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Photoelectronic Processes in ZnS Single Crystals*

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A simultaneous series of luminescence and photoelectronic measurements as a function of excitation energy, intensity, and temperature were made on ZnS:Cu:Cl single crystals grown by a chemical-transport method. Hall-effect measurements show that the charge carriers under steady-state excitation are electrons, and optical quenching of thermally stimulated luminescence and conductivity is found to be identical with steady-state optical quenching. Various models, such as those of Lambe and Klick, Klasens and Schön, Williams and Prener, and those involving unassociated pair transitions, are examined in view of all the evidence available, including the present measurements. It is concluded that a basic Klasens-Schön model is the most suitable. The measurements also show that the centers responsible for long photoconductivity lifetimes, i.e., the sensitizing centers, are not the same as the centers responsible for luminescence, i.e., luminescence-activator centers. Similar results are indicated in less detailed studies of ZnS:Cl and ZnS:Ag:Cl single crystals.

INTRODUCTION

THE luminescence of impurity- or imperfection-activated ZnS has been the subject of extensive investigation in the last two decades. Earlier research on powder samples has been succeeded to a large extent by research on single crystals. In spite of this effort, the following aspects of the luminescence centers remain to some extent uncertain: (1) their chemical and structural identities, (2) the location of their energy levels in the forbidden gap, (3) the role of free electrons and holes in the radiative recombination processes at these centers, and (4) their role in the photoconductivity process.

In contrast to other types of luminescence systems, such as KCl:Tl or KBr:F, in which the absorption and emission processes are confined to a localized center, luminescence in ZnS-type materials involves the transfer of charge between different centers. The determination of the sign of the charge carriers involved in luminescence is one of the key factors in understanding the luminescence mechanism. This possibility has not been fully exploited in past investigations because of difficulties in making reliable photoconductivity measurements on powders, in making reliable ohmic electric contacts to high-resistivity crystals, and in making Hall- and photo-Hall-effect measurements on high-resistivity crystals. Experimental methods have usually involved, principally, optical absorption, emission, and thermally stimulated luminescence (glow curves). When the results of such measurements alone are interpreted in terms of a band model, the data are sufficiently ambiguous that several different models can be constructed, each of which appears adequately to describe the data.[1]

Models constructed to describe luminescence processes in ZnS have been based on the nature of the luminescence-producing recombination transition. Three basic models are shown in Fig. 1. In the Klasens-Schön model,[2,3] luminescence results from the recombination of a free electron with a hole captured at an imperfection. In the Lambe-Klick model,[4] luminescence results from the recombination of a free hole with an electron captured at an imperfection. In the Williams-Prener model,[5,6] the luminescence results from the recombination of an electron captured by the donor member of an associated donor-acceptor pair with a hole captured by the acceptor member of the pair. In the more recent versions of the pair-recombination model, which we shall call the unassociated pair model,[7–11] luminescence results from the recombination of an electron captured by the donor member of an unassociated pair with a hole captured by the acceptor member of the pair, the actual energy and transition probability for the transition depending on the pair spacing in the crystal. It might be desirable at least to consider for completeness the possibility of a single-level scheme, looking like a Klasens-Schön model, in which the single level is to be related to an imperfection pair or complex[12]; we might refer to this as a one-level pair representation in contrast to the two-level representations of the Williams-Prener or unassociated pair models.

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Table I. Impurity content of ZnS crystals.

Impurity	ZnS:Cu:Cl(%)	ZnS:Ag:Cl(%)	ZnS:Cl(%)
Cu	0.07	0.002	0.0008
Ag	<0.0005	0.04	<0.0008
Si		<0.01	0.01
Mg		0.001	
Al		0.002	
Ca			0.001

In the present investigation, photoconductivity and luminescence were measured simultaneously whenever possible, and the sign of the free carriers was determined by Hall-effect measurements or some related technique. In addition to establishing criteria by which to judge the various possible models, the simultaneous luminescence and photoconductivity measurements also help to answer the question of the relative roles of activator centers and sensitizing centers in the same crystal. Some of the measurements described in detail for ZnS:Cu:Cl crystals were also carried out on ZnS:Cl and ZnS:Ag:Cl crystals with similar results.

EXPERIMENTAL

Crystal Growth

The technique of chemical-transport crystal growth, described by Samelson[13] and others[14,15] for ZnS, enables the growth of crystals at considerably lower temperatures than those needed for sublimation or melt growth, thus providing improved conditions for crystal purity and perfection. The ZnS powder charge was luminescence grade RCA 33-Z-19, and the transport agent was HCl gas, obtained by dehydrating HCl with concentrated H_2SO_4 and acetone–dry-ice cold traps. Crystal growth occurred at about 875°C, and single crystals of average size $5\times2\times2$ mm^3 were obtained.

Both x-ray diffractometer readings and back-reflection Laue patterns showed these crystals to have the wurtzite structure. This structure was found in crystals grown at as low a temperature as 750°C, in spite of the fact that the accepted temperature for the sphalerite-wurtzite transformation is 1020°C. There have been several reports on a strong dependence of this transition temperature on impurity content.[13,16] In fact, the accepted value of 1020°C was reported by Allen *et al.*[17] on ZnS containing 0.15% Fe.

No evidence was found for appreciable stacking-fault inhomogeneities, as is often reported for high-temperature–grown ZnS crystals, either by optical examination under polarized light or by photovoltaic-effect test.

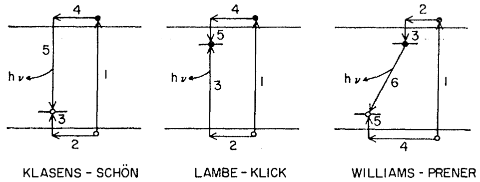

Fig. 1. Basic models for luminescence and photoconductivity in ZnS-type materials. The numbers indicate the chronological order of the transitions, except that in the Williams-Prener model, steps 4 and 5 could precede steps 2 and 3. The luminescence-emission transition is indicated in each model. The picture for the Williams-Prener model may be used also to describe a two-level unassociated-pair model, and the picture for the Klasens-Schön model may be used also to describe one-level pair models.

For incorporation of copper or silver impurity, a powder of these metals was mixed with the ZnS charge powder in an agate mortar and introduced into the reaction tube. It is believed that Cu and Ag were transported as chlorides during the crystal growth.

The ZnS:Cu:Cl crystals investigated most extensively were chosen from that batch with the least amount of undesired impurities. Spectrographic analyses are listed in Table I. It is assumed that a considerable proportion of Cl, of the same order as the Cu, was incorporated in the crystals during growth.

Measurements

Ohmic contacts to the ZnS crystals were made by heating indium metal in contact with the crystals in hydrogen.[18] Excitation sources were an Osram HBO 500-W Hg lamp and a GE 642-W Sun Gun lamp, used either directly with filter or with a Bausch and Lomb monochromator, as indicated. Emission spectra were measured either with the Bausch and Lomb monochromator and an RCA 1P21 photomultiplier tube, or with Eastman Kodak 103a-J plates. Photocurrents were measured with a Keithley micromicroammeter.

