APPENDIX C

We assume that the system is described by the density matrix

$$\rho=C\exp\{\mathcal{H}_{er1}/kT^{*}+[g\beta H_0\textstyle\sum_{j'}I_{j'z}+\mathcal{H}_L]/kT\},\qquad(109)$$

where $\mathcal{H}_{er1}$ contains all the time-independent terms of $\mathcal{H}_{er}$ [Eq. (53)] except the last. The reason for including all the spin-spin terms of $\mathcal{H}_{er}$ is discussed in Sec. III(d).

The ratio of external unprimed spin energy to internal spin-spin energy is obtained by evaluating $\langle\langle\mathcal{H}_{er1}\rangle\rangle$. Proceeding as in Appendix A, (55) easily follows.

The equation of motion of $\langle\langle\mathcal{H}_{er1}\rangle\rangle$ is given by (96) with the substitutions $\mathcal{H}_{er}\rightarrow\mathcal{H}_{er1}$ and the density matrix (109) for that of (86). Evaluation of the various terms is similar to the procedure of Appendix B. Equations (99) to (103) hold for the substitutions $j\rightarrow j'$ and/or $k\rightarrow k'$ under suitable additional substitution of $\mathbf{I}_0'$, T_1', and T_{2e}'. (48) and (56) then follow easily from the assumption $T_1=T_{2e}$ and $T_1'=T_{2e}'$.

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Theory of Electroluminescence

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The theoretical basis for exciting luminescence by the application of an electric potential to a crystalline dielectric or semiconductor is considered. Three mechanisms of excitation are each shown to be theoretically feasible in appropriate solids and with suitable local field conditions: (1) the ionization of impurity systems directly by an electric field, (2) the acceleration of conduction electrons or positive holes in the valence band to kinetic energies sufficient to excite or ionize impurity systems or valence electrons by inelastic collisions, and (3) injection of charge carriers. Radiative de-excitation is feasible by two mechanisms: (a) direct recombination of conduction electrons and holes in the valence band, and (b) optical transitions characteristic of impurity systems known as activators. The characteristics of electroluminescence proceeding by these processes are examined theoretically.

INTRODUCTION

ELECTROLUMINESCENCE of various crystalline phosphors has been reported in the literature over a period of twenty-five years.[1–5] Various mechanisms have also been proposed.[2,3,5–7] In this paper the general mechanisms for converting an electrical potential applied to a crystal into luminescence will be examined theoretically. Previously considered mechanisms are, of course, included as well as others which may have more significance as the number of types of electroluminescent crystals increases.

Electroluminescence is the excitation of luminescence as a result of the existence of an applied potential difference in the phosphor material. The definition includes luminescence induced by any mechanism of injection of electrons or holes into the phosphor or any mechanism of creating free charge carriers in the phosphor if the energy of the emitted radiation originates in the electric potential difference applied to the phosphor. Cathodoluminescence is excluded since in this case the excitation energy is supplied initially to electrons by an external field.

It is well known that solid-state luminescence usually originates from excited impurity systems called activators which have dimensions of the order of an interatomic distance. To radiate in the visible portion of the spectrum, the activator system must have an excited state at least 2 ev higher than the ground state. An electroluminescent mechanism utilizing an activator system must in some way localize 2 or 3 ev of the energy available in the applied potential to the atomic dimensions of the activator system and transfer this energy to the activator. If the activator is left in an excited state, it is then able to radiate a photon in returning to the ground state. Ionization of the center is also a permissible mechanism, provided conduction electrons are available or are made available subsequently.

The most straightforward mechanism of electroluminescent excitation is direct field ionization of the activator system. Since the ionized state of the activator system is at least 2 ev above the ground state, the field strength necessary to ionize these centers at a reasonable rate would normally be in excess of the dielectric breakdown strength of the crystalline matrix. Breakdown in materials with suitable band gaps for luminescence normally occurs by an avalanche mechanism, rather than by field ionization of the valence electrons. Nevertheless, direct field ionization of the activator system

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[1] O. Lossev, Phil. Mag. **6**, 1024 (1928).

[2] G. Destriau, Phil. Mag. **38**, 700 (1947).

[3] Lehovec, Accardo, and Jamgochian, Phys. Rev. **83**, 603 (1951).

[4] Payne, Mager, and Jerome, Illum. Eng. **45**, 688 (1950).

