PHYSICAL REVIEW VOLUME 98, NUMBER 4 MAY 15, 1955

Recombination Processes in Cadmium Sulfide*

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(Received January 28, 1955)

An experimental study has been carried out on the photoconductivity and luminescence of cadmium sulfide. The two main properties investigated were the photoconductive spectral response, and the relationship between luminescence and photoconductivity. It is found that the observed spectral response can be explained in terms of the dependence of lifetime of conduction electrons on the wavelength of exciting light. The rise and decay of photoconductivity and luminescence have been examined for silver-activated CdS, and for the red and green luminescence of unactivated CdS. It is found that the decay of luminescence is much more rapid than the decay of photoconductivity. An explanation for this behavior is offered, based on the assumption that the luminescence results from the recombination of localized electrons and free holes.

I. INTRODUCTION

THE photoconductive process can be conveniently discussed in terms of three subprocesses. These are excitation, conduction, and recombination. In the present work we shall be primarily concerned with the recombination process as it occurs in cadmium sulfide. The experimental approach used in this study is based on observations of the transient response of photocurrent and luminescence to varying excitation.

The general considerations involved in the study of recombination are indicated in the following discussion which is essentially that given by Gildart and Ewald[1] in connection with their work on CdS. We consider a homogeneous photoconductor in which the photoconductivity arises primarily from the motion of electrons in the conduction band. Free holes and electrons are liberated by the absorption of light in the fundamental absorption band. The electrons move in the conduction band and may be trapped, and also of course electrons previously trapped may be thermally ejected from traps. Similar considerations apply to free holes. Finally electrons and holes recombine. If n_c represents the number of conduction electrons, then

$$dn_c/dt = L - R - T + U, \tag{1}$$

where L = number of electrons excited per unit time, R = number of electrons recombining per unit time, T = number of electrons trapped per unit time, and U = number of electrons released from traps per unit time. Under steady-state conditions, we have $dn_c/dt = 0$, $T = U$, so that $L = R$. If the excitation, L, is cut off at $t = 0$, then momentarily the rate of decay of conduction electrons is

$$dn_c/dt = -R, \quad (L = R,\ t \leqslant 0;\ L = 0,\ t > 0). \tag{2}$$

By measuring dn_c/dt at $t = 0$, one may thus obtain a measure of R. If one also measures n_c, then the ratio of n_c to dn_c/dt gives a quantity which may be termed the lifetime of the conduction electron. This is the average time that an electron, which has been excited, will spend in the conduction band. Experimentally, one actually measures the photocurrent I, and dI/dt, but if one assumes that photoconductivity arises primarily from the motion of conduction electrons then one has

$$I = en_c\mu E,$$

and one obtains

$$\tau = \frac{n_c}{dn_c/dt} = \frac{I}{dI/dt}$$

$$= \text{average lifetime of the conduction electron.}$$

In addition to this method, one can obtain information regarding the recombination process from a study of luminescence since it comprises part of the recombination mechanism. In the present work recombination has been studied in relation to two properties of CdS: the shape of the spectral response curve of photoconductivity in CdS, and the relationship between photoconductivity and luminescent decay.

II. EXPERIMENTAL METHOD

For the measurement of photoconductivity, an alternating current method was employed at a frequency of 100 kc/sec. This ac method was used in order to avoid some of the difficulties of direct current methods. By this method the necessity for direct metallic contact to the CdS crystal is eliminated, and also the effects of polarization can be minimized.

The crystals used in this method were plate-like in shape, and were mounted in the manner shown in Fig. 1. The crystals were thus capacitively coupled to metallic electrodes. The measurements were made at 100 kc/sec to insure that this capacitive coupling impedance was very small in comparison to the photoresistance of the crystal. The ac photoresistance was then measured by means of a bridge (Fig. 2). The ac field applied to the crystal was of the order of 10 volts per cm. The transient behavior of the ac photocurrent was observed by means of an oscilloscope. The oscilloscope trace was photographed and measurements were made on these photographs.

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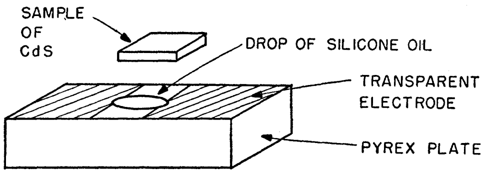
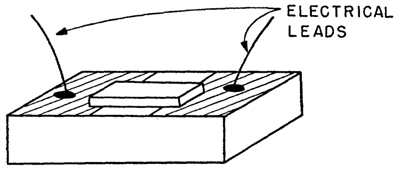
* A part of a dissertation submitted in partial fulfillment of the requirements for the Ph.D. degree at the University of Maryland.

[1] L. Gildart and A. W. Ewald, Phys. Rev. 83, 359 (1951).