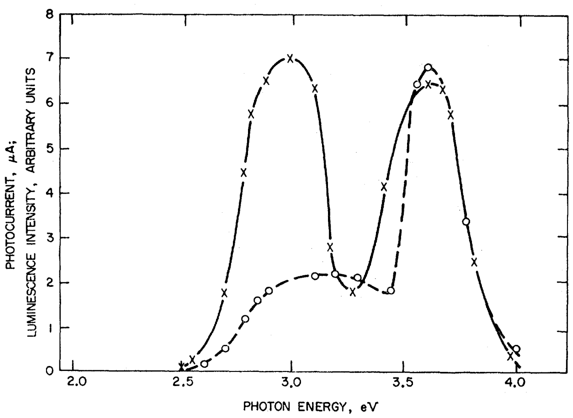

Fig. 2. Excitation spectra for photoconductivity (solid curve) and luminescence-emission intensity (dashed curve) for a ZnS:Cu:Cl crystal at 90°K.

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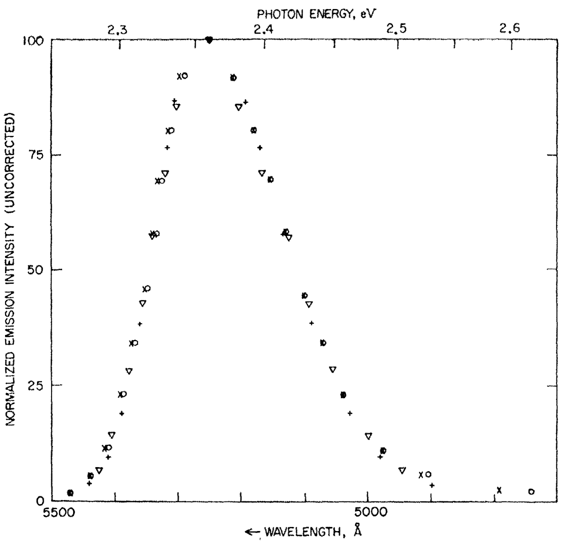

FIG. 3. The emission spectrum of a ZnS:Cu:Cl crystal as a function of excitation intensity. Excitation was by an Osram HBO 500-W Hg lamp through a Corning CS 7-60 filter. Points shown are taken from *uncorrected* densitometer traces on Eastman Kodak 103a-J film. Intensities were 100% (o), 20% (×), 8.2 %(▽), and 0.81% (+).

RESULTS FOR ZnS:Cu:Cl

Excitation Spectra

Spectral response curves of photoconductivity and luminescence at 90°K are shown in Fig. 2. The threshold energy is the same for both photoconducitivity and luminescence. Its value of 2.5 eV indicates a level lying 1.2 eV above the valence band, since the excitation produces free electrons as shown by Hall-effect measurements.

The magnitude of the photoconductivity in the extrinsic excitation region shown in Fig. 2 corresponds to a high-gain photoconductivity response involving photoconductivity sensitizing centers. Independent measurements[19] establish that the electron-capture cross section of these centers is of the order of 10^{-21} cm^2. Since the extrinsic excitation involves levels lying 1.2 eV above the valence band, extrinsic photoexcitation at 90°K produces free electrons and bound holes, which are not free to move from the center where excitation was initially produced. Since extrinsic excitation at 90°K does correspond to an electron lifetime characteristic of sensitizing centers, it may be concluded that sensitizing centers are being excited in the extrinsic excitation band. Whether the luminescence excitation is from the same centers, or from other centers with about the same energy-level position, cannot be determined by the present data alone.

Emission Spectra

The emission spectrum of ZnS:Cu:Cl is known to have a marked dependence on the relative concentration of Cu and Cl[20]: A green band results from Cu and Cl in equal proportions, a blue band for slight excesses of Cu over Cl of the order of 2:1, and a red band for heavy excesses of Cu over Cl. In the crystals of this investigation, the green band is dominant, with a maximum at 2.35 eV and a half-width of 0.32 eV. The spectrum, obtained by excitation through the monochromator, is essentially independent of temperature between 88 and 407°K, and of exciting wavelength between 3300 and 4390 Å; results are summarized in Table II.

Measurements were also made of the variation of the emission spectrum with excitation intensity, excitation being directly by the filtered HBO 500-W lamp, over an intensity range of 125 to 1. The results are summarized by the normalized data of Fig. 3. If a shift in the maximum of the emission band is present at all, it does not exceed 5 Å per order of magnitude of excitation intensity. A slight decrease in band half-width with increasing excitation intensity is found, corresponding to about 5% for two orders of magnitude of intensity variation.

Photo-Hall Effect

Photo-Hall measurements were made with an apparatus similar to one previously described,[21] in order to determine the sign of the charge carriers in steady-state photoconductivity. The results show clearly that these charge carriers are electrons for all exciting wavelengths. The magnitude of the Hall mobility was found to vary with excitation intensity as in CdS.[22] Data are given in Table III for a typical crystal. The values of Hall mobility obtained are in agreement with previously reported values.[23]

Optical Stimulation and Quenching

Infrared radiation, applied simultaneously with shorter wavelength radiation, often produces a marked change in the photoconductivity and luminescence of

TABLE II. Characteristics of spectral emission of ZnS:Cu:Cl crystals (excited through the monochromator).

		Energy at maximum (eV)	Half-width (eV)
		$\lambda = 3300$ Å	
T(°K)	88	2.35	0.32
	297	2.36	0.32
	407	2.36	0.35
		$T = 85$°K	
λ(Å)	3300	2.35	0.32
	4390	2.35	0.31

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ZnS single crystals.[24–26] The dynamic behavior of the luminescence emission and photoconductivity upon irradiation with infrared in addition to intrinsic excitation is shown in Fig. 4. At low temperatures, there is both a stimulation and a quenching of the luminescence, the stimulation having the faster time constant; under the same conditions, the photoconductivity shows only quenching. At room temperature, there is no stimulation in the luminescence, and the photoconductivity-quenching effect is much smaller. At higher temperatures, the photoconductivity is actually stimulated, and the luminescence is quenched.

The decrease in the photoconductivity quenching at higher temperatures is the result of the presence of thermal quenching, as is shown in a later section. Holes released by thermal quenching are no longer available for optical quenching. The stimulation of photoconductivity at 364°K could be the result of electron-trap emptying by the infrared, or possibly even the result of increased electron lifetime associated with the removal of holes from luminescence centers by the infrared.

