

Nature of Edge Emission in Cadmium Sulfide

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Experimental and theoretical evidence is reviewed to determine if edge emission in CdS is due to exciton recombination or is characteristic of a center. New evidence is presented which shows that edge luminescence may be produced in CdS at low temperatures by stimulating with infrared light, and simultaneous measurements have been made on the decay of edge luminescence and conductivity in single crystals at 4°K under this irradiation. It is concluded that emission occurs by recombination of a free hole with an electron shallowly trapped at an imperfection. The atomic nature of the imperfection is examined briefly.

I. INTRODUCTION

“EDGE” emission is luminescent emission in solids which occurs close to the fundamental absorption edge of the solid, and which may be resolved into a series of equally spaced lines when measured at low temperatures. Emission of this sort has been clearly observed in ZnO^{1,2}, ZnS, and CdS³; but it is on CdS that the largest range of investigation has centered. By comparison with phosphors of known efficiency it appears that the quantum efficiency of edge luminescence is appreciable, of the order of 30%.

The mechanism of edge luminescence is in doubt; some workers have argued that the emission is due to the luminescent decay of excitons^{3,4} while other investigators have suggested that the luminescence is associated with impurity centers.⁵⁻⁷ Since there are very few experimental phenomena which can unambiguously be shown to be due to excitons, it is important to find additional exciton effects. Should edge emission be due to excitons, a study of this luminescence would be a valuable tool in studying these elusive particles. It is for this reason that edge luminescence has been so widely investigated and it is for this reason also that it is important to determine the nature of the emission.

A statement of the specific problem may be worthwhile at this point, since a certain subtlety is involved. Surely there is no experimental evidence now existing, or even imaginable, which would argue that the energy put into the crystal by irradiation spends no time whatsoever in an exciton state. That is not the question. What we wish to ask is, are there any indications that excitons are an *essential* part of the luminescence process, and are there any measurements which one could make in the expectation of observing a dependence on the properties or even existence of excitons?

In this paper the previous experimental and theoretical work will first be reviewed and analyzed as to the information it offers on the mechanism of edge emission in CdS. Then new experimental results will be described; and finally there will be an attempt to reach a conclusion about this problem.

II. PREVIOUS RESULTS

In Fig. 1 there are presented experimental results obtained on single crystals of cadmium sulfide measured at 4°K.⁵ The emission spectrum falls into two parts: the first part, which is that generally called edge emission, is the series of equidistant “lines” beginning at 5180 Å and going to longer wavelengths; the second part ranges from about 5000 Å to shorter wavelengths and some of this emission falls well within the fundamental absorption band of the solid. For this reason this second part has been attributed to emission at the surface of the crystal.³ Another interpretation recently presented⁴ involves band-to-band transitions and higher exciton states. The emission “lines” are found to be about 10 Å in width at half-maximum for pure crystals.⁸ The relatively large width of the emission lines in Fig. 1 is due to the band pass of the monochromator which is indicated in the figure by a measurement on the 5461 Å Hg line. All the measurements of Fig. 1

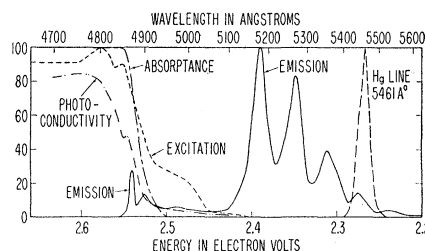


FIG. 1. Edge emission, excitation, photoconductivity, and absorptance (100 minus percent transmittance) for a CdS crystal measured at 4°K. The spectrum for the mercury 5461 Å line indicates the resolution of the monochromator used for all the measurements. These results are taken from reference 5.

¹ J. Ewles, Proc. Roy. Soc. (London) **A167**, 34 (1938).

² J. T. Randall, Trans. Faraday Soc. **35**, 1 (1939).

³ F. A. Kroger, Physica **7**, 1 (1940).

⁴ F. A. Kroger and H. J. G. Meyer, Physica **20**, 1149 (1954).

