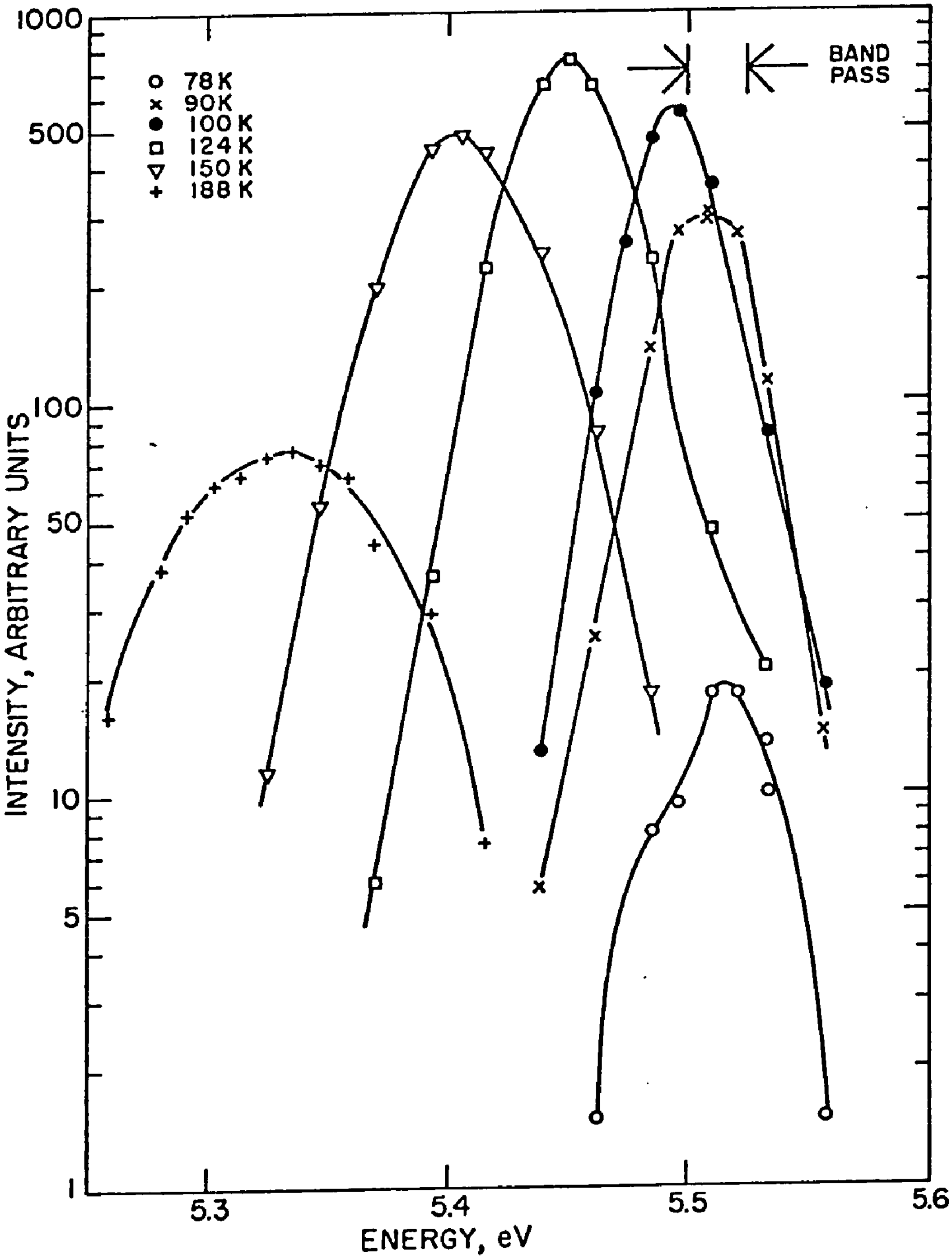

Figure 31. Pre-exposure Spectra of 425 nm Luminescence for Various Temperatures. These data were recorded on the Harshaw crystal. The pre-exposure time was two minutes and the dark time was two seconds.

found to obey Urbach's rule[108] in several alkali halides[61] and Emkey et al.[18] used Urbach's expression for NaI. Urbach's rule is $\alpha = \alpha_0 \exp(-\sigma(E_0 - E)/kT^*)$ where α is the absorption coefficient at some energy E, σ is a dimensionless constant, k is Boltzman's constant, α_0 and E_0 are specified values of the absorption coefficient and energy respectively. T^* is a temperature defined by $T^* = T_0 \coth(T_0/T)$ where T_0 is a specified temperature. Figure 32 is a graph of the peaks in the pre-exposure spectra of various luminescences as a function of T^* using $T_0 = 60$ K after Emkey et al. The slope of this line is $k \ln(\alpha/\alpha_0)/\sigma$. The good agreement to a straight line strongly suggests that the value of the absorption coefficient at which the peak in the pre-exposure spectrum occurs is a constant independent of temperature.

It can be seen that the data fall onto two lines. The data from the Bicron crystal has a less steep slope than that from the Harshaw crystal, but both lines have the same intercept of 5.735 eV at $T^* = 0$. This is further evidence that the temperature shift of the peak in the pre-exposure spectrum is due to the shift in the intrinsic absorption coefficient, as discussed below.

No stimulated impurity luminescence was observed after pre-exposure in the thallium "A" or "D" bands or in the copper excitation band at 4.85 eV. Stimulated 425 nm luminescence was observed in the thallium "C" band, however. (See Figure 33) This