The dissimilarity between the transient behavior of the photocurrent and the luminescence emission is definite evidence that the centers responsible for luminescence and the centers responsible for long electron lifetimes, i.e., sensitizing centers, are not identical. Other evidence for this conclusion is that the photoconductivity-quenching spectrum is quite similar in ZnS crystals with different luminescence-emission bands. The possibility that the luminescence activator and the photoconductivity sensitizing center may be physically different imperfections with quite similarly located energy levels has been suggested from work in CdS.[27]

The interpretation of the data of Fig. 4 proceeds as follows: At low temperatures, infrared excites electrons from the valence band to hole-occupied sensitizing centers. These released holes are captured partially by luminescence centers, the recombination traffic through luminescence centers increases, luminescence emission is stimulated initially, and photoconductivity is quenched. If the luminecsence center were the only important recombination center, the luminescence would decrease to the original value after the initial rise. Actually, the luminescence intensity decreases to a value about 10% below the original value. This result indicates that a nonradiative recombination center is also present in the crystal, the relative importance of which, in the recombination processes, is increased by the infrared. It is possible to have optical quenching of luminescence without actually exciting holes out of the luminescence centers, especially if there is a large concentration of nonradiative recombination centers in the crystal. Almost none of the investigations involving optical quenching of luminescence has allowed for this possibility.[24,25,28–30]

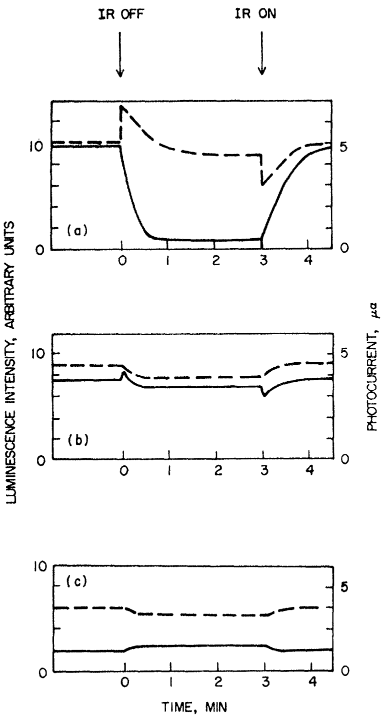

FIG. 4. Dynamic behavior of luminescence-emission intensity (dashed curves) and photocurrent (solid curves) in the presence of 7000 Å infrared radiation for a ZnS:Cu:Cl crystal. (a) 123°K, (b) 295°K, (c) 364°K.

TABLE III. Variation of Hall mobility with excitation intensity ($\lambda = 3650$ Å; $T = 300$°K; ZnS:Cu:Cl).

Hall mobility (cm^2/V sec)	Free-electron concentration (cm^{-3})	Location of electron quasi-Fermi level (eV)
193	2.3×10^{12}	0.37
180	1.3×10^{12}	0.39
159	4.4×10^{11}	0.42
124	1.2×10^{11}	0.45
120	5.0×10^{10}	0.47

If quenching of luminescence can be observed without concurrent quenching of photoconductivity or with enhancing of photoconductivity, then it can be concluded that holes are being optically excited out of luminescence centers. This is the case at higher temperatures, as is shown in Fig. 4. Under all conditions, therefore, we conclude that infrared is optically exciting holes out of both sensitizing centers and luminescence centers, an expected result of the fact that both have a similarly located energy level.

In order to represent the dependence of stimulation and quenching on infrared photon energy, we define a quantity R as the percent optically induced change for both luminescence and photoconductivity. Plots of R

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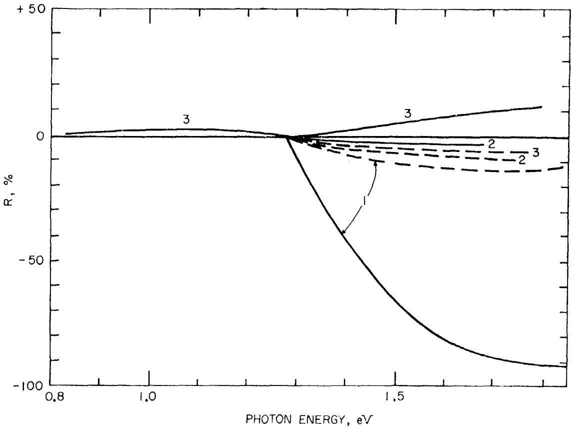

FIG. 5. Percent optically induced change as a function of secondary photon energy for a ZnS:Cu:Cl crystal. Primary excitation was by 3650 Å ultraviolet. Negative R corresponds to quenching, positive R to stimulation. Solid curves are for photocurrent, dashed curves for luminescence-emission intensity. (1) 123°K, (2) 295°K, (3) 364°K.

are shown in Fig. 5. A number of investigators have reported the quenching of luminescence and photoconductivity in ZnS.[24,25,28–31] All report two quenching bands with maxima at about 0.8 and 1.3 μ, the same for both luminescence and photoconductivity. In our ZnS:Cu:Cl crystals, quenching at 1.3 μ (0.95 eV) was not found. The magnitude of the luminescence quenching appears to be smaller in our crystals than in those previously reported, a fact than can be interpreted as evidence for the purity (density of nonradiative recombination centers is not very high) of our crystals. The threshold energy for optical quenching of photoconductivity and luminescence appear to be very close together, lying between 1.25 and 1.3 eV. This implies that the hole-occupied luminescence and sensitizing centers lie about 1.2–1.3 eV above the valence band, a value which is consistent with the excitation data of Fig. 2.

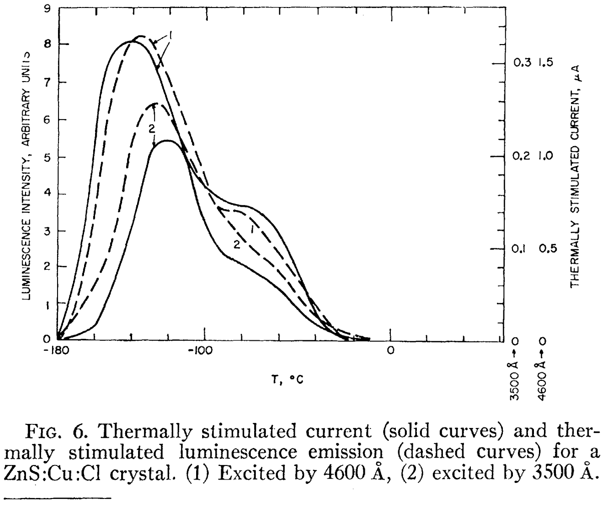

FIG. 6. Thermally stimulated current (solid curves) and thermally stimulated luminescence emission (dashed curves) for a ZnS:Cu:Cl crystal. (1) Excited by 4600 Å, (2) excited by 3500 Å.

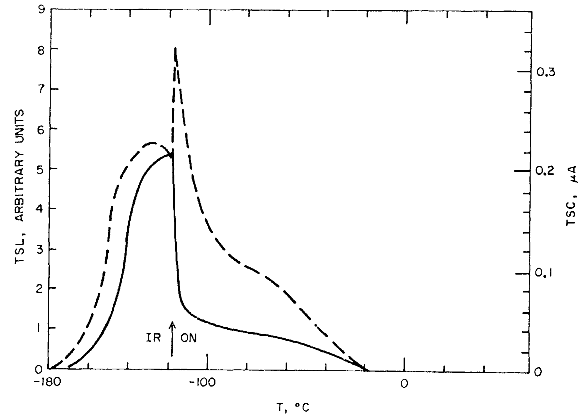

FIG. 7. Effect of infrared radiation in the quenching range on the thermally stimulated luminescence emission (dashed curve) and the thermally stimulated current (solid curve) for a ZnS:Cu:Cl crystal.