⁵ C. C. Klick, Phys. Rev. **89**, 274 (1953).

⁶ L. R. Furlong, Phys. Rev. **95**, 1086 (1954).

⁷ J. Lambe, Phys. Rev. **98**, 985 (1955).

⁸ C. C. Klick, J. Opt. Soc. Am. **41**, 816 (1951).

were made with the same monochromator and the same resolution.

In Fig. 1 there is also plotted the photoconductivity spectrum of a CdS crystal, the absorbance (100 minus percent transmittance) of a crystal 0.004 cm thick, and the relative efficiency of excitation for edge emission. The first peak of the edge emission (5180 Å) occurs at about 0.1 eV below the energy of the onset of strong absorption.

Evidence for an important band occurs in the excitation spectrum at about 4980 Å which does not appear in photoconductivity. It has been suggested⁴ that this band is an exciton absorption band and as such might not lead to photoconductivity at low temperatures. The position of this band is about 0.14 eV below the value taken for the band edge from photoelectromagnetic measurements⁹ at room temperatures and converted to low temperatures using the variation of absorption edge with temperature. This may be compared with a rough estimate of the energy between the lowest exciton state and the ionization continuum on the hydrogenic atom model.^{10,11} For CdS this estimate is 0.17 eV, which may be considered not in disagreement with the observed value. The emission would then likely be due to annihilation of these excitons. A serious difficulty with this interpretation is that the absorption band corresponding to the 4980 Å band is weak; it is certainly less than 100 cm^{-1} . This is in marked contrast to the values of about 10^5 cm^{-1} expected for allowed exciton transitions and found experimentally for the first absorption band in alkali and silver halides which is usually attributed to the creation of excitons.

An alternative explanation for this 4980 Å band is that it is connected with a low concentration of imperfections which lead to transitions of smaller energy than the normal band gap. Absorption at 4980 Å leads to excitation and subsequent luminescence of this center; under ultraviolet excitation, the recombination of free electrons and holes at this center may lead to the edge emission.

An argument for the exciton mechanism results from an analysis of the spacing of the edge emission lines. It has been shown⁴ that this spacing corresponds closely to interaction with the longitudinal optical vibrations of the lattice. The frequency of these vibrations may be computed from the frequency of the peak of the infrared absorption and the static and high-frequency dielectric constants.¹² In ZnS the observed spacing of the emission lines is 0.045 eV while the energy of the longitudinal optical vibrations is computed to be 0.043 eV. Corresponding figures for ZnO are 0.071 eV and 0.069 eV. It is not possible to make this same comparison for CdS since the infrared absorption peak has not been measured for this material; however, it appears

reasonable to assume that in this case also the spacing corresponds to a longitudinal optical vibrational frequency.

On the exciton model, the luminescence occurs in the pure lattice and vibrational interactions should be characteristic of the pure lattice, as they are observed to be.

If, however, the luminescent transition occurs between highly localized states of an imperfection, then the vibrational frequencies would be those characteristic of the imperfection and would not necessarily be the same as those of the pure lattice. Local interactions of this sort have been shown to be sizable in the case of KCl:Tl.¹³ On the other hand the optical properties of boron in silicon have been treated using interactions with the normal lattice vibrations.¹⁴ The type of interaction will certainly depend on the degree of localization of the initial and final wave functions describing the transition. In KCl:Tl both the initial and the final state are well localized, the usual configuration coordinate model seems satisfactory, and the vibrational energy quanta are not identical to those of the lattice modes. In Si:B the high dielectric constant leads to a large spatial extent of the electronic wave function and the interaction with lattice oscillations involves a sampling of a sizable region of the crystal so that the normal lattice vibrations are the natural ones to expect to be important. The case of CdS is an intermediate one, but from the fact that the emission is almost as energetic as the band gap, it is clear that a charge carrier making the transition at the imperfection would be only very slightly bound in its excited state, if at all. This result, coupled with the related circumstance of the good-sized dielectric constant of CdS, indicates a spatially extended wave function, which, as in Si:B, implies that the important interactions are with the normal modes of lattice oscillation.

