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PROPERTIES OF CADMIUM SULFIDE,  
ZINC SULFIDE AND MERCURIC SULFIDE

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PARTS I-III

VOL. I

AN ANNOTATED BIBLIOGRAPHY



SPECIAL RESEARCH BIBLIOGRAPHY  
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MARCH 1961

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**PROPERTIES OF CADMIUM SULFIDE,  
ZINC SULFIDE AND MERCURIC SULFIDE**

**PARTS I-III  
VOL. I**

**AN ANNOTATED BIBLIOGRAPHY**

**Compiled by  
HELEN M. ABBOTT**

**SPECIAL RESEARCH BIBLIOGRAPHY  
SRB-61-2**

**MARCH 1961**

WORK CARRIED OUT AS PART OF THE LOCKHEED GENERAL RESEARCH PROGRAM

*Lockheed*

**M I S S I L E S and S P A C E D I V I S I O N**

**LOCKHEED AIRCRAFT CORPORATION • SUNNYVALE, CALIF.**

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VOL. I - PROPERTIES OF CADMIUM SULFIDE, ZINC SULFIDE AND MERCURIC SULFIDE

Preface

This annotated bibliography contains selected references pertaining to the properties of the compounds CdS, ZnS and HgS.

References were obtained from a search of the following sources.

1. Science Abstracts (A): 1950 - 1960
2. Nuclear Science Abstracts: 1961 (Jan),  
1951 - 1960
3. Armed Services Technical Information  
Agency
4. Various periodicals translated  
from Russian

INTRODUCTION

Because of the vast number of references obtained, the bibliography is being issued in two volumes.

Volume I contains Part I: Crystal growth and crystalline properties. Part II: Electrical properties and Part III: Optical properties.

Volume II contains Part IV: Electro-optical properties.

CONTENTS

PREFACE. . . . . i  
INTRODUCTION. . . . . ii  
CONTENTS. . . . . iii

PART I

    CRYSTAL GROWTH. . . . . 1  
    CRYSTALLINE PROPERTIES. . . . . 17

PART II

    ELECTRICAL PROPERTIES. . . . . 22

PART III

    OPTICAL PROPERTIES. . . . . 47

PART I CRYSTAL GROWTH AND CRYSTALLINE PROPERTIESCRYSTAL GROWTH

1. Addamiano, A.  
A new type of zinc sulphide crystals.  
NATURE (LONDON) v. 179, p. 493-4, 1957.

ZnS crystals sublimed in a hydrogen atmosphere formed a number of spiral loops, about 3 mm in diameter.

2. Bean, K. E. et al  
RESEARCH IN PURIFICATION OF CADMIUM SULFIDE  
CRYSTALS. Eagle-Picher Co. WADC AF33(616)-  
6203 Eight Quart. Prog. Rept.

The general purpose of this Contract is to develop methods for the growth of cadmium sulfide crystals having optimum photovoltaic properties.

Specific objectives include:

1. Preparation of ultra-pure cadmium sulfide powder.
2. Growth of single crystals of cadmium sulfide which -
  - (a) are as large as possible, and
  - (b) are doped with the optimum amounts of selected materials to provide the desired photovoltaic properties.
3. Crystal growth studies are to include two separate and different processes, as follows:
  - (a) growth from the vapor phase, and
  - (b) growth from the melt,
 Studies of the growth of mixed crystals of cadmium sulfide, zinc sulfide, cadmium telluride, etc., are to be investigated by the melt process.
4. Evaluation of the crystals are to include -
  - (a) spectrographic analysis,
  - (b) electrical testing, and
  - (c) fabrication into solar cells with evaluation of photovoltaic conversion efficiencies.

The studies carried out in the eighth quarterly work period of this Contract are discussed in this report.

CRYSTAL GROWTH

3. Bishop, M. E. and Liebson, S. H.  
 Growth of cadmium sulfide crystals.  
 LETTER In J. APPL. PHYS. v. 24, p. 660-1,  
 May; ERRATUM v. 963, Jul 1953.

Two modifications of Freichs' technique for growing CdS crystals are briefly described. In the first, A replaces H<sub>2</sub> as the vehicular gas and passes at 1 cm/sec approx. over the molten Cd at 650°C. Best crystal growth occurred when a dense yellow fog of S appeared in the exhaust tube. The second method consists of passing A over molten CdS from one side and over molten S from the other side to combine within a quartz bulb. The reaction area is at 1000° C approx. The CdS crystals form inside the bulb and are 1 mm thick and several cm<sup>2</sup> in area. The gases used were at least 99.8% pure.

4. Boyd, D. R. and Sihvonen, Y. T.  
 Vaproization-crystallization method for  
 growing CdS single crystals. J. APPL. PHYS.  
 v. 30, n. 2, p. 176-9, 1959.

A self-refining method for growing three different forms of CdS single crystals is described together with fabrication details of the 1300 W three-temperature zone furnace employed. The growth chamber measuring 1 3/4 in. in diameter x 21 in. long is charged with CdS powder and either H<sub>2</sub>S or argon at a pressure of 1 atm or less, and subjected from 4 to 7 days to different temperatures (1250 ± 20°C maximum) and gradients depending on the type of crystal desired. Single crystals vary from thin plates, rods, and whiskers weighing fractions of a gram to 10-g polygonal chunks. The method is believed to be suitable for growing single crystals of many other elemental and compound semiconductors.

5. Czyzak, S. J. et al  
 THE STUDY OF PROPERTIES OF SINGLE CRYSTALS  
 FOR USE AS DETECTORS AND CRYSTAL COUNTERS.

CRYSTAL GROWTH

Detroit. Univ. Project NR-015-218.

Oct 55, 44 p. (Contract Nonr-1511 (01))

The properties of single crystals for use as detectors and crystal counters are discussed. Single crystals of CdS and ZnS with and without controlled impurity additions (In, Mn, Pb, and O) were grown. The crystals were examined for index of refraction, absorption coefficient, dielectric constant, resistivity, photoconductivity, rectification, and photovoltaic effects. Also, preliminary experiments on the radiation effects from high-energy electrons were made.

6.

Czyzak, S. J. et al

THE STUDY OF PROPERTIES OF SINGLE CdS AND

ZnS CRYSTALS FOR USE AS DETECTORS IN CRYSTAL

COUNTERS. Detroit. Univ. Technical Report

no. 4, 1 Oct 58, 57 p. (Contract Nonr-1511-(01))

Progress is reported on a theoretical and experimental study of the properties of single crystals for use as detectors and crystal counters. The latest procedure for growing single crystals as well as new techniques for powder preparation has resulted in the production of single crystals which are not only larger but of greater purity. Both hexagonal and cubic ZnS crystals were grown. Construction of a new furnace made it possible to reach 1550°C in approximately one hour and made it possible to grow mixed ZnS:CdS crystals with greater ease. Large thin prisms were cut from the relatively pure crystals. New techniques and more sensitive apparatus were employed in measurements of the electrical properties of CdS and ZnS crystals. An approximate method was developed for calculating the electronic charge distribution in the corresponding potential field.

7.

Czyzak, S. J. et al

On the properties of single cubic zinc sulfide

crystals. J. OPT. SOC. AMER. v. 44, n. 11, p. 864-

7, 1954.

Single cubic crystals of ZnS grown by a method previously reported have been investigated for optical and electrical properties, i.e. index of refraction,

CRYSTAL GROWTH

optical absorption, photoconductivity, dielectric constant and lattice parameters. The method of growing crystals has been refined so that large crystals and greater yield per individual run were obtained. Both hexagonal and cubic crystals have been grown.

8. Fischer, A.  
Production of crystals from unstable compounds.  
Z. NATURFORSCH. v. 13a, n. 2, p. 105-10, 1958.  
(In German)

Many crystals under normal pressures decompose at temperatures well below their melting point. An oven is described, which allows the melting of such unstable crystals; it operates up to temperatures of 2500°C and pressures of 150 atm. Some preliminary results are described of the growth of crystals of GaP, BP, ZnS and CdS.

9. Fochs, P. D.  
An improved method of growing CdS crystals from the vapor phase. J. APPL. PHYS. v. 31, n. 10, p. 1733-4, 1960.

The gradual increase in the difference in temperatures of two Kanthal heating elements enables CdS crystals to be grown directly on the inside of a silica tube, remote from one another, instead of a continuous polycrystalline CdS substrate as happens in most existing methods.

10. Fujisake, H. and Tanabe, Y.  
Crystal growth of CdS in the vertical furnace.  
J. PHYS. SOC. JAPAN 15, 204, 1960.

The sublimation method was used to grow CdS crystals in a vertical furnace. The crystals were formed from condensation of the vapor phase of CdS powder. They were of mosaic structure having boundaries formed by several single crystals. The surface structures are influenced by temperature, temperature gradient of growth location, and the cooling rate of the furnace. These

CRYSTAL GROWTH

results indicate that large single crystals of CdS may be obtained at a shorter time interval by heat treatment in the furnace and that the behavior of layer growth plays an important role in the mechanism of crystal growth.

11. Greene, L. C. et al  
Method for growing large CdS and ZnS  
single crystals. J. CHEM PHYS. v. 29, n. 6,  
p. 1375-80, 1958.

A new technique for growing single crystals of CdS and ZnS has been devised in which single crystals up to 115 g in weight are obtained. The conversion of sphalerite into wurtzite, and vice versa, is described. The growth mechanism of the single ZnS crystals is described and compared with that for CdS crystals previously reported.

12. Gross, E. F. and Suslina, L. G.  
Monocrystals of ZnS and the spectrum of  
their absorption region at low temperatures.  
OPTICS AND SPECTROSCOPY (U.S.S.R.) (ENGLISH  
TRANSLATION) v. 6, n. 1, p. 70-1, 1959.

A study was made of the absorption spectra of thin single crystals at 4.2, 77, and 293°K. In preparing ZnS crystals, the method of heating the powdered ZnS in a neutral gas atmosphere was used. The form and dimensions of the crystals obtained depend largely on such conditions as the vaporization temperature of the powder, the position of the quartz baffles, the velocity of the gas flow, and the temperature gradient near the baffles. Crystals grown for this study were thin colorless plates with maximum dimensions of 25 x 5 mm. The thickness varied from 0.1 mm to tenths of a micron. The crystals of varying thickness made possible a thorough study of the long wave natural absorption spectra of 3300 to 3100 Å. Heating the crystals from 4.2 to 77°K and then to 20°C displaces the lines in the direction of longer wave lengths and causes them to become diffuse. The position for the absorption lines for the ZnS crystals are tabulated for the various temperatures.

CRYSTAL GROWTH

13. Hamilton, D. R.

The synthesis of single crystals of the sulphides of zinc, cadmium and mercury and of mercuric selenide by vapour phase methods. BRIT J. APPL. PHYS. v. 9, n. 3, p. 103-5, 1958.

Experiments with the Reynolds-Czyzack method of growth are described for zinc sulphide and cadmium sulphide. A new application of the method to the crystallization of mercuric sulphide is discussed. Single crystals of mercuric selenide have been produced by a vapour-phase reaction and similar experiments attempted with mercuric telluride. The conditions of growth are examined in the light of recent theory; estimates of surface free energies are obtained.

14. Herforth, L. and Krumbiegel, J.

Observations on CdS crystals by microscopic examination and conductivity measurements. Z. NATURFORSCH. v. 9a, p. 432-4, May 1954. (In German)

It is found that single crystals can be better grown by sublimation of CdS than by direct preparation from Cd in an H<sub>2</sub>S atmosphere. The striations on the crystals run parallel to the c-axis of the lattice. Single crystals show in vacuo about 40% greater mean conductivity than twinned crystals. Crystal types can be sorted with interesting anisotropy of conductivity. In air the conductivity is enhanced with some rectification attributed to an adsorbed layer of water molecules.

15. Konozenko, I. D. and Ust'yanov, V. L.

Crystalline CdS gamma-radiation receivers. SOVIET PHYS. -SOLID STATE v. 1, p. 81-5, 1959.

The preparation of CdS specimens sufficiently sensitive to x and gamma radiation to be used without phosphors and amplifiers is described. Single crystals and polycrystalline samples of CdS grown from the vapor phase were

CRYSTAL GROWTH

resublimed in a quartz tube. Their dark resistance ranged from  $10^9$  to  $10^{13}$  ohms and their sensitivity ranged from  $0.8 \times 10^{-3}$  to  $7.0 \times 10^{-3}$   $\mu$  amp/ $\mu$  r/sec for a 24 mc ( $^{60}\text{Co}$  source).

16. Krehmeller, A.  
Growth and heat treatment of zinc sulfide  
single crystals. J. ELECTROCHEM. SOC. v. 107,  
n. 5, p. 442-7, 1960.

These crystals grow readily from the vapour phase if small traces of certain impurities, such as zinc oxide and copper, are present. The decrease of ambient impurity concentration leads first to very thin, flexible, ribbon-like crystals which are hexagonal, and finally to nucleation with little growth. The purity of crystals depend not only on the composition of the starting material but also on the purity of the combustion tube employed; contamination during growth leads to an impurity gradient in crystals and to impurity variations among crystals. Crystals usually exhibit disorder of the crystal structure, although pure cubic or hexagonal structure can be achieved by annealing or quenching. Heat treatment also changes the impurity content and attendant properties, such as physical colour, luminescence behaviour, electrical properties, and disorder of the crystal structure.

17. Lawrence, R.  
Cadmium sulphide photoconductive layers.  
BRIT. J. APPL. PHYS. v. 10, p. 298-300, 1959.

Notes on experience in the preparation of cadmium sulfide are presented. Layers exhibiting properties similar to those of single crystals can be prepared by evaporation of crystalline CdS onto heated substrates. Photoconductive layers can also be made from the oxide made by sputtering Cd on glass in air. The sputtered layer is baked at  $500^\circ\text{C}$  in  $\text{H}_2\text{S}$ , then in air. After cooling, the resulting layer is similar to the high-temperature substrate evaporated layers. Another preparation method involves the use of ordinary laboratory reagent cadmium salts. Salts, such as  $\text{CdCl}_2$ , are heated in a stream of  $\text{H}_2\text{S}$ ; upon cooling, a layer is formed which is immediately photo-sensitive.

CRYSTAL GROWTH

18. Matsumura, T., Fujisaki, H. and Tanabe, Y.  
Preparation of zinc sulfide single crystals.  
SCI. REP. RES. INSTS TOHOKU UNIV. A v. 10,  
n. 5, p. 459-71, 1958.

Rod crystals were prepared by the gas reaction (Frerichs) and the sublimation (Kremheller) methods. The former method was capable of growing crystals of nearly 8 x 0.3 x 0.1 mm from pure Zn metal kept at 1100°C for only half an hour in H<sub>2</sub>S gas atmosphere. The latter method enabled one to obtain crystals (5-8 mm in length and 0.3-1 mm in sectional diameter) from ZnS powder kept at 1220°C for 8 hours in an inert gas stream. It was found that relatively large crystals grew under steady condition at just above sublimation temperature. Crystals obtained by the sublimation method displayed electroluminescence with both a.c. and d.c. excitation, without any activator. The growth conditions of needle, twin and ribbon crystals are discussed.

19. Medcalf, W. E. and Fahrig, R. H.  
High-pressure, high-temperature growth of cadmium  
sulfide crystals. J. ELECTROCHEM. SOC. v. 105,  
n. 12, p. 719-23, 1958.

A process is described for growing crystals of uniform size, shape, and homogeneity from the melt. Structure and electrical characteristics of the crystals are discussed, and segregation data on several impurity species are given. A method is described for preparing high purity cadmium sulphide powder by the purification of cadmium and sulphur followed by direct combination of the elements.

20. Miller, R. J. and Bachman, C. H.  
Production of cadmium and of sulfide crystals by  
coevaporation in a vacuum. J. APPL. PHYS. v. 29,  
n. 9, p. 1277-85, 1958.

Apparatus was developed by which beams of cadmium and of sulphur were simultaneously directed to a common point on a temperature controlled substrate in a demountable vacuum apparatus. Cadmium sulphide crystals were obtained.

CRYSTAL GROWTH

The various types of crystals: spiroidals, globules, ribbons, and needles are described together with the conditions tending to produce each type. Crystal size can be increased by repeated exposure to the beams.

21. Ōtomo, Yoshiro

On the crystal growth of zinc sulfide phos-

phor. BULL. CHEM. SOC. JAPAN 32, p. 804-8, 1959.

The zinc sulfide, before firing, is a large aggregate of crystallites with the crystal diameter of about 150 Å and contains about 8% of  $\alpha$ -form. The crystal growth of zinc sulfide phosphor takes place at about 500°C regardless of whether there is flux or not, but the rate of the growth is much affected by the flux. Without flux, the crystal grows as step-wise piled layers, but, with flux, it grows isotropically showing no influence from the crystal symmetry. Concerning the above difference, there has been discussion, taking into account the density of kinks at the step-wise surfaces of crystals and the change of diffusion constant of zinc sulfide molecules adsorbed at the surfaces. The transition,  $\alpha$ -form  $\leftrightarrow$   $\beta$ -form, of zinc sulfide phosphor is rather easy, but becomes difficult without flux. Also, the transition is completed in thirty minutes of firing at 800°C with the flux of 2 wt.% of sodium chloride, but it is completed within ten minutes of firing at 1000°C. It is probable that there is a metastable state of  $\alpha$ -form at about 600°C, but it requires further consideration.

22. Piper, W. W.

Growth of zinc sulfide single crystals.

LETTER In J. CHEM. PHYS. v. 20, 1343, Aug 1952.

The crystal is grown in a sealed quartz tube in a furnace, at a rate of up to 5 mgm per day. The resulting crystals show some stacking disorder.

Powderly, J. E. and Bean, K. E. - Medcalf, W. E., ed.

RESEARCH ON GROWING OF CADMIUM SULFIDE CRYSTALS

FOR DOSIMETER PURPOSES. Eagle-picher Research Labs.

CRYSTAL GROWTH

Mining and Smelting Div., Miami, Okla.

Quarterly Report No. 2, DA Project No.

3-99-00-100. 17 Jul 57 to 17 Oct 57, 51 p.

(Contract DA-36-039-SC-73270)

Progress is reported in the development of a method of growing cadmium sulfide crystals with properties suitable for their incorporation into an electrically simple direct current instrument for measuring nuclear radiations. Fourteen runs were carried out during the period which resulted in production of single crystals of cadmium sulfide. Studies were made on the effects of crystal purity, doping materials, infra-red quenching, crystal size and homogeneity, and light and dark resistivities of the crystals on the sensitivity of the crystals to gamma rays.

23.

Powderly, J. E. and Bean, K. E. - Medcalf, W. E., ed.

