Optical Properties of Activated and Unactivated Hexagonal ZnS Single Crystals

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(Received March 13, 1959)

Single crystals of hexagonal ZnS, unactivated and activated with Cu, Al, or Mn, have been examined. The polarization effects in the transmission spectrum of unactivated ZnS were measured further into the fundamental absorption than were previously measured. The theoretical prediction that, for direct transitions at $k=0$, light polarized perpendicular to the c axis is more strongly absorbed than light polarized parallel to the c axis is born out throughout the fundamental absorption region except in the wavelength region between 290 and 325 mμ. The wavelength dependence and the polarization of the excitation and fluorescence spectra of the activated and unactivated crystals were measured at room temperature and at 77°K. The excitation spectra showed an agreement with the selection rule at the edge of the fundamental absorption, but there was a reversal of the selection rule deep in the absorption region. There was also an impurity absorption exhibiting the same polarization properties as the edge. Some fluorescent emissions were polarized perpendicular and some were polarized parallel to the c axis. Speculations are made on the reversal of the polarization deep in the fundamental absorption and on the symmetry and the nature of the sites causing the various fluorescence bands.

INTRODUCTION

IN a previous work[1] anomalously high photovoltages and their reversals with wavelength were measured on activated and unactivated single crystals of hexagonal ZnS. In order to answer questions as to what role the presence of certain activators played in the phenomena, we undertook an investigation of the optical properties of single crystals, pure and activated with various combinations of Cu, Al, and Mn. The optical studies consisted of measurements of excitation and emission spectra of pure and activated samples as well as transmission spectra of a single crystal plate of unactivated ZnS. (We denote by unactivated crystals, those samples to which no activators have been purposely added.)

In addition to these measurements we undertook to determine the effects of polarized light in the excitation spectra and the polarization of the fluorescence spectra. The selection rule for the fundamental absorption has been worked out by Casella[2] and independely by Birman.[3] Their work differs in that Casella's applies only to the absorption edge where the symmetries of the initial and final states are assumed different and the result is otherwise independent of their symmetries, whereas Birman's work is based upon detailed assumptions regarding the explicit symmetries of the bands. In agreement with this selection rule, the polarization effects in the transmission spectra of ZnS in the wavelength region between 328 and 700 mμ had been measured by Piper, Marple, and Johnson.[4] Recently, Lempicki[5] reported on the polarization of fluorescence of activated ZnS crystals, and Dutton[6] reported on the

polarization of edge emission and of fundamental absorption in CdS.

Since the Mn ion in Mn-activated hexagonal ZnS occupies a substitutional site, known from measurements of the anisotropy of its paramagnetic resonance absorption,[7] we could measure the polarization effects of a substitutional site by measuring these effects in the excitation and fluorescence of the Mn center. By comparing these polarization measurements with those of other emission bands, due to different activators and centers, we hoped to be able to make some statements about the nature of the site associated with the unknown centers. There have been many discussions in the literature of certain emission centers in ZnS. In the case of unactivated crystals we hoped that we could shed light on the nature of the green centers and the blue centers. These centers have been under examination for a number of years. Kröger and co-workers[8] at various times suggested that the green emission was due to either substitutional Cu^+ stabilized by Cl^-, to interstitial Zn, or to anion vacancies with trapped electrons. They suggested that the blue centers were due to cation vacancies with a trapped hole, $V_c{}^+$, or to $Cu_2{}^+$ at high Cu concentrations. Bube[9] associated the blue emission of pure ZnS with excess Zn. He further associated various green and blue emissions with Cu going into the lattice interstitially or substitutionally as either the monovalent or the divalent ion. In a later article Kröger[10] proposed that the green center was Cu^+ in a substitutional site and the blue center was $Cu_2{}^+$ contrary to Bube's[9] proposal of the green center being Cu^+ in an interstitial position and the blue center being Cu^+ in a substitutional posi-

[1] G. Cheroff and S. P. Keller, Phys. Rev. 111, 98 (1958).
[2] R. Casella, Phys. Rev. 114, 1514 (1959).
[3] J. L. Birman, Phys. Rev. Letters 2, 4, 157 (1959).
[4] Piper, Marple, and Johnson, Phys. Rev. 110, 323 (1958).
[5] A. Lempicki, Phys. Rev. Letters 2, 4, 155 (1959).
[6] D. Dutton, J. Phys. Chem. Solids 6, 101 (1958); Phys. Rev. 112, 785 (1958).

[7] Keller, Gelles, and Smith, Phys. Rev. 110, 850 (1958).
[8] F. A. Kröger and J. A. M. Dikhoff, J. Electrochem. Soc. 99, 144 (1952). F. A. Kröger and H. J. Vink, J. Chem. Phys. 22, 250 (1954).
[9] R. H. Bube, Phys. Rev. 80, 764 (1950); 80, 655 (1950); 81, 633 (1951); J. Chem. Phys. 20, 708 (1952).
[10] F. A. Kröger, J. Chem. Phys. 20, 345 (1952).

tion. In a later article Kröger[11] suggested that the green emission was caused by a $V_a{}^-$ (anion vacancy with a trapped electron) site resulting from firing the sample in a reducing atmosphere. He claimed that further reduction leads to a $V_a{}^=$ site with a decrease in the green emission and that the blue emission is due to a $V_c{}^+$ site resulting from firing the sample in excess sulfur or in oxidizing conditions. Bowers and Melamed[12] proposed that the green emission is due to substitutional Cu^+ sites whereas the blue emission is due to zinc vacancies. They rule out the possibility of Cu^{++} or $V_c{}^+$ being the emitting centers since either would be paramagnetic and they were unable to measure any paramagnetic susceptibility.

We felt that measurement of the effects of polarized light on the excitation of single crystals and measurements of the polarization of light emitted from single crystals would help clarify the question as to the nature of the centers causing the green and the blue emissions in unactivated crystals as well as the nature of other centers in activated crystals.

CHEMICAL PREPARATIONS AND INSTRUMENTATION

The preparation of the single crystals was described in detail earlier[1,7] where the materials investigated were single crystals of hexagonal ZnS, either pure or triply activated with Cu, Al, and Mn. The Mn is divalent and the Cu is probably monovalent due to the absence of a paramagnetic resonance absorption as mentioned in reference 7. The Al is assumed to be trivalent consistent with charge compensation arguments of Kröger, Klasens, *et al.*

In the present investigations, in addition to the unactivated and triply activated samples, we measured crystals singly activated by Cu, Mn, or Al. The crystals were all grown in the same fashion. The phosphor powder was sealed in a quartz tube with a room temperature pressure of 20 cm of H_2S. The tube was then inserted in a temperature gradient such that the charge was located in the hottest part of the furnace which was maintained at 1170°C. The tube remained in the furnace for 50 to 100 hours. The crystals that were obtained were either needles or plates. In both types there occurred birefringent banding perpendicular to the c axis which was contained in the planes of the crystals. We used the birefringent banding as an identification of the location of the c axis. In order to make the optical measurements, crystals of the same firing were cemented to quartz slides such that their c axes were all lined up. The sample slides were then cemented to a rotatable quartz tube which served as the inside wall of an evacuable quartz Dewar. The outer jacket was made of tubular quartz in which was mounted a flat quartz window. The inner tube could be filled with liquid N_2 and rotated so that different samples could be brought into the optical beam.