(a) SAMPLE HOLDER WITH CRYSTAL TO BE MOUNTED



(b) SAMPLE MOUNTED ON HOLDER

FIG. 1. Details of mounting of CdS crystals on sample holder.

The transient behavior of the luminescence was observed by means of a 6217 photomultiplier in conjunction with an appropriate filter for the color of luminescence being observed. The signal from the photomultiplier was also displayed on an oscilloscope and recorded photographically.

Temperature control was obtained as follows. For work at 300°K, samples were placed in a container which was then evacuated to about 10^{-5} mm of Hg and then filled with helium gas at 1 atmosphere pressure. At 4°K and 77°K the samples were immersed directly in liquid helium and liquid nitrogen respectively. Measurements at 200°K were made by suspending the samples above a bath of liquid nitrogen and determining the sample temperature by means of a copper-constantan thermocouple.

III. SPECTRAL RESPONSE OF PHOTOCONDUCTIVITY

The photoconductive spectral response of CdS is such that in most cases the peak in photoconductivity lies to the long wavelength side of the region of maximum optical absorption. This means that although the absorption decreases, the photoconductive response actually increases. Several explanations have been offered for this behavior. Leverenz[2] suggests that because the light in the fundamental absorption band is absorbed in a shallow surface layer ($\sim 10^{-5}$ cm), electrons liberated in this region move in a very imperfect surface region and have low mobility as compared with electrons excited by light which penetrates into the interior of the crystal. Another possibility is that electrons excited in the surface region have a shorter lifetime than electrons excited in the interior of the crystal.[3,4] This question has been investigated by several workers.[5–7]

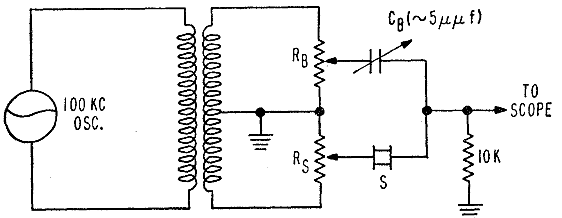


FIG. 2. Simplified diagram of bridge used in ac measurements. R_s varied the voltage applied to sample S. R_B and C_B were used to balance out any ac voltage across $10K$ resistor when sample (S) was in dark.

Fassbender and Seraphim[5] report no wavelength dependence of the photoconductive decay time on several crystals of CdS. They do not state whether or not these crystals show the usual peak in spectral response in the region of 5150 A. Gurevich, Tolstoi, and Feofilov[6] report finding a wavelength dependence of the photoconductive decay time in CdS crystals. Also Bube[7] has found wavelength-dependent effects in the decay time under the influence of water vapor. It appeared that a more thorough study of this matter would be useful in understanding the spectral response of CdS. Observations have been made on the optical absorption, the spectral response, and the decay rate of photoconductivity.

Consider a crystal being irradiated by L incident quanta per second at wavelength λ. Of these L quanta, AL will be absorbed by the crystal, where A is the absorptance of the crystal (i.e., fraction of incident light quanta which are absorbed). If we assume that each absorbed quanta gives rise to one conduction electron, then the number of conduction electrons under steady-state condition is

$$n_c(\lambda) = AL\tau, \tag{3}$$

where τ = lifetime of conduction electrons. If the mobility is not a function of the wavelength of exciting light, then we have for the photocurrent I as a function of wavelength:

$$I \propto AL\tau, \tag{4}$$

or

$$I(\lambda)/L(\lambda) \propto A\tau.$$

[$I(\lambda)/L(\lambda)$ is the photoconductive spectral response curve.]

Thus if the product ($A\tau$) yields a curve which is in good agreement with the observed spectral response, the above assumption about mobility is valid, and the observed spectral response can be explained in terms of the wavelength dependence of τ and A alone. This is the proposition which was tested experimentally by measuring τ, A, and the spectral response.

The measurement of $\tau(\lambda)$ was made as follows. The crystal was illuminated using a tungsten lamp in con-

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[2] H. W. Leverenz, *Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950).

[3] J. Fassbender, Ann. Physik. **5**, 33 (1949).

[4] A. Rose, RCA Rev. 362 (September, 1951).

[5] J. Fassbender and B. Seraphim, Ann. Physik **10**, 374 (1952).

[6] Gurevich, Tolstoi, and Feofilov, Doklady Akad Nauk U.S.S.R. **71**, 29 (1950).

[7] R. H. Bube, J. Chem. Phys. **21**, 1409 (1953).

junction with a monochromator to obtain light of a given wavelength. By means of a rotating sector the light was interrupted for a short interval. A measurement was then made of the time interval required for the photocurrent to drop to 0.95 of its initial value. If Δt is this time interval, then

$$\tau(\lambda)=\frac{I}{dI/dt}=\frac{I}{(0.05\times I)/\Delta t}=20\Delta t.$$

This method is approximate, of course, and will yield a value slightly larger than if a true measure of the initial slope were made. However, the error will be small, and since we are mainly interested in the relative value of τ at different wavelengths, this method is satisfactory.

