

CHAPTER II
THEORY



2.1 Luminescence.⁽⁴⁾

When a substance absorbs energy in some form or other, a fraction of the absorbed energy may be re-emitted in the form of electromagnetic radiation in the visible or near-visible region of the spectrum. This phenomenon is called luminescence, with the understanding that this term does not include the emission of black-body radiation, which obeys the laws of Kirchhoff and Wein. Luminescent solids are usually referred to as phosphors.

Luminescence is a process which involves at least two steps: the excitation of the electronic system of the solid and the subsequent emission of photons. Excitation may be achieved by bombardment with photons (photoluminescence), with electrons (cathodoluminescence), or with other particles. Luminescence can also be induced as the result of a chemical reaction (chemiluminescence) or by the application of an electric field (electroluminescence).

Fluorescence is a process in which the emission of light occurs during excitation; the emission of light after the excitation has ceased is then referred to as phosphorescence or afterglow. These definitions are not very exact since strictly speaking there is always a time lag between a particular excitation and the corresponding emission of a photon, even in a free atom. In fact, the lifetime of an atom in an excited state for which the return to the ground state is accompanied by dipole radiation is 10^{-8} second.

For forbidden transitions, involving quadrupole or higher-order radiation, the lifetimes may be 10^{-4} second or longer. The decay time of $\sim 10^{-8}$ second is the demarcation line between fluorescence and phosphorescence.

One of the most important conclusions in the process of luminescence, is the ability of a material to exhibit luminescence, in the presence of "activators". These activators may be impurity atoms occurring in relatively small concentrations in the host material, or a small excess of one of the constituents of the material which is self activation. The presence of a certain type of impurity may also inhibit the luminescence of other centers, in which case the former are referred to as "killers". Since small amounts of impurities may play such an important role in determining the luminescent properties of solids, studies aimed at a better understanding of the mechanism of luminescence must be carried out with materials prepared under carefully controlled conditions.

A number of important groups of luminescent crystalline solids may be:

- 1) Compounds which luminesce in the "pure" state should contain one ion or ion group per unit cell with an incompletely filled shell of electrons which is well screened from its surroundings. Examples are probably the manganous halides, samarium and gadolinium sulfate, molybdates, and platinocyanides.
- 2) The alkali halides activated with thallium or other heavy metals.
- 3) ZnS and CdS activated with Cu, Ag, Au, Mn, or with an excess of one of their constituents (self-activation).

4) The silicate phosphors, such as zinc orthosilicate (willemite, $Zn_2 SiO_4$) activated with divalent manganese, which is used as oscilloscope screens.

5) Oxide phosphors, such as self-activated ZnO and Al_2O_3 activated with transition metals.

6) Organic crystals, such as anthracene activated with naphthalene; these materials are often used as scintillation counters.

2.2 Excitation and Emission,^(4,5)

The key to luminescence is the tendency of electrons in atoms to jump from one energy state to another. Upon absorbing a quantum of energy from some outside source, an electron jumps to a higher, or "excited", state. It may then jump back to its original state, reemitting the absorbed energy. In a phosphor, part of this energy is emitted as light. But the process is complex, and certain conditions must be met to make the electron jumps produce light rather than merely heat or other radiations.

In a phosphor crystal, its closely packed atoms interact with one another, the electrons are occupying a band of energy levels, instead of the single, sharply defined energy level of an electron in an isolated atom. Nevertheless, just as a single electron in an atom is permitted only certain energy levels and is forbidden any intermediate energies, so there is a forbidden band of energy values which cannot be occupied by any electrons of the atoms of that phosphor, when the crystal is unexcited, the lowest energy band is completely filled with electrons. If exciting energy is supplied to the crystal, some of the electrons will jump from this

band across the forbidden band just above it into a permissible higher band. Now if an electron jumps back to the lowest band, it will emit energy - but not in the form of light. The quantum of energy required for a jump from one level to another depends on the width of the gap, and the size of the quantum determines the frequency, or wavelength, of the radiation emitted: the bigger the quantum, the higher the frequency. In this case the gap across the forbidden band is so wide that an electron jumping back to the lower band emits its energy at a frequency in the ultraviolet region rather than in the lower-frequency region of visible light. But the gap can be made narrow by inserting a new rung within the forbidden zone to shorten the step for the jumping electrons. The incorporation of an activator atom in a crystalline solid will in general give rise to localized energy levels in the normally forbidden energy gaps. These localized levels may be classified into two categories: (i) levels which belong to the activator atoms themselves and (ii) levels belonging to host atoms which are under the perturbing influence of the activators. The levels of group (ii) may be associated with host atoms in the immediate vicinity of the impurity atoms, but they may also be associated with lattice defects (e.g., vacancies) whose existence is tied up with the incorporation of the activator.