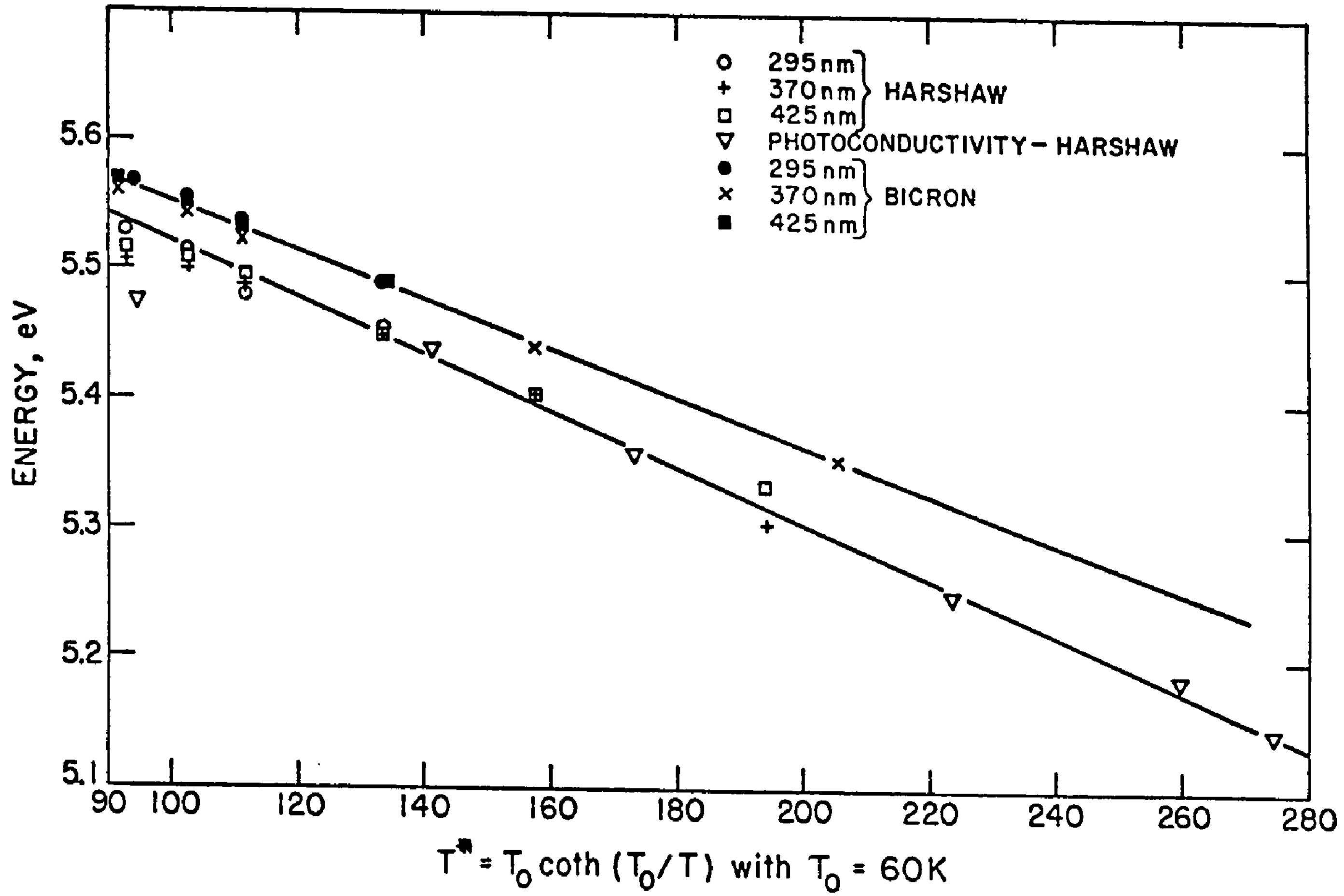

Figure 32. Pre-exposure and Photoconductivity Peaks as a Function of $T^* = T_0 \coth(T_0/T)$. The photoconductivity data were obtained from Emkey et al., reference 29, and not recorded using the same crystal as used in the other data reported in this section.