RESEARCH ON GROWING OF CADMIUM SULFIDE

CRYSTALS FOR DOSIMETER PURPOSES. Eagle-

Picher Research Labs. Mining and Smelting

Div., Miami, Okla. Quarterly Report No. 3,

DA Project No. 3-99-00-100. 17 Oct 57 to 17

Jan 58, 65 p. (Contract DA-36-039-SC-73270)

The theoretical and experimental aspects of the growing of single crystals of cadmium sulfide and the relationship of these aspects of crystal growth to such properties as conductivity; sensitivity to gamma rays, visible light, and other forms of energy; stability; and reproducibility are discussed.

CRYSTAL GROWTH

24. Powderly, J. E. and Bean, K. E.  
RESEARCH ON GROWING OF CADMIUM SULFIDE  
CRYSTALS FOR DOSIMETER PURPOSES. Quarterly  
Report No. 4. DA Project No. 3-99-00-100.  
17 Jan 58 to 17 Apr 58, 43 p. (Contract DA-  
36-039-SC-73270)

Studies were made of the growth of cadmium sulfide in alumina tubes replacing the quartz tubes previously used. The objective was to decrease the contamination of the cadmium sulfide with silica. Spectrographic analyses of the unvolatilized cadmium sulfide charge in the alumina tubes showed a much lower concentration of silicon, and the deposited cadmium sulfide single crystals also contained less silicon, although the deposition plate was polished quartz. Studies of the single crystals produced in this apparatus have not yet been sufficiently evaluated to state conclusively the effect of a lower concentration of silicon. The two crystals having the best properties from the standpoint of gamma-ray detection had a silicon concentration of 10 to 20 ppm which is less than the normal concentration. By the use of a secondary deposition plate during crystal growth the total recovery of usable crystalline cadmium sulfide was increased to 83% of theoretical. Studies of optimum seeding conditions indicated that the presence of a small amount of either zinc or silver improved the seeding characteristics of the cadmium sulfide. It was found that cadmium sulfide crystals of high resistivity ( $> 1 \times 10^8$  ohm-cm) gave better and more reproducible response to gamma rays when the sample was electroded parallel to the growth axis. The high resistivity portion of a crystal is usually found near the quartz deposition plate. By cutting away the cadmium sulfide of this area for a distance of 5 mm from the seed plate the crystal resistivity is reduced more than 50%. It was found that the dark quenched resistivities of cadmium sulfide crystals after remaining in the dark for several weeks were greater than the dark quenched resistivities obtained immediately after quenching with infrared. All crystals tested were of the same thickness, 2mm. The voltage gradient applied was the same for all samples, 175 volts/cm of length. A  $\text{Co}^{60}$  field of 1 r/hour, 7 r/hour, and 10 r/hour was used in the test series. Of fourteen samples tested in the 1 r/hour field, the two crystals having the fastest rise times, namely, 1 minute and 10 seconds, were from different runs but contained almost identical solute impurities. The two doping agents were indium and zinc with a concentration of 0.05 to 0.1% zinc and with a concentration of 0.004 to 0.005% indium. Each of these crystals also had the fastest response to visible light with 20 milliseconds rise time for 90% saturation for the better sample.

CRYSTAL GROWTH

25. Powderly, J. E. and Bean, K. E., - Medcalf, W. E. ed.  
 RESEARCH ON GROWING OF CADMIUM SULFIDE  
 CRYSTALS FOR DOSIMETER PURPOSES. Eagle-  
 Picher Research Labs. Mining and Smelting  
 Div., Miami, Okla. Final Report. DA Project  
 3-99-00-100. 17 Apr 57 to 15 Jul 58, 77 p.  
 (Contract DA-36-039-sc-73270)

The growth of cadmium sulfide single crystals of large size and with desirable properties was successfully carried out in a furnace consisting of an outer and inner chamber. By strategic location of the polished silica plates, total recovery of usable crystalline cadmium sulfide was 83 percent of theoretical. Single crystals weighing more than 100 grams were grown reproducibly. Obtaining large single crystals free of strain is accomplished only by obtaining precise temperature control and temperature gradient throughout the entire volatilization-deposition period of 100 hours. The optimum temperature conditions for crystal growth were determined. It was found, as a result of a statistical study in which 187 cadmium sulfide crystal specimens were irradiated with gamma rays, that crystals having dark resistivities in the range of  $5 \times 10^7$  to  $1 \times 10^8$  ohm-cm were in every case sensitive to gamma radiation but that a slightly lower resistivity range of  $1 \times 10^6$  to  $5 \times 10^7$  ohm-cm provided specimens with a greater maximum sensitivity. While not all the specimens in the latter range were sensitive to gamma radiation, those that were sensitive tended to have a higher degree of sensitivity than in any other resistivity range. Over 25% of the crystals showed an increase of more than 3 microamperes of current with irradiation of only 1 r/hr and with 175 volts DC applied across the electrodes.

26. Piper, W. W. and Roth, W. L.  
 Perfect crystals of zinc sulfide.  
 LETTER IN PHYS. REV. v. 92, p. 503, 1953.

Hexagonal ZnS crystals,  $5 \times 10^{-3}$  cm diameter and several mm long, grown by sublimation in a H atmosphere, appear free of dislocations and stacking faults; X-ray photographs showed no diffuse streaking. The needles are flexible, elastic strains up to 1.5% have been induced, Young's modulus =  $7 \times 10^{11}$  dynes/cm<sup>2</sup>. Photocurrent decay in these crystals was at least ten times faster than the usual decay time.

CRYSTAL GROWTH

27. Reynolds, D. C. and Czyzak, S. J.

Single synthetic zinc sulfide crystals.

LETTER In PHYS. REV. v. 79, p. 543-4, 1950

Crystals of size 2 x 2 x 10mm were grown in a H<sub>2</sub>S atmosphere at 1 150°C; they were of alpha-form (wurtzite). The optical absorption cut-off was at 3 350A, and they were entirely opaque for shorter wavelengths. A few specimens showed blue fluorescence; none showed phosphorescence.

28. Reynolds, C. C. et al

Properties of single cadmium sulfide crystals.

LETTER In J. OPT. SOC. AMER. v. 45, n. 2, p. 136-

8, 1955.

Crystals of CdS of average size 8 x 4 x 5mm were grown with various amounts of oxygen impurity up to 2% and their properties investigated. Oxygen affects the optical absorption edge structure and the spectral response for photoconductivity. The spectral response is different when measured by short to long wavelength traverse from that for long to short wavelength traverse. It is held that oxygen predominantly affects carrier mobility rather than carrier concentration.

29. Reynolds, D. C. and Greene, L. C.

Crystal growth mechanism in cadmium sulfide

crystals. J. APPL PHYS. v. 29, n. 3, p. 559-62,

1958.

Large cadmium sulphide crystals were grown from the vapour phase. The crystal growth was studied by observing growth patterns, chemical etch patterns, and vaporization patterns. The studies reveal a layer or lamellar type growth, the layers resulting form the coalescence of monoatomic steps into ledges of many atomic layers in height. The layers are generated at or near the crystal edge and move across the surface by edge nucleation. The exact mechanism by which the steps are generated is not known, however, it is believed that they result from screw dislocations or surface nucleation.

CRYSTAL GROWTH

30. Sears, G. W.  
A mechanism of whisker growth. ACTA MET.  
v. 3, p. 367-9, 1955.

Fine whiskers of zinc, cadmium, silver, and cadmium sulfide have been grown on pyrex and quartz glass substrates by vapor deposition. The maximum supersaturation ratio at which whiskers can be grown is in good correspondence with the calculated supersaturation at which two-dimensional nucleation occurs. This correspondence offers support for the generality of the growth mechanism first proposed for mercury whiskers.

31. Stanley, J. M.  
Vapor phase crystallization of cadmium sulfide  
crystals. J. CHEM. PHYS. v. 24, n. 6, p. 1279-  
80, 1956.

Single CdS crystals were prepared by heating CdS in fused quartz, Vycor and ceramic tubes in a N or A atmosphere to 900-1040°C for 16-48 hours. Plates of 22 x 25 x 1 mm<sup>3</sup> and prisms of 28 x 3 x 3 mm<sup>3</sup> were obtained. The absorption edge occurs at 525 mμ. The crystals have piezoelectric properties. CdSe crystals up to 28 x 14 x 0.8 mm<sup>3</sup> were grown by a similar method.

32. Tombak, M. I. et al  
Suitability of the thiosulfate procedure  
for preparation of ZnS for synthesis of phosphors.  
BULL ACAD. SCI USSR - PHYS. JER. 23 (11), 1345,  
Nov. 1959.

CRYSTAL GROWTH

33. Vitrikhovskii, M. I. and Mizetskaya, I. B.  
Preparation of mixed CdS.CdSe monocrystals  
from vapour phase and some of their properties.  
FIZ. TVERDOGO TELA v. 1, n. 3, p. 397-402, 1959.  
(In Russian)

CdS and finely powdered selenium were thoroughly mixed and heated for 5-6 hours at 400-450°C; selenium and sulphur not used up in the reaction were volatilized during this treatment. The product was ground and then sublimated in an atmosphere of argon at 980-1100°C. CdS.CdSe monocrystals prepared in this way were found to be substitutional solid solutions. Studies of photoconductivity showed that a stable position of the photocurrent maximum in a batch of CdS. CdSe monocrystals of given composition was a proof of uniform composition within that batch. The wavelengths at which the photocurrent maxima occurred depended linearly on the composition of the monocrystals.

34. Wilke, K. T.  
The activation of CdS crystals.  
Z. PHYS CHEM. (LEIPZIG) v. 205, n. 1-2, p.  
73-7, 1955. (In German)

Comparison experiments on the activation processes are made for cadmium sulphide phosphors produced by evaporating a mixture of CdS and activator sulphide to form crystals by vapour deposition and those produced by diffusion of the activator into the CdS. Higher activator contents occur in the latter method. A discussion of the results is given in terms of the sublimation and dissociation temperatures of the activator sulphides and the ionic sizes of the activators used (Cu and Ag).

35. Woods, J.  
Study of cadmium sulphide crystals grown  
from the vapour phase in a stream of argon.  
BRIT. J. APPL. PHYS. v. 10, n. 12, p. 529-33, 1959.

Crystals of cadmium sulphide have been grown by reacting a stream of argon containing cadmium vapour with a stream of hydrogen sulphide. The variations

CRYSTAL GROWTH

in crystal habit which occur are very similar to those reported for ice crystals by Hallett and Mason (see preceding abstracts). Growth features were studied using a metallurgical microscope. Although growth occurs in layers, spirals were only observed on rare occasions. The evidence indicates that ordinary two-dimensional nucleation over a plateau is more common, and is affected by the impurities added. Nucleation also occurs at sites on the edge of a crystal face or at the apexes of re-entrant angles between growth steps from neighbouring sources. Various types of cavity have also been observed in the volume of some crystals, and possible methods of formation are discussed.

36.

Yamashita, H. and Ibuki, S.

Crystal growth of CdS by vacuum sealed method.

J. PHYS. SOC. JAPAN v. 13, n. 2, p. 226, 1958.

A vapour-phase method of obtaining single crystals of CdS is described. Several plates are included which illustrate comments upon crystal growth directions and etch attack. .

CRYSTALLINE PROPERTIES

37. Addamiano, A. and Aven, M.  
Some properties of zinc sulfide crystals  
grown from the melt. J. APPL. PHYS. v. 31,  
n. 1, p. 36-9, 1960.

Hexagonal zinc sulphide crystals were obtained by controlled cooling of melted zinc sulphide. Both pure and activated zinc sulphide powders were used. The density of pure melt grown crystals was found to be higher than that of natural zinc blende crystals or crystals grown by evaporation. The stability of the pure hexagonal crystals towards transformation to the cubic zinc-blende structure in the interval of temperature 700-1150°C was investigated. A full conversion to the cubic phase was never observed. The experimental evidence indicates the transition point to be above 1150°C.

38. Aswegen, J. R. S., van. and Verleger, H.  
X-ray investigation of the system ZnS-FeS.  
NATURWISSENSCHAFTEN v. 47, n. 6, p. 131,  
1960. (In German)

The lattice spacing was measured for pure ZnS and for samples containing Fe up to 21.54%. The spacing varied considerably up to about 15% Fe but thereafter the change was small.

39. Aven, M. and Parodi, J. A.  
Study of the crystalline transformations in  
ZnS:Cu, ZnS:Ag and ZnS:Cu,Al. J. PHYS. CHEM. SOLIDS  
v. 13, n. 1-2, p. 56-64, 1960.

An e.p.r. study has shown that the formation of a separate phase of copper (or silver) sulphide in polycrystalline ZnS:Cu, ZnS:Ag and ZnS:Cu,Al triggers the rapid transformation of hexagonal to cubic zinc sulphide. It is believed that, after firing, cuprous sulphide precipitates from solution in hexagonal zinc sulphide and in so doing supplies the energy necessary for nucleation of cubic zinc sulphide. Once nucleation has begun, growth of the cubic phase will be selfsustaining, because energy is released in going from the hexagonal

CRYSTALLINE PROPERTIES

to the cubic structure. Supporting data for the postulated mechanism of nucleation and growth is provided by X-ray diffraction data on the effect of quenching and annealing on the crystal structure of  $\text{ZnS}:9 \times 10^4$  Cu phosphors. It was found that the optimum nucleation temperature lies close to  $700^\circ\text{C}$  and that at this temperature the growth of the cubic phase is reasonably fast.

40. Herforth, L. and Krumbiegel, J.

Some observations on cadmium sulphide crystals.

NOTE In NATURWISSENSCHAFTEN v. 40, n. 9, p. 270-1, 1953. (In German)

This note presents a macroscopic classification (by appearance) of 500 CdS crystals into five types and discusses some simple properties of these various types.

41. Krumbiegel, J. and Jost, K. H.

Conductivity measurements, spectrographic and X-ray investigations on zinc sulphide crystals.

Z. NATURFORSCH. v. 10a, n. 7, p. 526-9, 1955.  
(In German)

In all the crystals investigated, a conductivity maximum is seen at 3 520A, despite differences in luminous colour. Spectrographic analysis of the crystals is quoted, and X-ray investigations show that stacking faults occur; there are regions with two-fold, and three-fold and four-fold stacking repeats of the close-packed sheets.

42. Mansurova, Z. S.

Influence of the size of crystal grains on characteristics of the flash like rise of

CRYSTALLINE PROPERTIES

luminescence in ZnS-Mn phosphors.

OPTIKA I SPEKTROSKOPIYA v. 4, p. 529-32,  
1956. (In Russian)

An x-ray analysis was made of the crystal structure of crushed specimens of ZnS-Mn phosphors obtained at annealing temperatures of 1160° and 850°. From the observations it was shown that each fraction had its maximum flash magnitude; however, the optimal time of the maximum flash moment was constant for all fractions. It was shown that the drop in luminescence magnitude for the small or crushed grains of ZnS-Mn is not related to the transitions from one modification to another. The intensity of the Mn band stationary luminescence (with error) does not depend on the size of the grain. The differences in the behavior of the stationary luminescence and the absolute flash luminescence in crushed specimens show that the luminescence centers and the centers of the first and second localization react differently to the surface development during crushing. Hence, it was assumed that the magnitude of the relative flash depends on the crystal surface (i.e., on the exposure or isolation of the grain surface from contact with the atmosphere during annealing.

43.

Roth, W. L.

Spiroidal crystals of zinc sulphide.

LETTER In NATURE (LONDON) v. 173, p. 38-9,  
1954.

A new type of crystal form, for which the term "spiroid" is used to convey the topological character of the habit, is reported in zinc sulphide crystals grown by sublimation. Two typical spiroids are illustrated. They are hexagonal zinc sulphide, but disordered with a high density of stacking faults normal to the basal planes. The spiroid axis is (11·0). The crystallography of the forms was established by X-ray and microscope techniques. A hypothesis in terms of edge dislocations to account for the departure from the normal habit of hexagonal zinc sulphide is advanced.

CRYSTALLINE PROPERTIES

44. Rumsh, M. A., Shuvalov, Yu. N. and Smirnov, L. A.

The influence of illumination of the intensity  
of the X-ray reflections from a crystal of CdS.  
FIZ. TVERDOGO TELA v. 2, n. 2, p. 369-70, 1960.

(In Russian)

X-ray measurements of the intensities of reflections from a single crystal of CdS showed variations in the relative intensities which altered with changes in the intensity of the primary irradiating beam. By shining a beam of light onto the recording film (covered with black paper) in the places where some of the reflected X-ray beams fell, the local heating due to the absorbed radiation could be varied.  $1^{\circ}$  change in temperature changed the blackening by about  $1.5^{\circ}$ . It was thus shown that the observed variations were an instrumental effect and not due to radiation-induced changes in the crystal.

45. Smirnov, L. A. and Rumsh, M. A.

The change in intensity of X-ray reflections  
from a single crystal of CdS under illumination.  
ZH. TEKH. FIZ. v. 29, n. 6, p. 799, 1959.

English translation in: SOVIET PHYSICS-TECHNICAL  
PHYSICS (NEW YORK) v. 4, n. 6, p. 719-20, 1959.

In an attempt to improve upon the results obtained by Shuvalov (Abstr. 1738 of 1957) who used a photographic method, the authors have used the ionization method of recording to investigate the effect of illumination on the intensity of X-ray reflections from CdS. They conclude that Shuvalov's photographic method is not sufficiently accurate.

46. Votava, E.

Dislocations in CdS crystals and their effect  
on photoconductivity. Z. NATURFORSCH.

CRYSTALLINE PROPERTIES

v. 13a, n. 7, p. 542-4, 1959. (In German)

CdS crystals with well developed growth spirals were grown on heated sintered CdS discs. Dislocation configurations were revealed by etching in HCl. Measurements of conductivity, on scanning a small angle grain boundary with a light probe, confirmed that the presence of dislocations can reduce the electron lifetime.

47. Votava, E., Amelinckx, S. and Dekeyser, W.

Microscopic studies on deformed ZnS-crystals.

PHYSICA v. 19, p. 1163-72, 1953.

An optical and interferometric study was made of (111) faces of ZnS crystals grown at relatively high temperature. In addition to triangular growth terraces and incompletely developed growth spirals, an extensive substructure, covering the whole of the faces, was found. This substructure was proved by multiple beam interferometry to consist of steps. Evidence for movement of dislocations is also given. The substructure itself is divided into a fine-structure by lines of lower visibility, some of which are rows of etchpits. They are interpreted as polygonization lines (rows of Taylor dislocations), or very small steps.