In terms of the energy band picture of Fig.2.1 let G and A be two levels corresponding to one of the categories (i) and (ii) mentioned above. In the ground state level G is occupied by an electron and A is empty; in the excited state the reverse is true.

The excitation from G to A may be accomplished in at least three ways:

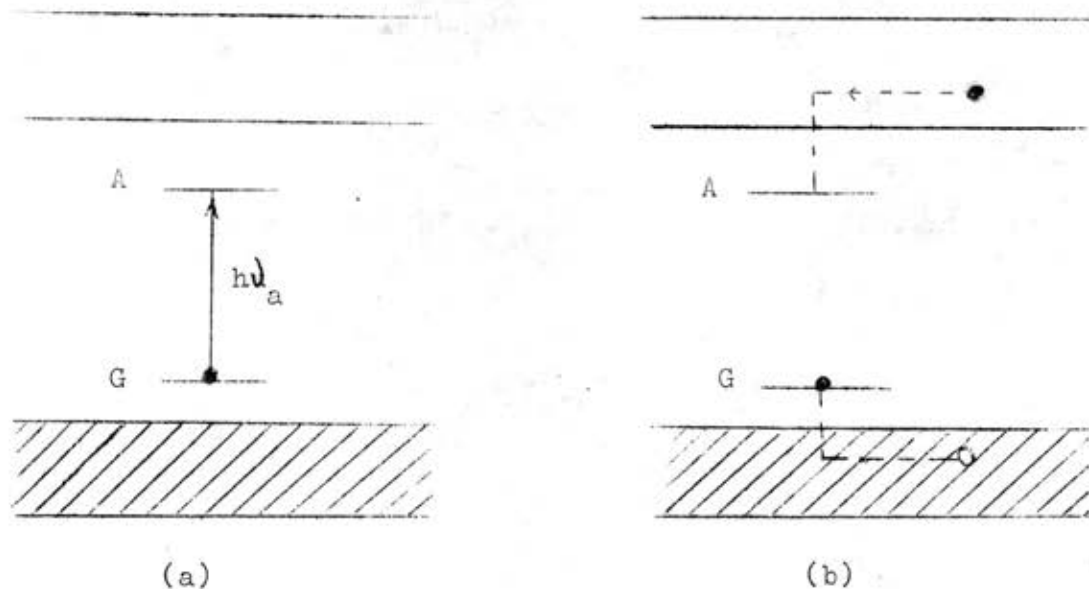


Fig.2.1 The Ground State G and an Excited State A of a Luminescence Center. In (a) excitation takes place by direct absorption of a photon $h\nu_a$. In (b) excitation is achieved by capture of a hole at G and of an electron at A.

a) It is possible that an incident photon of the proper frequency is absorbed directly by the electron in level G, whereupon it arrives in A, (Fig. 2.1 a) As a result of lattice vibrations the absorption will correspond to a band centering about a certain frequency ν_a .

b) The excitation process may also involve the diffusion of an exciton. In some part of the crystal an exciton is produced, since the exciton may diffuse about in the crystal, it may reach a center such as AG, whereupon it may give off its energy to the center,

resulting in excitation of the electron. Since it provides a mechanism whereby energy can be transferred from the exciting source to the impurities via the host crystal. In other words, the exciton mechanism makes it possible for the activators to receive more energy than they ought to on the basis of their relative concentration in the lattice.

c) The excitation process may also involve the motion of free electrons and holes. If electron-hole pairs be created somewhere in the crystal, as by bombardment with photons or electrons. If the center AG is in its ground state, the level G may capture a hole from the valence band and A may trap an electron from the conduction band. In this way, excitation of the center has been achieved, as indicated in Fig.(2.1 b.). Evidently this type of excitation process should be associated with conductivity, in contrast with process (a) and (b).

