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Electroluminescence in Zinc Sulfide

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Microscopic observations of electroluminescent emission from ZnS crystals activated with Cu, Cu:Pb, or Ag have shown that the typical emitting entity is a narrow line. These lines lie in $[1\bar{1}\cdot 0]$ directions of the wurtzite structure in planar regions associated with stacking faults or closely spaced alternations in crystal structure. A model of electroluminescence involving linear physical defects is proposed for the origin of the lines and their observed dependence on voltage, frequency, and phase of the applied electric field.

I. INTRODUCTION

A MAJORITY of the investigations of electroluminescence reported in the literature has been concerned with the macroscopic behavior of powders or of single crystals. Although several investigators have reported[1–14] that electroluminescence in ZnS crystals and crystallites is inhomogeneous, i.e., the emission originates from spots, streaks, or patches, these inhomogeneities have not been studied extensively. In previously proposed models of electroluminescence, physical defects have been of more importance in possible activation mechanisms than in explanation of the localization of emission.[15]

In the present work, extensive microscopic investigation of electroluminescent zinc sulfide crystals has shown that the emission typically takes place from localized regions which appear as discrete lines and spots. These emitting regions constitute an extremely small fraction of the crystal volume, of the order 10^{-6}. From these experimental findings it has been concluded that specific physical defects, in addition to the chemical-physical defects which serve as emitting centers, are necessary for the occurrence of electroluminescence, and a model is proposed to explain the existence of emitting lines and their observed dependence on experimental conditions.

Section II describes the basic experimental observations, Sec. III presents the proposed model, and Sec. IV contains a discussion of the model and some additional experimental data. Details concerning the materials studied and experimental techniques are contained in the Appendix.

II. BASIC EXPERIMENTAL OBSERVATIONS

A. Materials and Apparatus

The essential results of this paper are based on observation of electroluminescence at the microscopic level. Details of crystal preparation and handling, and of experimental apparatus are provided in the Appendix, while the most important features are noted here.

Vapor-grown crystals of ZnS doped with Cu were used. The crystals were of mixed sphalerite and wurtzite structures, the most active being 50–80% sphalerite. Crystal interiors were observed at magnifications up to 2000× through natural plane faces or polished plane surfaces.

Dependence of electroluminescence on voltage and frequency of excitation was studied from dc to 70 Mc/sec. Both sine waves and variable-length square waves were used. The phase relation between exciting voltage and emission from localized areas was also examined.

B. General Aspects of Microscopic Electroluminescence

Observations of many ZnS crystals have shown that the electroluminescent activity is generally confined to layers parallel to the basal plane of the wurtzite structure {(111) planes of sphalerite structure [See the Appendix for a description of the structure habit of the crystals examined.]}. In these basal layers the emission originates from tiny glowing lines and spots. Figure 1 shows a number of examples of these electroluminescent entities. The emission is not from the surface of the crystal but from the interior. The appearance of these sources in an alternating electric field is the same whether the electrodes are in contact with the crystal or are insulated from it. The lines have apparent widths of less than 5 μ, but range up to several hundred microns in length and frequently are arranged either parallel or at 60° to one another. The spots appear to be less than 2 μ in diameter. Comparison of electroluminescent patterns with x-ray orientation showed that the lines lie at 30° to the hexagonal a axes, i.e., along $[1\bar{1}\cdot 0]$ directions. The degree and extent of regularity of the

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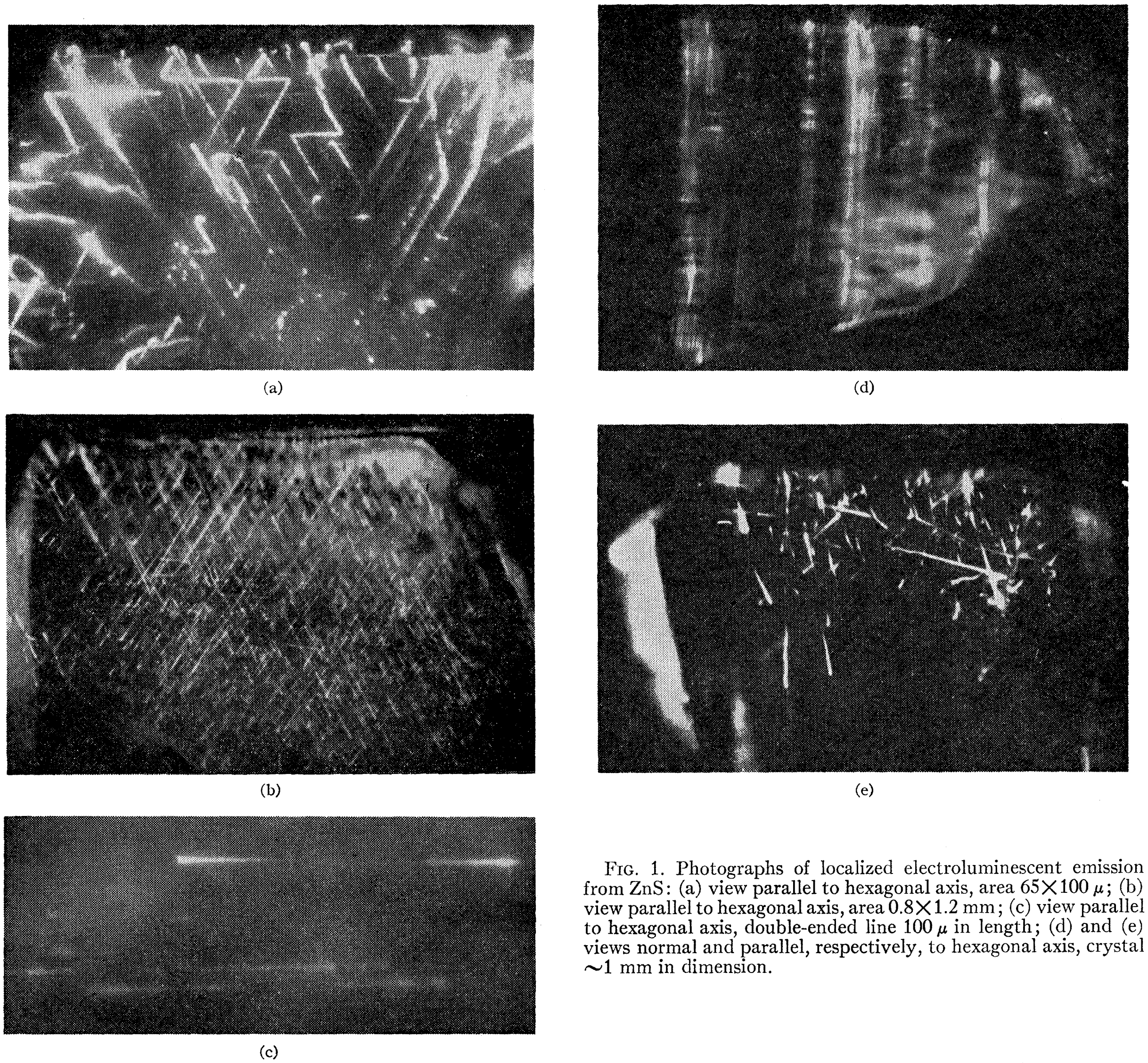

Fig. 1. Photographs of localized electroluminescent emission from ZnS: (a) view parallel to hexagonal axis, area 65×100 μ; (b) view parallel to hexagonal axis, area 0.8×1.2 mm; (c) view parallel to hexagonal axis, double-ended line 100 μ in length; (d) and (e) views normal and parallel, respectively, to hexagonal axis, crystal $\sim$1 mm in dimension.

pattern appear to be highest in the more perfectly formed crystals. Continuous zigzag lines composed of segments lying in $[1\bar{1}\cdot 0]$ directions were frequently observed.