PART II ELECTRICAL PROPERTIES

48. Arkhangelskaya, V. A. and Bonch-Bruевич, A. M.  
 Variation of the conductivity of cadmium  
 sulphide under irradiation with electrons.  
 DOKL. AKAD. NAUK SSSR v. 77, n. 2, p. 229-32,  
 1951. (In Russian)

The cathodic conductivity under electron bombardment was discovered by Kronig on Se (PHYS. REV., 24, 377 (1924)). The kinetics of the variation of the induced conductivity of both crystalline and amorphous Se could not be explained. An investigation on CdS was made by the authors with an intermittent electron beam, and the variations of the conductivity automatically recorded by c.r.o. The rise time of the electronic pulse was  $10^{-7}$  sec. The c.r.o. had an exponential time base and the method of analysis used was that of the "partial times." The absolute value of the dark conductivity of the CdS crystal was  $\sim 5 \times 10^{-11}$  ohm $^{-1}$ ; the electron velocity was kept at 2000 V. The drop of the value of the induced conductivity was slowed down by increasing the density of the electron current. Under a constant electron current the period of the induced conductivity remained constant after the initial reduction to about  $\frac{1}{2}$  the initial value taking about 10-15 min. The conclusion derived from the graphs is that the kinetics of the excitation of the cathodic conductivity by electron beams follows approximately a bimolecular law, with a deviation reminiscent of the degeneration of the bimolecular law of photoconductivity in the region of low luminescence of the specimen.

49. Auth, J. and Ridder, R.  
 Investigations on the diffusion of charge  
 carriers in CdS. Z. NATURFORSCH. v. 13a,  
 n. 5, p. 426-7, 1958. (In German)

The diffusion was determined by measuring the photocurrent between two probes as a function of their distance from the illuminated region. Two characteristic diffusion lengths,  $L_1$  and  $L_2$ , were found.  $L_1$  varied between 1 and 15  $\mu$  according to the origin of the crystal and was ascribed to ambipolar diffusion;  $L_2$  was 500  $\mu$  and temperature-independent, and was connected with the re-absorption of luminescent light.

ELECTRICAL PROPERTIES

50. Benda, H.  
 Measurements of the electrical conductivity  
 of CdS crystals irradiation with electrons of  
 moderate energy. ANN. PHYSIK. v. 6, n. 9,  
 p. 413-22, 1951. (In German)

The conductivity of CdS crystals irradiated with 800- to 3000-v electrons has been investigated. The currents measured were between 0.001 and 10  $\mu$ a. As in irradiations with light, the conductivity is related to the excitation intensity by a simple power law, the exponent of which lies between 0.5 and 1. In the region studied, each crystal had a specific exponent. The complex changes in conductivity with electron potential and the quantum yield are discussed.

51. Böer, K. W.  
 On the problem of electronic intrinsic con-  
 duction in semiconductors. Z. NATURFORSCH.  
 v. 10a, n. 11, p. 898-9, 1955. (In German)

By means of varying the heating rate of CdS crystals and measuring the electrical conductivity it is concluded from the results that no intrinsic conduction by the conventional model actually takes place at high temperatures but that conduction at these temperatures is by the motion of lattice defects which may be regarded as "intrinsic defect centres". This interpretation provides an explanation for the discrepancies found when mobility calculations are made on CdS crystals.

52. Böer, K. W. and Kümmel, U.  
 An experimental contribution to the problem  
 of dielectric breakdown in single crystals of  
 CdS. ANN. PHYS. (LEIPZIG) v. 16, n. 3-4, p. 181-  
 91, 1955. (In German)

An experimental study is made of the relation between "electrical" and thermal glow curves for a CdS crystal. Correlation is found for fields less than

ELECTRICAL PROPERTIES

one-half the breakdown value but above this the correlation breaks down and there is strong disturbance of defect levels by the relatively large current flow.

53. Böer, K. W. and Kümmel, U.  
On the electrostatic charging of CdS single crystals under the action of high electric fields. ANN. PHYS. (LEIPZIG), Folge 7, v. 2, n. 5-6, p. 217-24, 1958. (In German)

Both positive and negative charge accumulations were observed in crystals after a high current was passed through them. The dependence of this charge on the magnitude of the field and the frequency when a.c. fields were used (both in the dark and with weak illumination) and its independence of the nature of the electrode materials, can be explained on the basis of a non-homogeneous bulk conductivity which also gives rise to dielectric (polarization) after effects. It is argued that the conduction process at high fields cannot be explained in terms of space-charge limited currents initiated by electron injection from the cathode as stated by Rose and Smith.

54. Böer, K. W. and Kümmel, U.  
On the influence of the dielectric after-effect on the conduction process in CdS single crystals in the region of the breakdown field. ANN. PHYS. (LEIPZIG) v. 20, n. 1-6, p. 303-14, 1957. (In German)

Experiments on the decay of photoconductivity in single crystals which had been subjected to various high field pulses indicate the presence of dielectric after-effects due to nonhomogeneous samples. The results of the various experiments are given a qualitative interpretation. Such dielectric after-effects will influence the electrical conductivity at high field strengths.

ELECTRICAL PROPERTIES

55. Böer, K. W. and Kümmel, U.  
 Processis prior to electrical breakdown  
 in single crystals of CdS. Z. ANGEW. PHYS.  
 v. 12, n. 6, p. 241-4, 1960. (In German)

Breakdown is divided into two types, thermal and field breakdown. In relatively conducting crystals, Joule heating is followed by non-uniform heating forming "cannals" of high current density, the process being irreversible after their formation. For insulating crystals Joule heating is not in evidence until after the field breakdown effect which occurs at a critical applied voltage. The field breakdown is characterized by a very short relaxation time.

56. Böer, K. W., Kümmel, U. and Misselwitz, W.  
 Electric breakdown of CdS evaporated layers.  
 NATURWISSENSCHAFTEN v. 45, n. 14, p. 331,  
 1958. (In German)

The breakdown field strength of evaporated CdS layers with the Cr base as one electrode and a Hg drop as the other, increased from  $10^5$  V/cm at 2000  $\mu$ m (the bulk value) to about  $8 \times 10^5$  V/cm at 75  $\mu$ m thickness. Breakdown fields with the Hg electrode negative were 30% higher than for the reverse polarity.

57. Böer, K. W., Dziesiaty, J. and Kümmel, U.  
 On the electrical behaviour of CdS single  
 crystals with voltage pulses in the breakdown  
 region. NATURFORSCH. v. 13a, n. 7, p. 560-2,  
 1958. (In German)

Experiments with rectangular pulses of fixed height showed that the current decreased when either the pulse width (from 3 to 1000  $\mu$ sec) or the repetition frequency (from 10 to  $10^3$  c/s) were increased. Measurements on various samples, with fast (3  $\mu$ sec) single pulse gave currents proportional to a power of the voltage. The index decreased (ranging from about 5 to 1 for the various samples as measurements were carried out first in the dark and then with

ELECTRICAL PROPERTIES

increasing illumination. The results are related to dielectric (polarization) after-effects which occur if the crystals are nonhomogeneous.

58. Böer, K. W. and Lubitz, K.  
 Temperature-resistant barrier-free  
 contacts on CdS single crystals. Z.  
 NATURFORSCH. v. 15a, n. 1, p. 91-2, 1960.  
 (In German)

Vacuum-evaporated aluminium on single crystals of CdS, which are heated at 200°C during the deposition, can withstand a temperature of 350°C for 15 minutes in vacuo without forming a barrier layer.

59. Böer, K. W., Oberländer, S. and Voigt, J.  
 The evaluation of conductivity glow curves.  
 ANN. PNY. (LEIPZIG), Folge 7, v. 2, n. 3-4,  
 p. 130-45, 1958. (In German)

Glow curve equations are derived for a model with a single trapping level. Measurements were made with CdS:Cu and CdS:Co having single conductivity glow peaks. The approximate formula of Randall and Wilkins gives a good value for the position of trapping levels, even when re-trapping cannot be neglected.

60. Broser, I., Oeser, II. and Warminsky, R.  
 The conductivity of cadmium sulphide crystals  
 excited by medium and hard X-rays. Z. NATURFORSCH.  
 v. 5a, p. 214-15, 1950. (In German)

The conductivity of CdS crystals due to 40-200 kV X-rays was studied in comparison with an ionization chamber. Different wavelength-dependence occurred in each case, the CdS crystal showing a sensitivity max. for 130 kV X-rays.

ELECTRICAL PROPERTIES

61. Buttler, W. M. and Muscheid, W.  
The nature of the electrical contact by studies  
on single crystals of cadmium sulphide. II  
ANN. PHYS. (LEIPZIG) v. 15, n. 2, p. 82-111,  
1954. (In German)
62. Butler, W. M. and Muscheid, W.  
The nature of the electrical contact by studies  
on single crystals of cadmium sulphide. I.  
ANN. PHYS. (LEIPZIG) v. 15, n. 3-5, p. 215-19,  
1954. (In German)
63. Fassbender, J.  
The effect of a glow discharge on the conductivity of  
cadmium sulphide single crystals and the formation  
of ohmic contacts. Z PHYS. v. 145, n. 3, p. 301-  
18, 1956. (In German)

The effects of a glow discharge, run in various gases (pressure  $\sim 0.2$  mm Hg), on single crystals of CdS, are described. Dark currents and photoconductivities were measured, as a function of various discharge parameters. The results are shown, and discussed in terms of changes in surface layers of the crystals, and energy-level schemes therein.

ELECTRICAL PROPERTIES

64.

Frerichs, R.

On the conductivity produced in CdS crystals  
by irradiation with gamma-rays. PHYS. REV.  
v. 76, p. 1869-75, 1949.

By combining the theory of secondary photocurrents developed by Hilsch, Pohl, Schottky and others, with the model of a crystal phosphor by Johnson and Seitz and by Riehl and Schoen a theory of the photoconductivity in CdS crystals is given. The theory agrees qualitatively with the results of previous and present experiments. A quantitative energy scheme has been determined from measurements of the emission and absorption spectra of these crystals. According to the new determined sign of the thermal e.m.f.: CdS against Cu, the photocurrent in CdS is predominantly carried by electrons. The dark current follows the usual law:  $\log \sigma \propto 1/T$  the constants  $\epsilon = 0.67\text{eV}$  and  $\sigma_0 = 1.7 \times 10^{-3}$  mho  $\text{cm}^{-1}$ . In accordance with the theory the final current reached after prolonged irradiation is  $\propto$  the square root of the intensity of irradiation. The final current follows Ohm's law. The initial slope of the decay curve is  $\propto$  the intensity of irradiation. Under periodical irradiation with  $\gamma$ -rays the amplitude of the resulting alternating current slowly increases to a final value. If the electric field is temporarily removed the original conductivity is slowly restored. When a CdS crystal is heated and then cooled to liquid air temp. irradiation produces a small primary current of  $< 10^{-13}\text{A}$  at first. With continuous irradiation and after a slight delay this current suddenly increases until it reaches a constant value of  $10^{-8}\text{A}$ .

65.

Freyman, R. et al

Electrical and optical properties of some  
semiconductors: Zinc oxide, Zinc sulphide,  
selenium. J. PHYS. RADIUM v. 17, n. 8-9, p. 806-  
12, 1956. (In French)

I. Optical, photodielectrical and electrical summarized properties of the various types of ZnO. II. Study of the dipolar Debye absorption of several samples of ZnO in terms of frequency and temperature. The activation energies found by that method and by conductivity and thermoluminescence methods are in good agreement. III. Two types of photodielectric effect are proposed: photoconductivity (free carriers) and photodipolar effect (bound carriers). Impure selenium shows the second one, but the activation energy decreases under irradiation. ZnS(Cu) shows absorption bands only under irradiation. For ZnO, the phenomena are intricate.

ELECTRICAL PROPERTIES

66. Freymann, R. and Grillot, E.  
 Photodipolar absorption of zinc sulphide.  
 SEMICONDUCTORS AND PHOSPHORS. BRUNSWICK:  
 VIEWEG, p. 557-9, 1958.

The dielectric losses of various ZnS preparations, when excited by 3650 Å irradiation, were measured from 100 c/s to 1 Mc/s at temperatures from 80° to 300°K. Absorption bands are observed due to dipoles induced by the irradiation, and the activation energies determined agree well with those obtained from thermoluminescence studies. The growth and decay of the dielectric absorption were observed at various frequencies and temperatures.

67. Freymann, R. et al  
 On two distinct types of photodielectric  
 effect in cadmium sulphide. C.R. ACAD. SCI.  
 (PARIS) v. 245, n. 25, p. 2261-4, 1957. (In French)

Dipolar Debye absorption occurred under excitation in CdS powder, indicating the existence of a level at 0.02 eV below the conduction band. In addition an abnormal absorption band was observed, which did not obey the Debye relations.

68. Frohmeyer, G., Glocker, P. R. and Messner, D.  
 The dependence of the electrical conductivity  
 of cadmium sulphide single crystals on wavelength  
 under X-radiation and  $\gamma$ -radiation. Z. PHYS. v. 137,  
 n. 1, p. 117-25, 1954. (In German)

The variation of the conductivity of CdS crystals with wavelength over the range 2000 to 10XU was determined by measurement of the crystal current and the ionization current of the X-rays in air. The results confirmed the assumption that the effect is due only to the fraction of X-ray energy which is converted to energy of the photoelectrons and Compton electrons.

ELECTRICAL PROPERTIES

69. Frohnmeyer, G., Glocker, R. and Messner, D.  
 The wave length dependence of the electric conductivity of cadmium sulfide single crystals on radiation with X and  $\gamma$  rays. Z. PHYSIK v. 137, p. 117-25, 1954. (In German)

The wave-length dependence of the conductivity of CdS crystals on x and  $\gamma$  radiation in the range 2 to 0.001 kX was determined. There was confirmation of the theoretical assumption that only the fraction of the x-ray energy converted to Compton and photoelectron energies is effective.

70. Frohnmeyer, G., Glocker, R. and Messner, D.  
 On the wave length dependence of the conductivity produced in CdS crystals by X- and  $\gamma$  irradiation.  
 NOTE In NATURWISSENSCHAFTEN v. 40, n. 12, p. 338, 1953. (In German)

For crystals approximately 0.5 mm thick, the maximum conductivity change occurs in the region 1A for X-rays and about 1 MeV for  $\gamma$ -rays.

71. Fuchshuber, R., Guillien, R. and Roizen, S.  
 The dielectric properties of thin films of zinc sulphide. C.R. ACAD. SCI. (PARIS) v. 251, n. 1, p. 51-3, 1960. (In French)

Successive evaporations in a system in which a low pressure of  $10^{-7}$  torr could be maintained during an evaporation, enabled Al/ZnS/Al sandwiches to be made, with the Al layers about 200-600A thick and the ZnS from 1800 to 25000A. For applied voltages from 0.1 to 1V and frequencies from 1 to 50 kc/s, the dielectric constant is 10.3.

ELECTRICAL PROPERTIES

72. Garlick, G. F. J.  
 Infrared phosphor-semiconductors. J.  
 PHYS. CHEM. SOLIDS v. 8, p. 449-57, 1959.

Rochester Semiconductors Conference Paper. A review of progress over the past few years is given, with special reference to the emission of zinc and cadmium sulphide phosphors, lead sulphide, lead telluride and mercury sulphide. The infrared emission found in zinc sulphide is ascribed to electron transitions from the valence band to the ground states of visible emission centres. In mercury sulphide the characteristics of the excitation and emission spectra suggest a different mechanism. This also applies to lead sulphide and lead telluride. New results on cadmium telluride, made p- or n- type under controlled conditions, show a number of imission bands extending to  $2.6 \mu$ . Excitation and photovoltage excitation curves coincide with emission bands, there being no Franck-Condon shift. The results are given a tentative theoretical explanation.

73. Golynnaia, G. I. et al  
 Cadmium sulfide photoresistors of the type  
 FSK-Mi- with improved contacts. PRIBORY I  
 TEKHNIKA EKSPERIMENTS n. 4, p. 141-43, July-Aug  
 1960. ELECTRONICS EXPRESS v. 3, n. 4, p. 26, Dec  
 1960.

74. Gobrecht, H. and Bartschat, A.  
 On the optical and electrical properties of single  
 crystals of cadmium sulphide. Z. PHYS. v. 136,  
 n. 2, p. 224-33, 1953. (In German)

It is shown by measurements on single crystals of CdS that the lattice absorption edge must be at wavelengths less than  $5025\text{\AA}$ .

ELECTRICAL PROPERTIES

75. Greiner, R. A., Miller, R. F. and Retherford, R. C.

Effects of electrode materials and surface

preparation on CdS-metal contacts. J. APPL.

PHYS. v. 28, n. 11, p. 1358-9, 1957.

Experimental studies on the effects of contact materials and crystal surface preparation on the voltage-current characteristics of contacts to CdS single crystals are presented. Rectifying contacts are influenced by the surface preparation prior to electrode application. An artificially roughened or naturally rough crystal surface tends to reduce the rectification ratio of a contact. Two kinds of current fluctuations that may be attributed to the contacts are observed.

76. Hagène, B. and Le Fèvre, J. J.

Effect of the intensity and the excitation

time on the photodielectric properties of

zinc sulphide activated with copper. J. PHYS.

RADIUM v. 18, n. 6, p. 412-13, 1957. (In French)

After irradiating specimens of ZnS : Cu at 80°K at various intensities and for various durations, dielectric loss measurements were made at 1 kc/s while the specimens heated up in the dark and under irradiation. The maximum dielectric loss is proportional to the logarithm of both the intensity and the duration of irradiation, the constant of proportionality increases abruptly at a certain value of the intensity depending on the conditions of excitation.

77. Hollander, L. E., Jr.

Preparation of high-sensitivity cadmium sulfide

cells for gamma-ray detection. REV. SCI. INSTRUM.

v. 28, n. 5, p. 322-3, 1957.

Single synthetic CdS crystals 3 x 4 x 10 mm, having dark conductivities from  $10^{-9}$  to  $10^{-10}$  ohm<sup>-1</sup> cm<sup>-1</sup>, were prepared for gamma-ray detection. In a 50 r/hr Co<sup>60</sup> field the conductivity increased to  $10^{-6}$  ohm<sup>-1</sup> cm<sup>-1</sup>. The crystals were grown in a static system at  $930 \pm 5^\circ\text{C}$ . Indium electrodes were applied

ELECTRICAL PROPERTIES

by an ultrasonic soldering technique. The effect of constant excitation from radium to reduce the crystal rise time is illustrated. The time response and spectrographic analysis of crystals and commercial CdS powder is presented.

78. Jacobs, J. E.  
Electrical conductivity of cadmium sulphide  
exposed to pulsating X-radiation. ELECT.  
ENGG. v. 70, p. 667-71, 1951.

Cadmium sulphide crystals are used in the high-speed automatic X-ray inspection of homogeneous materials. A self-rectifying copper target X-ray tube (Be-window, 4 mA, peak 14.7kV) with more than three Ni-filters gives a practically monochromatic beam. CdS crystals retain their characteristics if bombarded with  $10^{12}$  quanta. The normally incident number of quanta is  $3 \cdot 10^3$  or of that order. Individual crystals may show a variation in sensitivity to incident X-radiation by a factor of 100. Illumination of the crystal with green light (5 200 A) greatly increases the a.c. component of the current. Red and blue light have the opposite effect. Superimposed green light also reduces substantially the time necessary to reach stabilized operating conditions. Annealing of the crystals in an O-atmosphere results in the ratio of output current/incident quanta being increased by a factor of 100. Irradiation of a region close to the negative electrode yields max. output. An explanation of the observed phenomena is given.