[11] F. A. Kröger, Suppl. Brit. J. Appl. Phys. **4**, 58 (1955).
[12] R. Bowers and N. T. Melamed, Phys. Rev. **99**, 1781 (1955).

For excitation and fluorescence spectra light from a Perkin Elmer model 112U Monochromator was focused onto the sample. The light source was a dc-operated high-pressure Xe lamp. The light emitted from the sample was focused into a perkin Elmer model 98 Monochromator, detected by an RCA 1P21 photomultiplier tube, and recorded. For excitation spectra the PE 112U was scanned while the PE 98 was held fixed. For fluorescence spectra the PE 98 was scanned while the PE 112U was held fixed. For the polarization measurements Polaroid films were used. The cellulose coatings were removed by dissolving them in acetone. In this way we were able to increase their transmission in the ultraviolet. The Polaroid film was placed before or after the sample, dependent on the desired run, with the optical axis either parallel or perpendicular to the crystal axis. In the measurements of the polarization of the fluorescence, all of the emissions occurred between 465 and 570 mμ. In this region the Polaroid films were between 94% and 99% effective at polarizing light. The data were appropriately corrected. In the measurements of the polarization effects in excitation spectra, the Polaroid films ranged between 60% and 85% effective and again corrections were made. The optics of the monochromators caused some polarization of the light and corrections were accordingly made. We will present only those data which exhibit effects greater than the corrections or opposite to the direction of the corrections.

For the transmission run the sample was located at the entrance slit of the PE 98 and both monochromators were scanned simultaneously with their wavelengths coincident. The Polaroid was placed in front of the sample with its optic axis parallel or perpendicular to the crystal axis. The results were corrected for the polarizing power of the Polaroid. Since the spectrum was corrected for the background light, the polarization effects introduced by the optics were cancelled. The single crystal plate, on which transmission measurements were made, was accidentally destroyed before its thickness could be measured. From fragments we estimated its thickness to be about 0.005 cm. One should normally treat with care data that are well within the absorption edge of a crystal of this thickness. However, our data, as will be seen, deal with polarization effects and not absolute transmission and the nature of the results and their reproducibility in repeated runs indicate their validity.

The impurity concentrations of the samples were determined by spectrographic analysis and will be presented in the appropriate sections.

EXPERIMENTAL RESULTS AND DISCUSSION

1. Polarized Transmission of a Single ZnS Plate

The measurement was made at room temperature. Following convention we plot $P=(I_{11}-I_\perp)/(I_{11}+I_\perp)$, expressed in percentages, where I_{11} is the transmitted
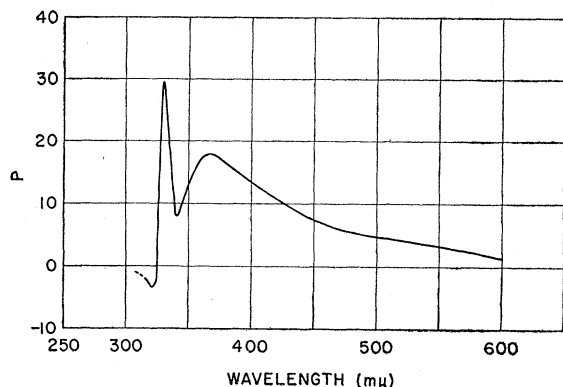
FIG. 1. Polarized transmission of a single crystal plate of hexagonal ZnS. $P = (I_{||} - I_{\perp})/(I_{||} + I_{\perp})$, expressed in percentages.

light when the incident light has its polarization parallel to the c-axis and $I_{\perp}$ is the transmitted light when the incident light has its polarization perpendicular to the c axis. It can be seen that P is proportional to $(\alpha_{\perp} - \alpha_{||})$ where $\alpha_{\perp}$ is the absorption coefficient for perpendicular polarized light and $\alpha_{||}$ is the absorption coefficient for parallel polarized light. When a difference is measured at a specific absorption peak, one expects this function to go through a maximum (or minimum) since $\alpha_{\perp} - \alpha_{||}$ goes to zero on either side of the peak. In the case of a measurement of the absorption edge, one also expects the function to go through a maximum (or minimum) since the absorption coefficients should go to zero on the long wavelength side of the edge and should approach each other on the short wavelength side. The data are presented in Fig. 1. The data presented go further into the fundamental absorption than do the data of Piper, Marple, and Johnson.[4] It is seen that near 335 mμ, the fundamental absorption is that predicted by theory[2,3] in that perpendicular light is more strongly absorbed than parallel. It can further be seen that there is impurity absorption peaked at 360 mμ following the same optical selection rule as the fundamental absorption. This is consistent with the data of Balkanski and Waldron.[13] An interesting feature of the data is the reversal of the selection rule in the short-wavelength region of the edge. Below 325 mμ, light polarized parallel to the c axis is more strongly absorbed than light polarized perpendicular to it. It is possible that this region of reversal is associated with excitonic absorptions, analogous to that reported by Dutton[6] for CdS. One normally expects excitonic absorption to occur at an energy which is less than the energy gap by an amount equivalent to the binding energy of the exciton. If we assume that for more complicated reasons excitons can be formed by energies greater than that of the gap, then there is no obvious reason why the optical selection rule should not break down nor on the other hand is there an obvious reason why it should reverse. We can offer no expla-

nation at this point for the reversal of the polarization selection rule.