The lines look somewhat like tiny comets, being brightest at one end and fading towards the other end. Sometimes several of these lines occur collinearly, all heading in the same direction, each with a uniform variation in brightness from the head to the tail. Lines often occur in collinear pairs, tail to tail, thus giving the appearance of a single line bright at both ends and faint in the center, as in Fig. 1(c). Occasionally, lines were observed that were curved, bent, wiggly, or had a random distribution of bright spots.

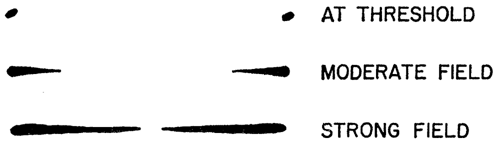

Fig. 2. Sketch of electroluminescent line emission as a function of field.

C. Voltage and Frequency Dependence

The position of the lines and spots is fixed in a given crystal, although the brightness depends on the direction of the applied electric field and is highest when the field is parallel to the lines. This directional effect is more pronounced at high than at low frequencies. As the applied field is increased from zero, those parts of lines which are brightest at high fields are seen first, so that the bright head of a line appears first, and then its tail forms and grows in length as shown in Fig. 2. Lines with bright points along their length appear first as rows of points. The longer lines are more easily excited and have thresholds as low as 1000 volts/cm average applied field. Shorter lines appear as the field is increased. Examination of several hundred electroluminescing zinc sulfide crystals has led to the conclusion that the bright-ended emitting line is the basic electroluminescent entity, and that observation of diffuse electroluminescence resulted from crystal imperfections or poor viewing conditions.

The observations described in the previous paragraphs were obtained with sine wave excitation at about 1 kc/sec. Further measurements were undertaken on selected crystals with sine wave excitation from 18 cps to 70 Mc/sec. At frequencies below a few hundred cycles, more electroluminescent lines are visible than at higher frequencies. They have a rather soft, diffuse appearance and relatively low intrinsic brightness. Many of them are long, 100 μ or more, and they are often quite crooked and may be disposed at large angles to the applied field direction. Generally, lines of this type are active only below about 500 cps. Often they are so numerous that even with very good optical viewing conditions resolution is difficult, because light emitted from regions outside the depth of focus produces a general background glow and reduces visual contrast. At frequencies of 1 or 2 kc/sec, the lower frequency lines have partially, and in some crystals completely, disappeared. Bright points at the ends of the remaining lines become still brighter relative to the lines themselves. The lines appear sharper or less diffuse and often develop irregularities in brightness along their lengths. Under the best optical conditions, many lines were found to be discontinuous, and some were composed of many short transverse segments less than a micron wide and spaced less than a micron apart in a "railroad tie" arrangement. As the frequency is raised above a few kilocycles the tails shrink and the lines condense into brilliant points or series of points, and at still higher frequencies may fade out altogether. Progressively higher frequencies lead to a succession of new lines which in turn disappear at still higher frequencies. Some of these changes are illustrated in Figs. 3 and 4.

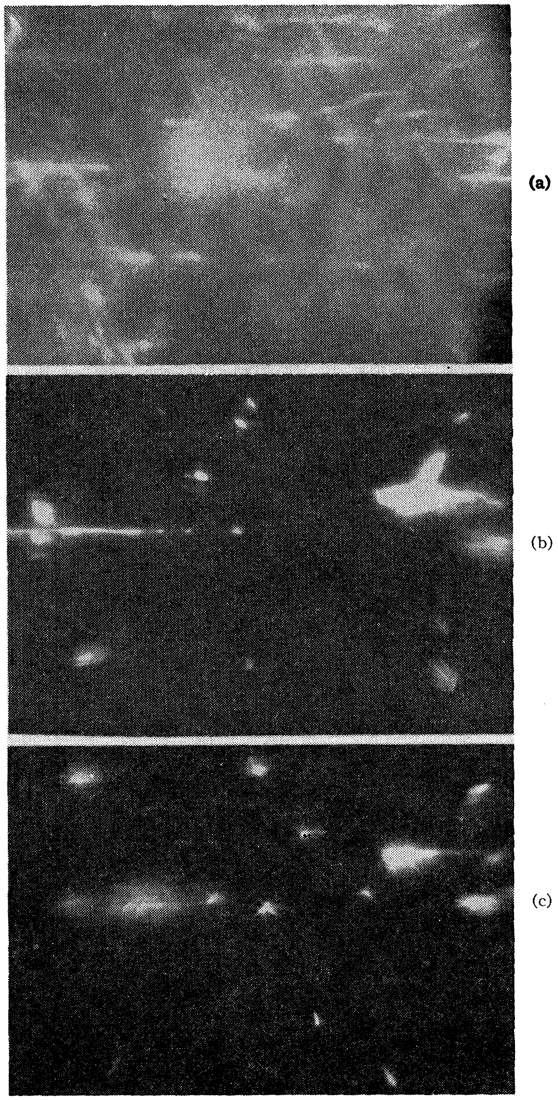

FIG. 3. Photographs showing change in aspect of electroluminescence with frequency, field 65×65 μ; (a) 200 cps, (b) 20 kc/sec, (c) 1 Mc/sec.

D. Excitation—Emission Phase Relation

The mechanical shutter discribed in the Appendix was used to observe the emitting activity of the individual electroluminescent lines during different phases of a square wave exciting voltage at frequencies from 50 to 1500-cps. It was found that each of the electroluminescent lines was active only for a field applied in one direction. The emission appeared suddenly for a positive voltage at the bright end of the line. The emission diminished with a decay time of about 1 msec, the applied voltage being constant. If the field was suddenly reversed, i.e., if a negative voltage was applied at the bright end before the emission had decayed normally, the emission abruptly ceased. The numerous lines active at low frequencies appear as two interlaced networks operating on alternate half-cycles. Opposite ends of double-ended lines also emit on alternate half-cycles, and the emission from spots is active only on one half-cycle. Rows of spots with spacings of a few microns emit in phase, but spots of wider spacings may emit alternately.