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essentially by quantum-mechanical tunneling is feasible if the high-field region in the neighborhood of the activator atom is sufficiently localized to prevent breakdown.

A second mechanism which does not require as large a field is the excitation of impurity systems by inelastic collisions. Electrons injected into the conduction band in the presence of a sufficiently strong electric field have an appreciable probability of attaining enough kinetic energy to excite or ionize an activator system by means of an inelastic collision. The excited activator could alternatively radiate a photon or become ionized either thermally or with the aid of the local electric field. Electrons may be injected into the conduction band in the presence of high fields either at the surface of the crystal or in the bulk of the crystal from donor levels or occupied traps too deep to be ionized thermally. In a completely analogous manner, positive holes can be injected into the valence band from the surface or from acceptor centers or hole traps and attain sufficient kinetic energy to excite an activator system by means of an inelastic collision.

A third method of exciting electroluminescence is the introduction of both types of free charge carriers into a particular region of a crystal. This may be accomplished by the injection of minority carriers into *p*-type or *n*-type material from the surface or at a *p*-*n* junction within the crystal. Alternatively both species may be injected into intrinsic material. A strong electric field is not required for the charge carrier injection mechanism.

Radiative de-excitation by means of an optical transition of an activator system is a well-known mechanism[8,9] of solid-state luminescence and will not be discussed further. In addition, the direct recombination of holes in the valence band and conduction electrons will be shown to be a possible source of radiation under conditions of large concentrations of charge carriers.

FIELD IONIZATION

If the activator center in the phosphor crystal is to be directly ionized by the applied field, the most serious problem is dielectric breakdown of the crystal before sufficient local field strength has been attained. The breakdown strengths of the alkali halides are approximately 10^6 volts/cm.[10] The breakdown field for most crystalline phosphors quite probably does not differ from this value by more than a factor of three.

It has been well established that the mechanism of breakdown of crystalline insulators is that of acceleration of conduction electrons to sufficient kinetic energy to ionize further valence electrons and thus multiply into a breakdown current. This mechanism dominates over Zener breakdown (field ionization of the valence electrons) except possibly for crystals with a forbidden band gap appreciably less than one electron volt. The field requirements for Zener breakdown increase as the square of the band gap and at larger band gaps exceed the field requirements for breakdown by avalanche.

Franz[11] has made calculations not only for field ionization of valence electrons but also for electrons trapped in a square well potential. His calculations for the field necessary to ionize this localized center reduces to good approximation to the expression

$$E_i=\frac{10^7\epsilon_g^{\frac{1}{2}}}{8+\log_{10}E_i\tau}\epsilon^{\frac{3}{2}}, \tag{1}$$

if E_i is measured in volts/cm, τ, the decay constant of the center in sec, and ϵ, the depth of the well in ev, and if the lattice constant is 5 A and the radius of the trap is 3 A. For example, with a band gap, ϵ_g, of 6 ev a field of 6×10^6 volts/cm is necessary to ionize with a decay constant of 10^{-3} sec a square well center 2 ev deep.

Both avalanche and Zener breakdown compete with the direct field ionization of a localized center. The breakdown strength of crystals ruptured by an avalanche of ionizing events is quite insensitive to crystal thickness except for very thin high-field configurations. If the assumption is made that a fixed number of multiplications must occur before breakdown, then the field strength increases as the high-field region becomes thinner. At the breakdown field strengths mentioned above, the mean multiplication distance has been shown to vary quite rapidly with the field[12] which means the field strength is not strongly dependent on thickness. However, in the region of very high fields, as pointed out by Wolff,[13] the mean multiplication distance, $\bar{\lambda}$, varies proportionally with the reciprocal of the field, and an ionizing event occurs for a potential difference equivalent to an energy not much larger than the band gap. Thus in this region the breakdown strength, E_B, may be written as

$$E_B=Na\epsilon_G/t, \tag{2}$$

where ϵ_g is the band gap energy; t, the thickness of the high-field region; $a\epsilon_g$, the mean energy for ionization; and N, the number of multiplications necessary to produce breakdown. An upper limit of thickness for direct field ionization can be calculated to the accuracy of the constants in (1) and estimates of the constants in (2).

$$t\leqslant\frac{Na\epsilon_g}{E_i}=\frac{Na\epsilon_g^{\frac{1}{2}}}{10^7\epsilon^{\frac{3}{2}}}(8+\log_{10}E_i\tau). \tag{3}$$

If one assumes a representative value of 4 for $a\epsilon_g^{\frac{1}{2}}$ and uses Seitz's estimate of 40 multiplications to cause rupture,[12] direct field ionization of a center 2 ev deep will have a time constant as small as 10^{-3} sec at fields

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[8] F. Seitz, J. Chem. Phys. **6**, 150, 454 (1938).