The return of the electron from the excited state A to the ground state G should be accompanied by emission of a photon of a frequency equal to the absorption frequency. In Fig 2.2 represented the levels A and G as function of a configurational coordinate q ; each value of q corresponds to a particular configuration of the nuclei in the vicinity of the luminescence center. During the optical excitation from G to A the nuclei remain essentially at rest, leading to an absorption energy $h\nu_a$. After the absorption act the nuclei do not occupy the equilibrium position proper for the excited state, and the system will move gradually to the minimum of the A curve, with emission of phonons. This process is possible since the

lifetime of the excited state is 10^{-8} second, as compared with periods of the order of 10^{-13} second associated with lattice vibrations. The emission act itself, like the absorption act, takes place vertically in Fig. 2.2(a), so that $\nu_c < \nu_a$. Thus luminescence centers are in general transparent, or nearly so, with respect to their own emission bands.

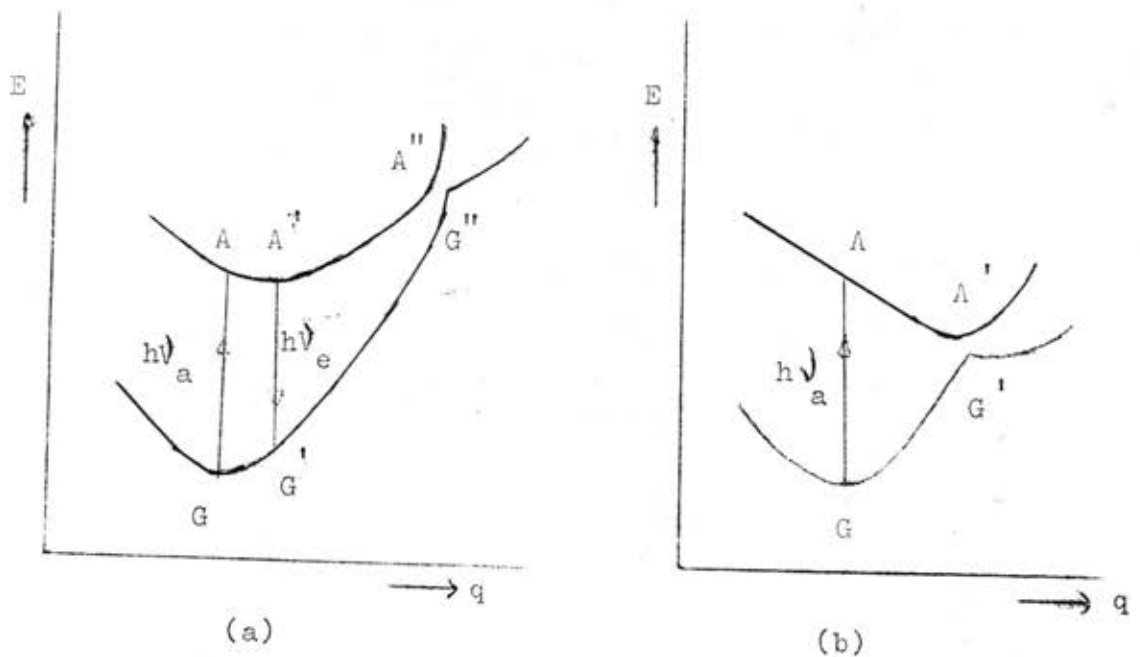


Fig. 2.2 Energy of the Ground State G and of an Excited State A as Function of a Configurational Coordinate q . The situation (a) gives luminescence; (b) corresponds to dissipation in the form of heat.

An excited center in a crystal can return to the ground state either with or without the emission of a photon. A model corresponding to the former case is the one represented in Fig. 2.2(a). For nonluminescent material, the model in which the return to the ground

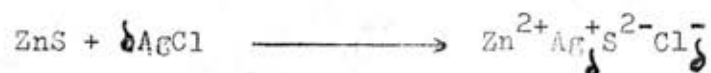
state of an excited center can take place by means of a radiationless radiation. Thus, in Fig 2.2(b) the system may move after the absorption act from A to A' and then cross the narrow gap to point G' associated with the ground state (perhaps with emission of a low-frequency photon). In this way the energy of the absorbed photon GA is essentially transformed into heat, i.e., into vibrational energy.