Lifetime measurements were carried out on two crystals of CdS, and they are shown in Fig. 3. Optical absorption measurements were made on these same crystals using a Beckman spectrophotometer. The product of the optical absorptance A and the lifetime τ was then plotted along with the measured spectral response as shown in Figs. 4 and 5 normalized to arbitrary scales. These curves indicate that a consideration of the lifetime as a function of wavelength can very nearly account for the observed spectral response, and therefore the wavelength dependence of mobility is not an important factor.

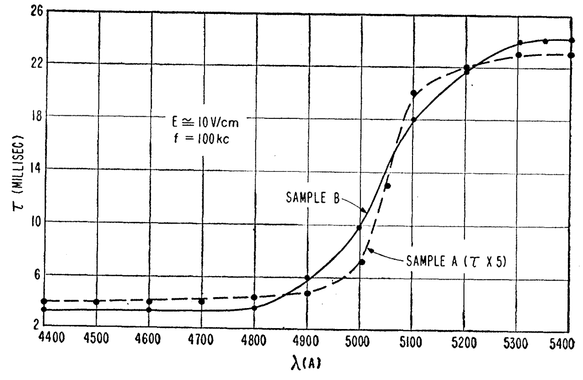

FIG. 3. Measurement of lifetime of conduction electrons as function of the wavelength of exciting light.

The cause of the wavelength dependence is not clearly understood, but it is of interest to point out some of the observations of others in this regard. Bube[6,8] has found that the presence of water vapor can reduce the photoconductivity in CdS. Moreover, he has found this effect to be wavelength dependent, being more pronounced at shorter wavelengths. He was able to show that the water vapor affected the recombination rate, and since light on the short wavelength side of the absorption edge is absorbed in a shallow surface layer, photoconductivity due to this light is quite dependent on surface conditions. Liebson[9] has found similar effects due to electronegative vapors, and has interpreted these results in terms of surface recombination processes. It thus appears that the wavelength dependence of the lifetime of the conduction electrons is related to surface recombination effects, the precise nature of which are as yet undetermined.

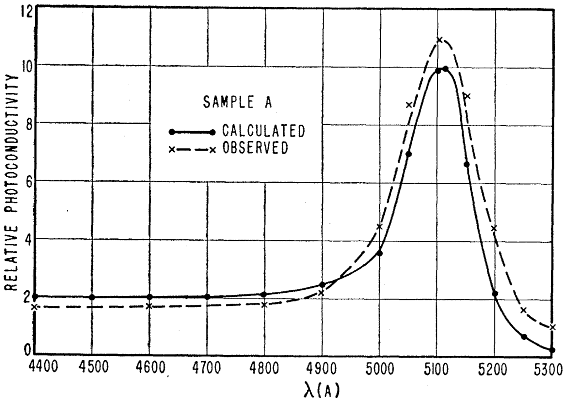

FIG. 4. Comparison of measured photoconductive response with the product ($A\tau$) for sample A. Curves have been normalized to arbitrary scales.

The observation of Fassbender and Seraphim[5] indicating the absence of any wavelength dependence of the time constant is also of interest. Unfortunately, they do not state whether the crystals they used showed the usual spectral response peak at 5200 A. Observations have been made in the course of this work of crystals which showed no peak in photoconductivity, and which showed no wavelength dependence of the time constant. This is a further indication the spectral response peak is associated with the time constant behavior.

IV. LUMINESCENCE AND PHOTOCONDUCTIVITY

In this section we shall discuss the relation between the decay of luminescence and the decay of photoconductivity. On the basis of the model often used for photoconducting phosphors (Fig. 6), it is seen that one should expect the luminescence and photoconductivity

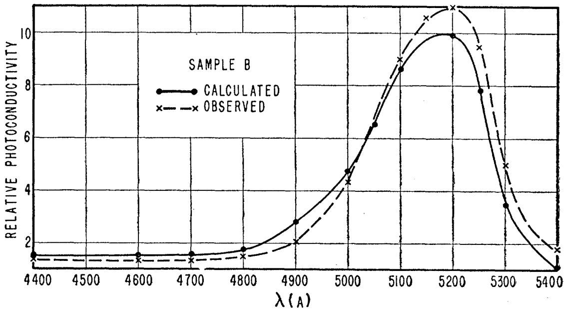

FIG. 5. Comparison of measured photoconductive response with the product ($A\tau$) for sample B.

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[8] R. H. Bube, Phys. Rev. **83**, 393 (1951).