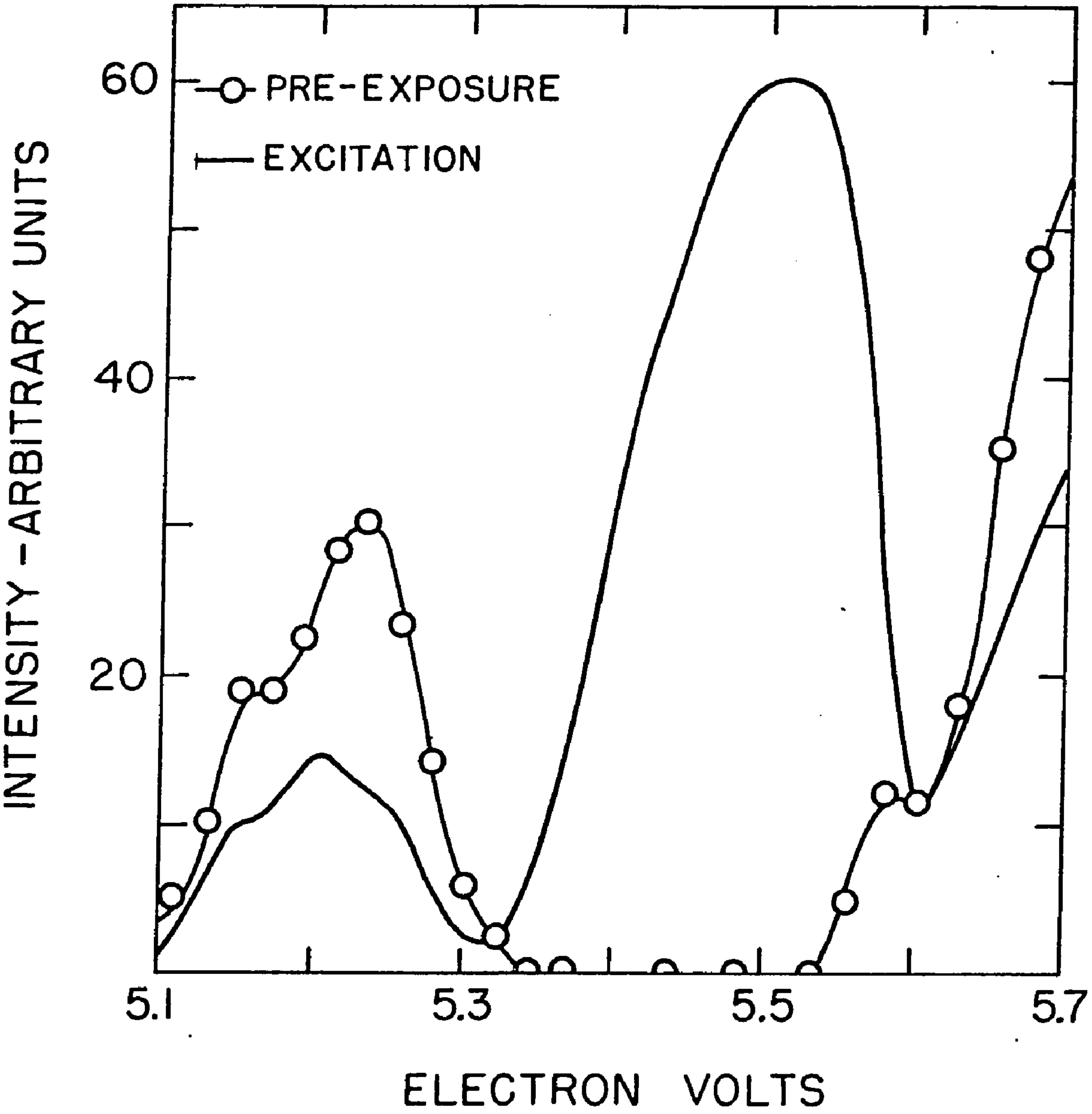

Figure 33. Excitation and Pre-exposure Spectra of 425 nm Luminescence. These data were recorded on the Isotopes crystal (8×10^{-8} molar fraction thallium) at 78 K. For the pre-exposure spectrum the pre-exposure time was 1 minute and the dark time 2 seconds.

stimulated luminescence has been observed in other alkali halides and has been attributed to excitation into an excited state from which radiative decay is forbidden.[21] We did not study this pre-exposure band further.

Stimulation spectra for the intrinsic and impurity luminescences were also recorded at energies below 1.8 eV. The results are shown in Figures 34 and 35. It can be seen that the intrinsic luminescence after pre-exposure in the low energy side of the exciton peak increases with increasing energy in this region. Stimulation spectra for the 370 nm luminescence in the Harshaw crystal and the 425 nm luminescence in the Isotopes crystal, pre-exposed in the same energy region were recorded, as well as the stimulation spectrum for the thallium "C" band.

9.4 Analysis of Results

9.4.1 Effects of Copper Impurity

As shown in Figures 23-25, both the excitation and pre-exposure spectra of intrinsic luminescence are apparently sensitive to minute concentrations of copper, and copper enhances, rather than reduces, the probability of intrinsic emission. This suggests a reaction of the form $I^- + Cu^+ + h\nu \rightarrow Cu^0 + I^0$; $I^0 + I^- \rightarrow I_2^-$ This is feasible because the electron affinity of Cu^+ (7.726 eV) is much greater than that of Na^+ (5.139 eV). If one considers that to a first approximation, an interband excitation is the transfer of an electron from an I^- ion to a distant Na^+, then the energy

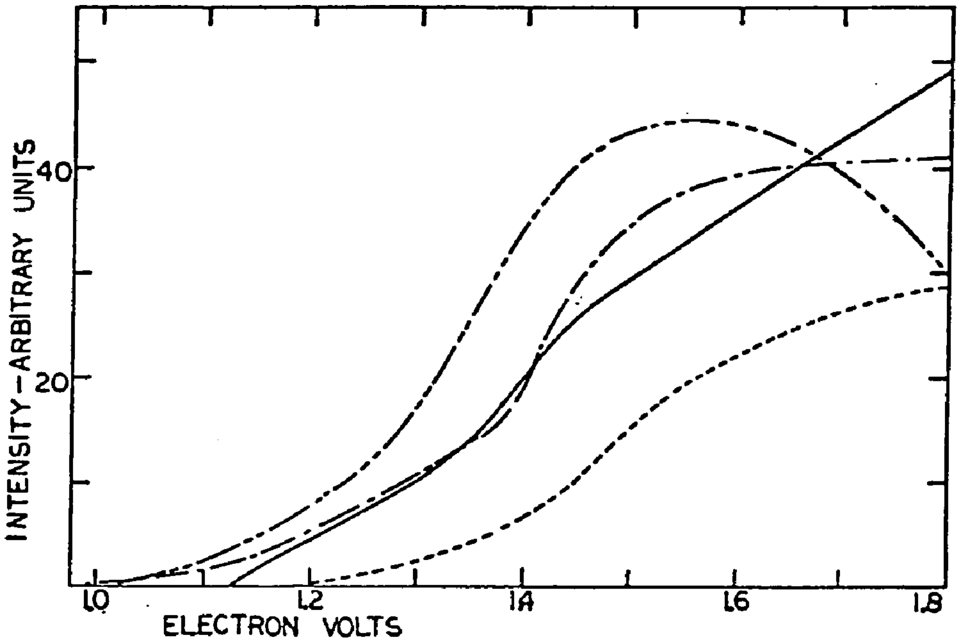

Figure 34. Stimulation Spectra of the Isotopes Crystal. This crystal contained 8 x 10^{-8} molar fraction thallium. ----- 295 nm emission pre-exposed in the low energy tail (LET) of the exciton absorption peak (EAP) at 78 K (x 0.5), —— 430 nm emission pre-exposed in the LET of the EAP at 78 K, —··— 430 nm emission pre-exposed in the Tl "C" band at 78 K (x 0.1), and —·— 430 nm emission pre-exposed in the LET of the EAP at 100 K (x 0.15). The pre-exposure time was 90 seconds and the dark time was 2 seconds.