2. Excitation and Fluorescence Spectra of Unactivated Crystals

The crystals were spectrographically analyzed and most of them contained between 0.0001 and 0.001% Cu. At times Fe, Sn, or Pb were reported in equivalent concentrations. The contaminations were introduced from the quartz.

a. Unpolarized Light

The data presented in this section represent data obtained from four different quartz sample slides on which were mounted crystals as mentioned earlier. One of the quartz slides contained the single-crystal plate discussed in Sec. 1. All data were obtained at room temperature (RT) and at 77°K (LT). We have chosen those data which we consider representative of the samples. Where there are distinct exceptions, note will be made of them. The RT excitation and fluorescent spectra are presented in Fig. 2. The solid line denotes the excitation spectrum in which region the abscissa represents the wavelength of the incident light and the dotted line denotes the emission spectrum in which region the abscissa represents the wavelength of emitted light. The excitation spectrum was determined for the emitted light located at 520 mμ. A comparison of the heights of the two curves is not meaningful. The curves have been corrected for constant incident energy. (These conventions will be maintained throughout the remainder of the paper.) Excitation by either 339- or 370-mμ light results in the emission shown. The 520-mμ emission is the well-known green emission and the emission near 455 mμ is the well-known blue emission. These are probably due to Cu$^+$ contamination but the exact origin is still in doubt. The 420-mμ excitation peak was seen with two of the sample slides. In the case of the single-crystal plate, mentioned in Sec. 1, the excitation spectrum showed the 339-mμ peak to be much higher than the 370-mμ peak.
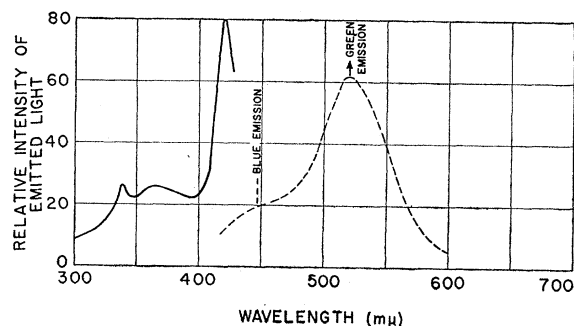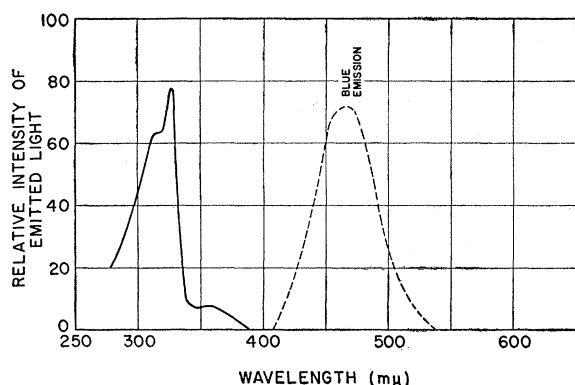

FIG. 2. RT excitation and fluorescence spectra of unactivated single crystals. The solid line represents the excitation spectrum of the 520-mμ emission and the dashed line represents the fluorescence spectrum resulting from either 339- or 370-mμ excitation.

[13] M. Balkanski and R. D. Waldron, Phys. Rev. 112, 123 (1958).

The LT excitation and fluorescence spectra are shown in Fig. 3. The solid line and broken lines have the same significance as in Fig. 2. The excitation spectrum was determined for the emitted light located at 465 mμ. The emission is the well known blue emission of "self-activated" ZnS. It is excited by either 328- or 358-mμ light. The excitation peaks are shifted to shorter wavelength at LT by an amount equal to the shift of the absorption edge. With one sample slide, the 358-mμ peak was about equal to the 328-mμ peak. It will be seen from future data and it will be pointed out again that there is an association between the structure near 319 mμ on the excitation peak in Fig. 3 and a reversal in the polarization of absorbed light in excitation measurements. It is possible that the 319-mμ structure is also related to the 320-mμ reversal in the fundamental optical selection rule governing the absorption of polarized light, as seen in Fig. 1. The latter reversal was measured at RT whereas the observed structure near 319 mμ was measured at LT. There should be a larger difference due to the temperature shift of the energy gap. Melamed[14] has reported on similar measurements and his excitation spectra for powdered samples, with only Cl as activator, have peak positions differing slightly from our data. He also reports structure on the excitation peak at shorter wavelengths than that ascribed to the fundamental absorption peak. It might be thought that our pure samples should be compared to Melamed's[14] Cu activator samples, since his Cu activated samples contain 0.0001 to 0.001 molar percent Cu. However, there is also disagreement with those results in that peak positions differ. He reports with these samples an excitation of the green center at LT similar to the 420 mμ peak shown in Fig. 2, which we shall discuss shortly.

We ascribe the RT 339-mμ and LT 328-mμ excitation to fundamental absorption and the RT 370-mμ and LT 358-mμ excitation to absorption by the blue emitting center. We further propose that the 420-mμ excitation
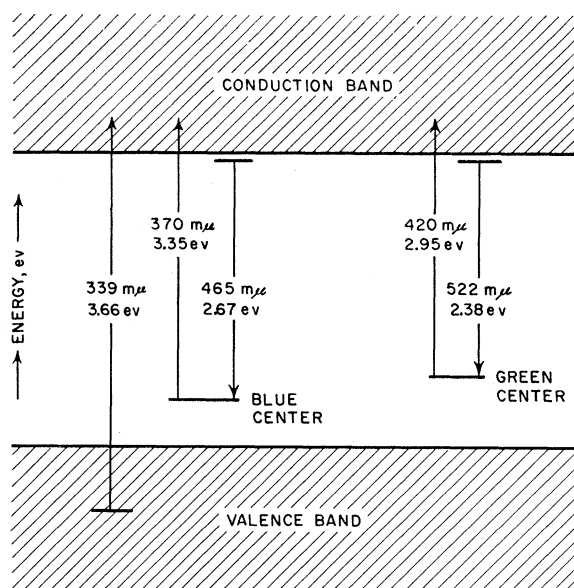

FIG. 4. Energy level diagram of unactivated ZnS. The upper-headed arrows represent absorption and the lower-headed arrows represent emissions.

of Fig. 2 is due to absorption by the green emitting center. Figure 4 presents an energy level diagram of the system. It is seen that the energy difference between the excitation and emission at the blue center is nearly equal to the energy difference at the green center. The explanation as to why the green emission predominates at RT but the blue at LT is one given in the past by many workers; namely, the blue center retains its hole at LT more readily than at RT whereas the hole is readily trapped by the green center at RT. Hence, LT favors the blue emission and RT favors the green emission. The dominance of the short-wavelength excitation peak at LT can be understood if one postulates (1) the existence of a thermal quenching center, and (2) proximity of the green center to the blue center which at RT become coupled. On this basis one can assume that at room temperature, holes created in the valence band either can be trapped at the blue center of the couple and subsequently transferred to the green center or they can be annihilated at the quenching center. During fundamental absorption the latter process is the dominant one whereas during the blue center absorption the former process is the dominant one. Hence, at RT 370-mμ light is as efficient at exciting green emission as is the fundamental 339-mμ light. At LT the thermal quencher no longer is the dominant hole trap since the blue center becomes a very efficient hole trap. In addition, those holes trapped by the blue center are no longer transferred to the green centers due to the lack of thermal coupling of the two centers. As a result holes generated in the valence band can be trapped only at the blue centers. In this case fundamental excitation at 328 mμ is more

FIG. 3. LT excitation and fluorescence spectra of unactivated single crystals. The solid line represents the excitation spectrum of the 465-mμ emission and the dashed line represents the fluorescence spectrum resulting from 328- or 358-mμ excitation.