[9] S. H. Liebson, J. Electrochem. Soc. **101**, 359 (1954).

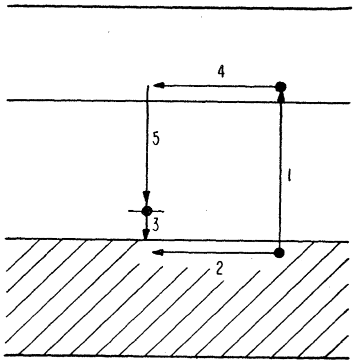

FIG. 6. Conventional model for photoconducting phosphor: (1) excitation; (2) hole migration; (3) capture of hole at luminescent center; (4) electron migration; (5) capture of electron leading to luminescent emission.

to have more or less equivalent decay times, or else the luminescence should persist longer than the photoconductivity. This is because luminescence is assumed to occur after the capture of a conduction electron by the luminescent center. In order to investigate this matter measurements were carried out on the decay of photoconductivity and the decay of the orange luminescence of silver-activated CdS, the green edge luminescence of CdS, and the red luminescence of "self-activated" CdS.

IV(a). Luminescence and Photoconductivity in CdS(Ag)

Silver-activated CdS shows a broad luminescence centered about 6100 A.[10] This luminescence can be observed at 77°K, but gradually disappears as the crystal is warmed to room temperature. The crystals used in this work were activated with silver by introducing silver vapor into the vapor phase growth of CdS crystals.

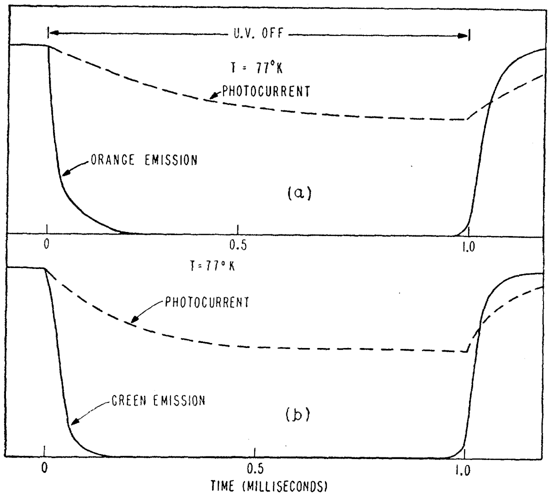

FIG. 7. Comparison of decay of luminescence and photoconductivity: (a) CdS(Ag) at 77°K, orange emission; (b) CdS at 77°K, green edge emission.

The first step in the present study was to observe the decay of photocurrent and luminescence at 77°K. The luminescence was observed by means of a 6217 photomultiplier in conjunction with a Corning 2-63 filter. The crystals were excited by light of 3650 A wavelength. This excitation was interrupted by means of a rotating sector, and the decay of luminescence and photoconductivity could then be observed by means of an oscilloscope.

The results of such observations are shown in Fig. 7(a). This shows clearly that the luminescence decay is much more rapid than the photoconductive decay. Further measurements indicated that the luminescence decay time (time required to drop to $\frac{1}{2}$ of initial value) is about 0.05 millisecond, while photoconductive decay time was about 5 milliseconds. The simple model of Fig. 6 does not afford an explanation of such a result.

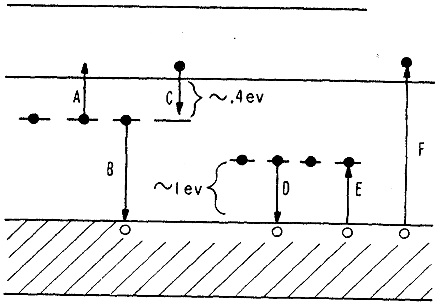

FIG. 8. Model proposed for CdS(Ag). (See reference 11.) The levels 0.4 ev below the conduction band result from silver activation. The levels 1 ev above the valence band are normally present in CdS. (*A*) infrared excitation of trapped electrons (3μ region); (*B*) luminescent recombination of trapped electron and free hole; (*C*) trapping of electrons; (*D*) trapping of holes; (*E*) freeing of trapped holes by excitation in 1μ region; (*F*) excitation.

In order to explain this behavior we shall consider a model which has recently been proposed for the luminescence process in CdS(Ag).[11] This model is illustrated in Fig. 8. Silver activation results in the formation of electron traps about 0.4 ev below the conduction band. These are the luminescence centers. In addition there are hole traps about 1 ev above the valence band. Such hole traps have been posulated in connection with infrared quenching effects in CdS.[4,12] In the model proposed, the following processes occur: (1) Irradiation in the fundamental band produces free holes and electrons. Some of the free electrons are then trapped in the luminescent centers, while some free holes are trapped by the levels 1 ev above the valence band. (2) As excitation continues, electrons in the luminescent centers recombine with free holes, resulting in lumines-

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[10] C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

[11] J. Lambe and C. C. Klick (to be published).