In addition to the edge emission lines in CdS with spacing of 0.040 eV as shown in Fig. 1, another weaker set of lines has been found with the same spacing as the main set but displaced from it by 0.025 eV to the high-energy side.⁶ A suggestion has been advanced that this weaker set of lines corresponds to additional interactions with transverse vibrational modes of the lattice⁴ and this explanation would be equally applicable to the exciton model and to an imperfection with sufficiently diffuse wave functions. The ratio of the energy separation between the two sets of lines to the energy of the transverse optical vibrations is 1.04 in ZnO but is only 0.78 in ZnS. Using this explanation there would be either 0 or 1 transverse phonon emitted during an optical transition and 0, 1, 2, longitudinal phonons emitted; however, no line is observed corresponding to the case where no phonon is emitted. On

⁹ Sommers, Berry, and Sochard, *Phys. Rev.* **101**, 987 (1956).

¹⁰ F. Seitz, *Phys. Rev.* **76**, 1376 (1949).

¹¹ H. Fröhlich and F. Seitz, *Phys. Rev.* **79**, 526 (1950).

¹² Lyddane, Sachs, and Teller, *Phys. Rev.* **59**, 673 (1941).

¹³ F. E. Williams, *J. Chem. Phys.* **19**, 457 (1951).

¹⁴ M. Lax and E. Burstein, *Phys. Rev.* **100**, 592 (1955).

the exciton model, it has been argued that the density of states is small for this case.⁴

Another explanation has been proposed for the two sets of lines using a configuration coordinate model.⁶ The main set of lines would correspond to a transition from the lowest vibrational level of the excited state to various vibrational levels of the ground state, and the smaller set of levels would correspond to transitions from the second vibrational level of the excited state. The vibrational frequency of the ground state would correspond to an energy of 0.040 eV and that of the system in the excited state to an energy of 0.025 eV. As mentioned above, it has subsequently been shown that the main lines are due to interactions with lattice photons. Under these conditions it appears difficult to explain another set of lines as being due to interaction with a localized vibrational mode. Also it is probably a poor approximation to use a configuration coordinate concept in the usual way to describe a center with energy levels so close to the band edges. Finally, it has been pointed out that the equilibrium population of the second vibrational level of the excited state should be negligible at 4°K.⁴

Since neither of these explanations seems completely satisfactory, other explanations may be proposed. One possibility is that there are two slightly different impurity centers; the one of highest concentration leads to the main lines and the other to the weaker set. The separation of the electronic energy levels of these centers would differ by 0.025 eV and the transitions in both would interact primarily with the longitudinal optical vibrations of the lattice. It is also conceivable that the two sets of lines arise from two excited electronic states of a center which have an energy difference of 0.025 eV. These possible explanations do not appear to be in disagreement with experiment.

Simultaneous measurements have also been made on the rise and decay of edge luminescence and photoconductivity in CdS crystals.⁷ The results of these measurements at 4°K have been interpreted to favor the imperfection model of edge emission. In this experiment a one-millisecond pulse of ultraviolet exciting light is placed on the crystal after 100 milliseconds in the dark and the process continues to be repeated. It is found that the rise time of photocurrent is much slower than that for luminescent emission. On the exciton model, the number of excitons formed should be proportional to the product of the number of free electrons and the number of free holes. Even if the number of free holes should reach its saturation value instantly with the application of light, luminescence should follow the photocurrent closely since electrons are the principal current carriers as shown by Hall effect measurements. A slower rise of the density of holes would lead to luminescence that rose more slowly than conductivity. However, it appears difficult to

imagine a situation in which the luminescence due to excitons could grow more rapidly than the photoconduction current as is observed in this case. On the other hand, the similarity of the rise and decay times of edge luminescence to that of CdS:Ag leads to the idea that edge luminescence arises from the recombination of a free hole with a trapped electron.⁷ Such a model^{15,16} may offer a somewhat simpler interpretation of rise and decay times than does an older model¹⁷⁻¹⁹ in which luminescence is attributed to the recombination of a free electron and a trapped hole; in the case of CdS:Ag a variety of experiments tends to support this new model.^{15,16,20}