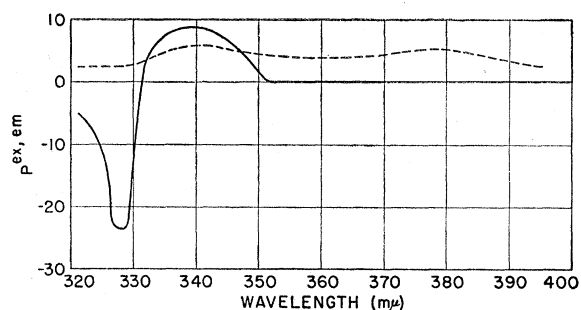[14] N. T. Melamed, J. Phys. Chem. Solids 7, 146 (1958).

FIG. 5. Polarization of exciting light and emitted light, for unactivated crystals. The solid curve represents P^{ex}, related to the polarization of the exciting light; and the dashed curve represents P^{em}, related to the polarization of the emitted light. In both plots the emitted light is peaked at 520 mμ and the data were obtained at RT.

efficient at exciting blue emission than is the blue center absorption at 358 mμ.

b. Polarized Light

Two types of polarized light experiments were performed. In one type, two excitation spectra were determined; one with the exciting light polarized perpendicular to the c axis and the other with the exciting light polarized parallel to the c axis. The other type of polarized light experiment involved the measurement of the polarization of the emitted light. For every wavelength of exciting light, we determined the polarization, relative to the c axis, of that wavelength of emitted light for which the excitation spectrum was being obtained. For the excitation spectra we have used as a measure of the polarization effects the difference between the intensities of the emitted light with the exciting light polarized perpendicular and parallel to the c axis divided by the intensity of the emitted light with the exciting light polarized perpendicular to the c axis. This ratio, $P^{ex}=I_\perp{}^{ex}-I_{11}{}^{ex}/I_\perp{}^{ex}$, expressed in percentages, is related to $\alpha_\perp-\alpha_{11}$, where α is the absorption coefficient as explained previously. The quantity P^{ex} is plotted as a function of the wavelength of exciting light.

For the emission spectra we have plotted the difference between the intensities of the emitted light polarized perpendicular to the c axis and polarized parallel to the c axis divided by the intensity of the emitted light polarized perpendicular to the c axis. This ratio, $P^{em}=I_\perp{}^{em}-I_{11}{}^{em}/I_\perp{}^{em}$, expressed in percentages, is simply the degree of polarization of emitted light and is plotted as a function of wavelength of exciting light.

In Fig. 5, we present both P^{ex} and P^{em} as $P^{ex,\ em}$ taken at RT for the unactivated crystals. In this case the emitted light was the green emission at 520 mμ. The RT blue emission was not strong enough in the three sample slides with which we made polarization measurements and hence we could not obtain P^{ex} and P^{em} data for this emission. In Fig. 6, we present $P^{ex,\ em}$ taken at LT for the blue emission at 465 mμ. (The data presented here

and elsewhere in the paper exhibit polarization effects that were larger than could be explained by the dichoric absorption shown in Fig. 1.) Related to Fig. 6, one sample slide showed a reversal in the polarization of the emitted light when the exciting light was located at 320 mμ, the region where the polarization of the exciting light reverses.

It can be seen that the polarization of the excitation of the blue center is different from that of the green center in that the blue center has a positive polarization in the LT 358-mμ excitation peak region. Light in the RT 370-mμ excitation peak, polarized in either direction is equally effective at exciting the green emission whereas light polarized perpendicular to the c axis is more effective at exciting the blue emission than light polarized parallel. A possible explanation for this is similar to what was given in the discussion of Fig. 4 involving coupled centers. At RT the green and blue centers are coupled such that the green center affects the absorption in the blue center. The results of the coupling are such that there is no preferential polarization. This would be true if the green centers are spatially randomly located with respect to the blue centers. At LT the centers are not coupled due to decreased lattice vibrations in which case the blue center can absorb according to its unperturbed selection rule which states that perpendicular light is more absorbed than parallel. The apparent difference between Fig. 5 and 6 at wavelengths shorter than 320 mμ is not real in that we could not carry the RT measurements of Fig. 5 into this region.

The emitted light for both centers indicates that the light is polarized perpendicular to the c axis. This is in agreement with Lempicki's[5] results for his crystals activated with Cu. In the case of the blue center for some samples, there appears to be a depolarization, or reversal, of the emitted light in that wavelength region where the optical selection rule governing fundamental absorption is not obeyed; i.e., at 320 mμ. One can interestingly speculate that if the 320-mμ region of negative P^{ex} is due to excitonic absorption, as suggested earlier, then when the emission at a center is due to free hole-electron recombination, the emission is polarized perpendicular to the c axis in accordance with some selection rule. On the other hand, when the exciting wavelength is such that excitons are generated and destroyed at emission
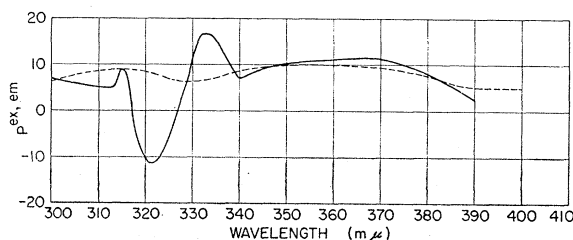

FIG. 6. Polarization of exciting and emitted light for unactivated crystals. The data were obtained at LT and the emitted light is located at 465 mμ. The solid curve represents P^{ex} and the dashed curve represents P^{em}.

centers, the resultant emission has no, or opposite, polarization. This breakdown of polarization of emitted light can be attributed to the influence of the symmetry of the field of the exciton on the emission center thus dominating the normal selection rule.

Aside from speculation there appears to be a strong correlation between the existence of structure around 319 mμ in the excitation curve, as seen in Fig. 3, and the reversal of polarization at 320 mμ as seen in Fig. 6. In some samples where the reversal in polarization was not strong there was little structure seen near 319 mμ on the excitation curve. On the other hand, whenever a 319-mμ structure was seen, there was also seen a strong reversal in polarization.