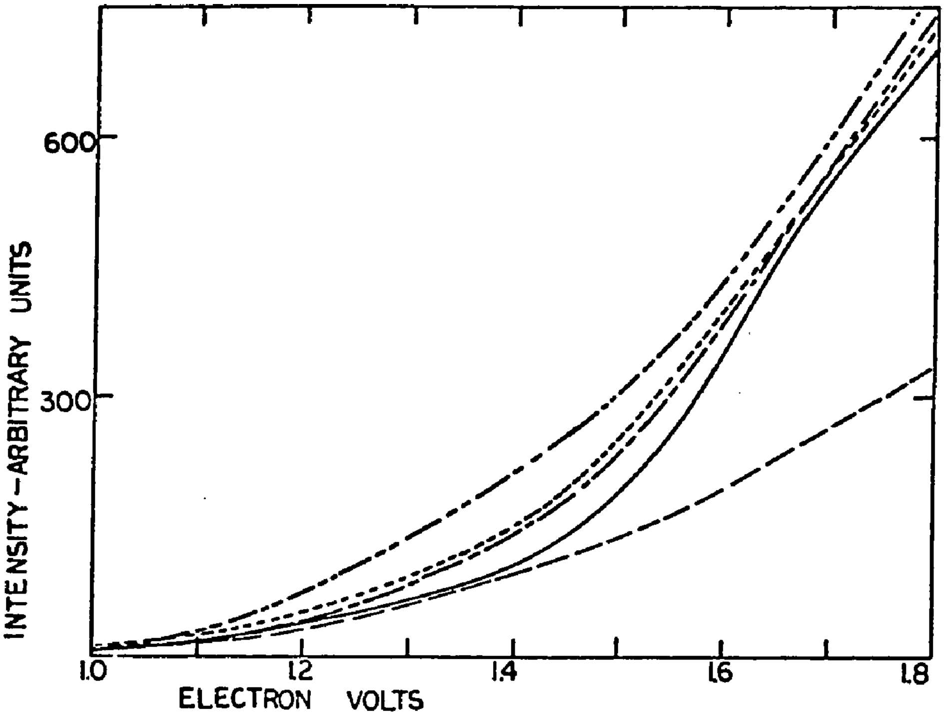

Figure 35. Stimulation Spectra of the Harshaw Crystal. This crystal contained 8 x 10^{-8} molar fraction Cu, 2 x 10^{-9} molar fraction Tl. —··— 295 nm emission at 80 K, ----- 295 nm emission at 85 K, — — — 370 nm emission at 80 K (x 2), —-— 370 nm emission at 85 K, and —— 370 nm emission at 100 K (x 0.5). All were pre-exposed in the low energy tail of the exciton absorption peak for 2 minutes with a dark time of 2 seconds.

necessary to remove an electron from an I^- ion to a not necessarily adjacent Cu^+ ion may be much less. While this argument is admittedly crude, it suggests that such a reaction is plausible. The experimental evidence strongly indicates that some such reaction occurs. Note that similar arguments could be applied to the Tl^+ ion, but in this case the electron affinity (6.108 eV) is less than 1 eV greater than that of Na^+. Tl^0 is known to exist in x-rayed NaI(Tl), however, and to be stable up to 105 K.[36, 58]

According to this model, the shift toward lower energy of the low energy tail of the excitation spectrum in crystals containing copper is the result of a two step process.. In the first step a V_k center is created near a copper impurity as described above. This process apparently occurs at an energy ~ 0.25 eV less than the energy necessary to create a V_k center in the perfect crystal. At some later time a second photon frees an electron from a shallow trap. This electron is captured by the V_k center, creating the luminescent center.

9.4.2 V_k Diffusion

The change in the shape of the stimulated luminescence spectrum pre-exposed in the low energy tail of the exciton absorption peak for different dark times is attributed to thermally activated V_k migration as studied by Popp and Murray.[15] From the data of Popp and Murray, a good straight line fit to their data over the temperature range 44-50 K gives the diffusion coefficient

$D \geq 1.9 \times 10^{-3} \exp(-0.163 \text{ eV}/kT) \text{ cm}^2/\text{s}$.

According to Waite[105] the concentration as a function of time for a bimolecular diffusion-limited reaction, in this case $I_2^- + Cu^+ \rightarrow 2\, I^- + Cu^{++}$, when the initial concentration of reactants is uniform is

$$C_B = \frac{(C_B^0 - C_A^0)\, C_A^0}{C_B^0 - C_A^0 \exp(-K(C_B^0 - C_A^0)(1 + \frac{2r_0}{(\pi D t)^{\frac{1}{2}}})t)}$$

where C_B^0 and C_A^0 are the concentrations of the reactants at time $t = 0$, r_0 is the capture radius of the reactants, D is the sum of the diffusion coefficients of the reactants and $K \equiv 4\pi r_0 D$. Thus the characteristic time at which a diffusion limited reaction occurs is $1/t_0 = 4\pi r_0 D(C_B^0 - C_A^0)$.

In our case we have no reason to assume uniform initial distribution of V_k centers with respect to impurities because of the non-uniform absorption of the pre-exposure light. If we assume, however, that the characteristic time constant of the reaction is inversely proportional to the V_k diffusion coefficient, then a plot of $1/t_0$ versus $1/T$ should give us a straight line with a slope of $-E/k$. This is done in Figure 36. From this data one obtains the value for the activation energy of diffusion of 0.163 ± 0.016 eV. Since this agrees, well within experimental error, with the value of the activation energy obtained from Popp and Murray, one may conclude that the decrease in stimulated intrinsic luminescence with dark time is due to diffusion of the