79. Kallmann, H., Kramer, B. and Mark, P.  
A.C. impedance measurements on CdS crystals.  
LETTER In PHYS REV. v. 99, n. 4, p. 1328, 1955.

Large increases in capacitances of light-irradiated condenser cells with CdS single crystals as dielectric are attributed to a fall in volume resistivity leaving  $10^{-6}$ cm wide surface barrier capacitances. The increase is quenched by increasing the applied a.c. field (probably due to surface barrier breakdown) and by infrared light. Contributions due to trapped electrons in the crystal volume are negligible.

ELECTRICAL PROPERTIES

80. Kallmann, H., Kramer, B. and Mark, P.  
De-excitation of ZnS and ZnCdS phosphors by  
electric fields. PHYS. REV. v. 109, n. 3, p. 721-9,  
1958.

The change of impedance (photoconductivity) of certain ZnS and ZnCdS powder phosphor samples, brought about by external a.c. (60 c/s) and d.c. fields (up to 15000 V/cm), applied both during and after excitation with ultraviolet light (3660 Å), is described and compared with impedance changes due to irradiation with infrared light. Application of a d.c. field simultaneously with the exciting radiation results first in a sudden drop in both the capacitance ( $\Delta C/C_0$ ) and the dissipation factor ( $D = 1/Q$ ) followed by a recovery to a new equilibrium level below the field-free case. Removal of the field is accompanied by another drop and a recovery to the original field-free values. The partial recovery is not seen during a.c. field application under the same conditions but the complete recovery also occurs upon field removal. Applied during the photoconductivity decay, both a.c. and d.c. fields accelerate the decay. The sudden drop and partial recovery under d.c. fields is also seen during the photoconductivity decay but to a lesser extent. These phenomena are explained by a consideration of the distribution of conduction electrons created by the application of the field. The sudden capacitance drop seen under a d.c. field is attributed to a polarization effect. The free charge is swept close to the electrodes leaving the bulk of the phosphor sample non-conducting. The partial recovery is due to the buildup of the back field as well as to an increase in the conductivity of the bulk of the phosphor grains due to the creation of additional free charge by the exciting radiation and the emptying of traps into the conduction band. There is no partial recovery during a.c. field application because of the absence of the polarization field. The finite recovery time after field removal when the phosphor is under excitation as well as the acceleration of the photoconductivity decay due to the field application is attributed to a quenching action brought on by an increase in the recombination rate in those regions of the phosphor powder sample where conduction electrons have been piled up by the action of the applied field.

ELECTRICAL PROPERTIES

81. Kallmann, H., Kramer, B. and Spruch, G. M.  
 A.C. impedance measurements on insulated  
 CdS crystals. PHYS. REV. v. 116, n. 3, p. 628-  
 32, 1959.

In order to study the induced conductivity in CdS crystals without charge injection at the electrodes, the crystals were insulated with Mylar and a.c. impedance measurements were made. The capacitance and resistance of the crystals were studied as functions of intensity and wavelength of excitation, and frequency and voltage of the a.c. field. The crystal-Mylar combination was found to behave in a manner similar to that of powdered samples in like experiments. With a model that treats the crystal as a capacitor shunted by a light-sensitive resistance, the capacitance was found to increase with intensity of excitation, and to decrease with voltage and frequency. The resistance of the crystal increased by factors of 4 or 5 as the intensity of excitation decreased by factors of 10. The limitations of the model are discussed and conclusions drawn regarding whether trapped electrons or only conduction electrons contribute to the impedance.

82. Kallmann, H. and Rosenberg, B.  
 Persistent internal polarization. PHYS.  
 REV. v. 97, n. 6, p. 1596-610, 1955.

Studies are reported on persistent internal polarization effects. This polarization can be produced, particularly in photoconductive, fluorescent substances of high dark resistance, by the action of various kinds of radiation in the presence of a d.c. electric field. It has been found that such polarizations, of more than 10000 volts/cm, will persist for many days if kept in the dark after field removal. A material so polarized is in many ways a photosensitive electret. Among the substances tested, a (Zn : Cd)S phosphor and anthracene were used most extensively. Measurements are reported on the effect of ultraviolet, visible and infrared light,  $\gamma$ - and  $\beta$ -rays on the production and removal of polarization. The increase of polarization with time is initially rapid and then shows saturation. It is almost a logarithmic function of the exciting radiation intensity, and a linear function of the polarizing voltage over a wide range. It is found that the equilibrium values of polarization are essentially determined by the applied voltage, and one parameter specific to the substance. Data are given on the long-time storage of polarization. It is shown that this polarization is due to a partial separation by the applied field of free mobile charges produced by the radiation inside the material and their localization in traps. It

ELECTRICAL PROPERTIES

is not a charge injection-ejection phenomenon at the electrodes since it occurs just as well in samples insulated from the electrodes. In powders at least, the polarization is distributed throughout the entire sample and is not a charge accumulation near the surfaces. A correlation is established between these phenomena and the mechanism assumed for these substances to explain photoconductivity and fluorescence. A phenomenological model is presented which quantitatively describes many of the results of these experiments. This polarization effect provides a new method to detect and study energy storage in crystals.

83. Klier, E.  
 Alternating current measurements on cadmium sulphide cells. ANN. PHYS. (LEIPZIG) v. 18, n. 3-4, p. 163-70, 1956. (In German)

An account of measurements of impedance of CdS crystals with ohmic and nonohmic contact electrodes by a bridge method described by Rose. For crystals cleaned by glow discharge treatment, a capacity due to space charge is not established. The measurements show that such crystals exhibit the same behaviour with a.c. as with d.c.

84. Konozenko, I. D., Ust'yanov, V. I. and Galushka, A. P.  
 Conditions required for appearance of " $\gamma$ -conductivity" in CdS monocrystals. FIZ. TVERDOGO TELA v. 2, n. 7, p. 1584-91, 1960. (In Russian)

It was found that  $\gamma$ -ray-induced electrical conductivity of CdS monocrystals is closely related to the presence of local centres of the shallow trap type ( $\Delta E_t = 0.08-0.14$  eV). In the absence of such traps irradiation with  $\text{Co}^{60}$   $\gamma$ -rays about 3000  $\mu\text{r}/\text{sec}$  intensity did not produce any noticeable " $\gamma$ -conductivity" (the change of current amounted to  $10^{-13}$  A). It is suggested that Compton electrons, produced on scattering of  $\gamma$ -rays, transfer current carriers from band to band and act upon excitons and electrons in the inner shells of Cd and S atoms. In the presence of shallow traps, excitons decompose at negatively charged centres and electrons are subsequently transferred to the conduction band.

ELECTRICAL PROPERTIES

85. Kröger, F. A., Vink, H. J. and Van den Boongaard, J.  
Controlled conductivity in CdS single crystals.  
Z. PHYS. CHEM. (LEIPZIG) v. 203, n. 1-2, p. 1-72,  
1954.

The electrical and optical properties of single crystals of pure CdS or of CdS containing Ga, In, Sb, Cl or Ag are found to depend markedly on the composition of the atmosphere in which they are prepared. Crystals exposed to an oxidizing atmosphere (e.g. sulphur vapour) are insulators or semiconductors and show photoconductivity; those exposed to a reducing atmosphere show quasi-metallic conductivity. In crystals containing Ga or Cl the concentrations of the charge carriers are equal to the respective concentrations of the foreign ions. Bands appear in the yellow region of the absorption spectrum of oxidized but not of reduced crystals. The theory of defect structures is extended to calculate the dependence of the concentration of defects (donors, traps, acceptors) on the concentration and nature of the impurities and the reducing power of the atmosphere. Satisfactory agreement with experiment is found.

86. Kröger, F. A., Vink, H. J. and Volger, J.  
Resistivity, Hall effect and thermo-electric  
power of conducting and photoconducting single  
crystals of CdS from 20-700°K. PHYSICA v. 20,  
n. 11, p. 1095-9, 1954.

For reduced or Cl-doped CdS the variation of Hall effect with temperature indicates conduction in a donor level band as well as in the conduction band. Photoconducting and semiconducting crystals show an increase in resistance and Hall effect at high and low temperatures due to hole motion at high temperatures and trapping processes at low temperatures.

ELECTRICAL PROPERTIES

87. Kröger, F. A., Vink, H. J. and Volger, J.  
 Temperature dependence of the Hall effect  
 and the resistivity of CdS single crystals.  
 PHILIPS RES. REP. v. 10, n. 1, p. 39-76, 1955.

The d.c. dark-conductivity and the Hall effect have been measured with single crystals of CdS, pure and doped with Cl and Ga, from 25 to 700°K. Peaks in the curves of the Hall constant as a function of the temperature indicate a double-band conduction mechanism. Analysis of the results shows that the data can best be interpreted by assuming conduction in a donor band in addition to that in the normal conduction band. In all cases electrons are found to be the current carriers. At room temperature the electron mobility in the normal conduction band, limited by thermal scattering, is found to be  $\mu_c \approx 210 \text{ cm}^2/\text{V sec}$ . The mobility in the donor band is found at low temperatures. It increases both with the concentration of donors and with the number of electrons. Thermoelectric-power data at room temperature and the variations of the Hall constant with temperature can be explained by an effective electron-mass ratio  $m^*/m_0 \approx 0.2-0.3$ . The depth of donor levels below the conduction band in CdS-Cd and CdS-Cl is 0.01-0.02eV at low carrier concentrations, and decreases to zero at concentrations exceeding  $10^{18} \text{ cm}^{-3}$ . For insulation crystals, the conductivity and the Hall effect were measured upon illumination with the green mercury line ( $0.5 \text{ W/cm}^2$ ). Irradiation with infrared in addition is found to cause a decrease in the concentration of free electrons present under stationary conditions. Capacity measurements with insulating crystals lead to a value of the static dielectric constant  $\epsilon_s = 11.6 \pm 1.5$ . The temperature variation of the electron mobility as limited by lattice scattering between 200 and 700°K can be quantitatively accounted for with  $m^*/m_0 = 0.2-0.3$ , a characteristic temperature of longitudinal optical modes  $\theta_0 = 250-300^\circ\text{K}$ , and a scattering at acoustical modes  $aT^{-3/2}$  with  $a = 3.8 \times 10^6 \text{ cm}^2 \cdot \text{degree}^{3/2}/\text{volt} \cdot \text{sec}$ .

88. Lampert, M. A., Rose, A. and Smith, R. W.  
 Space-charge-limited currents as a technique  
 for the study of imperfections in pure crystals.  
 J. PHYS. CHEM. SOLIDS v. 8, p. 464-6, 484-5, 1959.

Rochester Semiconductors Conference Paper. A brief theoretical treatment is given of the current-voltage relationship for a solid with plane parallel geometry. As applied to the observed characteristic for a single crystal of CdS this theory indicates that there is a discrete defect level lying above the Fermi level and at a depth of  $0.8 \pm 0.05 \text{ eV}$  below the bottom of the conduction band. The defect density is  $3 \times 10^{14} \text{ cm}^{-3}$ .

ELECTRICAL PROPERTIES

89. Landauer, R.  
 Pyroelectric effect in the Cubic ZnS  
 structure. J. CHEM. PHYS. v. 32, n. 5, p. 1784-  
 5, 1960.

The classical theory of pyroelectricity, which uses only the symmetry of the crystal class, is shown to be incorrect. The surface structure is also relevant. The case of cubic ZnS is discussed in detail.

90. MacArthur, J. W.  
 ELECTRICAL PROPERTIES OF THIN FILMS OF  
 CADMIUM SULFIDE. Servomechanisms Lab.,  
 Mass. Inst. of Tech., Cambridge. Rept.  
 no. 7848-7849-R-4. Sep 58. (Contracts  
 AF 33(616)5489 and AF 33(616)5477)

Results are given of an attempt to correlate the electrical and photoelectric properties of evaporated cadmium sulfide films with the deposition parameters. By comparison of observations of the photoconduction, photovoltaic, and rectification phenomena with predictions from the corresponding theories (given in the Appendices), the following tentative conclusions are drawn: (1) evaporated films of cadmium sulfide are n-type, the more rapid the evaporation, the greater the n-type characteristic; (2) the films consist of microcrystallinities whose dimensions are of the order of the film thickness; (3) the diffusion length is of the order of the film thickness and the mean free time of a carrier of the order  $10^{-8}$  to  $10^{-10}$  sec; (4) the distribution of trapping levels comprises a relatively sparse distribution throughout the forbidden band, plus a more dense, discrete level about a tenth of a volt from the conduction band.

91. Masumi, T.  
 Relaxation time anisotropy in cadmium sulphide  
 studied with electrical resistivity and magneto-

ELECTRICAL PROPERTIES

resistance effect. J. PHYS. SOC.

JAPAN v. 14, n. 1, p. 47-56, 1959.

Anisotropic temperature dependence of electrical resistivity and magneto-resistance effect in hexagonal CdS single crystals were observed in several impurity-doped conducting and photoconducting crystals. The experimental results indicate unusual anisotropic behaviours. They seem to suggest that the relaxation time anisotropy plays an important role in transport phenomena of cadmium sulphide crystals having hexagonal crystal structure.

92.

Piper, W. W.

Some electrical and optical properties of synthetic single crystals of zinc sulfide. PHYS.

REV. v. 92, p. 23-7, 1953.

The fundamental optical absorption edge and the temperature dependence of electrical conductivity of synthetic single crystals of hexagonal zinc sulfide have been measured, as well as the photoconductivity near the absorption edge. The fundamental absorption coefficient is  $1 \text{ mm}^{-1}$  at a photon energy of  $(3.58 \pm 0.02) \text{ eV}$  and increases exponentially by a factor of ten every  $0.07 \text{ eV}$  up to  $10^3 \text{ mm}^{-1}$ . The logarithm of the electric resistivity varies linearly as a function of the inverse absolute temperature with a slope of  $(3.77 \pm 0.1) \text{ eV}/2k$ . A peak in the spectral variation of photoconductivity has been observed at the optical absorption edge.

93.

Portis, A. M.

Microwave faraday rotation: measurement of the conductivity tensor. J. PHYS. CHEM.

SOLIDS v. 8, p. 326-9, 336-7, 1959.

Rochester Semiconductors Conference Paper. A microwave bimodal cavity method for the measurement of magnetoconductivity is described. The incident microwaves excite the first mode which excites currents in the sample. These currents excite the second mode, which is coupled to the detector. With high impedance samples, the sensitivity is 3 to 4 orders higher than with waveguide methods. The theory of the method is developed, and the limits of sensitivity set by the detector noise are discussed. The sensitivity is low compared with

ELECTRICAL PROPERTIES

direct measurements. A measurement of the mobility of photocarriers in CdS agrees well with published values. Some effects arising from a comparison of low-frequency and microwave measurements are briefly discussed.

94. Ryvkin, S. M. and Konovalenko, B. M.  
Dependence of the induced conductivity in  
cadmium sulphide on the energy of exciting  
electrons. FIZ. TVERDOGO TELA v. 1, n. 11,  
p. 1757-61, 1959. (In Russian)

Answering the criticisms of Bleil, Snyder and Sihvonen, the present authors show that their earlier results on the electrical conductivity of CdS induced by electron bombardment and the results of Bleil et al. agree quite satisfactorily, if differences in the experimental conditions are allowed for.

95. Ryvkin, S. M., Konovalenko, B. M. and Smetannikova, Yu. S.  
The energy-dependence of the conductivity  
induced in layers and single crystals of  
CdS during bombardment by electrons. ZH.  
TEKH. FIZ. v. 24, n. 6, p. 961-77, 1954.  
(In Russian)

Electron energies of 2-30keV were used. A plot of induced conductivity per unit energy flux against energy shows that the conductivity is almost constant in the range 10-30keV, but falls off sharply at lower energies. The fall in the effect at 10keV is connected only with the change in the penetration power of the electrons, since the ionizing power of the electrons does not change significantly in the range of energies used. The results are compared with a theory which assumes an insensitive layer approximately  $10^{-5}$ cm thick on the surface of the specimens. The drop in the photoconductive response on the short-wavelength side of the intrinsic absorption edge is also attributed to the failure of such light to penetrate this insensitive layer.

ELECTRICAL PROPERTIES

96. Sihvonen, Y. T. and Boyd, D. R.  
Ohmic probe contacts to CdS Crystals.  
J. APPL. PHYS. v. 29, n. 8, p. 1143-5,  
1958.

Wire probe contacts are found to be diodic upon first touching CdS, but can be permanently changed from diodic to ohmic by the passage of a moderately intense electric current pulse. This result obtained for ten metals supports the idea that an exhaustion barrier exists on the surface, and contradicts proposals that ohmic contact is solely dependent upon the relative metal and CdS work functions. It is postulated that the current pulse punctures the exhaustion barrier, thereby permitting electrons to tunnel more freely and in greater numbers.

97. Smith, R. W. and Rose, A.  
Space-charge-limited currents in single crystals  
of cadmium sulfide. PHYS. REV. v. 97, n. 6, p.  
1531-7, 1955.

Currents as high as 20 amperes per  $\text{cm}^2$  can be drawn through thin insulating crystals of CdS in the dark. A series of experiments demonstrate with a high degree of certainty that these are space-charge-limited currents-the solid-state analogue of space-charge-limited currents in a vacuum. This conclusion is contrary to a recently published interpretation of similar observations on CdS crystals by Böer and Kümmel. The use of pulsed voltages made possible the observation of currents close to those of a trap-free solid. The steady-stage currents are many orders of magnitude lower than these but still many orders of magnitude higher than would be expected from the low-field resistivity of the insulator. The presence of traps determines the form and magnitude of the steady-state current-voltage curves. Conversely, these curves become a sensitive tool for the measurement of trap densities. Trap densities computed independently from space-charge-limited currents and from photoconductive currents show reasonable agreement.

ELECTRICAL PROPERTIES

98. Smith, R. W.  
Radiation from CdS crystals generated by  
d.c. electric fields. PHYS REV. v. 93, p.  
347, 1954.

A red emission is obtained from relatively conducting crystals of CdS in d.c. fields of 150 V/cm or less and for operation near to thermal breakdown conditions.

99. Strakhov, L. P.  
The influence of surface states of PbS and  
CdS on the contact potential. FIZ. TVERDOGO  
TELA v. 1, n. 4, p. 583-8, 1959. (In Russian)

The author measured the contact potentials with respect to Pt and Au of various specimens of PbS and CdS as a function of temperature, illumination, and applied magnetic field. Kelvin's vibrating condenser method was used. The results showed a considerable variation of contact potential with orientation of the PbS films and with intensity of illumination. A field of 9000 G, applied in the plane of the specimens, produced a small change in contact potential.

100. Svechnikov, S. V.  
Comparison of some characteristics of photo-  
resistors FSK-M and FS-K under X-ray radiation.  
ZH. TEKH. FIZ. v. 27, n. 4, p. 656-62, 1957.  
(In Russian)

Sensitivity, dosimetric and current-voltage characteristics, stability of the basic properties, dependence of the photocurrent on the radiation level and the applied voltage, and inertia of CdS photoresistors prepared from pressed powder (FS-K) were studied and compared with the corresponding properties of photoresistors consisting of single crystals of CdS (FSK-M). The main differences observed were lower sensitivity, lower stability, higher inertia and shorter life of the polycrystalline photoresistors.