3. Excitation and Fluorescence Spectra of Crystals Activated with Cu

The crystals were grown as described previously. The concentration of Cu was determined by spectrographic analysis and was found to be between 0.01–0.1%. Cu is present presumably as Cu$^+$ since no paramagnetic resonance absorption was found.[7]

a. Unpolarized Light

The RT excitation and fluorescence is essentially that shown in Fig. 2. The excitation spectra did not show the 420-mμ peak and the peak at about 339 mμ is much higher than that at about 370 mμ. The emission spectrum is the same as that shown in Fig. 2. If one assumes the green and blue centers of unactivated crystals are due to Cu$^+$, then in the present crystals the increased Cu$^+$ centers would enhance the emission and one would also expect the 370-mμ absorption to be correspondingly increased, as can be seen in Fig. 4, contrary to observation. We can offer no explanation of this discrepancy at this time. The LT spectra are essentially the same as those presented in Fig. 3 with the exception that in the present case the excitation peak at around 358 mμ is approximately equal in height to that at 328 mμ. This is consistent with what would be expected based upon the increased Cu$^+$ concentration which presumably caused this impurity band absorption. There is again seen structure on the excitation peak near 319 mμ and from what has been said we would thus expect to see a reversal of polarization at about 320 mμ in the excitation spectrum. This will be seen to be true. Our results are again not in agreement with those of reference 14, both in peak positions and relative peak heights of the excitation spectra. The ratio of the intensities of the green to blue emissions are also not in good agreement with reference 14. This may partly be due to the fact that our activated samples have more Cu.

b. Polarized Light

The quantities P^{ex} and P^{em} obtained at RT are presented in Fig. 7 for which the emitted light is at 520 mμ.
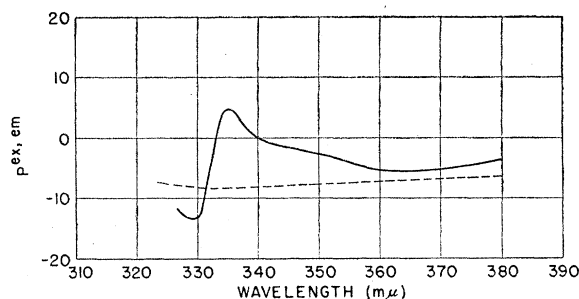

FIG. 7. Polarization of exciting and emitted light for crystals activated with Cu$^+$. The data were obtained at RT and the emitted light is peaked at 520 mμ. The solid curve represents P^{ex} and the dashed curve represents P^{em}.

There are several differences between these data and those of unactivated crystals shown in Fig. 5; (1) the present data show reversed polarization in the excitation spectrum at around 370 mμ, and (2) the emitted light has polarization reversed to that shown in Fig. 5 and opposite to that reported by Lempicki.[5] A possible explanation for these effects may lie in the increased concentration of the Cu$^+$ centers in the present case. If the Cu$^+$ is associated with the green and blue emission of so-called pure ZnS, as it is generally assumed, then association of these Cu centers can add a spatial symmetry with resultant light polarization that would be absent in crystals where Cu$^+$ centers are not associated. As an example the excitation at 370 mμ, which was assumed to be due to coupled blue and green centers, is not polarized in unactivated crystals as shown in Fig. 5. As more Cu$^+$ is added to the lattice they can associate with the green centers and effect an internal symmetry so that light polarized parallel to the c axis is more strongly absorbed than light polarized perpendicular, as shown in Fig. 7. However, the fundamental absorption still obeys the selection rule and is independent of the association. On the other hand, the emitted light, under all excitation will reflect the association and will be polarized parallel to the c axis, as shown in Fig. 7. As was stated before, we offer no explanation as to why the emitted light for unactivated crystals, shown in Fig. 5, is polarized perpendicular to the c axis. One can always assume as Birman[3] did that the emitting center's excited state and ground state have the same symmetry as the conduction and valance band respectively. (By excited state we mean the higher state that the center is in before an emission, and by ground state we mean the lower state that the system finds itself in after an emission. The states can be distinct and characteristic of the center as in the case of Mn centers. In the case of the Schön-Klasens model, the higher state would be the bottom of the conduction band and the lower state would be characteristic of the activator. In the case of the Lambe-Klick model, the higher state would be characteristic of the activator and the lower state would be the top of the valence band.) In other words, one can assume that the excited state is expandable in terms
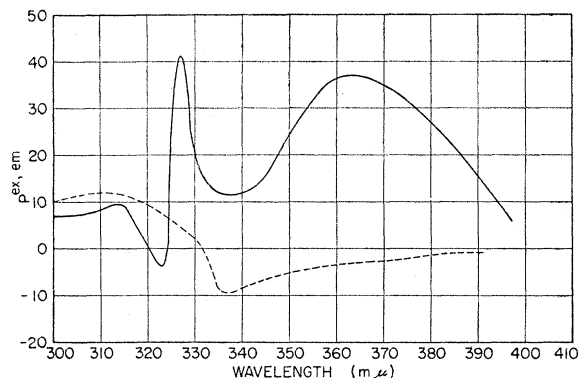
FIG. 8. Polarization of exciting and emitted light for crystals activated with Cu$^+$. The data were obtained at LT and the emitted light is located at 465 mμ. The solid curve represents P^{ex} and the dashed curve represents P^{em}.

of conduction band wave functions and the ground state is expandable in terms of valence band function. This explanation would account for the observed polarization of the emitted light for unactivated crystals shown in Fig. 5, being consistent with the polarization of the exciting light, at least in the excitation region around 340 mμ.

The LT measurements of P^{ex} and P^{em} are given in Fig. 8 for which the emitted light is at 465 mμ. The only difference between these data and those presented in Fig. 6 for the unactivated crystals is that in the present case the emitted light goes through a polarization reversal at 330 mμ in that the light emitted due to longer wavelength excitation is polarized parallel to the c axis and the light emitted at shorter wavelength excitation is polarized perpendicular to the c axis. The association argument offered for the RT data can explain the opposite signs of polarization of excitation spectra for RT and LT at 370 mμ. At RT the absorbing center experiences the effective field of associated Cu$^+$ ions and hence its excitation is polarized parallel to the c axis. (At low Cu$^+$ concentrations, for unactivated crystals, there is
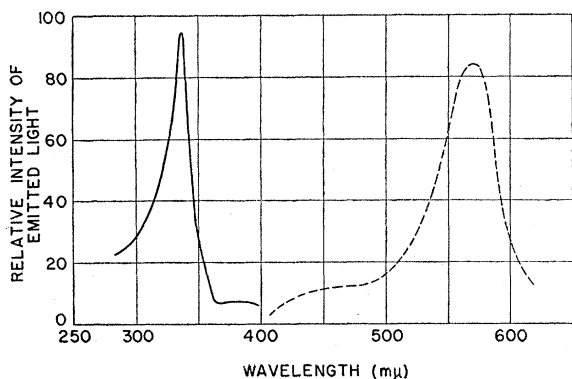

FIG. 9. RT excitation and fluorescence spectra of Mn activated single crystals. The solid line represents the excitation spectrum of the 570-mμ emission and the dashed line represents the emission resulting from 342-mμ excitation.