Finally, there exists evidence that slow annealing of the crystals destroys edge luminescence in CdS,²¹ as does heating in an atmosphere of sulfur.²² Heating in cadmium vapor appears to have no effect.²²

In addition to the experiments discussed in the foregoing, there exist two other pieces of information which have a bearing on the problem. First, it is found that edge luminescence may be observed in sulfide preparations even when fired in flux, ground to a powder, or with low concentrations of Ag activator.⁸ If the recombination of excitons were responsible for the luminescence, it would be remarkable that such drastic treatment should not greatly change the luminescent efficiency, since excitons interact strongly with many imperfections expected to be present under such conditions.²³ It would be particularly remarkable in view of the above-mentioned²¹ circumstance that such gentle treatment as slow annealing of the crystal destroys the luminescence. The second observation enables us to conclude that most of the excitons, if there are any, are not produced directly upon irradiation with light, but must come to exist by the junction of free electrons and holes, probably near an imperfection. That this is so is clear from the fact that the crystals are efficiently photoconductive for excitation wavelengths less than about 4900 Å at He temperatures. In the next section, another demonstration of this conclusion is presented.

III. EXPERIMENTAL RESULTS

Inasmuch as no really definite conclusion could be reached on the basis of the evidence reviewed in the last section, an experiment was undertaken which seemed capable of deciding the question of the necessity of imperfections in the luminescent process. According to one model, in which the luminescence is presumed to arise from the recombination of free holes with

¹⁵ J. Lambe and C. C. Klick, *Phys. Rev.* **98**, 909 (1955).

¹⁶ J. Lambe, *Phys. Rev.* **100**, 1586 (1955).

¹⁷ M. Schön, *Z. Physik* **119**, 463 (1942).

¹⁸ H. A. Klasens, *Nature* **158**, 306 (1946).

¹⁹ Klasens, Ramsden, and Quantie, *J. Opt. Soc. Am.* **38**, 60 (1948).

²⁰ A. W. Smith, *Phys. Rev.* **101**, 1263 (1956).

²¹ G. Wendel, *Fortschr. Physik* **1**, 45 (1953).

²² M. E. Bishop, unpublished work referred to in reference 7.

²³ D. L. Dexter and W. R. Heller, *Phys. Rev.* **84**, 377 (1951); D. L. Dexter and J. H. Schulman, *J. Chem. Phys.* **22**, 1063 (1954).

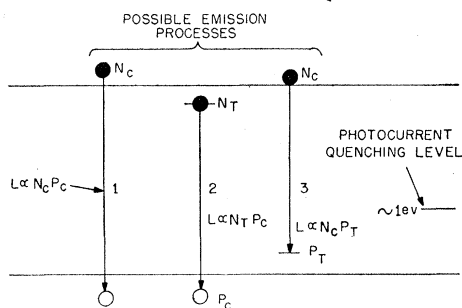


FIG. 2. Schematic representation of three possible recombination processes leading to edge emission. In process one, free electrons and free holes recombine either directly or by formation of excitons. In process two, trapped electrons recombine with free holes. In process three, free electrons recombine with trapped holes.

trapped electrons, edge luminescence should be stimu-
lable by the furnishing of free holes²⁴⁻²⁷ by infrared
radiation in a previously excited crystal. This predic-
tion, though not necessarily inconsistent with other
models, is at least not a natural one to make on the
basis of these models. As shown below, this prediction
was experimentally verified. That is, in a previously
excited crystal at liquid He temperatures, radiation of
about half the energy required to produce an exciton
gives rise to edge luminescence. Thus, whatever
excitons may come to exist by infrared radiation are
produced by the joining up of free electrons and holes,
and not directly, in accord with the tentative conclusion
at the end of the last section. This result will be used in
Eq. (1) below.