[12] E. A. Taft and M. H. Hebb, J. Opt. Soc. Am. **42**, 249 (1952).

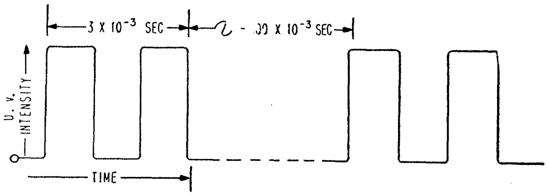

FIG. 9. Ultraviolet (3650 A) pulse pattern used in rise time studies.

cence. (3) When the excitation is removed, luminescence continues until the number of free holes is exhausted. If free holes have a short lifetime, the luminescence decay will be very rapid. (4) Electrons remaining in the conduction band after excitation ceases will continue to be trapped by empty luminescent centers, and also they may recombine nonradiatively with trapped holes. The photoconductivity will persist until the number of free electrons is exhausted.

Such a model was found to be consistent with observations on infrared photoconductivity and stimulation of luminescence in CdS(Ag).[11]

The proposed model affords a simple explanation of the difference in decay time of luminescence and photoconductivity. If one assumes that the lifetime of free holes is much shorter than the lifetime of free electrons, it is clear that luminescence, which is associated with the capture of free holes, will decay much more rapidly than photoconductivity which is associated with the motion of free electrons. The difference between free hole and electron lifetimes is presumed to be due to the existence of a large number of hole traps or to a larger cross section for hole trapping.

Since the proposed model is consistent with observations of infrared effects,[11] and also with the measurement of decay times reported here, let us examine some further observations in regard to the nature of the build up of luminescence and photoconductivity when CdS(Ag) is illuminated. In the experiments to be described, the CdS(Ag) crystal was kept in darkness for the major part of the time and was irradiated every 100 milliseconds by two short pulses of ultraviolet (3650 A) 1 millisecond apart (Fig. 9). The pulses were 1 millisecond in duration. We consider first the behavior of the photoconductivity and luminescence after many excitation cycles have elapsed. From Fig. 10(a) it is seen that at 77°K the rise of the luminescence was much more rapid than the photoconductivity for both pulses. The decay of luminescence is of course more rapid than the decay of photoconductivity as noted previously. At 200°K, however, this behavior has changed considerably. In this case it is seen from Fig. 10(b) that the rise of luminescence is much slower, and actually the rise of luminescence now parallels the rise of photoconductivity for the first pulse of the pair on each cycle. The decay shows the usual behavior. The rise of the second luminescence pulse of the pair is considerably steeper than the first pulse. It should be emphasized that these patterns are observed after many excitation cycles have elapsed and they are observed for each pair of excitation pulses.

The aforementioned behavior can be explained directly in terms of the proposed model. At 77°K electrons can be "frozen" in the luminescent levels, so that luminescence can occur as soon as free holes are generated. Thus, once a substantial number of the luminescent centers are filled, the rise of luminescence will be very rapid. At 200°K, however, electrons are not retained in the luminescent levels for a long period of time. During the time when the crystal is in darkness these levels are emptied and the ejected electrons recombine with trapped holes in a nonradiative manner. When excitation is applied free holes and electrons are generated. The luminescent levels are empty, however, so that the free holes cannot recombine immediately with electrons in these levels. Thus, before luminescence can occur these levels must be filled. At 200°K, it appears that the number of electrons in luminescent levels is roughly proportional to the number of conduction electrons so that the rise of luminescence follows the rise of photoconductivity. The steeper rise of the second luminescence pulse in Fig. 10(b) is understandable since a substantial number of traps remain filled in the short period following the first excitation pulse.

In Fig. 11 a qualitative picture of the observed luminescence pulse pattern is derived as the product of the number of electrons trapped in luminescent levels (n_T), and the number of free holes (assuming n_T is proportional to n_C and that free holes have a short lifetime due to hole trapping).

Two further observations are of interest in this connection. Suppose that CdS(Ag) be cooled from 300°K

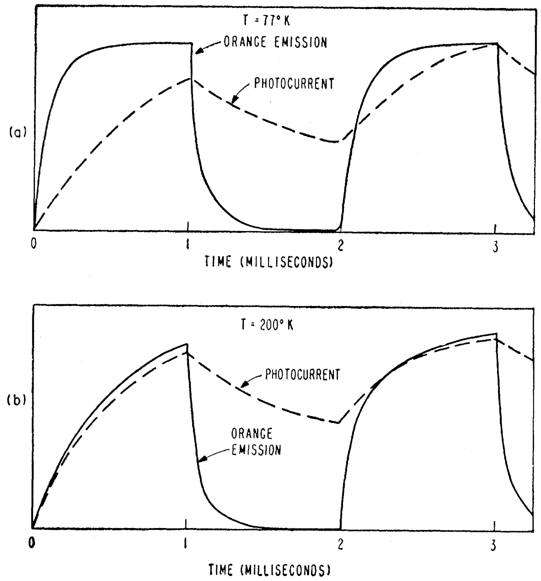

FIG. 10. Behavior of luminescence and photoconductivity at 77°K and 200°K under excitation by ultraviolet pulses (see Fig. 9 for ultraviolet pulse pattern) after many excitation cycles have elapsed.