Thermally Stimulated Conductivity and Thermally Stimulated Luminescence

The additional luminescence emission or conductivity produced by carriers thermally freed from traps provides information about both the trapping centers and the relation between photoconductivity and luminescence processes. Results for a ZnS:Cu:Cl crystal are given in Fig. 6. They suggest a close correlation between the stimulation of the current and of the luminescence. Release of either electrons or holes from traps must be responsible for both luminescence and current.

The sign of the charge carriers in thermally stimulated conductivity (TSC) was determined by testing the effect of infrared in the photoconductivity-quenching band on the TSC. A typical result is given in Fig. 7. The effect of infrared is found to be the same with the (TSC) and the thermally stimulated luminescence (TSL) as it was for the steady-state photoconductivity and luminescence, known to be associated with free-electron flow by Hall-effect measurements. It may be concluded, therefore, that the TSC and the TSL both involve electrons as the charge carriers.

Attempts were made to measure the Hall effect of the carriers released in the TSC measurement. Experimental difficulties were great, and only the qualitative observation of a small n-type Hall voltage could be made.

A comparison of the data of Fig. 6 with investigations of Hoogenstraaten[32] on traps in ZnS indicates that the trap with TSC peak at about −120°C can be associated with the chlorine level. The trap depth calculated from quasi-Fermi-level analysis applied to the maximum is 0.26 eV, and the trap depth determined from decayed TSC plots is 0.28 eV. An approximate value of 10^{17} cm^{-3} is obtained for the trap density.

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Temperature Dependence of Photoconductivity and Luminescence

The simultaneously measured photoconductivity and luminescence for a ZnS:Cu:Cl crystal are given as a function of temperature in Fig. 8. Photoexcitation was by 4100 Å light with a broad slit on the monochromator to minimize effects associated with changes in spectral response with temperature. The general behavior is quite similar to that reported for CdSe crystals.[33] The temperature for the onset of thermal quenching is slightly, but definitely, smaller for the photocurrent than for the luminescence. Since thermal quenching is associated with thermal excitation of holes into the valence band, either the energy level associated with the hole-occupied sensitizing center lies slightly closer to the valence band than that of the luminescence center, or the sensitizing center has a larger capture cross section for holes than the luminescence center.

A notable feature of the data of Fig. 8 is the constancy of the luminescence efficiency over a wide temperature range. This is a significant observation to be considered in deciding between one-level and two-level pair models.

Photoexcitation Intensity Dependence of Photoconductivity and Luminescence

Closely related to the temperature dependence at fixed excitation intensity is the intensity dependence at various temperatures. The difference between the luminescence and the photoconductivity behavior is found again here, this mode of presentation making the difference even more striking. Results are shown in Figs. 9 and 10.

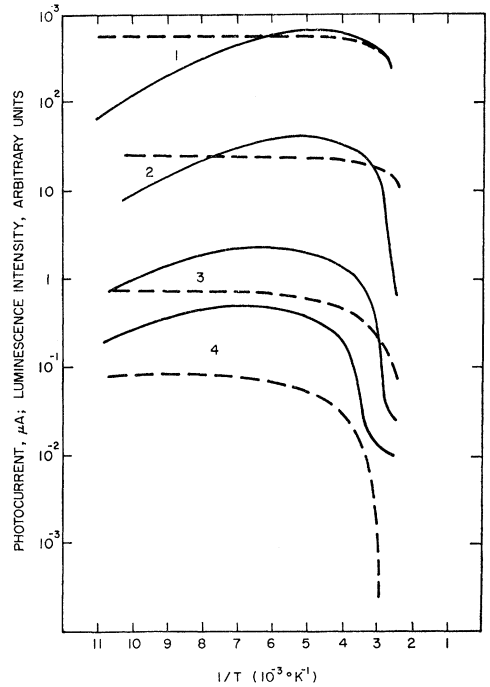

FIG. 8. Temperature dependence of luminescence-emission intensity (dashed curves) and photocurrent (solid curves) for a ZnS:Cu:Cl crystal. Excitation intensity had relative values of (1) 100, (2) 4, (3) 0.18, and (4) 0.036.

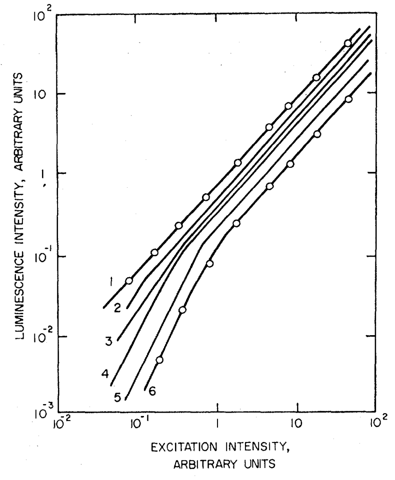

FIG. 9. Variation of luminescence-emission intensity with excitation intensity for a ZnS:Cu:Cl crystal. Temperatures are (1) 98°K, (2) 268°K, (3) 320°K, (4) 350°K, (5) 372°K, and (6) 408°K.

The luminescence intensity varies almost linearly with excitation intensity at all intensities and temperatures where thermal quenching of luminescence is not present. The photoconductivity variation with excitation intensity and temperature is again completely analogous to published data on CdSe.[33] Dussel and Bube[34] have analyzed the problem of superlinearity in a simple model involving a sensitizing center, a fast-recombination center, and trapping levels. Their results show that if the natural logarithm of the excitation intensity at the lower break point of the superlinearity curves is plotted as a function of reciprocal temperature, it is highly probable that the activation energy is the hole ionization energy of the sensitizing centers. Such a plot gives a straight line for the present data, corresponding to an activation energy of 0.75 eV. These results indicate that the thermal ionization energy for

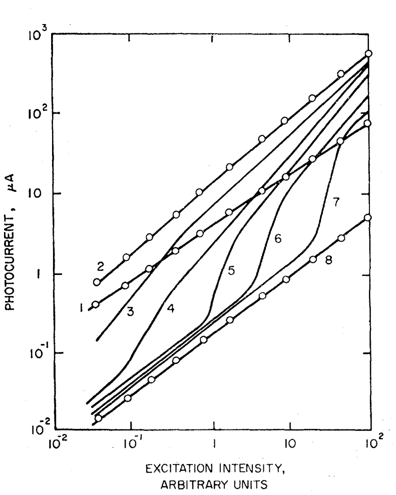

FIG. 10. Variation of photocurrent with excitation intensity for a ZnS:Cu:Cl crystal. Temperatures are (1) 98°K, (2) 187°K, (3) 268°K, (4) 300°K, (5) 320°K, (6) 350°K, (7) 372°K, and (8) 405°K.

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[33] Reference 20, p. 344.

[34] G. A. Dussel and R. H. Bube, J. Appl. Phys. **37**, 13 (1966).

holes is some 40% smaller than the optical ionization energy. Similar measurements on CdS have shown a thermal ionization energy about 25% smaller than the optical ionization energy.[35] The larger difference in the case of ZnS is consistent with a greater degree of ionic binding and hence a greater Franck-Condon effect due to readjustment of the atoms near a center upon ionization changes at the center.