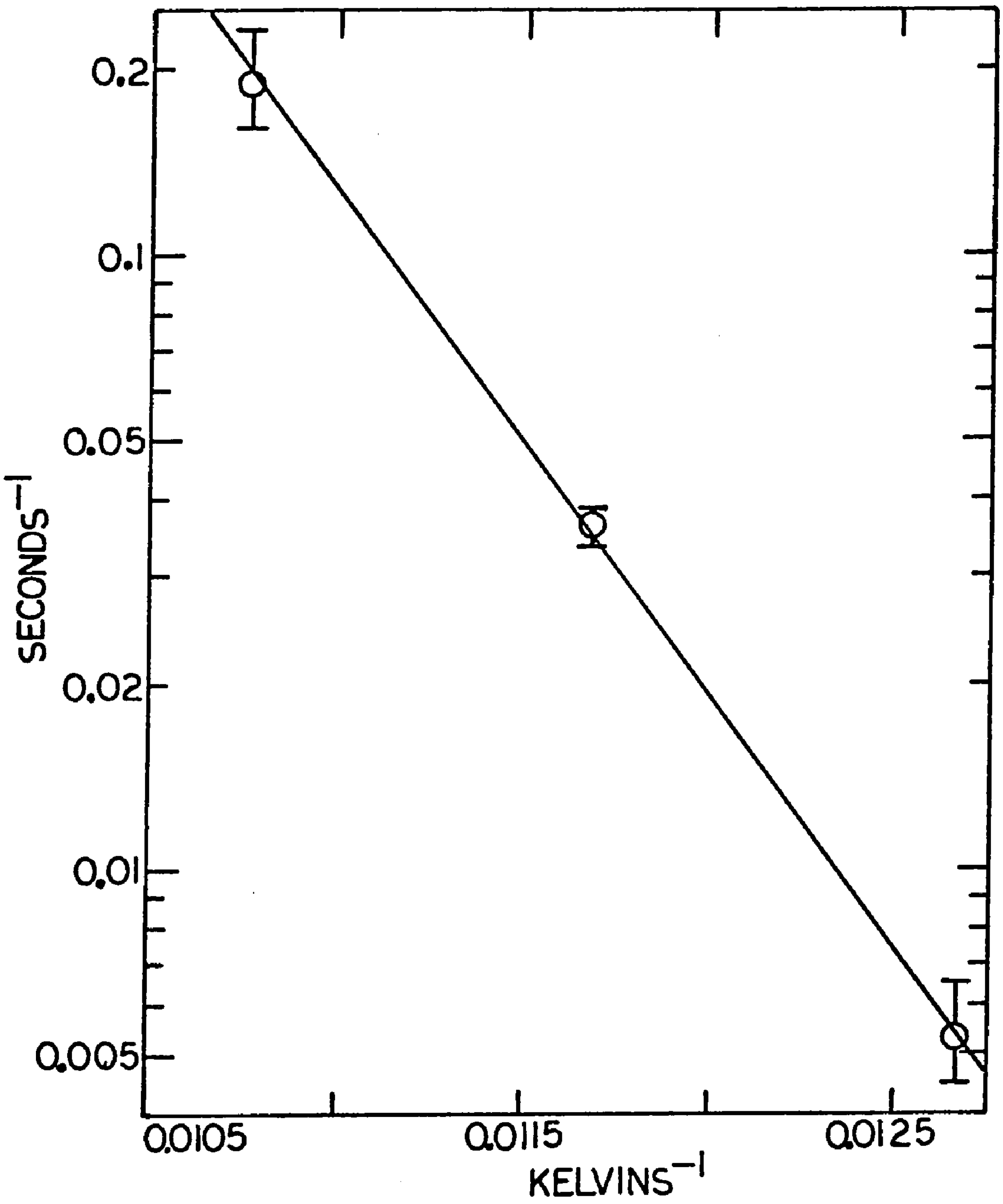

Figure 36. Graph of the Inverse of the Characteristic Time Constant at which the Concentration of V_k Centers Decreases During the Dark Time as a Function of Temperature. Data were recorded on the Harshaw crystal.

V_k centers to trapping centers. Further, it is apparent from Figure 27 that the trapping centers in this case are thallium and copper impurity ions.

9.4.3 Temperature Shift Of Pre-exposure Spectra

A. Absorption Coefficient Of Pre-exposure Peak

Urbach's rule can be expressed in the form $E = E_0 - (k/\sigma)\ln(\alpha_0/\alpha_M)\cdot T^*$ where α_M is the value of α at the energy of the maximum in the pre-exposure spectrum. Thus, assuming that σ has the value 0.79 appropriate for some other alkali halides,[61, 109] we can calculate the ratio of α_M/α_0 from the slope of the curves in Figure 32. Note that both curves have the same value of E_0, 5.735 eV. The results are $\alpha_M/\alpha_0 = 4.1 \times 10^{-8}$ for the Bicron crystal and 2.4×10^{-9} for the Harshaw crystal, or α_M (BICRON) = 17 α_M (HARSHAW). Absorption measurements were made with one mm thick crystals from both manufacturers. From the Harshaw crystal we get a value of α_M (HARSHAW) = 30 ± 10 cm^{-1}, thus the absorption coefficient for the Bicron crystal should be α_M (BICRON) ≈ 500 cm^{-1}. Although this high value of absorption coefficient could not be measured on a one mm crystal with the Cary 118CX, this is consistent with measurements at lower values of the absorption coefficient.

It may be observed that the data from the Harshaw crystal deviates from a straight line at lower temperatures. This is probably due to the fact that at lower temperatures the temperature broadening of the exciton absorption band becomes relatively less important than the impurity broadening. Even though the magnitude of α_M is unchanged at this temperature, the energy at which it occurs is not properly predicted by Urbach's rule.

B. Discussion Of The Temperature Shift

The shift in the peak of the pre-exposure spectrum with temperature agrees with the shift of a given value of the absorption coefficient predicted by Urbach's rule. This suggests two possibilities: 1. that the peak in the pre-exposure spectrum depends only on the absorption coefficient and therefore shifts as the absorption coefficient shifts, or 2. that the peak in the pre-exposure spectrum depends upon the energy of the pre-exposure, but that the energy at which the peak response occurs shifts in the same way as does a specific value of the absorption coefficient.

The first alternative was invoked by Emkey et al.[18] in order to explain the shift in the photoconductivity spectrum of NaI. Appendix III gives a model which semi-quantitatively predicts the observed shift. This model assumes that the maximum local concentration of trapped electrons, and therefore also that of positively effective charged species, is limited and independent of the intensity and of the energy of the uv light. The peak in the pre-exposure spectrum occurs when the absorption coefficient has a value large enough so that the light will not pass through the crystal, and yet small enough that a maximum volume of the crystal is reached.

The second possibility is that the reaction $2I^- + Cu^+ + h\nu \rightarrow I_2^- + Cu^0$ is sensitive to energy. At higher energies this reaction is not observed because the probability of exciton creation is large, thus the photons are absorbed by the unperturbed lattice. At lower energies the V_k center can only be created very close to the impurity center. Recombination occurs spontaneously and no stimulated luminescence is observed.

The shift with temperature of the pre-exposure spectrum is then due to the same cause as the shift in the intrinsic absorption, that is, phonon-photon interaction. The instantaneous configuration coordinates of the system in the vicinity of an impurity are altered by the presence of the phonon. This allows the transfer of the electron to the impurity. This model predicts no intensity or pre-exposure time dependence of the position of the peak in the pre-exposure spectra.