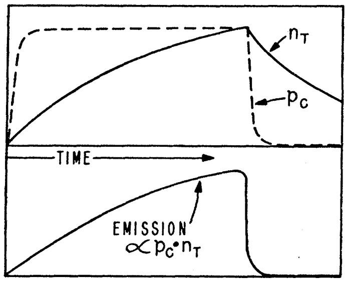

FIG. 11. Qualitative picture showing how the luminescence pulse observed in CdS(Ag) at 200°K can be derived as the product of n_t and p_c. n_t is the number of electrons localized in shallow luminescent levels and it is assumed that at 200°K, n_t is proportional to the number of conduction electrons. p_c is the number of free holes and it is assumed that free holes have short lifetimes.

down to 77°K in darkness. The luminescent levels would then be empty. If we then excite the crystal with ultraviolet, the rise of luminescence for the very first pulse should be slow since luminescence cannot occur until the luminescent levels are filled. Figure 12 shows what occurs on the very first excitation cycle under these conditions. The rise of luminescence is very slow compared to Fig. 10(a). After several excitation cycles, the luminescent levels become substantially filled (and remain filled at 77°K) and the rise of luminescence becomes very rapid [Fig. 10(a)]. Let the ultraviolet excitation now be removed, and let the crystal then be irradiated in the 1μ region. This radiation should liberate holes, and these free holes should then recombine with electrons in luminescent levels (giving rise to a burst of orange luminescence as has been reported[11]). The result of all this is to empty the luminescent levels. If we now remove the 1μ radiation and reapply the ultraviolet pulses, the rise of luminescence is again very slow for the initial pulses as shown in Fig. 12, just as was observed when the crystal was cooled in darkness from room temperature. Of course, after several excitation cycles, the rise of luminescence becomes rapid. This behavior is just what one should expect on the basis of the proposed model since a substantial number of luminescent levels will then be filled.

IV(b). Photoconductivity and Edge Luminescence

In this section experimental observations will be described on the relation between photoconductivity and the green edge luminescent band[13] of CdS at 77°K and 4°K. In these experiments the luminescence was observed with a 6217 photomultiplier in conjunction with a Corning 3-69 filter.

Figure 7(b) shows a comparison of the photoconductive and luminescent decay at 77°K. It is clear that the luminescent decay is much more rapid than the photoconductive decay. Again we have a situation which cannot be interpreted in terms of the simple model of Fig. 6. In order to clarify this matter, a study was carried out by means of the double-pulse method just as was done in the case of CdS(Ag). Let us first describe the series of observations which were made and then attempt to interpret them. Figure 13(a) shows the rise and decay of luminescence and photoconductivity at 77°K after many excitation pulses. The rise of photoconductivity and luminescence are nearly the same, while the decay of luminescence is much more rapid than the decay of photoconductivity. This is similar to what was observed at 200°K for CdS(Ag).

Figure 13(b) shows the behavior of green luminescence at 4°K. Here we see that the rise of luminescence has become quite rapid, and is now much faster than the rise of photoconductivity. At 4°K then, there is little apparent relation between photoconductivity and luminescence. This is very similar to what was observed for CdS(Ag) at 77°K.

In order to obtain more information on the slow rise of green luminescence at 77°K, the following experiment was carried out. Certain samples of CdS have been found to have very high dark conductivities. This conductivity is presumably due to a stoichiometric excess of cadmium. Such crystals have been studied by Kröger, Vink, and van den Boomgaard.[14] They find an activation energy of about 0.03 ev associated with this dark conductivity, and thus the number of conduction electrons can remain very large even at 77°K. In the samples used in these experiments the number of conduction electrons was roughly estimated at 10^{16}/cc at 77°K. Figure 13(c) shows the behavior of the green luminescence of such crystals under the double-pulse excitation after many excitation cycles have elapsed. It is to be noted in particular that the rise of luminescence is very rapid, and that the rise and decay times are equivalent.