Additional information on the phase behavior of electroluminescent lines was obtained from the following experiment. One of the electrodes on a test crystal was grounded, and a sequence of positive, negative, or ground voltages was applied to the second electrode. When a negative potential was applied, no electroluminescence was generated. However, when the second electrode was subsequently grounded, the comet-shaped

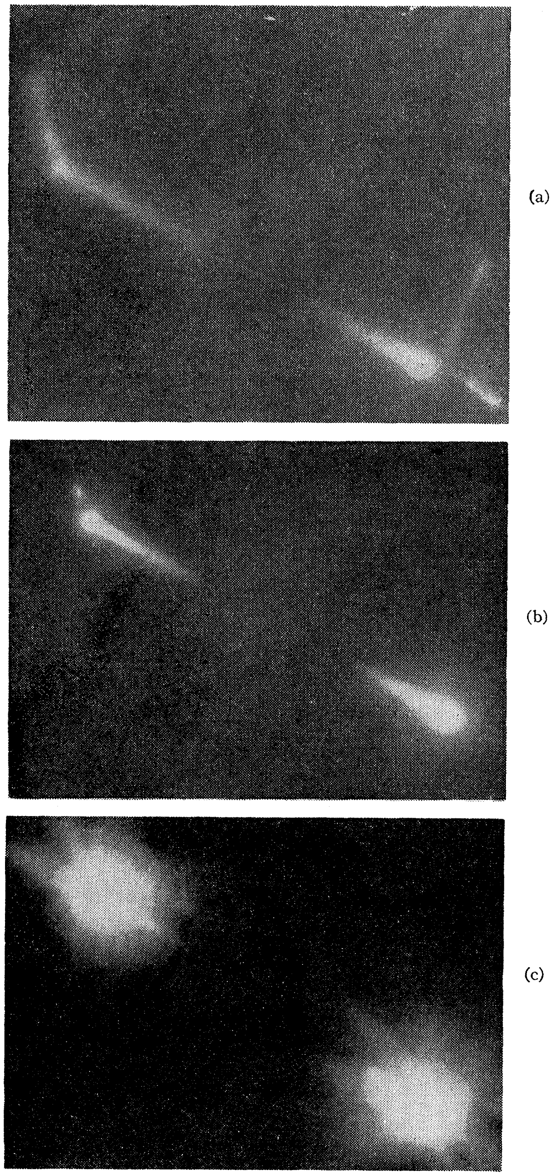

FIG. 4. Photographs showing change in aspect of electroluminescence with frequency, field 20×20 μ: (a) 2 kc/sec, (b) 20 kc/sec, (c) 10 Mc/sec.

lines heading toward that electrode were found to emit a single flash. If the second electrode was made positive and then grounded, these lines did not glow, but lines heading in the opposite direction were seen to flash. This relatively simple behavior was obtained only if the crystals were allowed to remain in the dark for several hours previous to the experiment or were exposed for several seconds to infrared light. If these precautions were not taken, space charge effects led to more complex behavior.

The normal ac electroluminescence appears to be a two-step process; it must first be primed by applying a negative voltage at the head of a line and then triggered by applying a positive voltage or grounding. The interval between the priming and triggering applications may be very long; with an interval of 1000 sec the intensity of emission decreases to only one-half that obtained for a half-second interval. Under infrared irradiation, the decay is more rapid; the intensity decreases to one half-maximum in about 6 sec and is lost altogether in about 500 sec.

E. Powder Particle Observations

Individual crystallites of ZnS:Cu:Pb and ZnS/Se:Cu:Pb powders, prepared by standard powder phosphor techniques, were examined in special holders (see Appendix) which provided an electric field perpendicular to the direction of view. Most of the crystallites were irregular in shape, and while they were actively electroluminescent, it was not possible to see into them because of their nonplanar surfaces. There were a few platelets (10–40 μ across) of hexagonal or triangular outline with flat faces through which their interiors could be viewed. Electroluminescence was observed only when the field was applied parallel to the flat face of a crystallite.

The electroluminescence in these phosphor powder crystallites appears to be quite the same as that in the large crystals. It occurs as tiny spots and lines of light. The lines are comet shaped, lie parallel to the large faces and a crystal edge, and occasionally occur in collinear, tail-to-tail pairs like those in Fig. 1(c). Study with a mechanical oscilloscope showed that the lines glowed when the adjacent electrode, i.e., the one nearest their bright end, became positive.

III. MODEL OF ELECTROLUMINESCENCE

It is proposed that specific linear physical defects are associated with, and are necessary for, the observed linear patterns of electroluminescence. These defects are presumed to be dislocations or dislocation-created defect lines as described below. The observed electroluminescent lines do not emit uniformly along their lengths but appear in the simplest case as lines with fixed ends, the interiors of which light up under certain conditions from the ends toward the center. The fixed ends and the extension of electroluminescence away from these ends under increased voltage or decreased frequency lead to the postulation of an additional defect which intersects the linear channel at these points; this additional defect is believed to be a *p–n* junction plane, with the *n*-type side of the plane toward the region from which electroluminescence is observed.

The proposed mechanism consists of a two-stage process which depends on the existence of effective *p–n* junctions and of linear defects with which there is associated a high density of acceptor levels. In the first or activating stage, the applied voltage is positive on the *n*-type side of the junction and negative on the *p*-type side, causing both electrons and holes to move away from the junction region. The second stage begins when the voltage is reversed and holes are injected into the *n*-type region where they are captured by the linear defect states and are transferred to chemical luminescent centers. The activated luminescent centers then emit light upon capture of an electron.

This mechanism leads to a depletion of the electron and hole concentrations, and these must be replenished by a primary activation mechanism dependent on the applied field. Acceleration of electrons to velocity sufficient for impact ionization of impurities or for pair production is a process frequently proposed,[15,16] although there is strong evidence against the impact mechanism.[17] Such processes would require carrier mobilities of $\sim 10^3$ cm^2/volt sec in fields of 10^5 volts/cm over distances of 100 μ. Such mobility is not unreasonable for electrons in ZnS; observed dependence of the electroluminescent line lengths as a function of frequency indicates hole mobilities $\sim 10^{-2}$ to 10^{-1} cm^2/volt sec, far below the required value. Regions of high field gradient, such as the postulated *p–n* junctions biased in the reverse direction, could provide the acceleration necessary for electrons to reach velocities for pair creation.

If dislocations in the basal plane of the wurtzite structure lie in the close-packed directions, $[10\cdot 0]$, then the linear defect involved in electroluminescence may be identified with a row of vacancies or of interstitials along $[1\bar{1}\cdot 0]$ created by interaction of screw dislocations.[18] Such a configuration would probably not be energetically stable, but a number of vacancies or interstitials may remain within a sufficiently localized region to appear as a line on the scale (approximately 5 μ wide) observed. Consideration of the energies involved in establishing a dislocation in various orientations in the wurtzite basal plane makes it seem possible that a dislocation may well lie not along the close-packed directions but along the $[1\bar{1}\cdot 0]$ directions. Such a dislocation could then be perpendicular to its Burgers vector and would be pure edge. We shall assume that such edge dislocations do exist; the alternative possibility of dislocation-created channels or rows of interstitials is not excluded, and similar behavior is expected for both kinds of defects. Associated with an edge dislocation will be a number of "dangling bonds" equal to the number of atoms along the dislocation edge.[19] These correspond to energy levels at some energy above the valence band and could serve as donor or acceptor centers depending on the position of the Fermi level. It will be assumed that these levels lie ~ 1 ev above the valence band and are acceptor levels. If the linear defects are indeed hollow channels created by dislocations, they will constitute essentially internal surfaces since the wave functions on atoms at opposite sides of a channel ~ 6 A in diameter do not overlap appreciably. Such a surface will possess energy states again arising from the atomic energy levels which can no longer participate in bonding. These Tamm states would be expected to lie slightly above the top of the valence band and would act as acceptor or hole trapping centers. In either case the linear defect would represent a high density of acceptor centers and would have a large effective cross section for hole capture.