[9] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).

[10] A. von Hippel and R. S. Alger, Phys. Rev. **76**, 127 (1949).

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lower than the field for breakdown by avalanche if the thickness is less than 0.7 micron. Crystals with larger band gaps can tolerate a larger value of thickness.

A minimum thickness of the high-field region is determined by the energy requirement for direct field ionization, and for the 2-ev transition is 30 A. The efficiency of electroluminescence by field ionization will be a maximum near this minimum thickness since energy is absorbed from the point of ionization to the edge of the high-field region.

A second limitation of the direct field ionization mechanism is competition with Zener breakdown of the lattice. Again using Franz's calculations, the following expression, similar to (1) but for Zener emission from the valence band, may be written for the field E_v necessary to induce valence electron emission with a time constant, τ_v.

$$E_v=\frac{6\times 10^6}{7+\log_{10}(E_v\tau_v)}\epsilon_g^2. \tag{4}$$

E_v is in volts/cm and ϵ_g in ev. The lattice constant is again taken as 5 A. For equal emission probability per unit volume of valence states and localized states which differ in concentration by 10^6, (ϵ/ϵ_g) is determined by (1) and (4) and is 0.6. This ratio changes to 0.7 for an impurity concentration of one percent. Hence the band gap requirements to prevent Zener breakdown are quite reasonable.

The possibility of direct field excitation without ionization exists for an activator system whose emitting state can be perturbed by the applied potential to an energy low enough to permit a reasonable occupation probability of this state from the ground state. If this perturbation, $\Delta\epsilon$, of the transition energy is due to a difference in polarizability, $\Delta\alpha$, of the two states, the difference in the induced dipole moments, Δp, will be

$$\Delta p=2(\Delta\epsilon)/E, \tag{5}$$

and

$$\Delta\alpha=\Delta p/E, \tag{6}$$

where E is the applied electric field. For an applied field as large as 10^8 volts/cm and $\Delta\epsilon=2$ ev, Δp and $\Delta\alpha$ are 20×10^{-18} esu cm and 30×10^{-24} cm^3 respectively. Both values are too high to be realized experimentally in the near future.

Activator systems having a minimum ionization energy in dielectric phosphors with large band gaps should be most suitable for electroluminescence by the direct field ionization mechanism. Observation of infrared electroluminescent emission by the direct field ionization mechanism is most probable because of the lower ionization energy and consequent lower field required. The emitting state of the activator system should be only a few tenths of an electron volt below the conduction band.

Unambiguous identification of the direct field ionization mechanism of electroluminescence has not yet been reported experimentally.

IONIZATION BY IMPACT

In order to produce electroluminescence by inelastic collisions of high-velocity electrons and activator systems, at least three conditions must exist. High-field regions capable of accelerating charge carriers to large kinetic energies must be produced, electrons or holes must be injected into this high-field region, and activator atoms must be suitably located to absorb by collision a significant fraction of the energy extracted from the field by the charge carriers.

The behavior of conduction electrons in high electric fields has been studied quite extensively by many investigators[10,13,14] in connection with the dielectric breakdown strength of solids. These investigators are in agreement on the main features of the mechanism. Electrons in an electric field are subjected to the force of acceleration of the field and a retarding force resulting from an interaction with the vibrational waves of the lattice. With sufficient field strength the electrons may overcome the frictional barrier and attain enough energy to ionize valence electrons. If occupied localized impurity states exist in the forbidden band of the crystal, the high-energy electrons will also have a certain probability of losing energy to these centers by inelastic collisions. The relative probabilities of this event and the ionization of valence electrons will depend on the energy and concentration of these impurity systems as well as the nature of the crystal lattice. The capture of holes by the localized systems following the ionization of valence electrons may also occur with appreciable probability.