There is some evidence for the former process. At 150 K the peak in the pre-exposure spectrum for the 425 nm emission could be shifted 0.024 eV toward lower energy by increasing the pre-exposure time from 15 to 300 seconds. Also note that the value of α_M/α_0 for the Harshaw crystal is less than that obtained for the Bicron crystal for the same pre-exposure and dark times. This may be due to different concentrations of electron trapping centers in the two crystals.

On the other hand, excitation and pre-exposure spectra for impurity luminescence are not the same. There are undoubtedly additional processes for host sensitized luminescence occurring when the crystal is excited in the low energy tail of the exciton absorption peak. It would be interesting to investigate these other methods of energy transfer.

9.4.4 Excitation Spectra

It is interesting to note that the shape of the excitation spectrum for the intrinsic luminescence differs for the different crystals. In particular the Harshaw crystal has a relatively higher quantum efficiency in the band to band region. The shape of the excitation spectrum is known to be sensitive to the angle between the illuminated crystal face and the direction of the luminescence detector;[8, 60] however, this spectrum was recorded from several angles and the relative increase in the band to band region of the Harshaw crystal relative to the Bicron and Isotopes crystals is apparently real. It may be that this is another effect of the copper impurity.

9.4.5 Summary

The study of pre-exposure and stimulated luminescence allows us to sort out some of the microscopic processes occurring in the luminescing crystal.

Specifically we have presented evidence that copper enhances the intrinsic luminescence excited in the low energy tail of the exciton absorption peak and possibly in the band to band region. This is explained by assuming that a V_k center can be created in the vicinity of a copper impurity with about 0.25 eV less than is required to create a V_k center in the perfect crystal. One may envision this process as a hole ionized from a Cu^+ by the uv light.

We have also observed stimulated luminescence at 370 nm. This is attributed to recombination of an electron and a hole at a copper impurity site in analogy with the process observed at thallium impurity centers.[36]

The temperature shift of the pre-exposure spectra with time has been explained using Urbach's rule.

10.0 Conclusion

10.1 Summary And Discussion

This research was initiated in an attempt to discover the cause for the dead layer, and in this respect was at least partially successful. It has been determined that electric fields do reduce the relative probability of radiative emission from the STE, but it has not been determined whether or not a uniform electric field exists in the surface region. It is possible that local random fields due to defects are concentrated in the surface region and that these are responsible for the dead layer. We found no evidence of a field due to a Dember effect. If there is a field built up because electrons are photoemitted by the uv light, its effect on the luminescence of a freshly cleaved crystal is hidden by the experimentally observed increase in luminescence. (The lower quantum efficiency of a freshly cleaved crystal has been attributed to a high concentration of unfilled shallow electron traps. When the crystal is first illuminated many electrons are captured by these traps. Thus the quantum efficiency rises until the rate of filling and of emptying traps are equal.)

Although the specific adsorbed gas has not been identified, adsorption has been shown to have a negative effect on luminescence excited above the exciton absorption peak. This is apparently not the major cause of the dead layer and in fact the luminescence excited in the low energy tail of the exciton absorption peak was observed to increase from its initial value in a freshly cleaved crystal.

Neither exciton diffusion nor exposure to I_2 gas is believed to be a significant factor in forming a dead layer.

Thus, in retrospect, the original attempt to find the cause of the dead layer was somewhat simplistic. This work has succeeded, however, in evaluating some of the possible mechanisms.

The stimulated luminescence experiments were very rewarding. This experimental technique has proved to be a powerful tool for detecting recombination luminescence. Specifically, it has permitted us to discover that the copper impurity acts as a "catalyst" for intrinsic luminescence excited in the low energy tail of the exciton absorption peak and possibly at higher energies. Also we found that some, but not all of the copper luminescence excited below the exciton absorption peak is due to electron and hole recombination at a copper center. The temperature shifts of the pre-exposure spectra were explained using Urbach's rule.

10.2 Suggestions For Further Research

One interesting fact is that the peak in the pre-exposure spectrum of the copper luminescence occurs at slightly lower energy, ~ 0.01 eV, than that of the intrinsic luminescence. This suggests the possibility that at the lower energy there is some local trapping of V_k centers in the vicinity of Cu^0 centers such that the stimulated luminescence is characteristic of the copper impurity rather than of the host. It would be interesting to study this phenomenon.

The Dember effect should be observable in NaI. Perhaps a different experimental procedure, such as using thin films, would be more suitable for measuring this effect. One problem may have been the high concentration of electron traps in the Harshaw crystal used in these experiments. Thus it might be productive to try these experiments on more perfect crystals.

Purer crystals would also be advantageous in a study of the electric field effects on the STE. By making some lifetime measurements at various field strengths and temperatures one could determine whether the electric field reduces the probability of radiative decay of the STE, increases the probability of non-radiative decay, or both.

Finally, the emission bands at 314 and 331 nm which appeared in the heat treated samples could be studied. Although they may be due to some impurity introduced during the heat treatment, it is possible that they are associated with an intrinsic defect such as a vacancy.

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Appendix I. Data from the INT Cleave Experiments

The data from the INT crystal cleave experiments are summarized in Table 1-1. This table shows the relative change in the luminescence intensity under the environmental conditions specified (see Section 4.2). The relative change in intensity is defined $\delta L \equiv (L_2 - L_1)/L_1$ where L is the luminescence intensity excited by an energy in the region specified. The subscripts 1 and 2 refer to the first curve recorded after cleaving and to the curve which is compared to the first, respectively.

			Excitation Energy			
Gas or Pressure	Temperature, Kelvin	Time Between Measurements (seconds)	Low Energy Exciton Peak	Exciton Absorption Maximum	High Energy Exciton Peak	Band To Band (5.92 eV)
~10^{-3} torr	~100	390	0.12	-0.27	-0.06	-0.15
~10^{-5} torr	90	262	0.03	0	-0.01	-0.04
~10^{-5} torr	90 → 93	1440	0.05	-0.08	-0.04	-0.12
3.3×10^{-7} torr	64	300	0.01	-0.08	0	-0.01
3.3×10^{-7} torr	64 → 72	2970	0.15	-0.04	0	-0.01
N_2 gas	80	300	0.01	-0.01	0	0
N_2 gas	80 → 79	3360	0	-0.01	-0.003	-0.02
He gas	82	185	0	0	-0.01	0.02
*N_2 + O_2 gas	91	420	0.04	0	0.02	-0.004
*N_2 + O_2 gas	91	3180	0.04	-0.18	0.003	-0.04
LN_2	73	300	0.03	-0.01	-0.03	-0.04
LN_2	73	2880	-0.01	-0.07	-0.08	-0.10

Table 2. Data from Crystal Cleaves at LNT. This table gives the relative change in intrinsic luminescence intensity excited at various energies as adsorption proceeds. The relative change in intensity is defined to be $(L_2 - L_1)/L_1$ where L_1 is the luminescence intensity recorded initially and L_2 is the luminescence recorded at a later time.