In the experimental work to be described here, an
attempt is made to decide among the three emission
processes illustrated in Fig. 2. Process number one is the
recombination of free electrons and holes either directly
or into excitons which then luminesce. The luminescent
intensity L is then governed by the relation

$$L \propto N_c P_c, \quad (1)$$

where N_c is the instantaneous number of free electrons
and P_c is the instantaneous number of free holes. Pro-
cess number two corresponds to a recombination of
a trapped electron with a free hole and for this case
the luminescent intensity is given by

$$L \propto N_T P_c, \quad (2)$$

where N_T is the number of trapped electrons. Finally,
process number three involves the recombination of a
free electron with a trapped hole and the luminescent
intensity is given by

$$L \propto N_c P_T, \quad (3)$$

where P_T is the concentration of trapped holes.

²⁴ A. E. Hardy, J. Electrochem. Soc. **87**, 355 (1954).

²⁵ A. Rose, RCA Rev. **12**, 362 (1951).

²⁶ E. A. Taft and M. H. Hebb, J. Opt. Soc. Am. **42**, 249 (1952).

²⁷ S. Tutihasi, Bull. Am. Phys. Soc. Ser. II, **1**, 110 (1956); J. Opt. Soc. Am. **46**, 443 (1956).

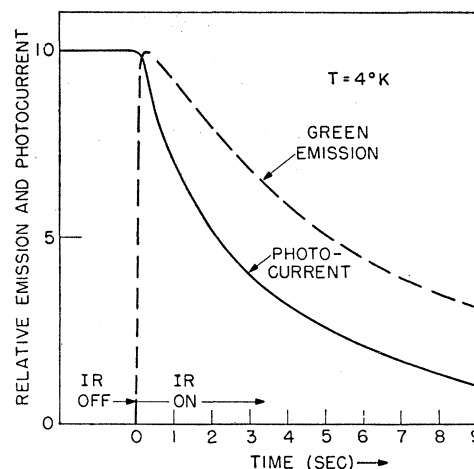


FIG. 3. Variation of edge emission and electronic conductivity with time after a CdS crystal, which has previously been excited with light in its fundamental absorption band, is irradiated with infrared light in the quenching band.

In Fig. 2 there is also drawn a level about 1 eV above
the filled band. This level is due to a "quenching center"
with well-known properties²⁴⁻²⁷ but undetermined
origin. Excitation with light of energy near 1 eV excites
electrons from the filled band into the quenching
centers thus producing free holes. These holes recom-
bine with electrons from the conduction band and
quench the photoconductivity associated with excita-
tion by more energetic radiation.

In these experiments a single crystal of CdS has
been investigated both for edge luminescence and for
conductivity at 4°K. The crystal is first illuminated
with ultraviolet light which is then removed. As is
typical of CdS, the luminescence quickly decays to
zero but the conductivity decays much more slowly.
While the conductivity is decaying, the crystal is
irradiated with light in the quenching band to produce
free holes. Figure 3 shows the results. Green edge
emission is observed. The luminescence rises quickly
and then decays more slowly than the photocurrent,
which is quenched. Interruption of the infrared light
always shows the same rapid rise or decay of the green
emission. This is important in that it demonstrates
that the time constant for the disappearance of free
holes is comparatively short, less than 0.1 second, so
that the build-up of free holes occurs in a comparable
time. In Fig. 4 current and luminescent intensity are
plotted on a logarithmic scale for almost two minutes,
at which time the phosphor is nearly exhausted. At all
times, the luminescence decay is less rapid than that
of the current.

These results may now be compared with the three
recombination processes of Fig. 2. Measurements of
Hall effect in CdS^{28,29} show that the conduction is

²⁸ R. W. Smith, RCA Rev. **12**, 350 (1951).

²⁹ Kroger, Vink, and Volger, Physica **20**, 1095 (1954); Phillips
Research Repts. **10**, 39 (1955).