no polarization since the presence of small amounts of Cu$^+$ was sufficient to negate any selection rules such that there resulted no polarization.) At LT the effect of the associated Cu$^+$ ions is removed by uncoupling them from the absorbing center. As a result the absorption is polarized in the same direction as the fundamental absorption and as the absorption in so-called unactivated crystals. With these speculations, it is difficult to reconcile the polarization of the emitted light at LT. At RT we gave the argument that the associated ions effected an over-all symmetry at the emission site and hence gave the negative polarization of the emitted light. If the above is correct the emission at LT should be independent of the associated ions due to uncoupling, and it should be polarized positively as in unactivated samples and should be of the same sign for all exciting wavelengths. We see that this is not true and can offer no explanation for the reversed polarization of emitted light, at long wavelengths, at this time.
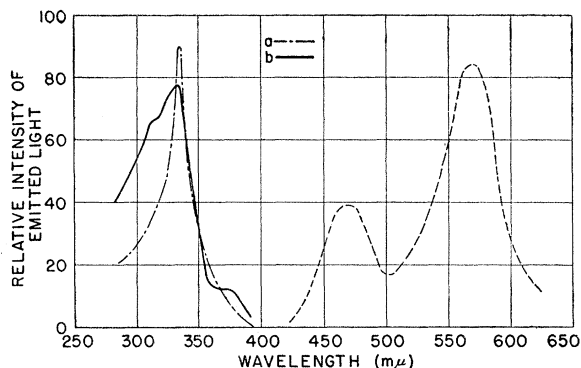

FIG. 10. LT excitation and fluorescence spectra of Mn activated single crystals. The curve a represents the excitation spectrum of 570-mμ light and the curve b represents the excitation spectrum of 465-mμ light. The dashed curve represents the emission spectrum resulting from 342-mμ excitation.

4. Excitation and Fluorescence Spectra of Crystals Activated with Mn

The crystals were grown as described previously. The concentration of Mn, as determined by spectrographic analysis, was between 1.0% and 10%. We know from a previous work[7] that Mn is present as the divalent ion and that it is present in the lattice in a substitutional site. It was hoped that the optical and polarization data of these crystals could be used as the reference for making conclusions about the nature of the lattice location of other centers.

a. Unpolarized Light

The RT excitation and emission spectra are presented in Fig. 9. The excitation spectrum was determined for the emitted light located at 570 mμ. The location of the excitation peaks, when comparable to those of other samples, at RT and at LT, are shifted to longer wave-

lengths by about 10 mμ. We have no explanation for this other than the fact that the inclusion of Mn into the lattice has so changed charge distributions and lattice spacings so as to shift the peaks. We assume that the 342-mμ excitation peak is due to the fundamental absorption. It is possible that there is green emission present at RT, but it is masked by the Mn emission at 570 mμ. As a result the 384-mμ excitation may result in unresolved 520-mμ emission and not in 570-mμ emission. In this way we can see why the 342-mμ excitation peak is so high. The excitation in the blue or green centers of Fig. 4 probably does not result in a transference of energy, by means of hole migration, to the Mn center. Hence, the fundamental absorption is the most efficient at exciting the Mn emission. This is born out by the LT data.

We present in Fig. 10 the LT data. There are two excitation curves, a and b. Curve a represents the excitation of 570-mμ light, whereas curve b represents the
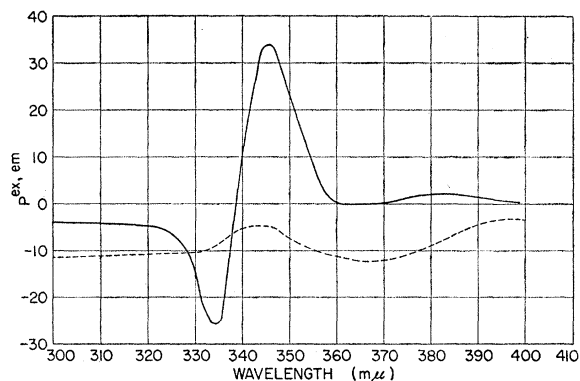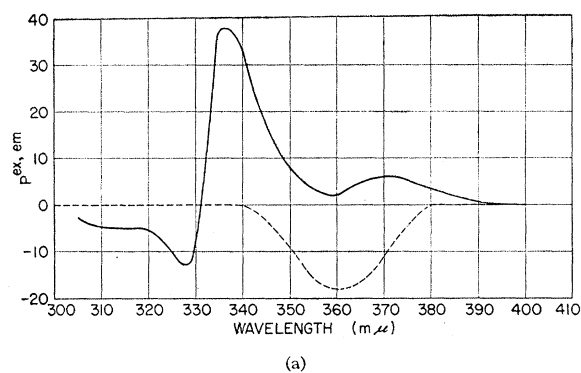

FIG. 11. Polarization of exciting and emitted light for crystals activated with Mn^{+2}. The data were obtained at RT and the emitted light is peaked at 570 mμ. The solid curve represents P^{ex} and the dashed curve represents P^{em}.

excitation of 465-mμ light. The emission is that due to 342-mμ excitation. These data afford an example of the nontransference of holes from the blue center of Fig. 4 to the Mn centers. If there were a transference we would see an excitation peak of the 570-mμ emission located around 370 mμ. From the structure shown near 319 mμ of the excitation curve b, we would expect to see an appreciable reversal of polarization in the excitation curve, which turns out to be the case.

b. Polarized Light

The quantities P^{ex} and P^{em} obtained at RT are presented in Fig. 11, in which the emitted light is at 570 mμ. The peaks in the polarization data have also been shifted to long wavelength as in the optical results. The data are slightly different from that of the Cu$^+$ centers shown in Fig. 7, in that there is a very small positive polarization to the excitation spectrum at around 384 mμ in the case of the Mn centers. The emitted light has negative polarization similar to Fig. 7.

(a)
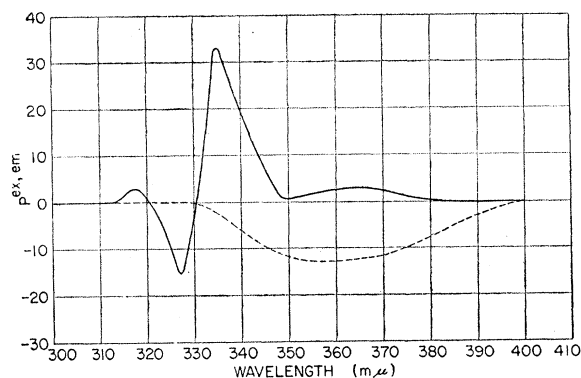
(b)

FIG. 12. Polarization of exciting and emitted light for crystals activated with Mn^{+2}. The data were obtained at LT. Figure 12(a) was obtained for the emitted light peaked at 570 mμ and Fig. 12(b) was obtained for the emitted light peaked at 465 mμ. The solid curves represent P^{ex} and the dashed curves represent P^{em}.