2.3 The Zinc Sulfide Phosphors.

2.3 a. The Principle of Charge Compensation; Coactivators. (4)

Zinc sulfide is usually obtained by precipitation from a solution of a zinc salt with H_2S or $(NH_4)_2S$. The actual phosphor is then prepared by firing the mixture of components at sufficiently high temperatures so that diffusion of the activators and recrystallization of the material may take place. To obtain a reasonable rate of recrystallization, it must require under normal circumstances temperatures of the order of $1200^{\circ}C$. However, if it is added by a flux, temperatures of, say, $800^{\circ}C$ may be sufficient, and for practical reasons this is usually done. For example, for activation of ZnS with monovalent metals such as Cu, Ag, Au, salts like NaCl or $CaCl_2$ are found to be suitable fluxes. The incorporation of activators such as Ag, Cu, Au, Li, Na in zinc sulfide is governed by the so-called principle of charge compensation.

When zinc sulfide is fired with Ag_2S , Ag^+ ions occupy positions normally occupied by Zn^{2+} ions. In order to conserve charge, the crystal must contain one sulfur vacancy for each two silver ions incorporated in the lattice. Since the creation of a vacancy requires a good deal of energy, the amount of silver incorporated in the lattice will be strongly limited. Similarly, a mixed crystal of ZnS and ZnCl_2 in which Cl^- ions occupy lattice sites normally occupied by S^{2-} ions, must contain positive ion vacancies. The formation of vacancies may be avoided, however, if in the case of ZnS:Ag a monovalent negative ion is incorporated for each Ag^+ ion. For example,



and no vacancies are required. The lack of positive charge associated with the Ag^+ ions is compensated by the lack of negative charge on the Cl^- ions. The chlorine ions presumably enhance the solubility of the monovalent metallic activator ions, resulting in a good phosphor. Similarly results are obtained with bromides as a flux. The Cl^- or Br^- ions are referred to as coactivators. From the principle of charge compensation it follows that trivalent metal ions such as Al^{3+} and Ga^{3+} should also be suitable coactivators for monovalent metal activators. This is indeed the case, the lack of positive charge is then compensated by an excess of positive charge.

2.3 b. The Nature of the Luminescence Centers in Impurity - Activated Zinc Sulfide Phosphors. (4,5)

By introducing a few copper atoms into the zinc sulfide crystal. An energy level permissible to copper's electrons lies within the band forbidden to those of zinc and sulfur. If a copper electron is excited to a higher energy level, it leaves a vacancy which can be filled by an electron dropping from the higher band. The drop to this level is short enough - that is, the quantum is of the right size - to produce emission of light. The electron berths provided by the copper atoms are therefore called luminescence centers.

There are other holes, within the forbidden band and close to the higher energy band, into which electrons may fall. They are called traps, and are created by imperfections in the crystal or by chlorine atoms, which are introduced to control the number of copper atoms dissolved in the crystal. Electrons falling into traps generate only heat, but they are easily excited out of the traps and then can fall into empty luminescence centers, producing light.

Energy bands of a zinc sulfide phosphor are schematically shown in Fig. 2.3. At bottom, the band occupied by unexcited electrons, is called valence band; at top, the band occupied by excited electrons is called conduction band. Between the two bands is a forbidden band which cannot be occupied by electrons in a pure crystal. If an electron in such a crystal jumps from the lower band to the upper and falls back again, it may emit ultraviolet radiation or simply radiate heat. If copper atoms are introduced into the

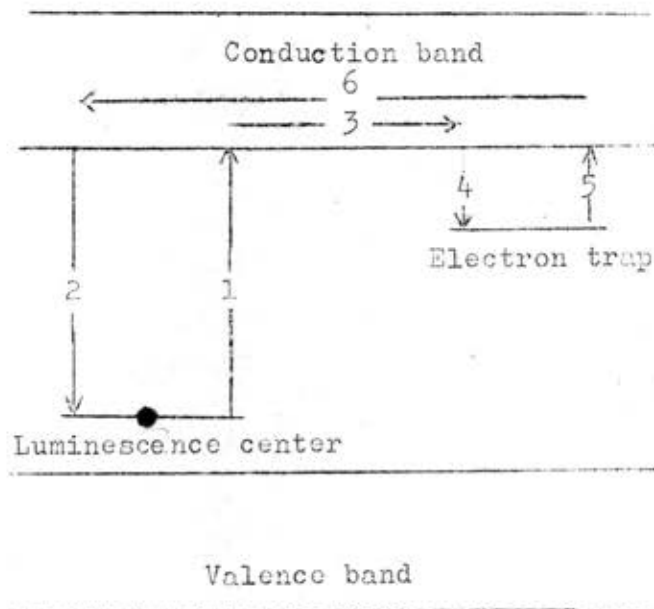


Fig. 2.3 Schematic Representation of the Electronic Levels in a Zinc Sulfide Phosphor.