Holes injected into an *n*-type region and captured at acceptor centers represent an excitation which could then be transferred to luminescent centers lying close to the channel. Such luminescent centers may consist of associated pairs of copper and chlorine ions,[15] but their exact nature is not critical to the mechanism proposed and they might in some cases be the linear defect acceptors themselves. The existence of *Z* or zigzag lines evenly illuminated over their length indicates that charge carriers generally do not move along the linear defects but through the bulk of the material, and are captured by acceptor sites associated with the defects. However, the intensity of emission from a given line has been found to vary with the magnitude of the projection of the electric field on the line, indicating that the electroluminescent process is dependent in some way on the field component along the line. This latter observation may be explained if it is assumed that the *p–n* junction planes tend to lie normal to the linear defects so that a field parallel to a channel provides the maximum voltage drop across the junction.

IV. DISCUSSION AND FURTHER OBSERVATIONS

A. Voltage and Frequency Dependence

The typical double-bright-ended electroluminescent line has fixed end points which are the brightest part of the line and "tails" which extend toward each other from these ends. As the frequency of applied voltage is increased, the tails shrink until at very high frequencies only the end spots remain. Such behavior would be expected on the basis of the model proposed here. Holes injected into the *n*-type region in which the electroluminescence occurs would have to travel through the crystal in order to activate regions along the observed electroluminescent line. The observed transient times are comparable to the period of the applied voltage at 20 kc/sec, and increases in frequency in the upper audio range and above shorten the average distance which holes travel and activate luminescent centers, thus causing a decrease in the length of the electroluminescent lines. If we take a typical line length of $\sim 5\times 10^{-3}$ cm, a field gradient of $\sim 10^4$ volt/cm, and a transient time $\sim 5\times 10^{-5}$ sec, the hole mobility is found to be $\sim 10^{-2}$ cm^2/volt sec. Total emission at low frequencies will increase with frequency since the number of emission periods is increased. At some higher frequency the

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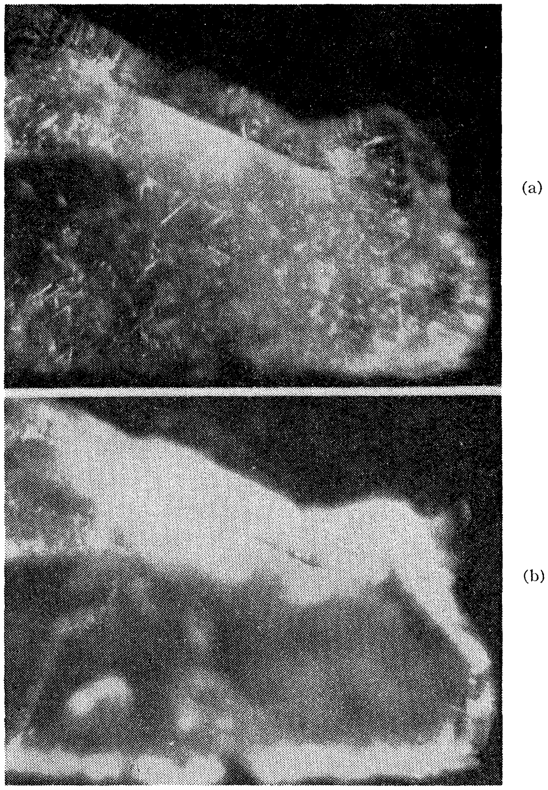

FIG. 5. Photographs of crystal in (a) normal electroluminescence and (b) electrode electroluminescence conditions. Field 0.8 ×0.6 mm.

total emission will begin to decrease since the activating carriers are more and more restricted in their extent of travel, becoming confined to the already saturated region near the *p–n* barrier.

Increase in voltage was observed to lead to an increase in the length of the tails constituting the double-ended line. At sufficiently high voltages, the tails merged to form a continuous line of fixed length. This behavior is expected as the voltage is increased and the activating holes move farther from the injection point. Required voltages for observation of electroluminescence depended strongly on the particular crystal and line under observation. At very low voltages only the two spots at the line ends could be distinguished and these usually seemed to become visible suddenly as if a threshold for their activation existed. The threshold level varied from crystal to crystal. Such a threshold may be connected with the height of the *p–n* junction and may represent not a uniquely critical voltage but rather a function which involves an exponential increase with voltage of the number of charges moving across a junction.

B. Relaxation; Temperature Effects

Observations of emission from individual lines and sections of lines, made by pulse measurements in which the length of pulse and repetition rate could be varied, showed that the major electroluminescent process required an activation stage with the voltage applied in the opposite direction to that in which it was applied during the emission process. The decay time of the activated state is $\sim 10^3$ sec, suggesting that space-charge effects with trapping of carriers are taking place.

The ac electroluminescence in a number of crystals was found to be reversibly altered by changes in the experimental conditions. Above 10–20 kv/cm. electroluminescence throughout the volume of these crystals spontaneously fades away, and emission develops at the crystal surfaces adjacent to the electrodes and to internal faults as shown in Fig. 5. This type of luminescence, which will be referred to as electrode electroluminescence, consists of many short lines, most less than 10 μ in length, which project inward from the surface. The time required for the spontaneous formation of this configuration decreases with increasing voltage. At fields just above the threshold for electrode electroluminescence, 20–30 minutes is required to complete the change, while at twice the threshold field, it is complete in less than a minute. The change from normal electroluminescence to the electrode electroluminescence can be induced immediately by a brief exposure of the crystal to 3650-A radiation. If the applied field is below the threshold for electrode electroluminescence, the normal electroluminescence redevelops a few seconds after the radiation is removed. Electrode electroluminescence is quenched, and the normal electroluminescence is restored, by irradiation of the crystal with infrared. The electrode electroluminescent behavior is the same whether electrodes are applied directly to the crystals or are insulated by mica sheets.

The change from the normal to electrode electroluminescence is presumed to result from space-charge formation. Under conditions for normal electroluminescence, the field gradient, at least on a macroscopic scale, is apparently uniform across the crystal. Under the conditions for electrode electroluminescence large field gradients appear near the electrodes, as indicated by formation of the thin sheets of very intense electroluminescence and by flashes due to breakdown that are sometimes seen to traverse these sheets. The effect of ultraviolet may arise from the liberation of sufficient electrons to prevent maintenance of the field gradient necessary for normal electroluminescence. The appearance of electroluminescence from a localized region next to the cathode has been reported[1,9,10] and interpreted[1,10,20] as emission from centers ionized by impact of electrons injected at the cathode and accelerated through a surface exhaustion layer. In the present experiments it was not necessary to place the electrodes in electrical contact, so that injected electrons would have to arise from charges trapped at the surface. In other re-

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spects the Piper and Williams model seems to explain the behavior and characteristics of the electrode electroluminescence.

The application of a narrow stripe of infrared radiation (ir) (about 100 μ wide) to the dark central portion of a crystal in its electrode electroluminescent condition slightly diminishes the emission at the electrodes and produces a stripe of normal electroluminescence in the infrared-irradiated part. When the ir is removed, the band of induced normal electroluminescence fades away in a few seconds. The action of the ir is presumably to release electrons and/or holes from traps so that they may participate in the electroluminescent process, the majority of previously available carriers having accumulated near the electrodes.

A spot of ultraviolet (uv) light (50 μ in diameter) placed anywhere on a normal electroluminescent line quenched all of the line on the side away from the "head" end; if the spot was moved up to touch the head end of the line from outside the line, the whole line was quenched.

Observation of localized emission with the appearance of "striations" has been reported by Oranovskii and Khmelinin,[11] who have investigated the effect of visible and ir irradiation on the striations. Their results are similar to those reported here, i.e., quenching by white light and enhancement by ir. These authors also suggest that their observed spots occur where the striations intersect *p–n* boundaries, as postulated here.