ELECTRICAL PROPERTIES

101. Talibi, M. A.  
Gamma and X-ray effects on electric prop-  
erties of CdS and CdSe. TRUDY INST. FIZ.  
I MAT. AKAD. NAUK AZERBAIDZHAN. S.S.R., SER  
FIZ. v. 9, p. 10-19, 1958. (In Azerbaidzhani)

Investigations show that with both high-energy quanta and visual light the effects of radiation on the electroconductivity of semiconductors are determined by the behavior of the current carriers liberated as a result of ionization, and not by the character of the ionization process itself.

102. Tanaka, S. and Masumi, T.  
Magneto-resistance effect in cadmium sulphide.  
J. PHYS. SOC. JAPAN v. 13, n. 3, p. 314, 1958.

Experiments on single crystals show that the relative change in resistivity is a linear function of  $H^2$  below 8000 Oe, and that there are oscillations in the values of relative resistance as the angle between the current and the magnetic field or between the field and crystal axes are varied.

103. Tanaka, S. and Tanaka, T.  
Effects of deuteron bombardment on CdS  
single crystals. J. PHYS. SOC. JAPAN  
v. 14, n. 1, p. 113-14, 1959.

Flake shaped pure CdS single crystals with a high dark resistivity were bombarded in air at room temperature by 2 MeV deuterons to a total flux of  $10^{16}$   $\text{cm}^{-2}$ . The resistivity of the crystals falls from  $10^{10}$  to  $10^4$  ohm cm and the donor levels produced lie about 0.4 eV below the conduction band. These levels are attributed to sulphur vacancies or interstitial cadmium ions. Also an increase in photosensitivity and shift in the absorption edge towards longer wavelengths is attributed to other defect levels at 2.0 eV below the conduction band. In addition the time dependence of the photocurrent suggests the formation of hole traps.

ELECTRICAL PROPERTIES

104. Thielemann, W.  
 Some field dependent effects during partial  
 irradiation of CdS single crystals. Z.  
 NATURFORSCH v. 12a, n. 12, p. 1023-4, 1957.  
 (In German)

Measurements of photocurrents flowing in an irradiated CdS crystal, part of which was covered by opaque foils, showed that above certain applied potential, space charge limitation occurs at the cathode side of the covered region.

105. Li Chzhi-Tszyan'  
 Electron energy dependence of induced  
 conductivity of cadmium sulphide and cadmium  
 selenide films bombarded with slow electrons.  
 FIZ. TVERDOGO TELA v. 1, n. 1, p. 77-81,  
 1959. (In Russian)

The variation of electrical conductivity of vacuum-deposited CdS and CdSe films approximately  $10^{-4}$  cm thick, bombarded with 0-15 eV electrons was studied. With increasing electron energy the induced conductivity increased in steps, the energy increment necessary to produce each consecutive rise of conductivity being approximately 2.5 eV for CdS and 1.8 eV for CdSe. This was taken to indicate that the induced conductivity was associated with electrons excited from the filled to the conductivity band.

106. Wlerick, G.  
 Optical variation of the contact potential of  
 cadmium sulphide. PHYSICA v. 20, n. 11, p. 1099-  
 103, 1954. (In French)

The contact potential is found by using a beam of slow electrons incident on a CdS crystal in vacuo and measuring the current v. voltage curves for the

ELECTRICAL PROPERTIES

system and without illumination. Results for strong illumination (red or blue light) can be explained by shift of the Fermi level in the crystal by light excitation; assumption of surface states is not necessary.

107. Woods, J.  
Changes in conductivity resulting from  
breakdown in cadmium sulphide single crystals.  
PROC. PHYS. SOC. B v. 69, pt. 10, p. 975-80,  
1956.

For small applied fields the resistivity of a pure cadmium sulphide crystal is very high. For fields greater than a critical value, however, dielectric breakdown occurs and large currents flow. If the crystal is protected from destruction by a limiting resistor it is found on re-measurement at small fields, after the passage of a high current, that the conductivity and photo-sensitivity have been greatly increased. The increase in conductivity is greater, the larger the current passed through the crystal after the initial breakdown.

108. Wright, G. T.  
Space-charge limited currents in insulating  
materials. NATURE (LONDON) v. 182, p. 1296-7,  
1958.

Measurements were made of the steady current-voltage characteristic of a thin cadmium sulphide crystal, with an indium cathode and graphite anode. In the forward direction, the current remains zero up to 2.5 V, increases rapidly up to 5.7 V, and then increases proportionally to the square of the applied voltage, in the manner predicted theoretically for a space-charge limited current. In the reverse direction, the current is negligible. The possibilities of using these properties for fundamental studies and for new solid-state devices are briefly discussed.

## PART III - OPTICAL PROPERTIES

109. Addamiano, A.  
On the fluorescence of self-activated  
zinc-sulphide. LETTER In J. CHEM. PHYS.  
v. 23, n. 8, p. 1541, 1955.

The effect of firing temperature and time on the blue band of ZnS is investigated. Support is given to the theory of Bube and of Kröger that the emission centre responsible is a cation lattice vacancy.

110. Airapetyants, A. V. and Ryvkin, S. M.  
On the effects of visible light sub-illumina-  
tion on the pulse heights in cadmium-sulfide  
 $\alpha$  counters. ZHUR. TEKH. FIZ. v. 27, p. 106-12,  
1957. (In Russian)

Attempts were made to show that a constant sub-illumination by visible light induces internal photoeffects which increase the conductivity. Comparisons were made of the CdS pulse magnitudes in relation to the increase of conductivity during sub-illumination by lights of various wave lengths and the CdS crystal heating.

111. Albers, K.  
The measurement of the temperature  
dependence of the luminescence of CdS.  
Z. NATURFORSCH. v. 14a, n. 11, p. 1002-3,  
1959. (In German)

CdS crystals which have lost their red emission by prior heating at 100-200°C have this luminescence restored by heating in the dark to 150-200°C, under a vacuum of  $10^{-4}$  to  $10^{-5}$  mm Hg, but the emission is fugitive. It is more permanent if the cooling after the heat treatment occurs under strong irradiation by yellow light.

OPTICAL PROPERTIES

112. Alentsev, M. N.  
 Dependence of the luminescence output of  
 the phosphor ZnS-Cu on the wavelength of  
 the exciting light. OPTIKA I SPEKTROSK.  
 v. 1, n. 2, p. 240-7, 1956. (In Russian)

The variation of quantum output of recombination luminescence of the phosphors ZnS and ZnS-Cu with wavelength of exciting light was measured taking account of factors which promote this luminescence or which lower output in the usual measurements. Output during the absorption of exciting light in the main substance is found to be considerably smaller than with absorption of exciting light by luminescence centres. This points to losses during transfer of excitation energy from the main substance to the centres. The variation of luminescence output with wavelength of exciting light for the phosphor ZnS-Cu, is explained by assuming that centres of blue luminescence transmit the energy absorbed by them to the copper centres exceedingly effectively.

113. Alentsev, M. N. and Panasyuk, E. I.  
 The absorption spectrum of ZnS monocrystals.  
 OPTIKA I SPEKTROSK. v. 5, n. 2, p. 207-8,  
 1958. (In Russian)

Crystals 2cm x 1mm x 1-10 $\mu$  thick were made by reaction of Zn vapour with H<sub>2</sub>S above 1000°C. They had high dark resistance and were non-luminescent. Above 3500 A all crystals had the same transmission, from which the refractive index was calculated as 2.6 at 3500 A and 2.3 at 6000 A. Between 3500 and 3130 A the absorption coefficient was determined.

114. Anthony, Jean-Pierre and Ambrosino, Georges  
 Response of a Zinc sulfide screen to  $\alpha$  Particles  
 of energy lower than 5 Mev. COMPT. REND. v. 236,  
 p. 1774-6, 1953. (In French)

The relation is established between the residual range of a beam of  $\alpha$  particles and the fluorescence they excite on striking a ZnS screen.

OPTICAL PROPERTIES

115. Antonov-Romanovskii, V. V. and Trapeznikova, Z. A.

Two recombination mechanisms of the luminescence of  $\text{Sm}^{+++}$  ion in the phosphor  $\text{ZnS-Sm Cu}(\text{NaCl})$ .

OPTIKA I SPEKTROSK. v. 1, n. 2, p. 204-15, 1956.

(In Russian)

Two groups of luminescence spectrum lines occur in this phosphor, the kinetics of which differ. One group behaves similarly to the green Cu band and presumably arises from the recombination of the thermal electrons. Reasons are summarized why the second group is not associated with optical electrons but in fact arises from recombination of a "hole" with a luminescence centre, due to  $\text{Sm}^{+++}$ , on which an electron has localized.

116. Apker, L. and Taft, E.

Field emission from photoconductors.

PHYS. REV. v. 88, p. 1037-8, 1952.

Field emission current was drawn from sharp needles of the photoconductors CdS and CdSe. It increased greatly when light that excited photoconductivity was incident on the emitting area. Possible mechanisms are mentioned.

117. Apple, E. F.

Effect of CdS addition in  $\text{ZnS:Cu}$ , in and  $\text{ZnS:}$

$\text{Ag}$ , in phosphors. J. ELECTROCHEM. SOC. v. 107,

n. 5, p. 418-22, 1960.

$\text{ZnS:Cr}$ , In and  $\text{ZnS:Ag}$ , In phosphors each can show two emission bands under 3650 A excitation, namely in the green (short) and orange (long) with Cu and in the blue and yellow with Ag activator. Addition of CdS causes the ratio of intensities of the short to long wavelength emission to increase. This observation is interpreted using the donor-acceptor associated pair model proposed recently for the long wavelength emission process.

OPTICAL PROPERTIES

118. Halsted, R. E., Apple, E. F. and Prener, J. S.  
Radiative energy transfer in ZnS. PHYS. REV.  
LETTERS v. 1, p. 134-6, 1958.

The results indicate that there are a radiative emission and absorption processes which overlap in most ZnS-type materials. An example of a radiative energy transfer process is presented.

119. Apple, E. F. and Prener, J. S.  
On the infrared emission in ZnS:Cu - Effect  
of sulfur pressure and aluminum. J. PHYS. CHEM.  
SOLIDS v. 13, n. 1-2, p. 81-7, 1960.

The intensity of the infrared emission in ZnS:Cu phosphors has been studied as a function of the sulphur pressure under which the phosphors were heated at high temperatures and of Al concentration in the phosphors. The observed dependence is interpreted using a model in which the infrared absorption and emission arises from hole transitions between states of a normally unionized Cu acceptor and the valence band, and in which sulphur vacancies behave as doubly ionizable donors in ZnS. The effect of Al impurities also follows from the model.

120. Apple, E. F. and Williams, F. E.  
Associated donor-acceptor luminescent centers in zinc  
sulfide phosphors. J. ELECTROCHEM. SOC. v. 106,  
n. 3, p. 224-30, 1959.

Zinc sulphide activated with copper or silver and coactivated with gallium or indium shows two emission bands. The shorter wavelength band does not involve the ground state of the coactivator or donor, whereas the longer wavelength band does. Both bands involve the ground state of the activator or acceptor. The factors contributing to the emission intensities from the various associated donor-acceptor pairs are discussed theoretically. The dependences on temperature and on concentrations of activator and coactivator are in accord with the longer wavelength band involving a highly associated donor-acceptor pair. In addition, the energy levels of the donors, as obtained from thermoluminescent data, are correlated on the basis of the model with the differences in the transition energies of the two emission bands of these phosphors.

OPTICAL PROPERTIES

121. Arbell, H. and Halperin, A.  
Thermoluminescence of ZnS single crystals.  
PHYS. REV. v. 117, n. 1, p. 45-52, 1960.

The blue and green components of the glow of ZnS:Cu:Cl crystals were recorded separately. Thermoluminescence-excitation spectra taken for each of the components were found to be identical with the excitation spectra for the blue and green luminescence at steady excitation. Other measurements included the spectral distribution of the glow, saturation effects, effects of infrared radiation, and computation of activation energies. The activation energy for the blue peak was found to be about 0.14 eV, and that for the green - about 0.20 eV. From the shape of the peaks it was concluded that the recombination process is bimolecular in character. Electrical glow curves were also recorded and were found to be similar to the green glow curves. The results are discussed and an energy model is proposed.

122. Arkhangel'skaya, V. A.  
Infrared emission bands and kinetics of  
emission and photoconduction in CdS in temperature  
region of quenching of luminescence. DOKL.  
AKAD. NAUK SSSR v. 100, n. 2, p. 233-5, 1955.  
(In Russian)

An investigation of growth and decay of luminescence in the red and infrared, and of photocurrents. Spectra at 20, 60 and 100°C show gradual development of longer waves up to 10140 Å with rising temperature, but above 200°C the infrared emission disappears. The existence of two bands in phosphorescence is shown by two decay curves. Infrared luminescence is not due to impurities. The dependence of instantaneous emission on exciting light is not linear but proportional to 1.5 power. Agreement between growth and decay of phosphorescence and of photocurrent indicates emission due to recombination of electrons with centre.

OPTICAL PROPERTIES

123. Asano, Sumitada  
 On the infrared-sensitive behaviors of some  
 doubly activated ZnS phosphors. J. CHEM. SOC. JAPAN  
 v. 9, p. 580-94, 1954.

The quenching and stimulation of phosphorescent brightness under infrared irradiation, and their spectral sensitivities about some ZnS doubly activated phosphors, have been investigated as well as the photocurrents induced simultaneously. A model is proposed which contains two types of electron traps, namely, traps associated with emission levels at the activator and isolated traps. Theoretical calculations based on this model are compared to the experimental results for nonstationary behavior. The comparison shows that nonradiative transitions from the conduction band to the filled band and so-called infrared-sensitive "quasi-direct transitions" from the associated traps to the activators become negligible a few minutes after the ceasing of ultraviolet excitation, and then the proposed theory becomes available exactly.

124. Asano, S.  
 On the spectral distribution of infrared-stimulated phosphorescence of Pb activated ZnS type phosphors. J. PHYS. SOC. JAPAN  
 v. 10, n. 10, p. 903-5, 1955; ERRATUM, n. 11,  
 p. 1027, 1955.

125. Asano, S.  
 On the infrared-responsive behaviors of (zinc: cadmium-sulphide: selenide)-type phosphor families.  
 III. Zinc-sulphide: selenide phosphors. SCI. OF  
 LIGHT (TOKYO) v. 4, n. 1, p. 16-31, 1955.

Some singly or doubly activated cubic or hexagonal zinc sulphide: selenide phosphors have been prepared. Their spectral infrared-responsivity and

OPTICAL PROPERTIES

spectral distribution of luminescence as well as their crystal structure are investigated. The results obtained are compared with those on other zinc sulphide : selenide phosphors, which are reported in the previous paper. Further, they are explained qualitatively by a model, which contains two types of electron traps, namely traps associated with emission centres and isolated traps.

126. Asano, S.

On the infrared-responsive behaviors of (zinc : cadmium-sulphide : selenide)-type phosphor families.

V. Zinc : cadmium-sulphide : selenide phosphors.

SCI. OF LIGHT (TOKYO) v. 4, n. 1, p. 48-60, 1955.

Some (Zn : Cd)(S : Se) phosphors activated with Pb, Mn, and Ag have been prepared. Their spectral infrared-responsivity and the decay of their natural and infrared-simulated or -quenched phosphorescence as well as their luminescence and crystal structure are investigated. The results obtained show that the infrared-responsive behaviour of the (Zn : Cd)(S : Se) phosphors are qualitatively similar to those of the Zn(S : Se) and (Zn : Cd)S phosphors, which are reported in the previous parts, and that the infrared-responsive mechanism of ZnS phosphors are not substantially altered by the addition of CdSe.

127. Asano, S.

On the infrared-responsive behaviors of (zinc : cadmium-sulphide : selenide)-type phosphor families.

VI. General survey and summary. SCI. OF LIGHT

(TOKYO) v. 4, n. 2, p. 163-85, 1955.

General features of i.r.-responsive behaviour of these ZnS-type phosphors are compared with one another and summarized. Further, the type of model which is most suited for the explanation of their behaviour is discussed. Quantitative conclusions based on the most suitable model, which contains shallow traps and deep traps, are compared with the experimental results reported in the preceding Parts. The comparison shows satisfactory agreement between them.

OPTICAL PROPERTIES

128. Auth, J., Krenzke, G. and Niekisch, E. A.  
A study of the field effect in CdS single  
crystals. Z. PHYS. CHEM. (LEIPZIG) v. 213, n. 1-2,  
p. 17-29, 1960. (In German)

Highly insulating crystals, illuminated either in the fundamental absorption region or in its tail, were investigated. A field effect was not detected in every crystal, and the magnitude of the effect depended on the ambient atmosphere, which was controlled. A theoretical interpretation is admitted to be difficult, but an attempt is made to consider the possible number of surface states and the influence of the donor states within the crystal on the field effect.

129. Auth, J., Niekisch, E. A. and Puff, H.  
The infrared quenching of the photoconductivity  
of CdS single crystals. Z. PHYS. CHEM (LEIPZIG)  
v. 212, n. 3-4, p. 175-204, 1959. (In German)

The infrared quenching spectra of photoconductivity between room temperature and liquid hydrogen temperature were obtained for pure CdS single crystals, and crystals doped with Mn, Sn, Cu and Ag. The quenching spectra consisted of two bands at 0.85-0.9 and 1.2-1.5 eV, the short wave band generally persisted down to 21°K, whereas the long wave band often disappeared at about 200°K. The general quenching properties were not greatly dependent on the doping of the crystals, but differences in detailed behaviour were observed. It is concluded that two classes of recombination centres exist, one of the classes consisting of a level at about 0.2 eV and one or two further levels at 1.1-1.2 eV above the valence band.

130. Aven, M. H. and Potter, R. M.  
The luminescence of self-coactivated ZnS:Cu.  
J. ELECTROCHEM. SOC. v. 105, n. 3, p. 134-40, 1958.

Phosphors prepared by firing ZnS with Cu in purified H<sub>2</sub>S show a simple orange emission band, with no other bands in evidence, even at 90°K. Excitation by u.v. radiation, cathode rays, and electric field gives identical emission

OPTICAL PROPERTIES

spectra. The emission-band has peaks at the same wavelength for samples with either hexagonal or cubic crystal structure, but is shifted to longer wavelengths by addition of CdS. The orange luminescence is strongly decreased by traces of H<sub>2</sub>O in the H<sub>2</sub>S firing atmosphere, but quite stable to firing in oxidizing or reducing atmospheres. Addition of Al to ZnS:Cu gives a series of phosphors showing various proportions of orange, blue and green emission. Firing ZnS with Ag in pure H<sub>2</sub>S gives a new yellow-emitting phosphor with properties very similar to the orange Cu-activated phosphor. Possible models for the orange centre are discussed.