RECOMBINATION MODELS FOR ZnS:Cu:Cl

Lambe-Klick Model

The model proposed by Lambe and Klick (LK) was based on their work on single crystals of Ag-activated CdS.[4] In general, the experimental data explainable by the LK model can also be explained by other models such as the Klasens-Schön (KS) model, when the roles of electrons and holes, and donors and acceptors, are reversed.[36] For this reason, it has been difficult to develop an optical experiment with truly unambiguous results.

The pertinent data of the present investigation are those that indicate the sign of the charge carriers. Hall-effect measurements show that electrons are the charge carriers during photoconductivity and luminescence with photoexcitation by extrinsic 2.8-eV light. The LK model requires the generation of free holes in the valence band in order to have luminescence. In the low-temperature photoexcitation experiment, photoexcitation by extrinsic 2.8-eV light creates either free holes and bound electrons, or free electrons and bound holes. The Hall-effect data make the second the most likely possibility. Continued support of the LK model requires the assumption that extrinsic 2.8-eV light creates both free electrons and free holes through interaction with two different centers, one involving a transition to the conduction band and the other involving a transition from the valence band, and that the mobility of electrons is much larger than the mobility of holes. Since the availability of states which are the terminus of the transition from the valence band should be strongly changed as the quasi-Fermi level is moved by varying the excitation intensity, a departure from a simple linear dependence of luminescence intensity on excitation intensity would be expected; this is not found.

The TSC and TSL measurements show that the current and the luminescence emission are strongly correlated. The same type of carrier must be the dominant one for both processes. The agreement between optical quenching of steady-state photoconductivity and TSC also indicates that the free carriers involved in TSC are electrons. Since the LK model requires that for luminescence emission to occur, holes must be freed from hole traps in TSL, the TSC current must be associated with free holes. The only way to maintain the LK model is to assume that electron and hole traps with identical depths occur; there is no evidence for such an assumption.

It may be concluded, therefore, that the LK model is not applicable to the green luminescence emission centers in ZnS:Cu:Cl.

Williams-Prener Model: Two-Level Associated Pairs

The Williams-Prener (WP) two-level associated pair model is based on the high probability of Coulombic attraction between positively charged ionized donors and negatively charged ionized acceptors, leading to pairing between these species at the temperatures of crystal growth. When the resulting pairs are sufficiently closely related, it is proposed that there is a transition from an upper state associated with the donor to a lower state associated with the acceptor. For very close pair spacing, the transition is proposed to be from the ground state of the donor to the ground state of the acceptor. For larger pair spacing, the transition is proposed to be from an excited state of the donor to the ground state of the acceptor. It is the latter situation which has been proposed for the green emission associated with Cu in ZnS,[5] as well as for the blue emission associated with Ag and self-activation.

Information available in the thesis of Van Gool[37] is extremely useful in evaluating the probability of pair transitions of any type in ZnS crystals. Van Gool has shown that for equal concentrations of Cu acceptors and donors chosen from the group Cl, Al, Sc, Ga, and In, the emission spectrum is independent of the donor used, for concentrations less than some critical value of the order of a few hundredths of a percent. The same is true for Ag or Au acceptors. When the concentration of acceptors and donors is increased, always keeping them equal, Van Gool reports that a new luminescence emission at lower energies is found for Sc, Ga, or In donors, which is dependent on both the particular acceptor and the particular donor. Furthermore, when the concentration of acceptor with Cl or Al donors is increased, keeping them equal, no new emission band is observed, even for high concentrations, sufficient to produce a new band for Sc, Ga, or In donors. Since work by Hoogenstraaten[32] has shown the energy-level separations from the bottom of the conduction band for the various donors to be Cl (0.25 eV), Al (0.25 eV), Sc (0.35 eV), Ga (0.42 eV), and In (0.50 eV), an interpretation of Van Gool's data in terms of a pair model is the following: For concentrations less than a few hundredths of a percent, pair transitions are unimportant and luminescence can be described in terms of a simple Klasens-Schön model. For concentrations greater than a few hundredths of a percent, associated pair transitions become important and a new luminescence band appears

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[35] R. H. Bube, J. Appl. Phys. **35**, 586 (1964).

[36] Reference 20, p. 373.

[37] W. Van Gool, Ph.D. thesis, University of Amsterdam, 1961 (unpublished).

if the relevant donor state for the transition lies appreciably below the bottom of the conduction band. This is the case for Sc, Ga, and In, and the new long-wavelength band which appears may be ascribed to a two-level pair. Consistent with this is Van Gool's observation that this new band is enhanced by decreasing the temperature. For the case of Cl and Al, however, the relevant donor state from which the transition is or would be made lies very close to or within the conduction band. Thus, the luminescence does not show any change upon the occurrence of pairs, except such perturbations in the ground-state energy of the acceptor as may occur because of the proximity of the donor. Since the concentration of Cu in the ZnS:Cu:Cl crystals of this investigation is above that for which Van Gool finds pairing important in the case of Sc, Ga, or In, it may be concluded that his work indicates that the active luminescence centers in our crystals are one-level pairs, describable by a simple KS picture.

Several measurements in the present investigation are difficult to describe in terms of a two-level WP model. The TSC and TSL data show that the introduction of Cl into ZnS leads to an electron-trap level lying about 0.3 eV below the conduction band. In the WP model, this trap is the ground state of the donor, which does not have sufficient overlap with the ground sate of the associated acceptor to give an appreciable transition probability. Since the emission is proposed to arise from the transition between the excited state of the donor, the electron trapped at the donor ground state must be thermally excited to the excited state for the radiative recombination detected in TSL. The TSC data show that the thermal escape of electrons from the Cl center is large at temperatures as low as −120°C. But if the probability of thermal escape from the excited state of the donor in the WP model is large at −120°C, then it is improbable that the luminescence efficiency will be constant with temperature, as observed in a crystal containing known competing nonradiative recombination centers. Van Gool's data on the red band associated with Cu-Sc pairs, for example, for which the relevant donor state lies about 0.4 eV below the conduction band from the emission data, show a continuous decrease in luminescence efficiency above −100°C.

A second difficulty with the two-level WP model arises from a consideration of the energy difference between the red and the green emissions associated with Cu in ZnS, and the temperature dependence of luminescence efficiency. According to the WP model, the red band is due to a transition from the ground state of the donor, and the green band to a transition from an excited state of the donor. Therefore, the separation between the excited state and the ground state should be given approximately by $(h\nu_{\text{green}} - h\nu_{\text{red}})$, or by about 0.5 eV. This value may be in error because of a shift in the ground state with pair spacing by an amount given approximately by $(e^2/Kr_{\text{DA}})(\frac{1}{3}-\frac{1}{6})$, where K is the dielectric constant, and r_{DA} is the distance between the donor and acceptor when they are paired as nearest neighbors. Following Prener and Williams,[38] a pair spacing of $3r_{\text{DA}}$ is assumed for the red band, and of $6r_{\text{DA}}$ for the green band. The magnitude of this correction is about 0.1 eV, so that the energy separation between the ground and excited state of the donor is between 0.4 and 0.6 eV. The measured depth of the Cl ground state, however, is less than 0.3 eV below the conduction band. It must be concluded that the indicated excited state lies very close to the conduction band, or even in the band. This is in accord with our interpretation of Van Gool's data, leading to the model of a one-level pair.