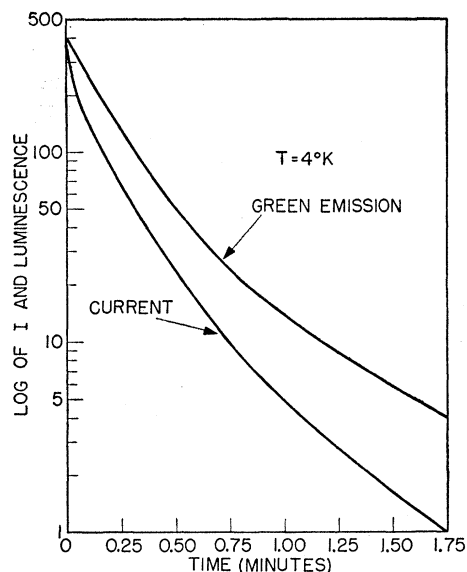


FIG. 4. Semilogarithmic plot of the variation of edge emission and conductivity in a CdS crystal during infrared irradiation after prior irradiation in the fundamental absorption band. At all times until exhaustion of the phosphor, the decay of edge emission is less rapid than that of the conductivity.

primarily the result of the free electrons. Attempts to find conductivity or rectification effects when holes alone are produced in undoped CdS by irradiation in the quenching center have been unsuccessful.⁷ Also, electromodulated photoluminescence experiments indicate a very much greater displacement distance for free electrons than for free holes.³⁰ It is probably an excellent approximation, then, to take the variation of current with time as being directly proportional to the variation of the number of conduction electrons. Thus there is an experimental measure of N_e . No direct measure of the number of free or trapped holes is available but an important characteristic of these populations can be deduced. As mentioned above, the rapid rise and fall of luminescence with changes in irradiation intensity in the quenching center indicate that an equilibrium concentration of holes is reached quickly. Furthermore, the number of free or trapped holes will decrease with time under infrared excitation or at most stay essentially constant for short periods of time. It seems clear that the hole concentration will not increase with time.

In recombination mechanism 1, then, N_e is given by the current decay and P_e is constant or decreasing so that the luminescence should decrease as fast as or faster than the conductivity. The same argument is true of process 3. Since the luminescence does not decrease as fast as the conductivity these experiments eliminate processes 1 and 3. This leaves process 2 for which no such difficulty exists. This experiment would then argue that edge luminescence is due to the recombination of a free hole with a trapped electron.

³⁰ R. E. Halsted, Phys. Rev. **99**, 1897 (1955).

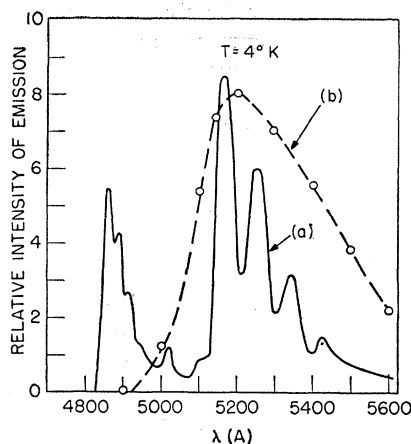


FIG. 5. Luminescent emission of a CdS crystal at 4°K. Curve (a) is for excitation with intense light in the fundamental absorption band and is taken with high resolution in the measuring instrument. Curve (b) is the emission resulting when a CdS crystal is stimulated with infrared light in the quenching band after previous irradiation in the fundamental absorption band. Because of the weak emission in the second case, the resolution of the measuring equipment was drastically reduced and the edge emission fine structure could not be observed.

In Fig. 5 the luminescence spectrum of the crystal used in these measurements is given in curve (a) for ultraviolet excitation; the emission on irradiation in the quenching center is given in curve (b). Because of the faint emission in the latter case, the resolution of the measurement had to be drastically reduced. This accounts for the absence of lines and the somewhat broader spectrum. It seems clear, however, that the peak of the emission is the same and that the emission observed is truly edge emission. It is interesting to note that the short-wavelength bands do not appear in curve (b). Since in this case the absorption of infrared light is small and excitation is throughout the crystal, surface recombination would be reduced from the case where the ultraviolet light is absorbed very close to the surface. This experiment gives added weight to the argument that the short wavelength lines are the result of surface effects.^{3,31}

Nothing has been said about the details of the recombination process after the free positive hole has joined the trapped electron. All one knows experimentally is that it does join, and that emission occurs very shortly thereafter. It is conceivable that the electron and hole leave the trapping center together, as an exciton, and recombine elsewhere. From the lack of strong dependence of luminescent efficiency on the impurity content and physical maltreatment, one would surmise that recombination occurs either at the center or very near to it. Certainly it appears that excitons are not necessary in an interpretation of these results, and equally certain that excitons without trapping sites are not sufficient.