131. Avinor, M.  
Gold-activated (Zn, Cd)S phosphors. J.  
ELECTROCHEM. SOC. v. 107, n. 7, p. 608-11, 1960.

Gold is shown to produce three emission bands in CdS at 640, 800 and 1150 m $\mu$ . The long-wave band appears only when a coactivator is used while the short-wave bands are observed with activation by gold alone. The 1150 m $\mu$  band in CdS is shown to correspond to the 530 m $\mu$  gold band in ZnS.

132. Avinor, M. and Meijer, G.  
Vanadium activated zinc and cadmium  
sulphide and selenide phosphors. J. PHYS.  
CHEM. SOLIDS v. 12, n. 3-4, p. 211-15, 1960.

Vanadium activated ZnS, ZnSe, CdS and CdSe powders were prepared. All these powders show a fluorescence at about 2  $\mu$ . Addition of copper and silver as auxiliary activators enhances the vanadium emission, while the well-known silver and copper emissions do not appear.

133. Bailey, G. M. and Prescott, J. R.  
Decay time of the luminescence of a zinc  
sulphide neutron detector for neutron and

OPTICAL PROPERTIES

$\gamma$ -ray excitation. AUSTRALIAN J. PHYS.

v. 2, p. 135-8, 1958.

The neutron detector consists of ZnS(Ag) molded in a lucite cylinder 1 in. in diameter by 3/4 in. thick, mounted directly on the face of a photomultiplier. The decay time for gamma excitation was determined from a measurement of the integrated pulse-rise time. Pulse-rise times were determined photographically from a short-time exposure spectrum.

134.

Baird, W. J.

EFFECT OF GAMMA RADIATION ON SINGLE CRYSTAL. (thesis).

Air force Inst. of Tech., Wright-Patterson, Ohio.

Mar 58, 38p.

Basic properties of cadmium sulfide are investigated with emphasis on  $\text{Co}^{60}$  gamma radiation effects. It was found that gamma irradiation of n-type cadmium sulfide causes an increase in conductivity and carrier concentration by introducing more donor than acceptor states.

135.

Warschauer, D. M. and Reynolds, D. C.

Edge and impurity emission in cadmium sul-

fide. PHYS. REV. LETTERS v. 3, p. 370-2, 1959.

A model was recently proposed for the band structure of CdS which purports to explain much of the observed optical phenomena in terms of conduction and valence band extrema centered around  $k = 0$ . A set of observations is described which cannot be explained in terms of this simple structure.

136.

Baker, W. M. et al

THE STUDY OF PROPERTIES OF SINGLE Cds AND

ZnS CRYSTALS FOR USE AS DETECTORS AND CRYSTAL

COUNTERS. Detroit. Univ. Technical Progress

OPTICAL PROPERTIES

Report No. 2. Project No. NR-015-218.

1 Sep 55 to 31 Aug 56, 56 p. (Contract Nonr-1511-(01)).

Progress is reported on a theoretical and experimental study of the properties of single crystals for use as detectors and crystal counters. A procedure for growing single synthetic crystals of CdS and ZnS is discussed. The optical, electrical, and structural properties of CdS and ZnS were studied. Measurements of the index of refraction, absorption coefficient, dielectric constant, dissipation factor, and lattice parameters of the unactivated crystals were made.

137. Balkanski, M. and Broser, I.

On the transport of excitation energy in ZnS and CdS crystals. Z. ELEKTROCHEM. v. 61, n. 6, p. 715-23, 1957. (In German)

Crystals were illuminated with a narrow beam of light and the density of excited states, at various positions and at various times, was determined by measuring the local conductivity. Two diffusion processes with different diffusion lengths were observed. The measurements showed that energy transport over larger distances (diffusion length about 0.3 cm) could not be due to charged carriers, but may arise from the diffusion of excitons (electron-hole pairs) or the scattering of luminescent light.

138. Barjon, R. and Brachet, C. et al

The irradiation of cadmium sulfide monocrystal photoconductors with 1.4-Mev PROTONS. COMPT. REND. v. 248, p. 83-6, 1959. (In French)

A cadmium sulfide photoconductor monocrystal exposed to a 1.4-Mev proton beam is the site of four phenomena: green luminescence, induced conductivity, permanent modification of its photoconductivity, and modification of its spectral response.

OPTICAL PROPERTIES

139. Bartenbach, M.  
 STEADY STIMULATION AND QUENCHING OF PHOTO-  
 CONDUCTIVITY IN CADMIUM SULFIDE BY INFRARED  
 RADIATION. Polish Academy of Sciences. Inst.  
 of Nuclear Research, Warsaw. Report No. 21/1-B.  
 Apr 58, 11 p.

The changes in the steady photocurrent produced by exciting light in CdS single crystals by simultaneous illumination with infrared radiation was investigated. Many authors have reported quenching of photoconductivity in CdS by infrared and some stimulation phenomena of a transient character. Steady stimulation was observed to occur when the photocurrent caused by light alone is small compared with the photocurrent caused by infrared alone. For some definite ratio of the light intensity to the infrared intensity, the illumination with infrared causes no change in the photocurrent. If the ratio is bigger than that mentioned the well known quenching phenomena occur. By using x-rays instead of the exciting light, similar stimulation and quenching phenomena were observed. These results can be explained using the model proposed by Rose which involves the creation of free holes by infrared radiation and assuming that the current caused by infrared radiation only is associated with holes.

140. Bateman, S. K.  
 The formation of luminescent films by  
 evaporation, VACUUM p. 329, Sept. 1960.

Evaporated films of some phosphors may retain their luminescence if the components volatilize without separation, or are made to diffuse into the correct lattice position by baking.

141. Belikova, T. P.  
 Phosphorescence of the crystal phosphor  
 ZnS-Cu during excitation by an electron  
 beam. SOVIET PHYS. JETP v. 2, p. 776-7,

OPTICAL PROPERTIES

1956. (In English) ZHUR. EKSPYL. I  
 TEORET. FIZ. v. 29, p. 905-6, 1955. (In  
 Russian)

The continuous decay of luminescence of a ZnS-Cu phosphor was measured during excitation by an electron beam and, for comparison, under excitation by light with  $\lambda = 365 \text{ m}\mu$ . It was shown that the decay takes place nonspecifically with regard to the type of excitation and that the difference in observed decay curves can be explained by the difference in density of excitation during the various types of excitation.

142. Bertoldi, W. and Kleint, C.  
 Outer field emission of single crystals of  
 ZnS. ANN. PHYS. (LEIPZIG), Folge 7, v. 4,  
 n. 6-8, p. 388-95, 1959. (In German)

Field emission was observed in the dark and under illumination, after electron bombardment and after evaporating barium on to the crystals. Currents of up to  $2 \times 10^{-4} \text{ A}$  were obtained. The field dependence of current is discussed and compared with the theoretical work of Stratton on the effect for semiconductors.

143. Birman, J. L.  
 Polarization of Fluorescence in CdS and ZnS  
 single crystals. J. ELECTROCHEM. SOC. v. 107,  
 n. 5, p. 409-17, 1960.

Various symmetry properties of the wurtzite structure are discussed; the band structure of CdS and ZnS at  $k = 000$  is discussed. These symmetry and band structure considerations are used to set up and consider various models, Lambe-klick, Schoen-Klasens, etc., which would be in accord with observation of polarization. It is concluded that the Lambe-Klick model is the simplest which is in accord with the presently available observations. Some experimental tests are proposed which should help the decision among the various models. In conjunction with other single crystal optical, electrical, and magnetic measurements, polarization studies may prove decisive in obtaining quantitative knowledge about the centres in sulphides.

OPTICAL PROPERTIES

144. Birman, J. L.  
Polarization of fluorescence in CdS and ZnS  
single crystals. PHYS. REV. LETTERS v. 2, n. 4,  
p. 157-9, 1959.

The polarization of fluorescence in CdS and ZnS (see preceding abstract) is explained using the Lambe-Klick model. Consideration of energy levels of the wurtzite structure for CdS indicate that the polarization of the 6200 A emission should obey the same law as that of the edge emission. The ZnS case is more complex because of crystal disorder and zinc blende-wurtzite mixtures.

145. Bleil, C. E. and Snyder, D. D.  
Some effects of low fields on luminescence  
of CdS. J. APPL. PHYS. v. 30, n. 11, p. 1699-702,  
1959.

The effects produced on luminescence and conductivity in pure CdS crystals by application of electric fields up to  $\sim 1000\text{V/cm}$  are reported. A shift in the red and green cathodoluminescence peaks of  $\sim 0.1\text{A(V/cm)}^{-1}$  is observed. After application of the low fields, some crystals required over 90 min to recover their "prefield" luminescence. Fine structure in the luminescent peaks at room temperature is reported. A V-I plot shows a sublinear relation in this voltage range for several different levels of irradiation. An explanation of the observations is suggested based on self-trapping of electrons.

146. Bleil, C. E. and Snyder, D. D.  
Bombardment of Cadmium sulfide crystals with  
30-TO 60-Kov electrons. PHYS. REV. v. 111, p.  
1522-6, 1958.

The dependence of induced conductivity in CdS crystals on the rate of arrival and the energy of impinging electrons is reported. These results lead to a qualitative picture of the conduction, excitation, and recombination phenomena in CdS which is satisfied by the simple model of a sulfur vacancy, and an analytical expression which involves the mobility of carriers, their effective

OPTICAL PROPERTIES

masses, the number of ground states in the forbidden gap (for pure but not perfect crystals) and their positions as a function of temperature. The red and green luminescence observed under irradiation by electrons is qualitatively explained. The equation for the induced conductivity is derived from the expression for two-carrier conductivity and the definitions of the steady-state Fermi levels for holes and electrons. An empirical fit to the observed data yields  $\sigma = e\mu_n N_C \exp(kT\alpha I - E_{fn}^0)/kT$  for  $I < I_S$  and  $\sigma = e(\mu_n + \mu_p)N_V \exp(kT\beta(I - I_S) - E_{fp}^0)/kT$  for  $I > I_S$ . The data reported herein were obtained by using monoenergetic bombarding electrons in the range of 30 to 60 kev. An interesting field effect is reported but no clear interpretation is available to the authors. Corroborating data employing ultraviolet irradiation are described.

147. Böer, K. W., Borchardt, E. and Borchardt, W.

On slow changes of conductivity with time for single crystal at high temperatures and under additional optical irradiation. A contribution to the clarification of the conduction-mechanism. Z. PHYS. CHEM. (LEIPZIG) v. 203, p. 145-62, 1954. (In German)

It is found that the time variation of conductivity after irradiation or heating up is not of the expected similar form. Experiments on this effect are described including the dependence of the build-up and decay on temperature, light intensity, and previous heat treatment. Experiments analogous to the thermoluminescence glow curves are also described.

148. Böer, K. W. and Gutjahr, H.

Optical absorption of CdS single crystals at the lattice absorption edge. Z. PHYS. v. 155, n. 3, p. 328-31, 1959. (In German)

The optical absorption of CdS at the band edge is determined by indirect band to band transitions involving phonons. At room temperature optical absorption occurs with the emission or absorption of a phonon. The characteristic phonon energy is given.

OPTICAL PROPERTIES

149. Böer, K. W., Rummel, U. and Rompe, R.  
 A contribution to the problem of breakdown of  
 solid insulators. Z. PHYS. CHEM. v. 200, p. 180-9,  
 1952.

The effects of irradiation with visible light, on the conduction current and electric strength of CdS single crystals, are discussed in relation to the theories of thermal and intrinsic breakdown.

150. Boldt, W. and Seiwert, R.  
 The temperature dependence of the luminescence  
 of Cds crystals. II : Crystals with Mn, Fe, Co  
 or Ni incorporated. v. 212, n. 5-6, p. 319-44,  
 1959. (In German)

For Pt I see preceding abstract. The crystals probably contained  $\approx 0.01\%$  of foreign atoms; their emission bands were measured at 5150, 6250, and 7700Å, and some data obtained on the visible end of an infrared band. Curves show the temperature dependence of the bands between -184 and +200°C, and the whole spectral distribution at various temperatures. Few crystals had the green emission, the orange band was at a maximum at -100°C, and the red band (peak  $\sim 7850\text{Å}$ ) showed variable behaviour. Overall light output was highest for crystals containing Mn, with maximum at -50°C, whereas for Fe impurity the maximum was at 100°C. Co and Ni produced only low efficiency. The temperature dependence of efficiency is discussed, especially for the red band which also varies in position.

151. Borisov, M.  
 A sensitive method of investigating the internal  
 photoeffect in powdered simiconductors by dielectric  
 loss measurements. IZV. BULG. AKAD. NAUK. v. 3, p. 91-  
 8, 1952. (In Bulgarian)

The method presented determines the variations of the dielectric losses under illumination which produce variations of the grid current of an h.f. oscillator,

OPTICAL PROPERTIES

the oscillation circuit of which contains a capacitor the dielectric of which is the substance investigated. The actual measuring method is a compensation method by which variations of the order of  $10^{-6}$  of the initial grid current may be observed. The variations of the grid current depend linearly on the variations of the equivalent h.f. admittance of the oscillation circuit. The author presents the curves of the variations of the dielectric losses under illumination and darkening of Zn25%CdS, Cu, and the corresponding curves plotted for infrared irradiation, and also the recorded curves of the internal photoeffect of ZnS.Zn and ZnO.

152.

Borisov, M., Kynev (Kunev), S., and Zlateva, A.

Some experimental results of investigations on  
the internal photoeffect in mixed (ZnS, CdS):

Cu crystal phosphors. C. R. ACAD. BULG. SCI.

v. 8, n. 1, p. 13-16, Jan-Mar 1957. (In Russian)

Presents the results of experiments with powder specimens at room temperature and at 230°C, using the dielectric-loss method. Four phosphors were studied, containing 0, 25, 50 and 100% CdS, respectively, and activated with 0.01% Cu; the wavelength of excitation light varied between 365 and 578  $\mu$ . In the case of phosphors with 0 or 25% CdS the regular kinetics of the internal photoeffect was observed; with the two other phosphors and wavelengths 546 and 578  $\mu$ , more involved kinetic curves were obtained. It was also established that the conductivity v. temperature curves of phosphors with 0 and 25% CdS showed maxima at temperatures above room temperature; these maxima were shifted towards higher temperatures when the phosphor remained in darkness for a relatively long period between excitation and heating. The maxima flattened out when the phosphors were irradiated with infrared light between excitation and heating.

153.

Bowers, R., and Melamed, N. T.

Luminescent centers in ZnS: Cl phosphors.

PHYS. REV. v. 99, p. 1781-7, 1955.

Measurements of the magnetic susceptibility and emission spectra have been made on zinc sulfide activated by copper and/or chlorine. The results of these measurements demonstrate that the luminescent centers are diamagnetic in the absence of optical excitation, and that of the five previously reported emissions, only three are distinct. These are a blue emission resulting from

OPTICAL PROPERTIES

the addition of chloride, a green emission when copper and chloride are simultaneously present, and a red emission when copper alone is present. The results are discussed on an ionic model and on a semiconductor model. We conclude that the blue emission is due to zinc vacancies, the green emission to substitutional copper, and the red emission to interstitial copper.

154. Brauer, P.  
Photoelectromotive forces in phosphors.  
Z. NATURFORSCH v. 14a, n. 5-6, p. 555-9,  
1959. (In German)

Irradiation of ZnS phosphors by monochromatic light in the lattice absorption region produces free carriers and a current resulting from their diffusion, which identifies them as electrons. In the tail of the absorption the current varies in direction but the carriers are usually holes. With either Cu or Ag activator and either Ga or Al coactivator, the displacement current changes sign at  $\sim 3350 \text{ \AA}$ , with a comparatively small reversed current due to holes at longer wavelengths. The effect becomes zero at  $\sim 4800 \text{ \AA}$  for Cu and  $\sim 4100 \text{ \AA}$  for Ag, in agreement with relative activator levels, whereas the different trap depths of Ga and Al have no effect.

155. Brophy, J. J.  
Trapping and diffusion in the surface region  
of cadmium sulfide. PHYS. REV. v. 119, n. 2,  
p. 591-6, 1960.

For previous work, see Abstr. 9991 of 1960. In lightly doped single crystal CdS illuminated with  $4400 \text{ \AA}$  radiation hole-electron pairs generated at the surface diffuse into the crystal until the hole is trapped. The electrons experience multiple retrapping until they disappear through recombination. Current noise and photo-conductivity measurements were used to study these processes. The noise data establish the ambipolar diffusion length as 30 microns, confirm that diffusion is important though the appearance of a  $f^{-3/2}$  trend in the noise spectra, and show that discrete traps are located the same distance below the conduction band in the surface regions as in the bulk. Discrete trap levels at 0.35, 0.40 and 0.43 V below the conduction band are observed in the surface region. Trap densities of  $10^{16}$  traps  $\text{cm}^{-3} \text{ V}$ , an order of magnitude greater than that in the bulk, are determined. The trap frequency factors are of the order  $10^{10} \text{ sec}^{-1}$ .

OPTICAL PROPERTIES

156. Broser, Immanuel and Warminsky, Ruth  
 Modifications produced by  $\alpha$ -particle  
 irradiations in CdS crystals. Z.  
 NATURFORSCH v. 6a, p. 85-102, 1951.

(In German)

Changes produced by irradiations with  $\alpha$  particles in the luminescence properties and electrical conductivity of synthetic CdS crystals were measured. Whereas the luminescence is always reduced by the action of  $\alpha$  rays, the conductivity is modified by some combination of both an increasing and a decreasing effect. An explanation of these actions of  $\alpha$  particles on the position of crystal electrons, based on the band model of the lattice (Riehl and Schön, Z PHYSIK 114, 682(1939)), is offered.

157. Broser, I., and Broser-Warminsky, R.  
 Concerning the problem of exciton diffusion  
 in photoconductors. J. PHYS. CHEM. SOLIDS  
 v. 8, p. 177-9, 193-5, 1959.

The photocurrent and the luminescence in optically shielded regions of an irradiated CdS crystal are quantitatively compared. The results negate the validity of exciton diffusion theories for such crystals.

158. Broser, I., and Broser-Warminsky, R.  
 On the energy level scheme of phosphorescent  
 crystals. J. PHYS. RADIUM v. 17, n. 8-9,  
 p. 791-6, 1956. (In French)

The emission, absorption, stimulation and quenching spectra of ZnS and CdS single crystals are investigated. The importance of making all these experiments on the same sample is pointed out. The energy-levels scheme is derived for self-activated or Cu-activated ZnS and CdS.