The identity of the long-wavelength threshold of the luminescence and photoconductivity excitation spectra also indicates that the excitation is to either a very shallow level or a level in the conduction band itself.

The Two-Level Unassociated-Pair Model

Luminescence emission resulting from recombination between relatively unassociated pairs of donors and acceptors has been investigated particularly in GaP.[7–9] A large number of sharp emission lines or a relatively narrow emission band is found corresponding to recombination between donors and acceptors with a wide variety of different spacings. The energy of the emission and the transition probability for the recombination process are largest for the smallest donor-acceptor spacings. This model has been proposed for ZnS:Cu:Al and ZnS:Cu:Cl luminenscent powders by Shionoya *et al.*[10] on the basis of the observation of an apparent shift in the emission spectrum to lower energies with increasing decay time following photoexcitation.

The work of Van Gool described in the previous section can also be used to evaluate the applicability of the unassociated pair model to ZnS:Cu:Cl crystals. Since for low concentrations no pair effects are found, and for high concentrations associated pair effects are found, it is only in the region of intermediate concentration that unassociated-pair effects would be detectable if present. The depth of both donor and acceptor levels in ZnS is sufficiently deep that long-range interaction between such impurities should be relatively unimportant.

Reasons for discounting the unassociated pair model for ZnS:Cu:Cl may be summarized as follows: (1) general reasons on the basis of available data like that of Van Gool, (2) specific reasons on the basis of data on our own crystals, and (3) some comments on the data of Shionoya *et al.*

General evidence against the applicability of the unassociated pair model to ZnS:Cu:Cl crystals, in addition to the work of Van Gool, is the following: (1) The luminescence efficiency is constant as a function of temperature over the whole temperature range below the

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[38] J. S. Prener and F. E. Williams, Phys. Rev. **128**, 1427 (1956).

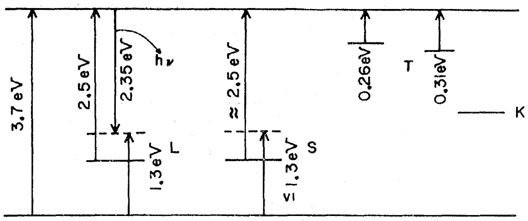

FIG. 11. Apparent energy-level scheme for ZnS:Cu:Cl from the results of the present investigation, indicating *L*, luminescence center; *S*, sensitizing center; *T*, electron traps; and *K*, nonradiative recombination center. Although the level for the excited *S* center lies at about the same energy above the valence band as the excited *L* center, when excitation is optical, the thermal excitation energy from the valence band to the *S* center (0.75 eV) is slightly less than the corresponding thermal transition for the *L* center (or, alternatively, the *S* center has a larger capture cross section for holes than the *L* center).

principal thermal-quenching temperature. It is unlikely that this behavior would be found with a two-level unassociated-pair model, in a crystal with known competing nonradiative recombination centers. In those cases of unassociated-pair emission investigated in GaP, there is a marked temperature dependence, the efficiency of luminescence emission decreasing rapidly above some temperature typically about 100°K. (2) The green emission associated with Cu in ZnS:Cu:Cl is independent of Cu concentration, at least between 10^{17} and 10^{19} cm^{-3}.[39,40] (3) The emission spectrum measured for the green Cu emission from ZnS:Cu:Cl is independent of the wavelength of the exciting radiation, and of the temperature, as indicated by the present investigation in agreement with the literature.[41]

Even if the two-level unassociated-pair model must be discarded for a variety of reasons, it is possible that an equivalent one-level unassociated-pair model exists, in which the ground state of the acceptor is perturbed by various donors at different distances from the acceptor. In such a system, it would be expected that a shift in the emission spectrum with excitation intensity would be found. Our experimental results, given in Fig. 3, show that, at least for the Cu concentration in our ZnS:Cu:Cl crystals, no such effect is found.

Shionoya *et al.*[10] present data showing a shift in the emission spectrum of a ZnS:Cu:Al luminescent powder to lower energies with longer decay times after the cessation of photoexcitation. It is possible to ascribe the observed shift to the contribution of a rapidly decaying blue band in a two-band emission spectrum, and not to an intrinsic shift associated with unassociated-pair emission. In support of this conclusion are the following observations: (1) The consistent evidence from the literature, as well as from our investigation, is that the green emission of Cu in ZnS:Cu:Cl material with a hexagonal crystal structure has an emission maximum at 2.35 eV which is temperature independent.[39–42] If the emission maximum given by Shionoya *et al.* for the zero-decay situation is to be attributed to the Cu green emission, then this maximum shifts from 2.43 eV at 300°K, to 2.53 eV at 77°K, to 2.50 eV at 4°K. If the experimental maximum, however, is the result of contributions from both a green band and a blue band, present in different proportions at different temperatures, the apparent discrepancy is removed. (2) Shionoya *et al.* show that the maximum of the emission spectrum becomes 2.35 eV at every temperature for long decay times. This is consistent with the measurement of the actual green-emission maximum at times sufficiently long for the coexisting blue band to decay away. (3) The shift in emission maximum with decay time reported by Shionoya *et al.* is much smaller at room temperature, where the blue band has been appreciably thermally quenched, than at lower temperatures, where the blue band is still an efficient emission. Also, the reported half-width at room temperature decreases by 10% with decay, from a value of 0.37 eV for zero decay to 0.33 eV for 1.1-msec decay. This is contrary to our measurements on the green band, which show an increase in half-width by 5% upon reduction of the excitation intensity by two orders of magnitude.

In conclusion, it may be stated that if the above assessment of the data of Shionoya *et al.* in terms of a two-band system is not fully adequate to account for all of their results, then it appears that they have measured the properties of a new emission brought about by the unusually high intensity of their excitation source—an emission possibly associated with pair-perturbed one-level acceptors or two-level unassociated pairs, or even with the Cu-blue band—and not the properties of the normal green emission in ZnS:Cu:Cl.

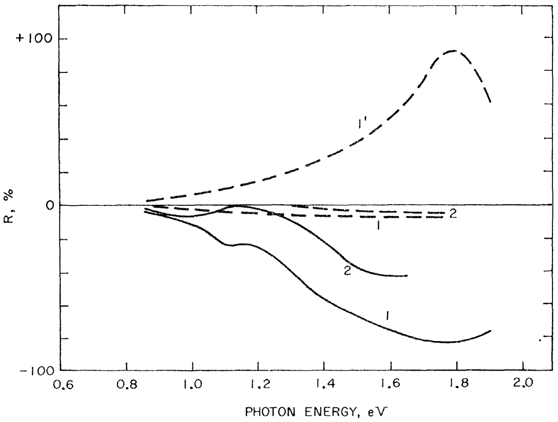

FIG. 12. Percent optically induced change as a function of secondary photon energy for a ZnS:Ag:Cl crystal. Negative *R* corresponds to quenching, positive *R* to stimulation. Solid curves are for photocurrent, dashed curves for luminescence-emission intensity. (1) 110°K, (2) 295°K. (1') shows the initial rise in the luminescence-emission intensity at 110°K.

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[39] H. W. Leverenz, *Luminescence of Solids* (John Wiley & Sons, Inc., New York, 1950), p. 209.