Measurements of the temperature dependence of brightness by several experimenters[21–23] indicate that brightness changes depend largely on changes in available carrier concentration as influenced by thermal activation and recombination. As the temperature is decreased from room temperature, the brightness will increase with the mobility of charge carriers provided that the number of carriers is constant and the mobility is limited by lattice scattering. At temperatures such that appreciable trapping of charge carriers takes place, the brightness will decrease with decreasing temperature. In the absence of knowledge of the temperature dependence for either electron or hole mobilities, a simple speculative interpretation of the present experiments may be made. In crystals a decrease in brightness was observed from 300°K down to 200°K, indicating a trapping of carriers available at room temperature. Below this temperature the brightness again increased, suggesting a constant concentration of carriers and increasing mobility. At still lower temperatures, below 100°K, the brightness again decreased, indicating the presence of further trapping or of mobility limited by impurity scattering. In similar measurements on ZnS powder phosphors, the minimum in the region of 200°K was not observed. This may be due to a mobility limited by impurity or boundary scattering even at the higher temperatures. In the model proposed above, changes in carrier density of either electrons or holes can be important depending upon the relative concentrations on either side of the *p–n* junctions.

The color of electroluminescent emission in ZnS crystals was observed to change with decreasing temperature or with increasing frequency from green or blue-green to blue or blue-white. A possible explanation might be as follows. If the luminescent trapping centers activated by injected holes are of two energies, corresponding to levels ~2.5 ev (green) and ~2.7 ev (blue) below the conduction band, the observed behavior will result if blue levels have capture cross sections larger than those for green. In equilibrium, the green centers, lying higher in energy, will tend to be populated in preference to the blue centers by holes moving into the *n* region. At low frequencies or high temperatures, equilibrium will lead to greener emission. At high frequencies or low temperatures equilibrium will not be attained, and the relative capture cross sections of the centers will cause preferential activation of the blue centers and consequent blue emission. This behavior is similar to hole-migration-based explanations of color changes with temperature and excitation conditions proposed by Schön,[24] Klasens,[25] and others.

C. Physical Defects, Junctions

Dislocations presumably could arise due to the strain induced by the transition from wurtzite to sphalerite which the crystal undergoes upon cooling after formation. It would be expected that formation of additional dislocations would result in increased activity. Attempts to increase dislocation density by various mechanical methods of cold working did not, however, result in increased activity. Attempts to observe changes in the electroluminescent emission patterns during application of forces up to those sufficient to fracture the crystal have also been unsuccessful. The negative results of these experiments are presumably due to the high energies required to create or move dislocations in this material at room temperature. At the higher temperatures traversed during the cooling process from growth temperature of the order of 1100°, formation and movement of dislocations may well take place. Very good correlation has been obtained between electroluminescent activity and the concentration of stacking faults in zinc sulfide.[6,26–29] Stacking fault regions presumably have associated with them more strain than pure cubic

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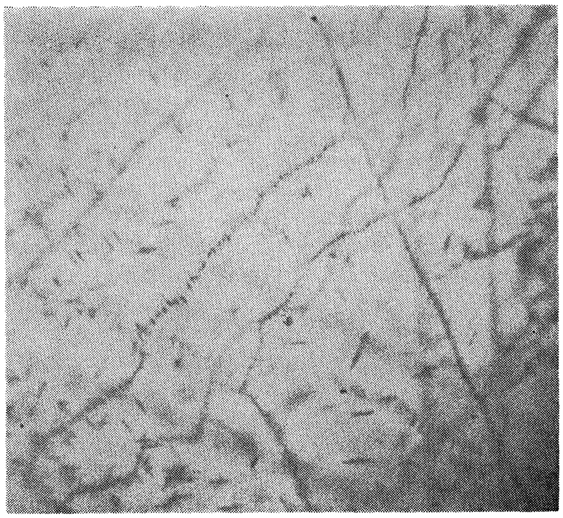

FIG. 6. Photograph of precipitate in ZnS:Ag crystal achieved by diffusion of copper. View parallel to hexagonal axis, field 75×70 μ. Depth of focus less than 1 μ.

or pure hexagonal regions, and the concentration of dislocations resulting from attempts to alleviate such strain would be higher in such faulted regions. Alternatively, the linear defects may be partial dislocations which, with the stacking faults, arise from strain-induced primary dislocations.

Decoration was obtained in nonactive ZnS:Ag crystals which were coated with copper by wetting with copper sulfate solution or by vacuum evaporation of copper metal, and were then heated to 400–750°C. for 15–30 minutes. The body color of decorated crystals was a deep blue. The decoration consisted of lines of a dark precipitate 5–100 μ in length usually lying in basal planes, and often arranged in patterns containing 60° angles. Another common feature was a row of short parallel lines in a "railroad tie" arrangement. Some of these rows were several hundred microns long and had a rather sinuous shape.

Most of the crystals were not decorated throughout. A peripheral layer contained the precipitate while the central part remained clear. In some such crystals, electroluminescence having the same appearance as that in crystals activated during growth was induced in the clear parts. No electroluminescence occurred in the darkened regions. Reheating the blued crystals to 800–900°C for 30 minutes clarified them and usually produced electroluminescence in the previously blued regions. Although there is similarity between the decoration patterns (Fig. 6) and those of electroluminescence, a correspondence between decorated and previously active electroluminescent regions was not established.

A number of microscopic ridges were found on a natural (00·1) face of a decorated crystal. The widest ridges were less than 2 μ across, and some were as long as 200 μ. Some were straight and others were curved, some were broad at one end and tapered away toward the other. Many terminated at holes at one or both ends, while others had holes along their lengths. There were also isolated holes in the surface, occasionally in rows, but usually randomly distributed. A photomicrograph of these surface features, Fig. 7, shows their resemblance to electroluminescent patterns.

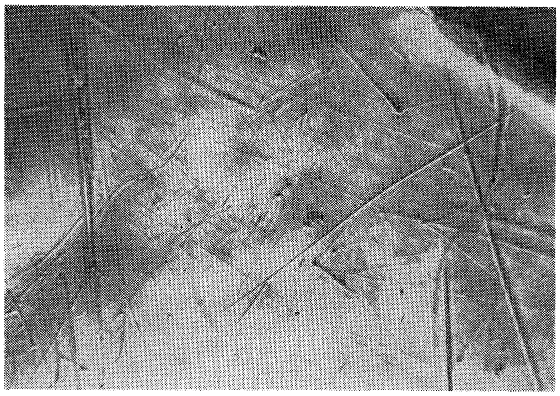

FIG. 7. Photograph of microscopic ridges on ZnS surface normal to hexagonal axis. Field 90×60 μ.

It is possible that local fluctuations in stoichiometry during growth lead to the formation of regions containing alternately sulfur or zinc in slight excess, and the boundaries between such regions correspond to *p–n* junctions. Similar effects might alternatively be brought about by local variation in impurity content. Evidence for rapid alternation of *n* and *p* type with the resulting formation of numerous junctions in zinc sulfide is found in the large photovoltages observed by Ellis *et al.*[30,31] These, however, have only been observed in directions parallel to the *c* axis and, therefore, at right angles to those junctions postulated here.