The quantities P^{ex} and P^{em} obtained at LT are presented in Figs. 12(a) and 12(b). The emitted light in the former is located at 570 mμ and the emitted light in the latter is located at 465 mμ. One should compare the data for the 465-mμ emission in Fig. 12(b) with the data for the same emission for the unactivated samples in Fig. 6 and with the data for the same emission for the Cu activated samples shown in Fig. 8. The results compare well with those shown in Fig. 8, except for P^{em} excited below 330 mμ. Since the Mn occupies a substitutional site it would do well to compare the data in Fig. 12(b), and other data obtained at RT, with those data in Fig. 12(a), obtained for the Mn centers. One sees that in Fig. 12(a) the P^{ex} curve is negative at short wavelengths and it is positive in the same region of Fig. 12(b).

From the previous RT data one can conclude that the green center in pure crystals does not have the same symmetry as the green center in crystals doped with large concentrations of Cu and neither does it have the same symmetry as substitutional Mn sites. The green centers in concentrated Cu samples also are not the same as the Mn substitutional sites.

The LT data indicate that the blue centers in unactivated crystals have a different symmetry from the blue centers in Cu activated crystals and different from
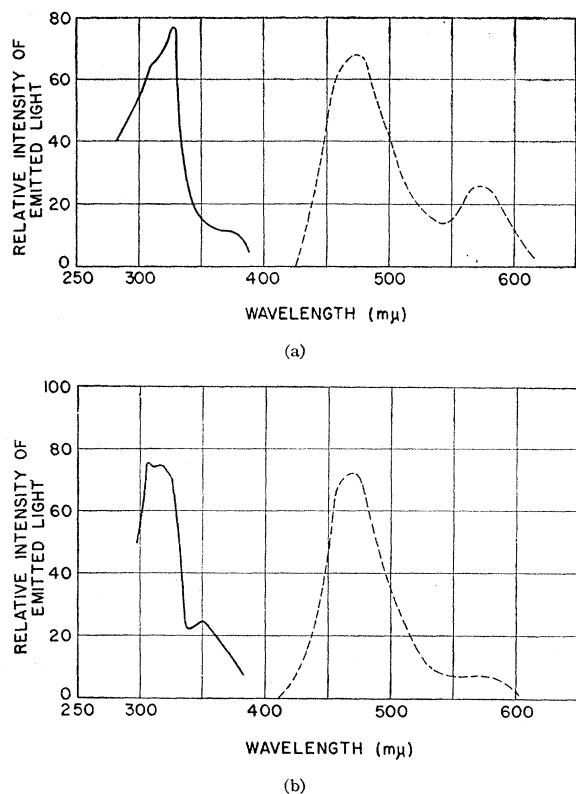
(a)

(b)

FIG. 13. LT excitation and fluorescence spectra of crystals activated with Cu, Al, and Mn. The solid curves represent excitation spectra and the dashed curves represent emission spectra. Figure 13(a) presents the excitation of the 570-mμ emission and the emission resulting from 328-mμ excitation, while Fig. 13(b) presents the excitation of the 465-mμ emission and the emission resulting from 358-mμ excitation.

the Mn^{+2} substitutional sites. Furthermore, the blue center in Cu activated crystals is slightly different from the substitutional Mn centers. The difference is in the short wavelength region in which the emitted light for Mn is not polarized whereas for Cu it is. This difference in behavior may be due to either (1) a difference in the method of transference of energy from the fundamental absorption to the Mn or Cu center, and (2) the difference in the polarization of the short wavelength excitation spectra as can be seen in Figs. 8 and 12(a).

5. Excitation and Fluorescence Spectra of Crystals Activated with Al

The crystals were grown with more difficulty than the others. We tried to get more Al doping into them but could only get between 0.001 and 0.01%. The crystals also contained Cu contamination between 0.0001 and 0.001%. We assume the Al is present in the trivalent state.

The optical data were essentially the same as the unactivated crystals and the spectra were essentially the same as that given in Figs. 2 and 3. In the RT excitation curve there was a structure at 532 mμ in addition to the

structures of around 420, 370, and 339 mμ shown in Fig. 2. The emission at RT was the typical green emission and that at LT was the typical blue emission. There was no structure seen near 319 mμ on the LT excitation spectra. Because of the similarity of the optical spectra between the present sample and unactivated samples we did not undertake any polarized light experiments.

6. Excitation and Fluorescence Spectra of Crystals Activated with Cu, Al, and Mn

The crystals were grown in the same fashion as the others. The percentages of the activators were as follows: 0.001–0.01% Cu; 0.001–0.01% Al; 0.01–0.1% Mn. There was also present from trace to small amounts of Ge, Ag, and In, presumably introduced from the quartz. The latter contaminants did not seem to affect the optical properties.

a. Unpolarized Light

The RT emission was the same as that presented in Fig. 9 for Mn activation. The excitation of the 570-mμ peak was the same as that shown in Fig. 9 with a shift of peak positions to shorter wavelengths, thus bringing them more in line with those of the unactivated phosphor of Fig. 2 and Fig. 3. Perhaps the perturbation to the crystal parameters introduced by Mn, as discussed in paragraph 4, has been compensated by the introduction of the other activators. The excitation spectrum of the 465-mμ emission is the same as that discussed in paragraph 3 for Cu activation.

The LT spectra are presented in Fig. 13(a) and 13(b). The former contains the excitation of the 570-mμ emission and the emission resulting from 328-mμ excitation while the latter contains the excitation of the 465-mμ emission and the emission resulting from 358-mμ excitation.

The conclusions that one can derive from the spectra are similar to what had been derived earlier. It appears as if the collective optical properties of the crystals activated with Cu, Al, and Mn are simply additions of the properties of crystals activated with Cu alone, and of crystals activated with Mn alone. A feature to be noted is the structure near 310 and 319 mμ on the excitation curve in Fig. 13(b). We have noticed frequently structure at 319 mμ which we have correlated with the negative polarization of the excitation spectra at about 320 mμ. We suspect that the 310-mμ structure should be associated with the positive polarization peak at 315 mμ in Fig. 6, the 314-mμ peak in Fig. 8, the 317-mμ peak in Fig. 12(b), and the positive peaks, to be reported in Figs. 14 and 15, at 315 mμ and 313 mμ, respectively.

b. Polarized Light

The quantities P^{ex} and P^{em} obtained at RT are presented in Fig. 14 in which the emitted light is located at 570 mμ. The results are similar to what were shown

in Fig. 11 for the sample activated with Mn alone and for which the data are also for the 570-mμ emission. (One sample, not shown, had no negative polarization at 325 mμ and its positive peak at 330 mμ had a magnitude of 85% and its emitted light was 30% polarized and flat over most of the exciting wavelengths.)