[40] R. H. Bube, Phys. Rev. **80**, 655 (1950).

[41] Reference 39, p. 190.

[42] R. H. Bube, Phys. Rev. **90**, 70 (1955).

The Klasens-Schön Model

The experimental data for the green band may be conveniently described in terms of a Klasens-Schön (KS) model, as indicated in Fig. 11. The acceptor level associated with the luminescence center corresponds to a nonpaired Cu center for low concentrations of impurity, and to a one-level Cu-Cl pair center for high concentrations of impurity, probably the case of significance for our crystals. The band gap of ZnS is 3.7 eV. The position of the excited luminescence-center level is derived from the maximum of the emission spectrum and from the threshold of the optical quenching of luminescence spectrum. The position of the unexcited luminescence-center level is derived from the threshold of the excitation spectra. The position of the excited sensitizing level is derived from the threshold of the optical quenching of photoconductivity, with a thermal-quenching activation energy 40% smaller. The position of the unexcited sensitizing-center level is approximately the same as that of the unexcited luminescence-center level, although an exact value is difficult to obtain because of the overlap with photoconductivity resulting from excitation from the luminescence-center levels. Two electron trapping levels are found from TSC and TSL data, one associated with Cl and the other of unknown origin. The presence of nonradiative recombination centers can be inferred from the observation of quenching phenomena, but their level positions cannot be determined from these data.

RESULTS FOR ZnS:Ag:Cl AND ZnS:Cl

Some of the measurements made on ZnS:Cu:Cl crystals were repeated for ZnS:Ag:Cl and ZnS:Cl crystals. The impurity contents of the crystals of the latter two types are given in Table I. The Ag-activated crystals had an emission peak at 2.8 eV, and the self-activated crystals had an emission peak at 2.65 eV, both in agreement with commonly given values. Evidence for a green Cu band could also be detected in some crystals of both types. We have described, in the previous section, how the work of Van Gool indicates a common behavior for Cu and Ag acceptors in ZnS; from the concentration of Ag in our crystals we would conclude that we are in the high-concentration one-level pair region.

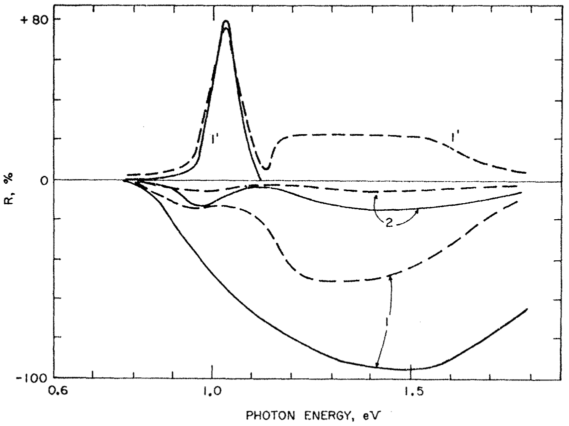

FIG. 13. Percent optically induced change as a function of secondary photon energy for a ZnS:Cl crystal. Negative R corresponds to quenching, positive R to stimulation. Solid curves are for photocurrent, dashed curves for luminescence-emission intensity. (1) 90°K, (2) 295°K, (1') shows the initial rise at 90°K.

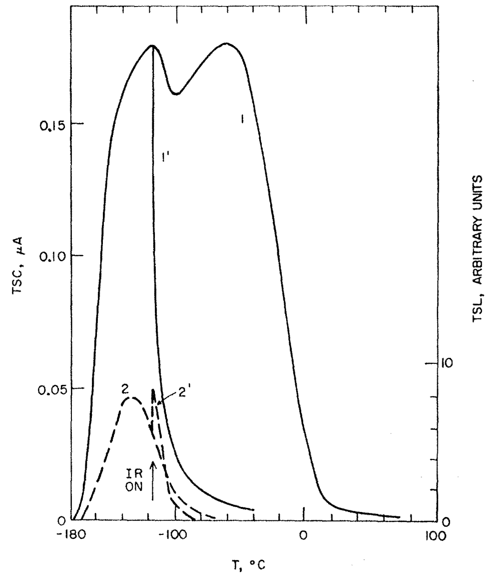

FIG. 14. Thermally stimulated current (1) and thermally stimulated blue luminescence emission (2) for a ZnS:Ag:Cl crystal. Effect of infrared radiation in the quenching range is shown in (1') and (2') for the TSC and TSL, respectively.

Sign of the Charge Carriers

The sign of the charge carriers participating in these emission processes was determined through an investigation of the effect of optical quenching on TSC and TSL, as in the case of ZnS:Cu:Cl crystals.

The infrared quenching spectra for ZnS:Ag:Cl and ZnS:Cl crystals are given in Figs. 12 and 13, respectively. In both cases, strong quenching of photoconductivity was observed. The low-energy threshold for optical quenching occurs at about 0.8 eV, thus showing the low-energy quenching band commonly found in ZnS and CdS,[25,30,31] but which could not be measured in the ZnS:Cu:Cl crystals of this investigation. This low-energy band is presumably due to a transition (or transitions) of the hole to excited states of the sensitizing center, as has been studied in detail in the CdS-CdSe system.[35]

Optical-quenching effects during TSC and TSL are shown in Figs. 14 and 15, where the data are for the blue emission only. The results are identical to those found in ZnS:Cu:Cl, and lead to the similar conclusion that the charge carriers participating in the luminescence process are electrons. The LK model is again rendered unlikely.

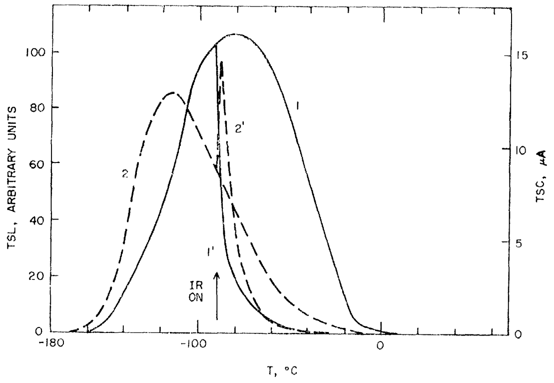

FIG. 15. Thermally stimulated current (1) and thermally stimulated luminescence emission (2) for a ZnS:Cl crystal. Effect of infrared radiation in the quenching range is shown in (1′) and (2′) for the TSC and TSL, respectively.

Certain details of the TSC and TSL data, such as the fact that two peaks are found with Cu or Ag activator, but only one peak with self-activation, and the fact that the TSL maximum is displaced from the TSC maximum in the self-activated crystals, merit further investigation. The TSL curve for the self-activated crystal is very similar to that reported by Samelson and Lempicki[43] for similarly grown ZnS:Cl crystals.

Identity of Luminescence and Sensitizing Centers

It was concluded that for ZnS:Cu:Cl crystals the activator centers for luminescence emission are not the same as the sensitizing centers for photoconductivity; this conclusion was reached after observation of opposite dynamic behavior at low temperatures under optical quenching, and of different thermal-quenching temperatures for the two types of phenomena. Both of these effects are found also in ZnS:Ag:Cl and ZnS:Cl crystals. At liquid-nitrogen temperature, irradiation with 0.8-μ light, in addition to primary excitation, produces an initial increase in luminescence, but only quenching of photoconductivity. In both ZnS:Ag:Cl and ZnS:Cl crystals, it was found that thermal quenching of luminescence occurred at a lower temperature than that of photoconductivity. Figure 16 shows typical results for the ZnS:Cl crystals.