OPTICAL PROPERTIES

159. Broser, I., Kallmann, H., and Warminsky, R.  
On the theory of the conductive mechanism in  
cadmium sulphide crystals. Z. NATURFORSCH  
v. 4a, p. 631-7, 1949. (In German)

A model is proposed which takes account of the connection between conductivity and luminescence. The efficiency of luminescence phenomena is observed to increase with conductivity. Both properties are a function of impurity content and of the life-time of the charge carriers. Many crystals have high electron multiplication factors under light or nucleon bombardment. This process is often associated with pronounced inertia. In highly activated CdS excitation by  $\alpha$ -particles is most effective near the cathode. Photo-conductive properties are influenced by preillumination of the crystal before application of the electric field. These and other observations are accounted for by assuming that a narrow partially filled band exists below the main conduction band of the crystal.

160. Broser, I., and Warminsky, R.  
The variation of luminescence and electrical  
conductivity of CdS crystals with alpha-  
particle irradiation. Z. NATURFORSCH v. 5a,  
p. 85-102, 1951. (In German)

The change of luminescence and electrical conductivity due to alpha particles and to photons in various CdS crystals is investigated after prolonged exposure to Po alpha particles. Results show that alpha particles produce empty electron trapping states in the crystals in which electrons can make non-radiative transitions to the ground state. The results can be interpreted by use of the Riehl-Schön band model and provide new information on the differences between particle and photon excitation of crystals.

OPTICAL PROPERTIES

161. Broser, I., and Warminsky, R.  
Theory of luminescence and electrical  
conductivity of cadmium sulphide crystals.  
ANN. PHYS. LPZ. v. 7, n. 6, p. 289-311,  
1950. (In German)

A quantitative study is made of the mechanisms of luminescence and electrical conductivity in CdS crystals in terms of the Riehl-Schön energy-band model. Factors such as the temperature, impurity concentration and thickness of excited crystal layer are accounted for. Agreement is shown with experimental results.

162. Broser, I., and Warminsky, R.  
On the electrical conductivity accompanying  
the phosphorescence of cadmium sulphide  
crystals. Z. PHYS. v. 133, n. 3, p. 340-61,  
1952. (In German)

The influence of electron traps on the conductivity and luminescence of well activated CdS crystals is discussed in terms of the band model. Experiments are made to determine the decay of phosphorescence and corresponding decay of conductivity.

163. Broude, V. L., Eremenko, V. V., and Medvedev, V. S.  
Photoconductivity excitation and luminescence  
spectra of CdS crystals. ZHUR. TEKH. FIZ.  
v. 28, p. 2263-5, 1958. (In Russian)

It was shown that there is a close connection between the photoconductivity of CdS crystals and their green luminescence. For some specimens the excitation spectra coincide. The spectral distribution of the quantum yield, which in contrast to the spectral distribution of photocurrent is not complicated by the dependence of free electron lifetimes on the wavelength, is close to the

OPTICAL PROPERTIES

green luminescence excitation spectra. Two types of orange luminescence excitation were observed which indicate the presence of two luminescences of different origin. In some crystals the orange luminescence is accompanied by green and is induced by absorption in the 20,600 to 20,700  $\text{cm}^{-1}$  region. Other specimens with strong orange luminescence have a supplementary long wave band of absorption.

164. Broude, V. L., Eremenko, V. V., and Chikovani, N. N.

The structure of spectra of absorption and

photoconductivity of CdS crystals at 20°K. DOKL.

AKAD. NAUK SSSR v. 119, n. 5, p. 911-13, 1958.

(In Russian)

Optical absorption,  $K$ , was measured to 20 860  $\text{cm}^{-1}$  for light polarized parallel, and to 20 680  $\text{cm}^{-1}$  for light polarized perpendicular to the c-axis. Above 20 600  $\text{cm}^{-1}$  similar spectra were obtained from all crystals, but appreciable local differences in  $K$  were possible at lower frequencies. Comparison is made between features in the absorption spectrum and photoconductivity, e.g. the absorption line near 20 600  $\text{cm}^{-1}$  (polarized parallel to c-axis), which may be connected with surface deformation and which was found to vary in strength with different crystals, appeared to have no photoconductivity associated with it. The hypothesis that the photocurrent should be the same for the same value of  $K$  in different parts of the spectrum did not appear to be valid.

165. Browne, P. F.

Infra-red luminescence of zinc and cadmium

sulphide phosphors. J. ELECTRONICS v. 2,

n. 1, p. 1-16, 1956.

New luminescence emission bands have been found in the infrared region at 1.8  $\mu$  for cadmium sulphide phosphors. The emission is analogous to that recently found for zinc sulphide phosphors at 1.6  $\mu$ . A systematic study has been made of the infrared emission in a large number of zinc sulphide, zinc-cadmium sulphide and cadmium sulphide phosphors. It is excited by raising electrons from the valence band of the phosphor lattice into the ground states of the normal luminescence centres. The latter are either empty in the normal state or must

OPTICAL PROPERTIES

first be emptied by suitable excitation giving rise to the well-known visible and near visible luminescence of these phosphors. The return of electrons to the valence band gives rise to the infrared emission. The excitation spectra for the infrared emission correspond to the quenching spectra for the visible luminescence and for the photoconduction of the above phosphors. A new infrared stimulation band of the visible emission of ZnS has been found at about 2.55  $\mu$ , which may well correspond to the single thermal glow peak of these phosphors.

166. Browne, P. F.  
Luminescence of the sulphide phosphors.  
J. ELECTRONICS v. 2, n. 2, p. 154-65, 1956.

Detailed theoretical and experimental studies suggest that cation vacancies cause the 0.46  $\mu$ , 0.54  $\mu$  luminescence bands of ZnS, the 0.8  $\mu$ , 1.01  $\mu$  bands of CdS and the 0.92  $\mu$ , 1.2  $\mu$ , bands of CdSe. Both the blue and green bands arise from the same centre. Anion vacancies in the lattice are thought to provide the centres for the 0.67  $\mu$  red emission of ZnS and the 2.5  $\mu$  emission of HgS. All these are interionic transitions between ions of the fundamental lattice. Overlap due to partially covalent binding ensures that there is appreciable probability of such transitions. Two energy levels in the forbidden zone are created by breaking a double homopolar bond and these are undisturbed by the presence of Cu<sup>+</sup> ions in the vacancy. The recently investigated infrared emissions of the sulphides are assumed to be transitions between 3p-3s mixed states, which have been perturbed by the absence of a neighbouring cation into the forbidden zone. The binding is found to be about 36% covalent.

167. Browne, P. F.  
Infra-red luminescence of zinc and cadmium  
sulphide phosphors. J. ELECTRONICS v. 2,  
n. 1, p. 1-16, 1956.

New luminescence emission bands have been found in the infrared region at 1.8  $\mu$  for cadmium sulphide phosphors. The emission is analogous to that recently found for zinc sulphide phosphors at 1.6  $\mu$ . A systematic study has been made of the infrared emission in a large number of zinc sulphide, zinc-cadmium sulphide and cadmium sulphide phosphors. It is excited by raising electrons from the valence band of the phosphor lattice into the ground states of the normal luminescence centres. The latter are either empty in the normal state or must first be emptied by suitable excitation giving rise to the

OPTICAL PROPERTIES

well-known visible and near visible luminescence of these phosphors. The return of electrons to the valence band gives rise to the infrared emission. The excitation spectra for the infrared emission correspond to the quenching spectra for the visible luminescence and for the photoconduction of the above phosphors. A new infrared stimulation band of the visible emission of ZnS has been found at about  $2.55 \mu$ , which may well correspond to the single thermal glow peak of these phosphors.

168. Bube, R. H.  
Luminescence and trapping in zinc sulfide  
phosphors with and without copper activator.  
PHYS. REV. v. 80, p. 655-66, 1950.

A comprehensive study of ZnS : (Zn) and ZnS : (Zn) : Cu phosphors has been carried out with the use of glow curves, phosphorescence-emission decay curves, and spectral distribution curves of emission during excitation by  $3\ 650\text{\AA}$  u.v. The principal contributions of the study are: glow curves and spectral emission curves for 9 samples each cubic and hexagonal ZnS with copper activator in proportions from zero to 3 000 parts per million; a direct proof for ZnS-type phosphors of the equation of emptying proposed by Randall and Wilkins; a detailed extension of the study of retrapping by the method indicated by Wilkins and Garlick; a determination of the number of electron traps in ZnS as a function of heating temperature in preparation; an analysis of glow and decay curves by means of the equation of Randall and Wilkins; suggestions concerning the identity of traps and luminescence centres on the basis of a study of the crystal structures of cubic and hexagonal ZnS.

169. Bube, R. H.  
A comparative study of photoconductivity  
and luminescence. PHYS. REV. v. 83, p.  
393-6, 1951.

Measurements of luminescence emission and photoconductivity as a function of (1) operating temperature during excitation, (2) time during decay, and (3) temperature during thermostimulation were made for a ZnS crystal. The results indicate that the processes of luminescence and photoconductivity are dissimilar. Evidence is presented for the presence of surface conductivity, especially important in measurements made with acicular crystals.

OPTICAL PROPERTIES

170. Bube, R. H.  
Electronic transitions in the luminescence of  
zinc sulfide phosphors. PHYS. REV. v. 90, p.  
70-80, April 1, 1953.

The electronic transitions involved in the processes of absorption, excitation, emission, trapping, and photoconductivity, at room temperature, have been measured for ZnS phosphors, without added impurity, and with Ag, Cu, and Mn impurity. Three types of excitation transitions are found: (1) from the filled band to the conduction band, (2) from an impurity level above the filled band to the conduction band, and (3) from a ground-state level to an excited-state level of an impurity ion. The first two transitions result in trapping and photoconductivity; the third does not. Emission transitions occur from a level below the bottom of the conduction band to a level above the filled band. The same five major trap depths are common to all ZnS phosphors regardless of the nature of the impurity. Optical-trap emptying by visible light, like thermal trap emptying, involves a process of stimulation in which trapped electrons are raised into the conduction band before returning to luminescence centers to produce emission. A tentative energy-level diagram is constructed from the data obtained.

171. Cherepnev, A. A.  
Zinc oxide in zinc sulphide phosphor.  
OPTIKA I SPEKTROSK. v. 1, n. 2, p. 272-4,  
1956. (In Russian)

On the subject of the part played by oxygen compounds in the ZnS luminophor system there has been a considerable amount of work done and the author here discusses it critically. The partial volatilization of components (e.g. Zn, SO<sub>2</sub> S) which occurs during their mutual interaction suggests the formation of defects in the crystal lattice which aid the development of luminescent properties by creating places for the activator and for electron capture.

OPTICAL PROPERTIES

172. Cherpnev, A.A.  
 Physico-chemical properties of silver activator  
 in a zinc sulfide luminophor. IZVEST. AKAD. NAUK. S.S.S.R.,  
 SER. FIZ. v. 23, p. 1334-40, November 1959. (In Russian)

The physico-chemical properties of a silver activator as a function of interactions between the components (ZnS, Ag<sub>2</sub>S, Ag, Zn, ZnO, calcination, and atmosphere) during preparation were studied. Various compositions of ZnS-Ag were prepared at 800 to 1100°C with NaCl and H<sub>3</sub>BO<sub>3</sub> flux, and their luminescence properties at  $\lambda = 365$  m $\mu$  excitation at room temperature were analyzed. Absorption spectra were measured.

173. Cheroff, G., Enck, R. C. and Keller, S. P.  
 Effects of polarized light on photocurrents and  
 photovoltages in ZnS. PHYS. REV. v. 116, n. 5, p. 1091-  
 3, December 1, 1959.

The anomalous short-circuit photocurrents in ZnS were measured using polarized light. In spite of the fact that for a given wavelength, light polarized perpendicular to the c-axis is more strongly absorbed than light polarized parallel to the c-axis, there are wavelength regions in which the absolute magnitude of the short-circuit photocurrents are smaller for perpendicularly polarized light. The data are consistent with a double valence bande model.

174. Li Chzhi-tszyan'  
 Investigation of the intercrystal energy barriers  
 in thin CdS layers by means of bombardment with  
 low-energy electrons. FIZ. TVERDOGO TELA v. 1,  
 n. 1, p. 82-8, January 1959. (In Russian)

The effect of irradiation with 0-15 eV electrons on the electrical resistance of very thin ( $10^{-7}$ - $10^{-5}$  cm) CdS layers was studied. It was found that above a certain critical electron energy  $E_c$  the resistance of CdS layers fell after electron irradiation, while below  $E_c$  electron irradiation increased the

OPTICAL PROPERTIES

resistance. The value of  $E_c$  decreased with increase of thickness of the layers, but it was independent of thickness in the case of layers thicker than  $3 \times 10^{-5}$  cm. After heating to 300°C or a higher temperature the value of  $E_c$  rose or became indeterminate. Illumination of CdS layers with blue light (4800 Å) raised the value of  $E_c$ , indicating anisotropy of CdS crystallites; illumination with light of 6500 Å wavelength did not affect the value of  $E_c$  very greatly. Increase of the resistance on electron irradiation was ascribed to attachment of electrons at the crystallite surfaces in the layers. The resistance was lowered by electrons with energies higher than  $E_c$  because such electrons were able to penetrate or lower the intercrystalline energy barriers and increase in this way the electron density inside the crystallites. CdS layers thinner than  $3 \times 10^{-5}$  cm were found to consist of separate grains which joined together in thicker layers.

175. Clayton, C. G., Haywood, B. C. and Fowler, J. F.  
 Conductivity induced by radiation in poly  
 crystalline cadmium sulphide and poly-  
 ethylene. NATURE v. 183, p. 1112-13, April  
 18, 1959.

Ionizing radiation on insulators or semiconductors produces electron-hole pairs; when irradiation is stopped, electrons are released from traps into the conduction band. The curve of conductivity decay resulting is hyperbolic. Results of studies with CdS and polyethylene are cited to support the idea of photoconductive trapping and decay.

176. Coche, A. and Henck, R.  
 Effects of alternating and continuous electric  
 fields on the luminescence of certain sulphides of  
 zinc excited by  $\alpha$ -rays. J. PHYS. RADIUM v. 20,  
 n. 10, p. 827-9, Oct 1959. (In French)

The  $\alpha$  particle luminescence of ZnCdS:Mn is enhanced by an a.c. field if the Mn content is 1% or 0.1%, but decreased for 0.01%Mn. Increase of field causes roughly linear enhancement of the yellow emission band, and decrease of the blue band if present. Under a d.c. field time effects are observed, and high Mn content leads to enhancement while low Mn leads to quenching. "Memory" effects are described.

OPTICAL PROPERTIES

177. Collins, R. J.  
 Mechanism and defect responsible for edge  
 emission in CdS. J. APPL. PHYS. v. 30. n. 8, p.  
 1135-40, Aug 1959.

The nature of the green and blue emission at 78°K in CdS has been investigated. On the basis of the wavelengths of absorption and emission lines the blue component is assigned as exciton decay. Measurement of the decay of the blue luminescence, following excitation by a  $10^{-8}$  sec pulse of 1 MeV electrons, gave an exciton lifetime  $< 10^{-8}$  sec. Similar measurements have shown that the green component has a slower decay with emission occurring as long as 20  $\mu$ sec after the excitation has ended. These results have been used to support the recombination of a free electron with a trapped hole as the mechanism for green edge emission. Heating in sulphur vapour quenches the green luminescence in a controllable fashion. From the infrared reflection spectra of CdS in the region 10 to 50  $\mu$  the optical phonon frequencies were determined. The value of  $305 \text{ cm}^{-1}$  for the longitudinal phonon is in good agreement with the prediction of Kröger and Meyer from edge emission measurements.

178. Coogan, C. K.  
 The measurement of the optical properties  
 of zinc sulphide. PROC. PHYS. SOC. B  
 v. 70, pt. 9, p. 845-61, Sep 1957.

The knowledge, to date, of optical absorption in ZnS is surveyed and discussed. The method used for determining the optical absorption and refractive index of a solid over a range of wavelengths is discussed and equations deduced for the transmittance and reflectance of a thin absorbing film on a thick substrate. The practical determination of the refractive index and extinction coefficient from the measured values of transmittance and reflectance is discussed in some detail. A description is given of the experimental procedure and precautions used in determining the optical constants of evaporated layers of ZnS. The results are discussed in relation to previous work. The effects of change of temperature at which the measurements are made, and of exposure of the films to air are noted and discussed.

OPTICAL PROPERTIES

179. Cox, J. T., Waylonis, J. E., and Hunter, W. R.  
 Optical properties of zinc sulfide in the  
 vacuum ultraviolet. J. OPT. SOC. AMER. v. 49,  
 n. 8, p. 807-10, 1959.

The reflectance and optical constants of films of zinc sulphide vacuum deposited on to glass were measured for the wavelength region extending from 2200 to 584 A. The effects of different deposition conditions and ageing in normal and dry air were studied. In the wavelength range from 2200 to 1100 A the reflectance is relatively high ( $\cong 33\%$ ) and uniform. Beyond 1100 A it decreases and at 584 A is only 3.8%. The refractive index,  $n$ , decreases rapidly from a value of 3.13 at 2200 A to a minimum of 0.64 at 735 A. The absorption coefficient,  $k$ , has a maximum value of 1.75 at 1800 A and decreases with decreasing wavelength to a value of 0.23 at 584 A. In contrast to many other materials the variation of deposition conditions has very little effect on the reflectance of zinc sulphide. The films also show almost no ageing in normal or dry air. Under the best conditions these films are durable enough to stand washing with cotton and detergent many times without damage.

180. Curie, G.  
 Study by interference filters of the action  
 of infrared on ZnS (Cu, Pb). J. PHYS. RADIUM  
 v. 17, n. 5, p. 453-4, 1956. (In French)

By using interference filters the action of various regions of near infrared radiation on the trapped electrons in ZnS (Cu, Pb) is studied. The thermoluminescence curve is used as an indicator of changes in trapped electron distributions following irradiation.

181. Curie, G., and Curie, D.  
 The green and blue emission bands of ZnS(Cu).  
 (Faculté des Sciences, Paris). J. PHYS.  
 RADIUM v. 21, p. 127-9, 1960. (In French)

It is suggested, at least as a first approximation, that the same fundamental level plays its part in both the "blue centers" and "green centers" of ZnS(Cu).

OPTICAL PROPERTIES

The emitted light quantum depends on the excited level "associated" with the fundamental level; the transition occurs between these two states. Experimental arguments are given supporting this model, especially resulting from electroluminescence studies

182. Czyzak, S. J., et al  
On the properties of single cubic zinc sulfide crystals. J. OPT. SOC. AMER. v. 44, n. 11, p. 864-7, 1954.

Single cubic crystals of ZnS grown by a method previously reported have been investigated for optical and electrical properties, i.e., index of refraction, optical absorption, photoconductivity, dielectric constant, and lattice parameters. The method of growing crystals has been refined over the previously reported method so that larger crystals and greater yield per individual run were obtained. Both hexagonal and cubic crystals have been grown.

183. Czyzak, S. J., et al  
Refractive indexes of single synthetic zinc sulfide and cadmium sulfide crystals. J. OPT. SOC. AMER. v. 47, n. 3, p. 240-3, 1957.