Junctions are believed present as planes spaced 1–100 μ apart and having thicknesses of 1 μ or less. Junctions formed in elemental semiconductors can be made as thin as 1 μ with some difficulty. Diffuse junctions may give rise to the electroluminescence observed at low frequencies; thin junctions are necessary for higher frequency response.

V. CONCLUSIONS

The electroluminescent emission sources in a number of zinc sulfide crystals and crystallites were found by microscopic observation to be fine lines and spots. Study of the behavior of these emitting entities under variations of voltage, frequency, and phase of the exciting ac electric field has led to a model of electroluminescence in zinc sulfide. This model requires the existence of linear defects ∼100 μ in length, lying in particular directions, i.e., $[1\bar{1}\cdot 0]$, in the wurtzite structure, and with which are associated a high density of acceptor levels. The model also requires local variations

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[30] S. G. Ellis *et al.*, Phys. Rev. **109**, 1860 (1958).

[31] W. J. Merz, Helv. Phys. Acta **31**, 625 (1958).

from p- to n-type material, with consequent narrow p–n boundaries or junctions.

The complete electroluminescence cycle is envisaged as follows. During the first step, with few available carriers, the higher mobility electrons are accelerated to velocities sufficient for pair creation. Free electrons and holes might also be produced with greater efficiency by impact ionization of impurities followed by liberation of the hole by thermal energy. At the beginning of the second step holes migrate across p–n junctions into n-type regions where they are trapped predominantly at the linear defect acceptor levels. This excitation is transferred to nearby luminescent centers, presumably by hole migration, and emission occurs upon combination of an electron with the activated center. The shrinking of the lines to fixed spots with increasing frequency or decreasing voltage, and the phase relation between emission and applied ac or dc electric fields are in agreement with the proposed model.

ACKNOWLEDGMENTS

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APPENDIX

Experimental Materials and Apparatus

Single crystals of zinc sulfide, of average size 0.5×0.5×1.0 mm, were prepared at temperatures in the range 900–1200°C by sintering of ZnS powder or by sublimation and deposition on a cooler surface. Heating was carried our in evacuated and sealed silica tubes placed in gradient furnaces. In the vapor deposition process the charge was normally between 1100° and 1200°C and the crystals formed on the tube walls at a temperature from ten to several hundred degrees lower. The starting material was phosphor-grade ZnS to which 0.01 to 0.1% of an activator was added. Silver, manganese, copper, lead, and gold were used as activators; the greatest activity was obtained with copper or copper plus lead. For a given starting phosphor and activator, it was found that the threshold voltage for electroluminescence of the vapor-grown crystals varied systematically with the deposition substrate temperature, showing pronounced minima at intervals of ~150°C for deposition temperatures from 950° to 1200°C. Crystals studied in this paper usually were chosen from those at minimum threshold. Additional activation was sometimes achieved by heating single crystals for 24 hr at 400° to 900°C in a phosphor medium to which activator metal chlorides had been added.

The majority of crystals were of mixed sphalerite and wurtzite structures with the relative concentrations depending on furnace conditions. The most actively electroluminescent crystals were 50–80% sphalerite. The crystals generally formed as prisms with axes parallel to the hexagonal [00·1] direction (cubic [111]), i.e., perpendicular to the close-packed plane. Microbeam x-ray diffraction showed that structures other than pure cubic or pure hexagonal also occurred. For example, Fig. 8 shows a prism in which the structures vary from point to point as indicated by bands of striae on its surface. The clear regions were entirely hexagonal, giving sharp x-ray spots, while the banded regions exhibited mixed structure, showing diffuse spots with long streamers trailing off toward the positions on the x-ray film where spots for sphalerite would be expected. Study of the crystal structure by means of optical birefringence[29] confirmed these structure conclusions.

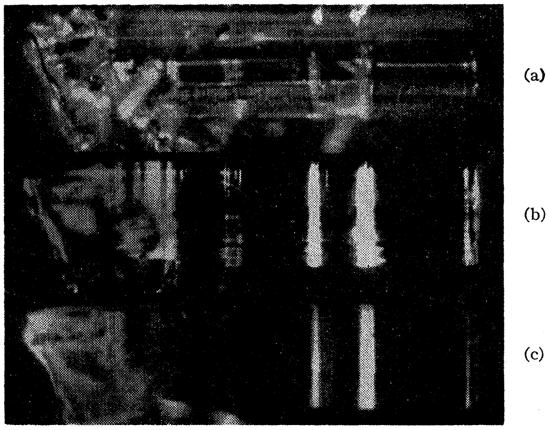


FIG. 8. Comparison of (a) reflected, (b) electroluminescent, and (c) fluorescent light from 0.8-mm long ZnS crystal.

Preliminary examinations were made by placing crystals on a conducting plate which served as one electrode and moving up a loop of fine wire mounted on a micromanipulator which served as the second electrode. Observations were then made with a binocular microscope providing magnifications up to 150×.

Crystal mountings similar to that of Fig. 9 were used for more detailed studies at magnifications up to 2000× utilizing a monocular microscope fitted with an oil immersion objective. Photomicrographs were taken with a 35-mm Exakta camera using Adox KB14 or Kodak Microfile film. Electroluminescence exposures ranged from 2 to 30 minutes. Some crystals had plane natural faces which permitted a clear view of their

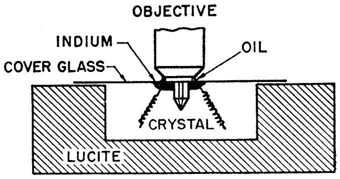


FIG. 9. Experimental arrangement for observation of electroluminescence at high magnification.

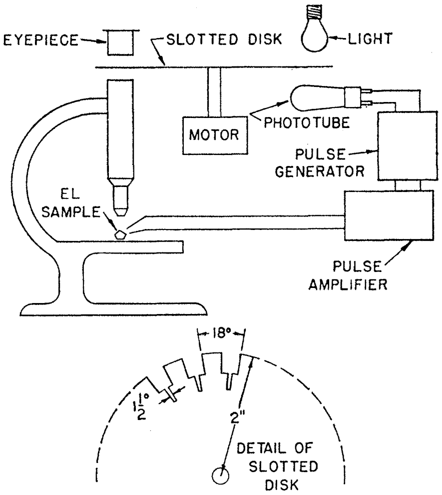


FIG. 10. Schematic diagram of mechanical oscilloscope for study of phase relation between excitation and emission.

interiors; in others, suitably flat surfaces were prepared as follows. The crystal was worked into the desired position in a rosin-filled machine screw nut using a hot needle. This assembly was then ground down to the desired level with 600-grit carborundum, given a fine grind with 6-μ garnet, and finally polished with 0.3-μ alumina on dampened, hard filter paper.

Sine wave excitation voltages were provided by an audio oscillator-power amplifier system for frequencies from 18 to 50 000 cps and by fixed radio-frequency oscillators at 1, 10, and 70 Mc/sec. In addition, subaudio frequency square wave excitation voltages from 0.001 to 20 cps were produced by mechanical or electromechanical switching of dc power supplies.

The experimental arrangement used to measure the phase relation between emission from localized areas of the crystal and the exciting voltage is shown in Fig. 10. Slots in the periphery of a rotating disk passing through the axis of a microscope at the focal plane of the eyepiece served as stroboscopic shutters, and also interrupted light falling on a photomultiplier to produce an alternating voltage synchronous with the shutter. The photomultiplier output drove a pulse generator-amplifier that delivered rectangular pulses to the crystal with rise and decay times of a few microseconds. The angular position of the photomultiplier could be changed so that the phase of the voltage cycle could be shifted more than 360 degrees with respect to the viewing point. The viewing slot gave a time resolution of 0.08 of the total voltage cycle.