Seitz[12] has emphasized the importance of nonpolar modes of lattice vibration at high energies even in an ionic crystal. These modes impose a frictional barrier at high kinetic energies of a conduction electron. Thus, with an electric field applied to the crystal, there may be a group of electrons which possess energies large compared with kT. If this barrier occurs at an energy close to the excitation or ionization energy of the impurity, there then will be an enhanced relative probability of excitation of the impurity.

Since this mechanism of electroluminescence is operating at field strengths not greatly inferior to the strength necessary for dielectric breakdown, field configurations contributing to stability against breakdown are important. For example, a thin high-field region in series with a thick low-field region would permit operation over a broader range of applied voltages without reaching an unstable breakdown condition. If the crystal possessed a high-impedance barrier region, this condition would be realized. A crystal with nonlinear characteristics such that the width of the high-field region, as well as the magnitude of the field, is

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[14] H. Frohlich, Proc. Roy. Soc. (London) **188**, 521, 532 (1947).

dependent on the applied voltage, is particularly stable against dielectric breakdown.

Several types of barriers are physically possible, each having different electrical characteristics which might aid in the experimental identification of the mechanism for a specific phosphor system. A Mott-Schottky exhaustion-type barrier has already been proposed by Piper and Williams[5] to explain the characteristics of single crystals of ZnS:Cu. The barrier to be effective must be close to a conducting electrode. Charge from donor levels is swept from the volume in front of the electrode and further charge cannot flow into the crystal from the electrode due to a difference of work function or the presence of an insulating layer. As the potential difference across the crystal is increased, the exhaustion layer broadens and the barrier fields increase as the square root of applied potential.

An insulating intrinsic layer is another suitable type of barrier. This barrier would remain constant in thickness and the field which would be independent of position in the barrier would vary linearly with applied voltage.

A further possibility is a *p-n* junction biased in the reverse direction. An idealized example of a junction is a linear variation of the difference of donor and acceptor concentrations through the junction. The exhaustion region increases in width with increasing applied voltage, and for this example the field strength would vary as the two-thirds power of the voltage.

In order to produce electroluminescence, free charge carriers must be injected into the high-field region of the crystal after the field has been established. This can be accomplished in a variety of ways. The carriers may be injected from the surface of the crystal. Donors, acceptors, and filled traps are also a source of free carriers. The position of these sources may be in the high-field region itself if their binding energies are sufficient to permit the field to reach an appropriate value without the charge carrier being prematurely released. The sources may also occupy an adjacent volume if the carriers are swept into the high-field region after being released. The release of the carriers may occur thermally or the ionization may occur due to the presence of the high field. Photon absorption is also possible. If the absorption is in the fundamental band, a localized center is not needed and two free charges of opposite sign are released for each absorbed photon.

If the mean distance for the acceleration of a carrier up to an ionization event is less than the width of the barrier, then the effects of multiplication must be considered. The size of the avalanches will, of course, depend critically on the field strength. Postulating the creation of carriers by the absorption of photons in the fundamental band, or by thermal or field ionization of impurity systems excited by the absorption of photons, the interesting possibility of light amplification was predicted by Williams.[14a] The amplification depends on sufficient local field so that either the charge carriers created by the incident radiation attain sufficient kinetic energy for the excitation by impact of the activator systems several times in their mean lives or the charge carriers created by the incident radiation form avalanches of prebreakdown magnitudes and excitation by impact of a number of activators per incident photon is attained. The electroluminescence of ZnS:Cu phosphors has been identified with the impact mechanism of excitation.[5] Light amplification in ZnS:Mn phosphor films has recently been observed experimentally by Cusano.[15]

CHARGE CARRIER INJECTION

In semiconducting material, charge carrier injection provides a third mechanism for electroluminescence. The charge carrier can be injected either through the surface of the crystal or from a *p-n* junction biased in the forward direction.

In the case of *n*-type material, the Fermi level would be well above the ground state of the activator centers so that these centers would have their ground state occupied. The injection of a hole in the valence band if trapped by an activator would ionize this center. The center would then electrostatically attract and trap a conduction electron. The trapped electron would initially occupy an excited state and upon returning to the ground state emit a photon. Other localized centers would constitute competitive mechanisms for hole annihilation. These alternate mechanisms would not necessarily result in the radiation of visible light.

For *p*-type material, free holes are available to ionize the activator system for activators with ground states above the valence band. In this case, injected conduction electrons if captured by the activator center would result in luminescence. The supply of holes in the valence band would reionize the activator system in preparation for the next radiative event.