*This crystal was cleaved in N_2 gas. L_1 was recorded when O_2 was added to the coolant gas.

Appendix II. Data from the Effects of I_2 Gas on NaI Experiments

These data were recorded on a crystal exposed to I_2 gas at 500°C and on a control sample which received only a heat treatment as described in Section 5.2.2. Data were recorded on uncleaved crystals and on crystals cleaved at LNT in N_2 gas. In an attempt to compensate for the known sensitivity of the shape of the excitation spectrum to angle of observation, the signal from each crystal was maximized at several excitation energies by rotating the crystal.

If there was a relative increase in the quantum efficiency of luminescence excited above the band gap in the crystal exposed to I_2 gas at 500°C, it would show up as an increase in the intensity of luminescence of this crystal, relative to the control crystal, excited with energies above 5.8 eV. Although there is some scatter in the data, no such effect is observed.

Excitation Energy At Which Signal Maximized (eV)	Crystal, Surface	Excitation Energy, eV				
		5.55	5.60	5.87	6.14	6.76
5.55	C, A	39	33	51	31	10
	C, B	41	20	39	22	5
	I, B	50	14	31	17	1
	I, A	41	22	40	25	5
5.67	C, A	39	31	53	28	8
	C, B	39	18	47	23	4
	I, A	37	15	47	27	4
	I, B	37	24	50	28	7
5.77	C, A	38	29	53	33	6
	C, B	37	20	45	22	2
	I, A	37	16	47	23	2
	I, B	38	25	49	26	5
5.87	C, A	40	31	55	30	8
	C, B	37	20	49	25	4
	I, A	36	20	55	32	4
	I, B	38	28	55	32	7
6.76	C, A	40	33	58	31	10
	C, B	45	35	57	30	8
	I, A	53	42	57	30	5
	I, B	40	32	56	30	9

Table 3. Effect of Exposure to I_2 Gas at 500°C on the Intrinsic Luminescence of NaI. This table lists the intensity of intrinsic luminescence in arbitrary units, excited at various energies and normalized to the intensity excited at 5.70 eV. The data are grouped according to the excitation energy at which the luminescence signal was maximized by rotating the crystal. Data were recorded on the control crystal (C) and the crystal exposed to I_2 gas at 500°C (I), both before (B) and after (A) cleaving the crystal at LNT. The crystal temperature was 79 K.

Appendix III. Model for the Energy of the Peak in the Pre-exposure Spectrum

A crude model which provides a semi-quantitative explanation for the dependence of the peak in stimulated luminescence of the pre-exposure spectrum in the low energy tail of the exciton absorption peak on the absorption coefficient is given. Let N be the concentration of trapped electrons at some point in the crystal. Since the crystal is neutral the integral over the crystal of N must equal the sum of the integrals of the V_k, Cu^{++} and Tl^{++} concentrations. Thus the stimulated luminescence is proportional to the integral of N over the crystal.

At a given distance x from the illuminated surface, the rate at which photons are absorbed is $\alpha I e^{-\alpha x}$ where α is the absorption coefficient in cm^{-1} and I is the intensity of the uv light in photons $\cdot$ cm^{-2} $\cdot$ s^{-1}. The mechanism by which electrons become trapped must be 1. capture of a free electron from the conduction band and 2. ionization of a hole from a Cu^+ ion leaving a Cu^o. Rather than consider the details of the various capture and ionization processes, we will assume that the rate at which electrons become shallowly trapped is proporational to the energy absorbed with a proportionality constant β. The mechanisms for emptying electron traps are 1. ionization by an incident photon, 2. ionization by collision with a mobile exciton, and 3. recombination with a migrating V_k center. Again, rather than trying to sort out the ionization and capture cross sections, we will lump these processes into a single trapped electron lifetime t_0, which may also depend upon the rate of energy absorption. Thus the rate equation for N becomes

$$\frac{dN}{dt} = \beta\alpha I\exp(-\alpha x) - \frac{N}{t_0}$$

which has the solution

$$N = \beta t_0 \alpha I\exp(-\alpha x) - t_0 K\exp(-t/t_0)$$

where K is an integration constant. Choosing the initial condition $N(t = 0) = 0$ and solving for K,

$$N = \beta t_0 \alpha I\exp(-\alpha x)(1 - \exp(-t/t_0))$$

The concentration of trapped electrons must saturate at some value N_0, at long exposure times. If we assume that N_0 is independent of absorbed light intensity and is constant throughout the crystal, then, solving for t_0 in terms of N_0,

$$t_0 = \frac{N_0}{\beta\alpha I\exp(-\alpha x)} \qquad \text{and} \qquad N = N_0(1 - \exp(-t/t_0)).$$

N_0 must depend upon the concentration of available electron traps of all kinds, and must be of the same order of magnitude as the total impurity concentration of the crystal.

In order to obtain the total number of trapped electrons, we integrate over x and multiply by the illuminated area, A. Letting A = 1,

$$T \equiv \int_0^d N dx = \int_0^d N_0(1 - \exp(-\beta\alpha I\exp(-\alpha x) \cdot t/N_0))dx .$$

The solution is

$$T = (N_0/\alpha)(S(\beta\alpha It/N_0) - S(\beta\alpha It\exp(-\alpha d)/N_0))$$

where the series S is defined

$$S(z) \equiv z - \frac{z^2}{2\cdot 2!} + \frac{z^3}{3\cdot 3!} - \frac{z^4}{4\cdot 4!} + \cdots\cdot (-1)^{n+1}\frac{z^n}{n\cdot n!}\cdots\cdot$$

A better qualitative feeling for $S(z)$ is obtained by noting that $\frac{dS(z)}{dz} = \frac{1 - \exp(-z)}{z}$. Thus $S(z)$ is similar to a logarithmic function. See Figure 37. It can be shown that T does peak for some value of α when all other parameters are kept constant. Also as $\frac{\beta It}{N_0}$ increases, T peaks at smaller values of α.