The LT measurements of P^{ex} and P^{em} are shown in Figs. 15(a) and 15(b). The emitted light in the former is located at 570 mμ and the emitted light of the latter is located at 465 mμ. The data shown in Fig. 15(a) are similar to the analogous data presented for the Mn activated sample in Fig. 12(a). Figure 15(b) presents data which are comparable to those presented in Fig. 12(b), for Mn activated samples, and Fig. 8, for Cu activated samples.

CONCLUSIONS

We have seen that in the case of the transmission spectrum through a single crystal, the selection rule governing direct transitions at $k=0$, resulting in the fact that $\alpha_\perp(\lambda_i) > \alpha_{\|}(\lambda_i)$, is obeyed at the fundamental absorption edge but it is reversed at shorter wavelength regions. Further, this reversal of polarization is also seen in the excitation spectra of activated and unactivated crystals and this reversal is associated with short-wavelength structure in the excitation curves obtained using unpolarized light.

The polarization of the light emitted from some samples especially unactivated samples, is in agreement with the results obtained by Lempicki.[5] Most of the activated samples emit light polarized parallel to the c axis, contrary to the results of Lempicki. In any case the polarization of the emitted light is a function of the wavelength of incident light and in those samples activated with Cu the polarization of the fluorescence can change sign as the wavelength of the exciting light is varied.

The exact meaning and consequences of these reversals of P^{ex} and P^{em} is not clear. One expects that in the fundamental region the light polarized perpendicular to the c axis to be more strongly absorbed than the light polarized parallel to the c axis, for direct transitions.
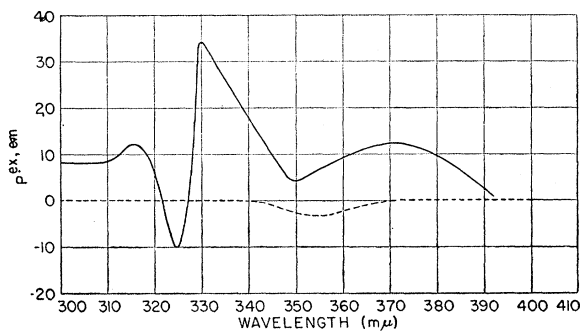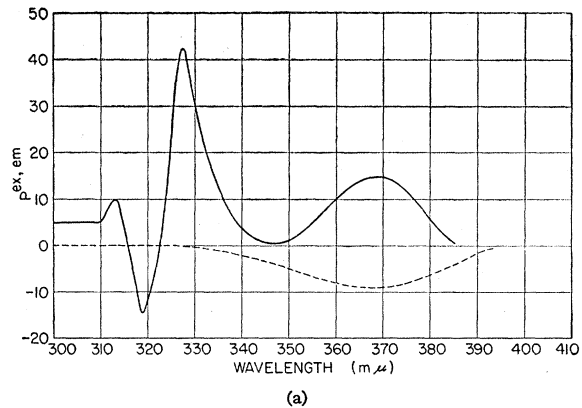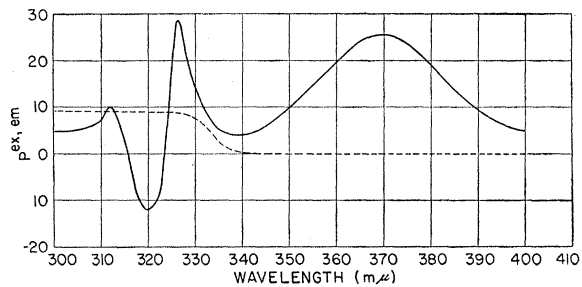
FIG. 14. Polarization of exciting and emitted light for crystals activated with Cu, Mn, and Al. The data were obtained at RT and the emitted light was peaked at 570 mμ. The solid curve represents P^{ex} and the dashed curve represents P^{em}.

FIG. 15. Polarization of exciting and emitted light for crystals activated with Cu, Mn, and Al. The data were obtained at LT. The solid curves represent P^{ex} and the dashed curves represent P^{em}. Figure 15(a) is for emitted light peaked at 570 mμ and Fig. 15(b) is for emitted light peaked at 465 mμ.

The reversal of this selection rule at shorter wavelengths is not understood. An interesting speculation associates these reversals with excitonic absorption. From a classical point of view one would expect the emitting center, if a substitutional site, to be influenced by the polar field of the crystal and hence emit light polarized parallel to the c axis. For the crystals activated with Mn, which is known to occupy a lattice site, the light emitted from the Mn center is polarized parallel to the c axis, consistent with the classical argument. This is also true for crystals activated with Cu, at least in certain spectral regions. As a corollary to the classical reasoning, one would expect that if a center emits light polarized perpendicular to the c axis then the center would be something other than substitutional, or that it at least feels a local field other than the polar one of the normal lattice. We find the emitted light to be polarized perpendicular to the c axis for those centers which supply the normal green and blue emission of unactivated crystals at all exciting wavelengths. It is similarly polarized in Cu doped samples for short-wavelength excitation.

From comparisons of the polarization of the various emissions to that of Mn, we conclude that the green center and the blue center of unactivated ZnS do not have simple substitutional symmetry, but our measurements do not enable us to conclude the nature of these centers. The centers associated with Cu, at least in

crystals with large concentrations of Cu, are also different from the green and blue centers of unactivated ZnS and are slightly different from the Mn centers as shown in polarization of the emission resulting from short-wavelength excitation. If we assume that the Cu, like the Mn, is substitutional, a possible explanation for the difference in the emission for Mn and Cu centers, even though they may be of the same symmetry, perhaps involves the nature of the energy transfer to the centers; i.e., the transfer of energy to the Cu center may reflect the nature of the absorbed energy directly whereas the transfer of energy to the Mn center goes via a different mechanism[15] and only less directly reflects the nature of the absorbed energy.

[15] R. Leach, J. Electrochem. Soc. **105**, 27 (1958); D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

It is possible that the dominant influence in the polarization of the emitted light for various centers lies in the symmetry of their excited and ground states, rather than the symmetry of the crystalline field.

There appears to be a connection between the existence of the reversal in polarization of exciting light near 320 mμ with changes in polarization of emitted light resulting from excitation at this wavelength (e.g., the change in sign of polarization of emission for Cu activated samples, decreases in degree of polarization of emitted light, for unactivated samples, etc.). We plan to investigate further the short wavelength polarization reversal. As yet we have been unable to correlate the results presented here and the photovoltages reported in reference 1.