The absence of a local field and applied potential threshold leads to several characteristics of the charge carrier injection mechanism of electroluminescence. For the *p-n* junction, for example, with no applied potential thermal excitation leads to some injection and consequent light emission, limited in radiation density, however, by the characteristics of a black body at the lattice temperature. With small applied potentials the injection process will be markedly temperature-dependent. The electroluminescent efficiency will depend on the carrier lifetime of the injected charge carriers. Modulation by photon absorption should be possible for the carrier injection mechanism of electroluminescence. In addition, if the photons create charge carriers which are trapped, thereby yielding a space charge facilitating the transport of carriers of opposite sign which are

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[14a] F. E. Williams, Phys. Rev. **98**, 547 (1955).

[15] D. A. Cusano, Bull. Am. Phys. Soc. **30**, No. 1, 30 (1955); Phys. Rev. **98**, 546 (1955).

subsequently captured by the activator systems, light amplification is feasible. The electroluminescence of SiC has been attributed to the charge carrier injection mechanism.[3]

DIRECT RADIATIVE RECOMBINATION

The activator centers would not be necessary in a crystal whose band gap lies in the appropriate range. Holes and electrons are capable of direct recombination by the mechanism of photon emission. This process can compete successfully with the nonradiative mechanism in material of sufficiently high purity and high carrier concentration. Emission of this sort has already been observed in the infrared in germanium.[16] Smith recently reported injected electroluminescence in CdS and attributes the emission to direct radiative recombination.[17] Van Roosbroeck and Shockley have developed a formula for the total rate of radiative recombination.[18] Applying this expression to an intrinsic material whose absorption coefficient abruptly rises to 10^5 cm^{-1} at 2 ev and which has a refractive index of $\sqrt{10}$ near the absorption edge, one obtains a rate of recombination, $\mathcal{R}$, under conditions of thermal equilibrium at room temperature of

$$\mathcal{R}=5.3\times 10^{-7}\ \mathrm{cm}^{-3}\ \mathrm{sec}^{-1}. \tag{7}$$

For an arbitrary concentration of holes and electrons, the recombination rate is

$$\mathcal{R}_c=(np/n_i^2)\mathcal{R}, \tag{8}$$

where n_i is the equilibrium concentration of holes and electrons in intrinsic material, n, the free electron concentration, and p, the free hole concentration. This is clearly a bimolecular mechanism. The nonradiative recombination rate is essentially bimolecular as long as the probability of thermal dissociation following capture of a charge carrier by the center is large compared to the probability of capture of a charge carrier of opposite sign. However, at sufficiently high concentrations of free charge carriers, the mechanism becomes monomolecular and the ratio of radiative and nonradiative rates will favor the radiative process. This ratio reduces to

$$(\mathcal{R}_c/\mathcal{R}_{NR})=n_c\sigma_c/(\delta N\sigma_{NR}), \tag{9}$$

where the subscript NR refers to the nonradiative rate of recombination, n_c and N the concentrations of the majority injected carriers and nonradiative centers and σ the cross sections of the two mechanisms. Depending upon the ratio of holes and electrons, δ varies between 0.5 and 1.

The cross section for the radiative process for the case of the 2-ev band gap is

$$\sigma_i=\mathcal{R}/(n_i^2 v), \tag{10}$$

where v is the thermal velocity of the free electrons and holes. At room temperature σ_i is approximately 10^{-16} cm^2. If the nonradiative cross section has a conventional atomic value of the order of 10^{-15} cm^2, then the injected carrier concentration must rise to ten times the nonradiative center concentration for the recombination rates to be equal.

SUMMARY

The threshold fields required for electroluminescence distinguish the three excitation mechanisms. Approximate local fields of 10^7 and 10^5 volts/cm are necessary for the direct field ionization and the impact excitation mechanisms respectively. The charge carrier injection mechanism does not have a field threshold. The sequence of events necessary for impact excitation and carrier injection indicates that modulation by incident radiation of electroluminescence occurring by these mechanisms is feasible. Only for the carrier injection mechanism operating with small applied potential is a pronounced temperature dependence of electroluminescence predicted. There is good reason to believe that additional electroluminescent materials will be devised and that the three general mechanisms analyzed theoretically are sufficiently comprehensive to include all experimentally realizable systems.

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