We have made many approximations in this model and have neglected the energy dependence of the process, so we cannot expect quantitative agreement, however we feel that the qualitative results are correct. Thus, for example, we may expect that for long exposure times or low electron trap concentrations the peak in the pre-exposure spectrum will more toward lower energies.

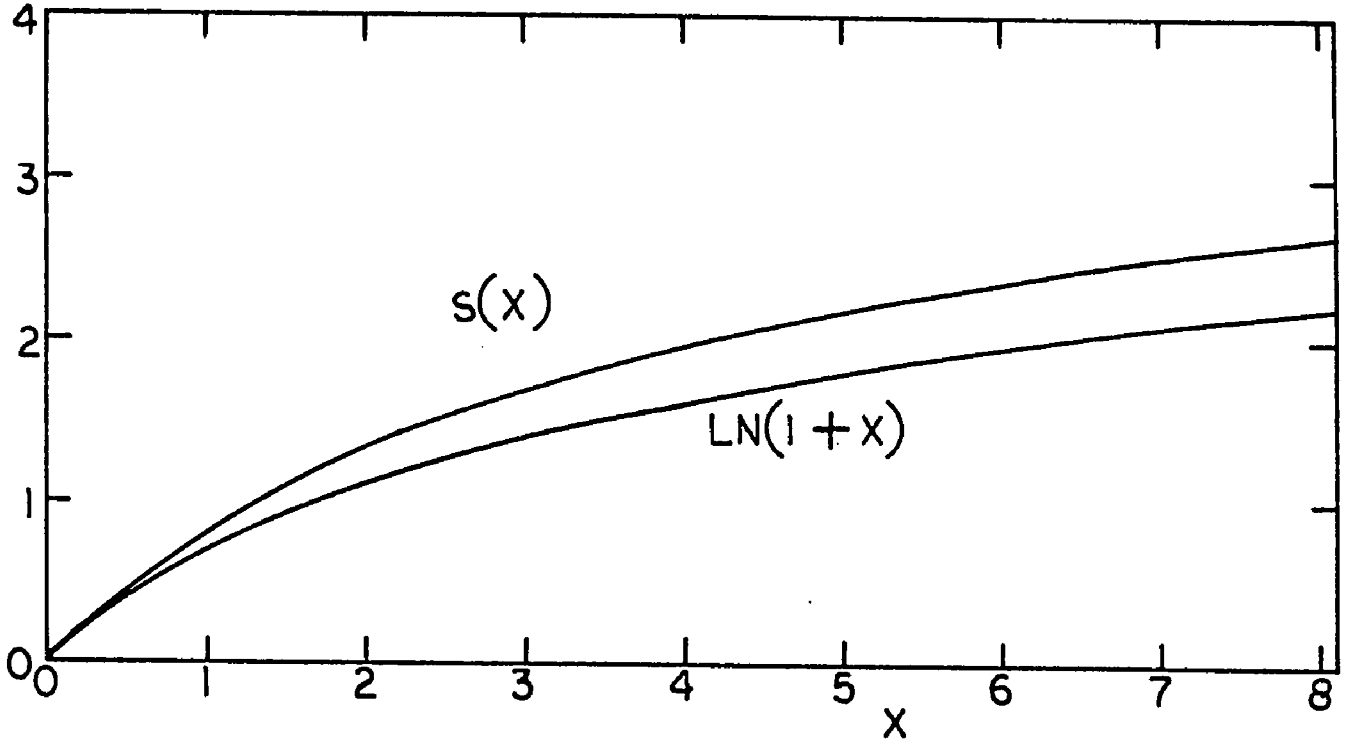

Figure 37. Plot of S(x). This is a numerical calculation of $S(x) \equiv \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n \cdot n!}$ from numerical integral of $((1 - \exp(-x))/x) \cdot \delta x$ with $\delta x = 0.01$. The natural logarithm of $1 + x$ is shown for comparison.

Vita

Peter Van Zandt Meyers was born on August 3, 1947 in Buffalo, New York. He is the son of Hubert Charles Meyers, a dentist from Hudson, New York, and the former Harriet Ruth Van Zandt, a laboratory technician from Hutchinson, Kansas. The author has a sister, Janet Alice, and a brother, Edmund Charles.

During the author's childhood the family resided principally near the rural town of Wassaic, New York. Peter graduated from Dover Plains Junior-Senior High School in 1965. After graduating from Muhlenberg College in 1969 with a B. S. in physics, Peter entered the U. S. Navy. In October, 1969 he was commissioned an Ensign after completing Officer Candidate School at Newport, Rhode Island. He spent two years, first in the Weapons Department and later as Air Transfer Officer, aboard the aircraft carrier Intrepid. During this time, Peter married the former Carole Ann Schneider of Allentown, Pennsylvania.

In February, 1972 he entered Lehigh University with an interest in oceanography. Working under the direction of Professor Adrian Richards he published the article "Theory of Nuclear Transmission Densitometry Applied to Sedimentology and Geotechnology". While completing a summer project under Professors Wesley Van Sciver and William Emkey, with whom he published

"Anisotropic Luminescence in Sodium Iodide", Peter's interest turned to solid state physics. He received an M. S. in physics from Lehigh University in 1974 and began his thesis project with Professor Van Sciver as his advisor.

On February 18, 1974 Peter and Carole had their first son, Gregory James and on May 25, 1976 a second son, Peter Terrill was born.

During his stay at Lehigh University the author was a teaching assistant, instructing freshmen and sophomore physics laboratory, as well as a research assistant. From September 1975 through August, 1977 he was awarded a Sherman Fairchild Fellowship in Solid State Studies. In January 1976 Peter was chosen by the faculty of the Physics Department at Lehigh University to receive a cash award from the Eastman Kodak Company for excellence in research.

As of February, 1978 Peter will be employed as a staff physicist with the Ametek Corporation based in Paoli, Pennsylvania.