crystal, they form a luminescence center whose energy level is in the forbidden band. If an electron jumps from this level (1) and falls back again (2), it emits light. The electron can also wander through the crystal (3) and fall into an electron trap (4). Such a trap is created by an imperfection in the crystal or by chlorine atoms which are introduced to control the number of copper atoms. The electrons are easily dislodged from the trap (5) and can then fall back to the level of the luminescence center (6 and 2).



2.4 Mechanisms of Electroluminescence.

2.4 a The Gudden - Pohl Effect. (3,4,5)

In 1920 Gudden and Pohl discovered that a momentary flash of light is emitted when an electric field is applied to a zinc sulfide phosphor during the after glow (phosphorescence). When a D - C field is applied, a flash is observed; the same is true when the field is switched off. This indicates that after a static field is applied to a phosphor, an internal field is set up, due to polarization, which rapidly reduce the external field to zero before all the traps can be emptied. Removal of the applied field causes a sudden increase in the internal field which again decreases rapidly to zero, producing another flash of emission. The same effect may also be observed by removal of a field which is applied before or during excitation.

The Gudden - Pohl effect is evidently due to the emptying of electron traps. This may occur as a result of tunneling of electrons from the traps into the conduction band or it may be due to ionization of the filled traps by free electrons accelerated by the field in the conduction band.

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The effects of polarization can obviously be avoided by the use of alternating fields. In this case the emission consists of light pulses at twice the field frequency and decreasing in amplitude. A second light flash is often also observed at removal of an alternating field. The higher the voltage the more rapid is the decrease in output; the decay is thus more rapid than the normal phosphorescence.

The process of electroluminescence is more indirect when compared with the process of luminescence, such as fluorescence. The ultraviolet rays in a fluorescent tube excite electrons contained in the phosphor to the higher permitted energy band, and the excited electrons then fall into empty luminescence centers. In electroluminescence, the alternating electric field cannot kick electrons out of the centers directly, but it accelerates free electrons, and these accelerated particles then knock electrons out of the luminescence centers, creating vacancies into which electrons can fall with emission of light. If the method is to produce much light, the phosphor has to be specially treated to increase the effectiveness of the electric field. Small particles of copper sulfide are introduced into the phosphor. Because copper sulfide is a good conductor, each of these particles concentrates and intensifies the electric field around it and so enhances the acceleration of electrons. The field, though not strong enough to dislodge electrons from luminescence centers, can free electrons from the traps and so start an avalanche. Once started, the avalanche excites many of the electrons out of the centers by means of collisions. It slows down as it reaches areas of low field strength. The electrons then fill nearby traps, only to be liberated again by the reverse build-up of the alternating field, which accelerates them back toward the empty centers. When electrons drop into the centers, they emit light.

2.4. b. The Destriau Effect ⁽⁴⁾

The emission of light by a phosphor resulting solely from the action of an electric field applied to a suspension of luminescent

particles in an insulator was first discovered by Destriau. In this case one may speak of intrinsic electroluminescence, since the effect does not involve previous photo-excitation, nor the injection of charge carriers from an external source. In order to transfer power to the dielectric consisting of the luminescent powder embedded in an insulator, alternating voltages or pulses must be used. A possible explanation of intrinsic electroluminescence presumably involves the emptying of traps by the field, subsequent acceleration of electrons in the conduction band, and excitation of centers by these electrons.