Although the mechanism responsible for green luminescence is not yet clearly established, it is possible to give a phenomenological explanation of the foregoing observations based on a model similar to the one used for CdS(Ag). That is, let us assume the green luminescence arises from the recombination of trapped electrons and free holes just as was done for CdS(Ag). In the

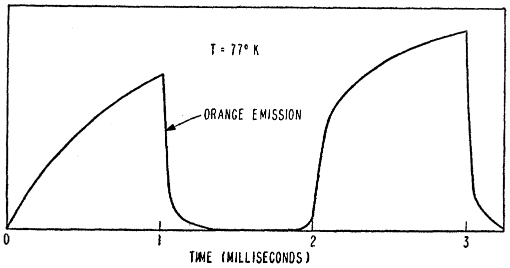

FIG. 12. Initial luminescence pulse for CdS(Ag) crystals at 77°K for a crystal cooled in darkness from room temperature or for a crystal pre-irradiated with 1μ infrared at 77°K.

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[13] C. C. Klick, Phys. Rev. **89**, 274 (1953).

[14] Kröger, Vink, van den Boomgaard, Z. physik. Chem. **203**, 1 (1954).

green luminescence case the electron traps would not be as deep as in the CdS(Ag), since the green corresponds to a higher-energy transition than the orange luminescence of CdS(Ag).

The rapid decay of green luminescence would then be ascribed to a short lifetime for free holes, just as was discussed for CdS(Ag). The slower decay of photoconductivity is due to the longer lifetime of free electrons.

The results of the double-pulse observations can also be interpreted on the basis of the CdS(Ag) model. The electron traps responsible for green luminescence are such that at 77°K electrons are not "frozen" in for a long period of time. Thus before luminescence can occur, these traps must be filled. This is the reason for the slow rise of green luminescence at 77°K. This is analogous to the behavior of CdS(Ag) at 200°K.

At 4°K, electrons can be "frozen" in the traps responsible for green luminescence so that the rise of luminescence becomes quite rapid, once these traps have been filled by previous excitation pulses. This is just what occurred at 77°K in the case of CdS(Ag).

The behavior of high dark-conductivity crystals at 77°K can also be interpreted on the CdS(Ag) model. In high dark-conductivity crystals there are a large number of conduction electrons so that a substantial number of the trapping levels would be filled. This means that luminescence can occur as soon as free holes are generated, so that the rise of green luminescence is very rapid in these crystals even at 77°K.

It is clear that on the basis of a model similar to the one proposed for CdS(Ag) one can explain the behavior of green luminescence and photoconductivity under a variety of conditions. This explanation does not offer any description as to the details of the center or mechanism of the luminescence. It is of interest to note that Kröger[15] has offered arguments to support the view that the green luminescence results from the recombination of free holes and free electrons by means of the formation of excitons. On such a picture the green emission would be proportional to the product of the number of free electrons and the number of free holes. Such an exciton picture is consistent with the observations made here at 77°K. The relation between photoconductivity and luminescence and the effect of high dark conductivity could be explained on such a basis. However, the results at 4°K do not appear to be consistent with the exciton model.

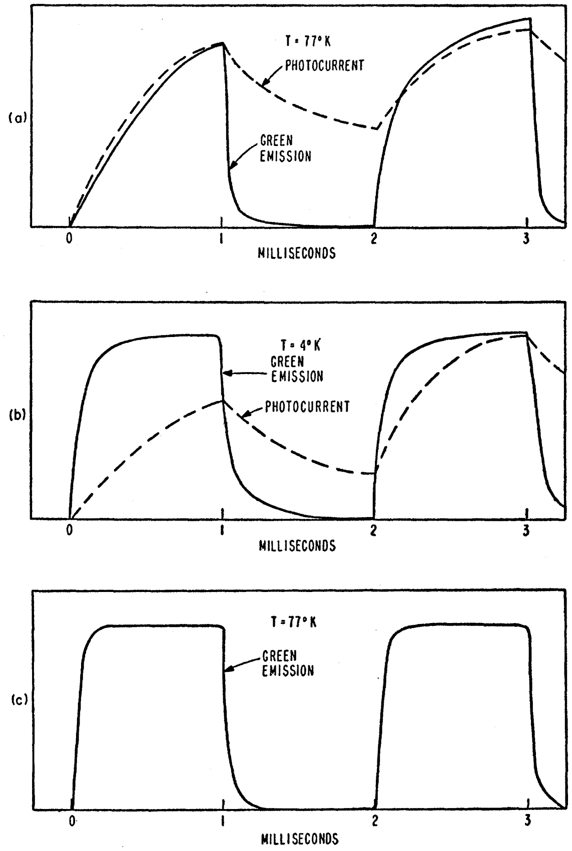

FIG. 13. Pulse patterns obtained for CdS at 77°K and 4°K under excitation by ultraviolet pulse pattern shown in Fig. 8. (a) for samples of CdS with low dark conductivity at 77°K; (b) for CdS crystals with low dark conductivity at 4°K; (c) for CdS crystals of high dark conductivity at 77°K.