³¹ L. R. Furlong and C. F. Ravilius, Phys. Rev. **98**, 954 (1955).

If edge luminescence involves an imperfection, as seems evident, it is important to attempt to identify the center. Although several suggestions have been made,^{5,7,32} it does not appear possible to be certain about the atomic nature of the center at present. It may, however, be worthwhile to describe the evidence and point out the difficulties of making an assignment.

Edge luminescence is observed in "pure" materials; addition of chemical impurities does not enhance the emission but eventually reduces it. From this one might conclude that the imperfection responsible for edge emission in CdS is not a chemical impurity. The effects of heating in sulfur or cadmium vapor referred to previously²² would indicate that the center is associated with a sulfur ion vacancy or an interstitial cadmium atom or ion. However, it is generally now believed that most impurities are substitutional rather than interstitial in ZnS³³ and ZnO.³⁴ The depth of the trap does not prove to be especially helpful in the determination of a center. Using a hydrogenic model of a center, the binding energy of an electron to a center with a single positive charge is $13.7/n^4$ ev, where n is the index of refraction. For CdS this would be approximately 0.3 ev. The observed thermal activation energy for an electron bound to a chlorine ion in CdS which acts as a single positive charge is only about 0.05 ev.³⁵ On the other hand the optical trap depth of an electron bound to a neutral Ag_+S_- center, which might be expected to be even less, is about 0.4 ev.¹⁵ It does not appear, therefore, that simple arguments about Coulomb binding are decisive.

From the similarity of the rise and decay of the luminescence and photoconductivity of edge lumines-

cence in CdS with that of CdS:Ag,⁷ it might be inferred that the empty edge luminescence center is neutral as is the Ag_+S_- center. Also, sensitive magnetic measurements have been made on pure sulfide samples at 4°K³⁶ which failed to show evidence for paramagnetic centers. These considerations are in agreement with the model of a sulfur vacancy with two electrons. On this model a third electron would be trapped at the sulfur vacancy and the recombination of this electron with a free hole would lead to edge luminescence. This picture does not appear to be compatible, however, with data on semiconducting properties of CdS with sulfur vacancies.³⁵ It is argued that a sulfur vacancy with electrons has a binding energy of 0.03 ev for a second electron. The possibility of then trapping a third electron does not seem to be reasonable. As a result of these factors it does not seem possible to give a conclusive argument for the identity of the center at this time.

IV. CONCLUSION

The experimental and theoretical evidence on edge luminescence in CdS appears to indicate the following.

1. Edge emission occurs as the result of the recombination of a free hole with an electron trapped at some imperfection.
2. The electronic transition interacts primarily with the longitudinal optical vibrational modes of the pure lattice rather than with any which might be peculiar to the imperfection.
3. The weaker set of emission lines may be due to another imperfection with slightly different energy levels, or to a higher excited state of the center.
4. Emission to the short-wavelength side of 5000 Å is due to recombination at the surface.
5. With present information, no conclusive argument can be made as to the identity of the center.

³² J. S. Prener and F. E. Williams, *Phys. Rev.* **101**, 1427 (1956).

³³ A. Kroger and J. F. Hellingman, *J. Electrochem. Soc.* **93**, 156 (1948); **95**, 68 (1949); F. A. Kroger and J. Dikhoff, *Physica* **16**, 297 (1950).

³⁴ S. E. Harrison, *Phys. Rev.* **93**, 52 (1954).

³⁵ Kroger, Vink, and van den Boomgaard, *Z. physik. Chem.* **203**, 1 (1954).

³⁶ R. Bowers and N. T. Melamed, *Phys. Rev.* **99**, 1781 (1955).