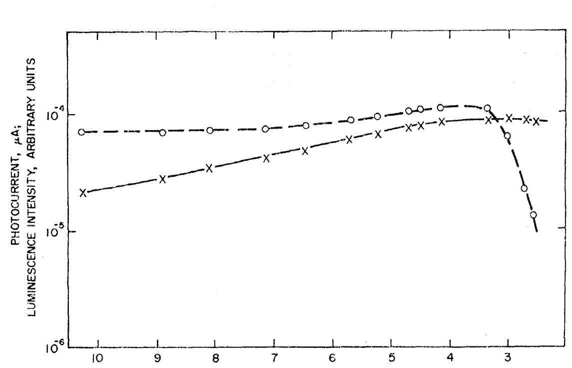

FIG. 16. Temperature dependence of luminescence-emission intensity (dashed curve) and photocurrent (solid curve) for a ZnS:Cl crystal.

These results lead again to the conclusion that luminescence and sensitizing centers are not identical in ZnS:Ag:Cl and ZnS:Cl crystals. The temperature independence of luminescence efficiency, together with the other evidence previously presented, also argue against two-level pair models.

CONCLUSIONS

The principal findings of the present investigation on ZnS:Cu:Cl crystals are the following:

(1) Excitation spectra show that the threshold energy of 2.5 eV is the same for luminescence and photoconductivity.

(2) The green-band emission spectrum has a maximum at 2.35 eV and a half-width of 0.32 eV, which are essentially independent of excitation temperature or wavelength.

(3) The green-band emission spectrum shows no more than 5 Å shift in maximum with an order-of-magnitude change in excitation intensity, and shows a 5% increase in half-width with a two order-of-magnitude decrease in excitation intensity.

(4) Photo-Hall measurements show that the carriers during steady-state intrinsic and extrinsic excitation are electrons with mobility between 100 and 200 cm^2/V sec.

(5) At low temperatures, luminescence emission is initially stimulated by infrared, whereas photoconductivity is quenched.

(6) Infrared quenches both luminescence and photoconductivity with a minimum threshold energy of 1.3 eV.

(7) TSC and TSL curves correspond to a chlorine-associated trap with depth of about 0.3 eV, and a second unidentified trap.

(8) The same infrared that quenches the stready-state photoconductivity also quenches the TSC.

(9) Luminescence efficiency is almost independent of temperature from liquid nitrogen to room temperature.

(10) The temperature for the onset of thermal quenching of luminescence is greater than that for the photoconductivity.

(11) The activation energy for thermal-quenching photoconductivity is 0.75 eV, 40% smaller than the optical energy.

When standard models, such as the Lambe-Klick, Klasens-Schön, Williams-Prener two-level associated pair, two-level unassociated pair, and one-level pair, are investigated in the light of the above results and the other evidence available in the luminescence literature, it is concluded with reasonable conviction that the

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[43] H. Samelson and A. Lempicki, Phys. Rev. **125**, 901 (1962).

TABLE IV. Summary of suggested centers in ZnS (for equal donor and acceptor concentrations).

Imperfections	Concentration range	Type of center	Function of center
Cu and Cl, Al, Sc, Ga, In	Low	Nonpaired compensated Cu	Green emission (2.35 eV)
Cu and Cl, Al	High	One-level Cu-Cl, Cu-Al pairs	Green emission (2.35 eV)
Cu and Sc, Ga, In	High	Two-level associated Cu-Sc, Cu-Ga, Cu-In pairs	Red emission ($\approx$1.9 eV)
Ag and Cl, Al, Sc, Ga, In	Low	Nonpaired compensated Ag	Blue emission (2.82 eV)
Ag and Cl, Al	High	One-level Ag-Cl, Ag-Al pairs	Blue emission (2.82 eV)
Ag and Sc, Ga, In	High	Two-level associated Ag-Sc, Ag-Ga, Ag-In pairs	Orange emission ($\approx$2.2 eV)
Cl, Al and Zn vacancy	?	One-level V_{Zn}-Cl, V_{Zn}-Al pairs	Blue emission (2.68 eV)
Donors and Zn vacancy or S interstitial	?	Probably complex compensated acceptor-type	Sensitizing center

green-emission band in our ZnS:Cu:Cl crystals is to be associated with a one-level pair, describable adequately by a simple Klasens-Schön picture. For low concentrations of Cu and Cl impurity in ZnS:Cu:Cl crystals (about 10% that in our crystals and less), it is expected that no pairing effects would be present.

The results also show that the luminescence center is not the same as the sensitizing center for photoconductivity.

Experiments corresponding to (5), (8) ,(9), and (10) above were carried out also on ZnS:Ag:Cl and ZnS:Cl crystals. These results indicate that the LK model is not suitable for these crystals, that two-level pair models are inappropriate, and that the activator and sensitizing centers are different. In these crystals, the thermal quenching of luminescence occurred at lower temperatures than that of photoconductivity, indicating that the energy level for the Ag center and the self-activated center lie below that for the sensitizing center. This is consistent with the energies of the emission and the apparent equality of level position between the Cu center and the sensitizing center.

This difference in identity between the activator and sensitizing centers, which now appears to be fairly definitely established in several II-VI compounds, offers a direct explanation for one of the basic observations that led to the formulation of the LK model: the marked difference in decay rate for luminescence emission and photoconductivity, the former being much faster. The sensitizing center has a very small electron-capture cross section to be effective in sustaining long electron lifetimes, whereas the luminescence center must have a cross section at least large enough to compete favorably with other nonradiative centers in the crystal.

The observation by a number of investigators that the position of the sensitizing-center level does not vary with the particular impurities incorporated in II-VI crystals[44–46] indicates that this center is associated with an intrinsic defect. Research on the identity of the luminescence center in ZnS:Cl crystals has also led to the suggestion that these centers are associated with compensated cation vacancies,[47,48] and indeed that these centers are identical to the sensitizing centers.[49] The present results indicate that this simple identification is not justified. Kasai and Otomo,[50] and Schneider *et al.*[51] have found through electron paramagnetic resonance studies in ZnS:Cl crystals that photoexcited holes are localized in the environment of a Cl-vacancy pair. The report of anisotropy in luminescence emission by Koda and Shionoya[52] is also consistent with the hypothesis that a Cl-vacancy pair is the luminescence center in ZnS:Cl, as proposed by Kasai and Otomo, and by Schneider *et al.* The integrated understanding of luminescence and sensitizing centers, as a result of these previous investigations and of the present work, is summarized in Table IV.

ACKNOWLEDGMENT

The authors are indebted to Dr. Guy A. Marlor for helpful discussions, as well as for the measurement of the intensity dependence of the green-emission band of ZnS:Cu:Cl.

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[44] R. H. Bube, Solid State Phys. **11**, 223 (1960).

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