Since the observations presented here can be interpreted on the basis of the recombination of a trapped electron and free hole, it may be worthwhile to speculate as to a possible center which could give rise to such behavior. Kröger and his co-workers[14] have indicated that sulfur vacancy which has trapped one electron, acts as a shallow trap for an additional electron. This additional electron, trapped at the sulfur defect, could then recombine with a free hole to give the observed luminescence. Kröger[15] has shown that the vibrational structure in the edge luminescence is associated with the longitudinal modes of vibration of the lattice. The theory of Huang and Rhys[16] indicates that in the *F* center for example, the electronic transitions are coupled to the longitudinal modes of vibration of the lattice. Further, the wave function of a weakly bound electron in a material of high dielectric constant may be expected to extend over several lattice spacings so that the vibrational modes with which it interacts could be characteristic of the lattice rather than the specific center to which the electron is bound. It would appear, therefore that the luminescent center proposed here could show the vibrational structure which is observed. Another interesting observation in this connection has been made by Bishop[17] at this laboratory. It was found that by firing CdS crystals in sulfur vapor at 800°C, the green edge luminescence can be removed. Similar treatment in cadmium vapor or in vacuum did not produce this effect, leading one to conclude that the

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[15] F. A. Kröger (to be published).

[16] K. Huang and A. Rhys, Proc. Roy. Soc. (London) **A204**, 406 (1950).

[17] M. E. Bishop (unpublished).

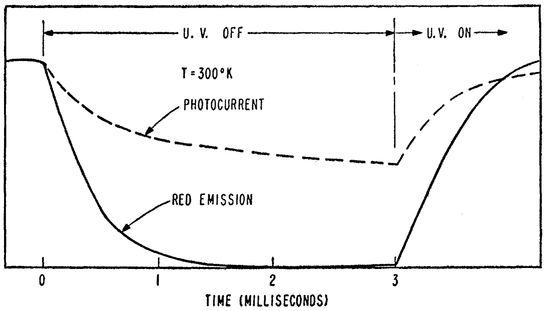

FIG. 14. Comparison of the decay of red luminescence and photoconductivity of CdS at 300°K.

formation of sulfur defects may be needed to observe the luminescence. A more thorough investigation of the effect of sulfurization on the edge luminescence would be useful in determining whether or not sulfur defects are the centers involved.

IV(c). Red Luminescence of CdS

CdS, without the intentional addition of any activator, shows a broad red luminescence at room temperature. This emission corresponds to an energy of 1.4 to 1.8 ev.[18] The crystals in these experiments were excited with ultraviolet at 3650 A and the red emission observed with a 6217 photomultiplier in conjunction with a Corning 2-64 filter. As before, the excitation was interrupted for a short interval and the decay of red luminescence and photoconductivity was observed.

Figure 14 shows the results of such observations. Here again, the luminescent decay is considerably faster than the photoconductive decay. Measurements made using the double pulse method showed that the rise and decay of red luminescence are equivalent, both being much more rapid than the photoconductivity.

This behavior can be interpreted in a rather simple manner if one assumes that the luminescence arises from the recombination of an electron in a donor level and a free hole. That is if we have a donor level ~1.5 ev above the valence band, an electron in such a level could recombine with a free hole in a radiative manner so that luminescence could terminate before photoconductivity. Conductivity would terminate when an electron was captured by the empty donor level. This is essentially the same type of model which is proposed for CdS(Ag).

Since little is known of the center responsible for red luminescence, the above picture is purely phenomenological. For the present, however, it does offer a simple explanation of the difference in decay times between red luminescence and photoconductivity.

V. CONCLUSION

The measurements of the wavelength dependence of the recombination process show that the spectral response of the photoconductivity is clearly related to such a dependence. The reasons for this wavelength dependence have not been definitely established, but indications are that surface recombination effects may play an important role.

Measurements on the relation between photoconductivity and luminescence show that luminescence decay is much more rapid than the photoconductive decay in CdS. A detailed study of CdS(Ag) indicated that this result is explicable on the basis of a model in which luminescence results from the recombination of trapped electrons and free holes. Such a model could also explain the results obtained in the case of green edge luminescence, and the red luminescence of "pure" CdS.

ACKNOWLEDGMENT

I would like to thank M. E. Bishop, who grew the crystals used in this work, and other members of the Electromagnetics Branch of the Naval Research Laboratory for their advice and assistance on various aspects of this problem. I am also indebted to Professor R. D. Myers, Dr. Jules DeLaunay, and Dr. Clifford C. Klick for their helpful interest in the course of this work.

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[18] R. Frerichs, Phys. Rev. **72**, 594 (1947).