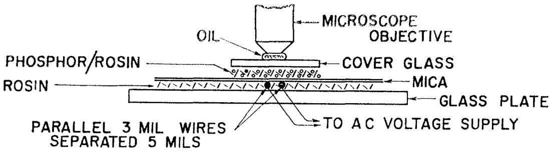
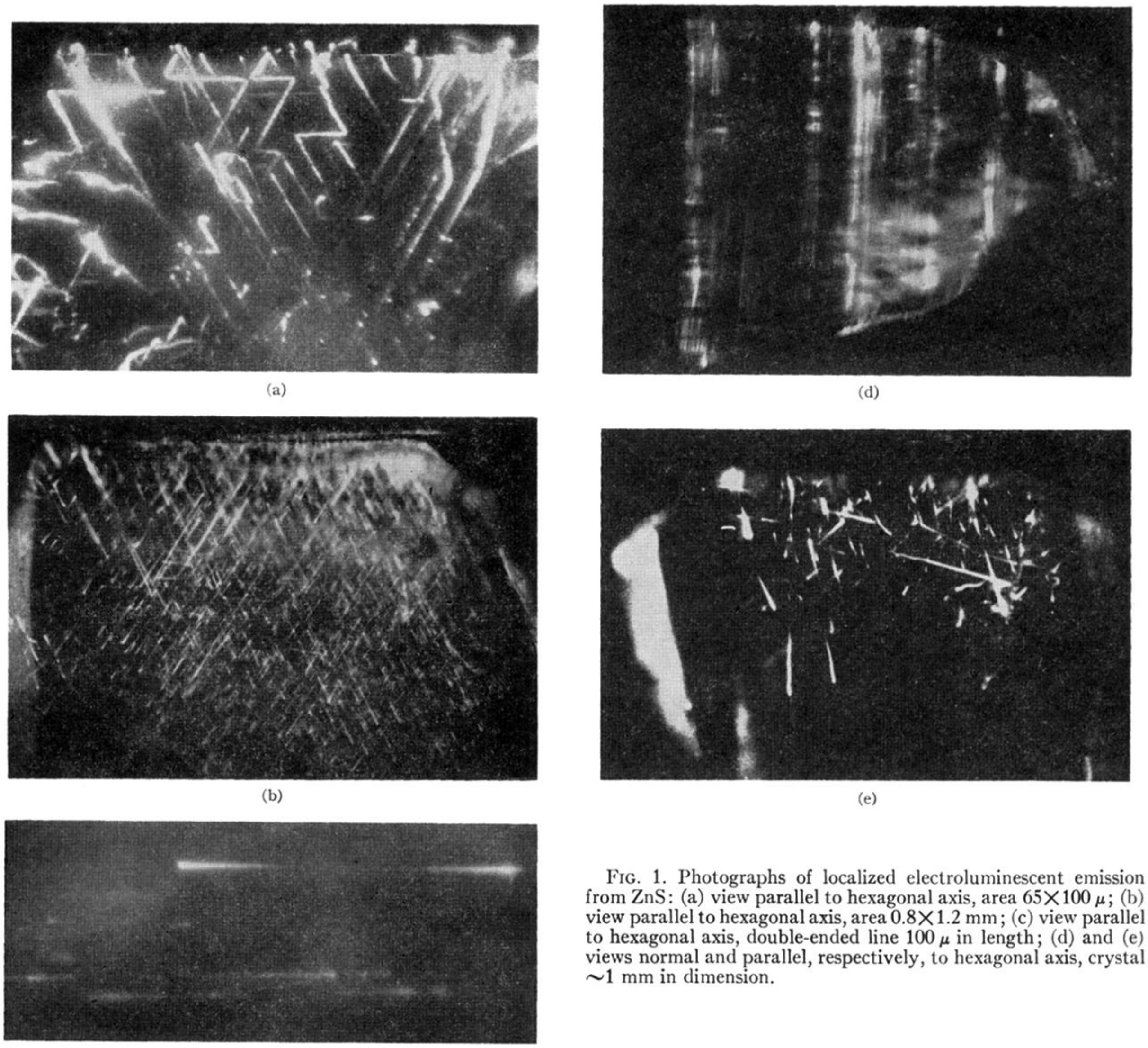


FIG. 11. Viewing arrangement for observation of electroluminescence in powder phosphors.

Although most of the observations were made at room temperature, electroluminescence in a number of crystals was examined over a range of temperatures using an apparatus in which the crystals were supported in vacuum, under a horizontal window, on the end of an inclined metal tube which was cooled with liquid nitrogen or heated electrically. Crystals could be observed through the window with a binocular microscope at temperatures from $-196°C$ to 250°C.

A special holder was found necessary for good observations on powder phosphor crystallites due to the double requirements of high magnification, and field perpendicular to the direction of view. As shown in Fig. 11, the required field component is obtained by using as electrodes two 3-mil wires placed close together under the phosphor suspension, thus avoiding interference with the viewing arrangement. Only the crystallites in a small volume above the electrodes are excited suitably for observation of emission details.



(a)

(d)

(b)

(e)

(c)

FIG. 1. Photographs of localized electroluminescent emission from ZnS: (a) view parallel to hexagonal axis, area 65×100 μ; (b) view parallel to hexagonal axis, area 0.8×1.2 mm; (c) view parallel to hexagonal axis, double-ended line 100 μ in length; (d) and (e) views normal and parallel, respectively, to hexagonal axis, crystal ~1 mm in dimension.

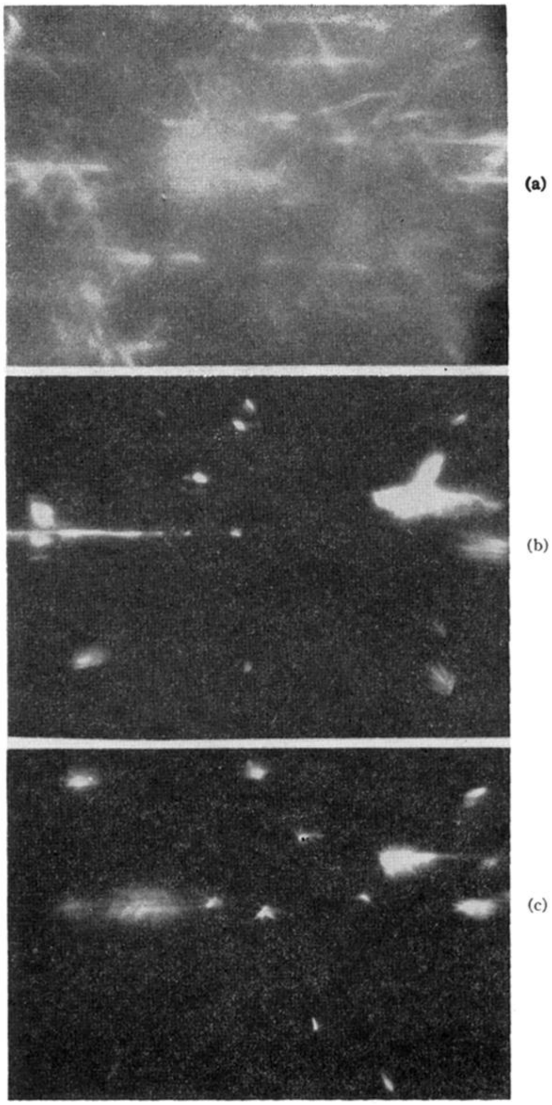


FIG. 3. Photographs showing change in aspect of electroluminescence with frequency, field 65×65 μ; (a) 200 cps, (b) 20 kc/sec, (c) 1 Mc/sec.