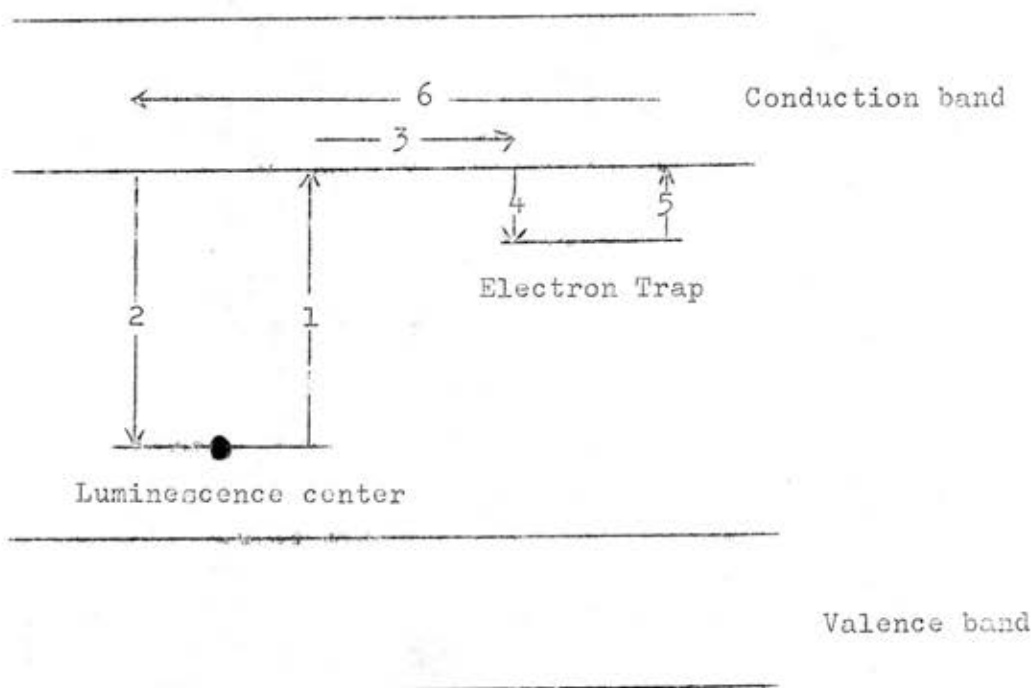


Fig. 2.4. Schematic Representation of the Electronic Levels in a Zinc Sulfide Phosphor.

If one assumes that the luminescent particles are spheres, one can show that the local field E_2 in the phosphor is given by the expression

$$E_2 = \frac{3 \epsilon_1 E}{2 \epsilon_1 + \epsilon_2 - f_1 (\epsilon_2 - \epsilon_1)}$$

where E is the applied field, ϵ_1 is the dielectric constant of the phosphor, ϵ_2 is the dielectric constant of the matrix, and f_1 is the fraction of the volume occupied by the phosphor particles. By using various matrices of widely different dielectric constants, Roberts⁽⁶⁾ showed that the observed brightness is a function only of the local field E_2 . The brightness varies only slightly with temperature, indicating that thermal excitation is of little importance in the mechanism.

The colour of the light could be changed instantly by tuning the applied electricity to a different frequency. The available colours depend on the substances introduced into the phosphor to provide luminescence centers. Copper gives blue or green. The brightness of the green band becomes saturated as the frequency increases whereas the brightness of the blue band increases linearly. Thus at low frequencies the green band dominates the colour of emission, whereas at higher frequency the colour becomes blue.

2.5 Dependence of Brightness on Voltage and Frequency. (1,2,3,4,5)

Many equations have been proposed to account for the observed dependence of electroluminescent brightness upon applied voltage. If the variation of brightness is small a power law relation of the form

$$B = aV^n, \text{ where } 3 < n < 4$$

adequately represents the voltage dependence.

G. Destriau originally proposed an equation,

$$B = a \exp - (b/V)$$

which was modified later to account for a slight curvature in the plot to

$$B = aV^n \exp - (b/V)$$

where a, b and n are constants, the value of n being between 1 and 3 but generally 2. If the range of observation only extends over one or two decades of brightness the exact form of the equation is not critical. An equation which fits the observations over nine decades for power and crystal electroluminescent phosphor is:

$$B = a \exp - \left\{ b / \sqrt{v} \right\}$$

The frequency dependence varies from phosphor to phosphor. In the case of electroluminescent panels this dependence of the phosphor may be obscured or complicated by variation in the dielectric properties of the plastic in which the phosphor is suspended. In

general, phosphors with a single emission band increase in brightness linearly or sublinearly with frequency. At high frequency there is a tendency for the brightness to saturate or decrease because too short a cycle will not give the electrons time enough to emerge from their traps.