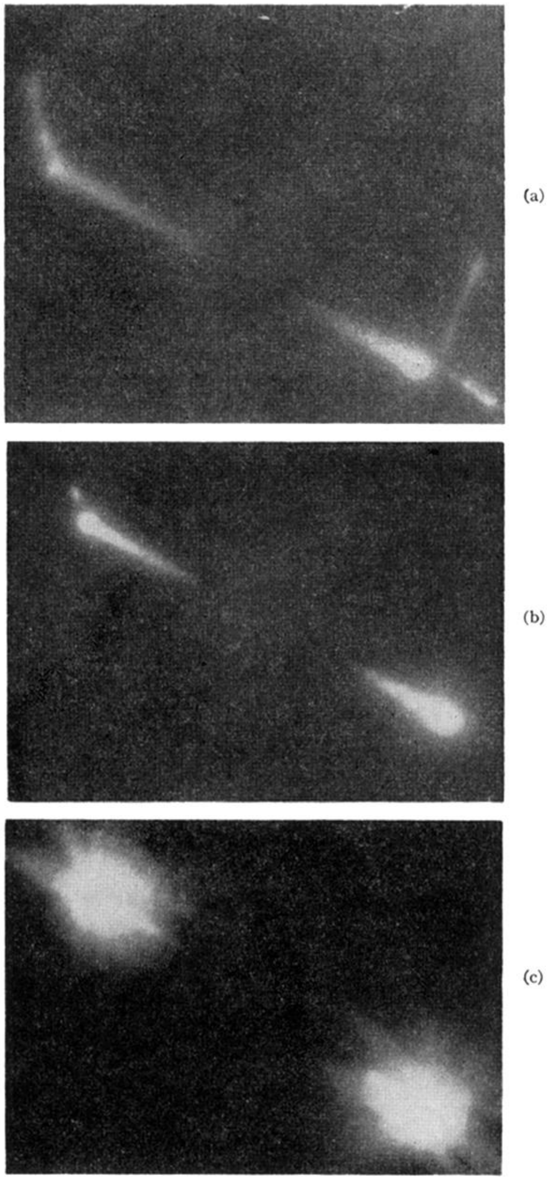


FIG. 4. Photographs showing change in aspect of electroluminescence with frequency, field 20×20 μ: (a) 2 kc/sec, (b) 20 kc/sec, (c) 10 Mc/sec.

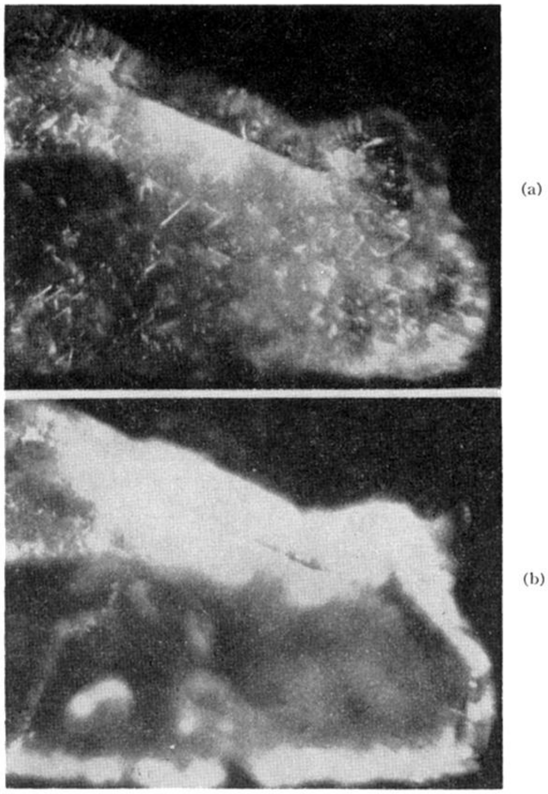


FIG. 5. Photographs of crystal in (a) normal electroluminescence and (b) electrode electroluminescence conditions. Field 0.8 ×0.6 mm.

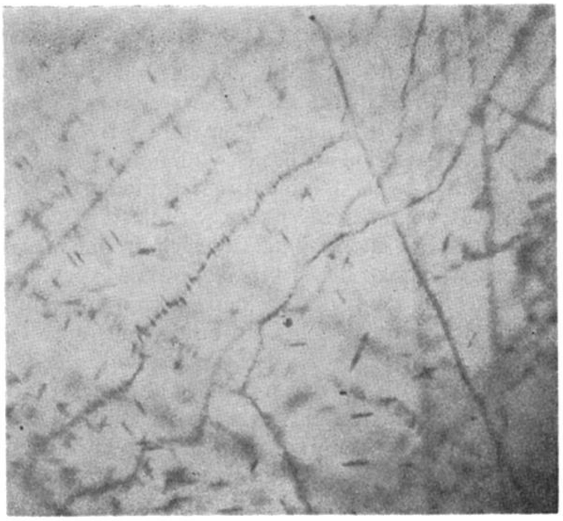


FIG. 6. Photograph of precipitate in ZnS:Ag crystal achieved by diffusion of copper. View parallel to hexagonal axis, field 75×70 μ. Depth of focus less than 1 μ.

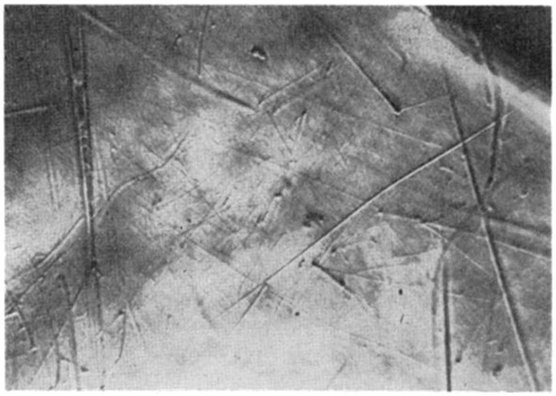


FIG. 7. Photograph of microscopic ridges on ZnS surface normal to hexagonal axis. Field 90×60 μ.

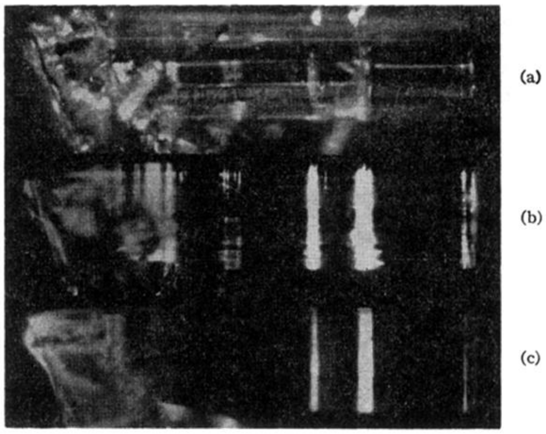


FIG. 8. Comparison of (a) reflected, (b) electroluminescent, and (c) fluorescent light from 0.8-mm long ZnS crystal.