A new method has been devised for measuring refractive indexes of crystals in the visible and infrared region. In this method thermocouples with CaF<sub>2</sub> or KBr windows have been used to detect the chopped (10 c/s) refracted beam. Single synthetic crystals of CdS and ZnS grown by the vapour phase method have been examined from their absorption cutoffs to 1.4  $\mu$ . In comparing the results obtained, in the visible region, to the visual method of determining refractive indexes, the thermocouple detector method has duplicated these to within an index of refraction of  $\pm 0.001$ . For data extended to the infrared region it is found that the calculated results compare very closely with the experimental data. Index of refraction measurements may now be extended considerably into the infrared region being limited only by the sensitivity of the detector and the intensity of the transmitted monochromatic beam.

OPTICAL PROPERTIES

184. Czyzak, S. J., et al  
THE STUDY OF THE PROPERTIES OF SINGLE CdS  
AND ZnS CRYSTALS. Technical Report No. 6.  
1 Sep 60, 47p. Project NR 015-218.  
(Contract Nonr-1511 (01)).

The progress in the theoretical and experimental investigation of single-crystal properties is reported. The studies during the period were particularly concerned with the optical, electrical, and structural properties which might suit them to applications such as detectors and crystal counters. Dielectric constant measurements on CdS and ZnS single crystals at 25° and -65°C were completed. Index-of-refraction measurements were also completed to 1.4  $\mu$  and extension of these measurements to 25  $\mu$  is in progress. Thermal-conductivity studies will receive major attention during the next report period.

185. Destriau, G.  
Spectral distribution of the electro-  
enhancement effect of CdS-ZnS mixtures activated  
by manganese and silver. J. PHYS. RADIUM v. 17,  
n. 8-9, p. 734-6, 1956. (In French)

The magnitude of the "electro-enhancement effect" (the increase in the X-ray excited fluorescence of certain phosphors when in electric field is applied) is quite different according to the spectral region observed. The maximum enhancement for the samples used (70% ZnS, 30% CdS) is obtained at about 6000 A; here the brightness is increased by a factor which may be as high as four when the field is applied. For shorter wavelengths (below about 6000 A), however, the enhancement effect disappears and, in some cases, is even replaced by a quenching effect.

OPTICAL PROPERTIES

186. Destriau, G.  
 Reinforcement by electric fields of the  
 sensitivity to x-rays of certain luminescent  
 products, and photoelectroluminescence.  
 C. R. ACAD. SCI. (PARIS) v. 245, n. 21,  
 p. 1797-800, 1957. (In French)

The luminescence of ZnDcS:Mn under X-rays is enhanced by a simultaneous a.c. field, and the effect is similar whether the field is in phase with the X-ray pulses, or  $90^\circ$  out of phase. With ZnS:Ag an extinction replaces the enhancement, though only if the X-rays and a.c. field are in phase. These results conflict with the mechanism of photoelectroluminescence advanced by Cusano and Williams. Wave forms of the luminescence are shown.

187. Dexter, D. L.  
 Optical investigation of semiconductors at  
 the University of Rochester. J. PHYS. CHEM.  
 SOLIDS v. 8, p. 473-81, 1959.

A survey is given of recent investigations at this institution of optical properties of non-metals. The fundamental absorption of the alkali, silver, and thallos halides and of cadmium sulphide; intrinsic photoconductivity in the alkali halides; electron multiplication in lead sulphide and selenide; and the theory of excitons in the tight binding approximation are among the topics discussed.

188. Diemer, G., and van der Houven van Oordt, A. J.  
 Nature of blue edge emission in CdS. PHYSICA  
 v. 24, n. 8, p. 707-8, 1958.

The green and blue edge emissions from CdS crystals, and the electron concentration vary with light intensity at  $77^\circ\text{K}$  as the powers of 0.7, 1.5 and 0.4 respectively. Free charge carriers must be involved in the recombination processes.

OPTICAL PROPERTIES

189. Dobrowolski, J. A., and Weinstein, W.  
Optical aspherizing by vacuum evaporation.  
LETTER In NATURE (LONDON) v. 175, p. 646-7,  
1955.

The use of zinc sulphide films, giving retardations of 30-40 $\lambda$  mercury green light, is described. The films were stable and showed no signs of weathering. A few practical details are given, together with figures for the accuracy obtained.

190. Drozd, L.  
The influence of composition on the luminescence  
of non-activated ZnS-CdS phosphors. IZVEST.  
AKAD. NAUK. S.S.S.R., SER. FIZ. v. 23,  
p. 1300-3, 1959. (In Russian)

Interactions of natural activators were studied in mixed ZnS-CdS phosphors with various contents of CdS (0; 0.01; 0.1; 0.3; 1; 5; 10; 15; 20; 50; 80; 90; 95; 99; 99.7; 99.99; and 100%). Crystals were fused with NaCl (2%) and calcined at 900°C for 15 min. The brightest luminescence was achieved with specimens calcined at 850 to 900°C in oxide media.

191. Dutton, D.  
Fundamental absorption edge in cadmium sulfide.  
PHYS. REV. v. 112, n. 3, p. 785-92, 1958.

The absorption and reflection spectra of CdS were determined in the temperature range 90-340°K by photoelectric measurements on single crystals, using polarized light. The temperature and frequency dependence of the absorption coefficient in the edge, over a substantial range of absorption magnitudes, are well described by expressions of the form

$$\alpha(\nu) = \alpha_0 \exp \left[ -\beta(E_{00} - CT - h\nu)/kT \right],$$

where the energy  $(E_{00} - CT)$  is closely associated with the position of an absorption peak. For light polarized, with E vector parallel to the crystalline c-axis, there is one such peak, at  $\lambda$  4844 Å at 90°K; for light polarized with

OPTICAL PROPERTIES

E vector perpendicular to the c-axis, the 4844 Å absorption is again present in about equal strength and a stronger line appears at  $\lambda$  4874 Å, shifting the absorption edge toward longer wavelengths by a corresponding amount. These absorption lines, or sharp bands, are observed in the reflectance spectrum, and correspond to absorption lines observed photographically by Gross and others. These results are discussed in the light of the present theoretical picture of absorption in insulating crystals, and it is noted that an exponential absorption edge of this kind, characteristic also of other ionic crystals, cannot be adequately explained in terms of existing models.

192.

Eliashberg, G. M.

Investigation of the initial stages of  
luminescence rise in the ZnS:Cu,Co phosphor.

OPTIKA I SPEKTROSK v. 4, n. 1, p. 66-75,  
1958. (In Russian)

A thin layer ( $4 \text{ mg/cm}^2$ ) of the phosphor, excited with 313, 365, 405 and 436 m $\mu$  radiation, was studied over a wide range of excitation intensities and at various temperatures. Increase in the intensity of excitation E decreases the length of the linear portion of the rise curve in inverse proportion to E. The gradient of the linear portion increases as  $E^{1.6}$ . Similar results are obtained at the 4 excitation wavelengths. Increase of temperature from 20° to 100° C increases the rate of rise of luminescence, but the form of the rise curve in the initial stages is practically unchanged. It is concluded that the initial stages of the luminescence rise are related to the presence of a small number (about  $10^{14} \text{ cm}^{-3}$ ) of very deep capture levels (T-traps) and that in the excitation process almost all T-traps are filled, mainly by optical electrons.

193.

Eremenko, V. V.

Luminescence of cadmium sulphide crystals.

OPTIKA I SPEKTROSK v. 4, n. 3, p. 348-53,  
1958. (In Russian)

The luminescence spectra of monocrystals of cadmium sulphide have been measured at 20° K. The spectrum varies from sample to sample, but usually two regions are observed: a "green" luminescence consisting of a series of bands originating at  $19\,550 \text{ cm}^{-1}$ , and a "blue" luminescence consisting of

OPTICAL PROPERTIES

narrow lines overlapping the absorption spectrum. Usually one region is intense and other weak. In some samples intense "orange" luminescence is observed. The "green" luminescence is affected by surface treatment. It is concluded that luminescence emission from up to six types of spatially separated centres may be observed, two being responsible for the "green", and four for the "blue" luminescence.

194. Eve, C. F., and Duckworth, H. E.  
The luminescent response of silver activated ZnS to lithium ions of different energies. CANADIAN J. PHYS. v. 34, p. 896-7, 1956.

195. Fehr, E. B., et al  
The multiple emission bands in zinc cadmium sulfide phosphors. J. OPT. SOC. AMER. v. 42, p. 917-22, 1952.

Unexpected emission bands have been observed for ZnCdS Ag high in cadmium. With high Ag, the main emission band under cathode-ray excitation at 10kV appeared to be shifted to shorter wavelength on increase in current density. Under ultraviolet excitation at  $-196^{\circ}\text{C}$ , the apparent shift was resolved into two emission bands, one of which corresponded to the new band that appeared under cathode rays; the other, to the normal band of the unactivated phosphor. With low Ag, edge emission bands appeared under high current-density cathode rays and sodium bands under ultraviolet at  $-196^{\circ}\text{C}$ .

196. Feinberg, R.  
Rise and decay of intensity of luminescence of short-persistence phosphors. NATURE (LONDON) v. 183, p. 1546-7, 1959.

The luminescence rise-time  $\tau_{r1}$  and the luminescence decay-times  $\tau_{d1}$  and  $\tau_{d2}$  of the slow and fast components, and their relative magnitudes  $k_{d1}$  and  $k_{d2}$  have been measured for ZnS·Ag, ZnS·Ag,Ni and ZnS : 36% CdS·Ag phosphors excited by 30  $\mu\text{sec}$  pulses of 15 kV electrons. In general  $k_{d1} > k_{d2}$ ,  $\tau_{d1} >$

OPTICAL PROPERTIES

$\tau_{d1}$ . Increase in the electron current density in each case decreases  $\tau$ . The ultraviolet component (0.30  $\mu$ -0.43  $\mu$ ) of the luminescence has lower values of  $\tau$ , than the visible component. It is proposed that the ratio  $\tau_{d1}/\tau_{r2}$  is a measure of the probability of non-radiative de-excitation.

197.

Feldman, C., and O'Hara, M.

Formation of luminescent films by evaporation.

J. OPT. SOC. AMER. v. 47, n. 4, p. 300-5, 1957.

Luminescent films of ZnS[Mn], Zn<sub>2</sub>SiO<sub>4</sub>[Mn], Zn<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>[Mn], CaF<sub>2</sub>[Mn], and CaWO<sub>4</sub>[W] have been formed by evaporation in a vacuum and a subsequent heat treatment. Most of the films may be made either transparent or fogged depending on the post-heat treatment. The luminescent brightness of the fogged films, under cathode cathode-ray excitation, approaches the brightness of the bulk powdered material. The brightness of the transparent films is limited chiefly by internal reflection. In general, the phosphor chemistry of the powdered materials has been found to be applicable to thin films.

198.

Fok, M. V.

On recombination-interaction of the centres

of blue and green luminescence in the phosphor

ZnS:Cu. OPTIKA I SPEKTROSK v. 2, n. 4, p. 475-9,

1957. (In Russian)

The interaction of centres of blue and green luminescence comes about through the migration of holes in the valence zone from one centre to the other. In agreement with the calculation presented it is found that with stimulation in the blue-centre absorption band quenching of the blue band, starting at a certain instant, is slowed down, and proceeds parallel to that of the green. It is also possible to stimulate the blue band with absorption by the centres of green luminescence. In this case the blue band from the start quenches almost parallel to the green.

OPTICAL PROPERTIES

199. Ford, R. A., and Williams, M. M. R.  
 Fluorescence of trivalent dysprosium  
 in hexagonal zinc sulphide at 77°K.  
 SPECTROCHIM. ACTA v. 16, p. 721-9, 1960.

The low-temperature fluorescence of  $Dy^{3+}$  in hexagonal ZnS was reported. Systems around 17,000 and 20,500  $cm^{-1}$ , due to return from the resonance level to the  ${}^6H_{3/2}$  and  ${}^6H_{13/2}$  levels of the ground multiplet, were studied in detail. The assignment  ${}^4I_{15/2}$  was made for the resonance level. The fluorescent lifetime of the  ${}^4I_{15/2} \rightarrow {}^6H_{13/2}$  transition was found to be  $8 \times 10^{-5}$  sec, which is considerably shorter than the calculated radiative mean life. This result was discussed in terms of vibronic interaction with the crystal lattice.

200. Francis, A. B., and Carlson, A. I.  
 Cadmium sulfide infrared optical material.  
 J OPT. SOC. AMER. v. 50, n. 2, p. 118-21,  
 1960.

Cadmium sulphide is investigated as an i.r. optical material. Properties of the crystal presented include index of refraction, percent transmission, hardness, coefficient of thermal expansion, solubility, workability. CdS is also compared with other common i.r. materials.

201. Freymann, R., et al  
 Electrical and optical properties of some  
 semiconductors: zinc oxide, zinc sulphide,  
 selenium. J. PHYS. RADIUM v. 17, n. 8-9,  
 p. 806-12, 1956. (In French)

I. Optical, photodielectrical and electrical summarized properties of the various types of ZnO. II. Study of the dipolar Debye absorption of several samples of ZnO in terms of frequency and temperature. The activation energies found by that method and by conductivity and thermoluminescence methods are in good agreement. III. Two types of photodielectric effect are proposed:

OPTICAL PROPERTIES

photoconductivity (free carriers) and photodipolar effect (bound carriers). Impure selenium shows the second one, but the activation energy decreases under irradiation. ZnS(Cu) shows absorption bands only under irradiation. For ZnO, the phenomena are intricate.

202.

Fridkin, V. A.

The photoelectret state and the luminescent afterglow in ZnS. DOKL. AKAD. NAUK SSSR v. 129, n. 4, p. 773-6, 1959. (In Russian)

Polycrystalline ZnS was activated with Cu and Cl, and polystyrene was used as binder. The light sum stored in the specimen when excited with light in the absence of a field, and the photoelectret charge arising in the same specimen in identical conditions, but with a field, were measured simultaneously. The latter was measured by the method of Nadzhakov and Kashukeev (1951, 1952); the light sum was measured with a photomultiplier and an oscillograph. It was found that the photo-polarization/logarithm-of-exposure curve (for  $E = 400 \times 10^{-6} \text{ W/cm}^2$ ) shows saturation at  $E t = 10^{-3} \text{ W sec/cm}^2$ , whereas, for the same E, the light-sum/logarithm-of-exposure curve shows saturation at  $10^{-4} \text{ W sec/cm}^2$ . Moreover, while the processes of formation of the photoelectret state in ZnS are associated with the fulfilment of the law of interchangeability, deviations from this law are observed for the light-sum. The afterglow in ZnS lasts only a few seconds, whereas the photoelectret charge in ZnS keeps on decreasing for a few tens of hours. An attempt is made to explain the mechanisms of the two phenomena.

203.

Fridkin, V. M.

Some effects observed in an investigation of the luminescence of electrets made of ZnS. DOKL. AKAD. NAUK SSSR v. 131, n. 2, p. 290-2, 1960. (In Russian)

It was found that the luminescent luminance was changed by the presence of a field. On warming the specimens an analogue of thermoluminescence was observed in the degree of electric polarization. These phenomena were considered in terms of the tunnel effect occurring in the specimens.

OPTICAL PROPERTIES

204. Frohnmeyer, G., Glocker, R., and Messner, D.  
The wave length dependence of the conductivity of cadmium sulfide crystals irradiated with x rays and  $\gamma$  rays. NATURWISSENSCHAFTEN v. 40, p. 338, 1953. (In German)

CdS crystals, varying in thickness from 0.05 to 0.5 mm, were irradiated in the range from 1-A x rays to 1-Mev  $\gamma$  rays in an ionization chamber. The change in the conductivity of the crystals with respect to the wave length of the irradiation light was in good agreement with theory.

205. Furlong, L. R., and Ravilious, C. F.  
Low-temperature luminescence and absorption of CdS. PHYS. REV. v. 98, n. 4, p. 954-5, 1955.

Measurements of the emission and absorption of CdS single crystals have been made at several temperatures. At 4°K a set of emission lines in the range 4850-5020Å has been found. A study of these lines together with observations at other temperatures suggests that they are emitted by a system consisting of the combination of a gas and CdS, the gas being adsorbed on the crystal.

206. Galanin, M. D., and Raevskii, A. V.  
Temperature damping of ZnS-Ag phosphor crystal luminescence in excitation by light or  $\alpha$  particles. IZVEST. AKAD. NAUK. S.S.S.R., SER. FIZ. v. 23, p. 1280-2, 1959. (In Russian)

The effects of temperature on luminescence damping in ZnS-10<sup>-4</sup>Ag phosphors calcined at 800°C were studied. Experimental curves of temperature damping were plotted for both Po<sup>210</sup>  $\alpha$  particle excitation and light ( $\lambda = 365 \text{ m}\mu$ ) under constant and slowly changing thermal conditions.

OPTICAL PROPERTIES

207. Payen de la Garanderie, Hughes, and Curie, D.  
Emission spectrum of copper-activated zinc sulfide  
in the partial thermal extinction region.  
COMPT. REND. v 248, p. 3151-3, 1959. (In French)

The emission spectrum of irradiated ZnS ( $7 \times 10^{-5}\%$  Cu, 3% NaCl) was examined. The width observed is attributed to a color center-lattice interaction.

208. Garlick, G. F. J.  
Infrared phosphor - semiconductors. PHYS. AND  
CHEM. SOLIDS v. 8, p. 449-57, 1959.

The development of sensitive photoconducting detectors for infrared radiation has made possible the study of luminescence emission from a new variety of solids including those of considerable interest as semiconductors. A review of progress over the past few years is given with special reference to the emission of zinc and cadmium sulphide phosphors, lead sulphide, lead telluride and mercury sulphide. The infrared emission found in zinc sulphide is ascribed to electron transitions from the valence band to the ground states of visible emission centers. In mercury sulphide the characteristics of the excitation and emission spectra suggest a different mechanism. This also applies to lead sulphide and lead telluride.

209. Garlick, G. I. J., and Dumbleton, M. J.  
Phosphors emitting infra-red radiation.  
PROC. PHYS. SOC. (B) v. 67, p. 442-3, 1954.

Investigations in producing phosphors with emission spectra lying in the infra-red region beyond  $\mu$ .

OPTICAL PROPERTIES

210. Gergely, G.  
Notes on the cathodoluminescence efficiency  
of zinc sulphide type phosphors. J. ELECTRONICS  
AND CONTROL v. 5, n. 3, p. 270-2, Sep 1958.

It is concluded that energy conversion efficiencies in cathodray tube phosphor screens ( $\approx 21\%$ ) approach the estimated theoretical limit, although quantum efficiencies for photoluminescence can be greater ( $\approx 90\%$ ). The difference is attributed to non-radiative energy losses of primary and secondary electrons which appear to be independent of primary electron velocities over a wide range.

211. Gergely, G.  
The calorimetric determination of the efficiency  
of ZnS-type luminescent materials. ACTA. PHYS. HUNGAR.  
v. 7, n. 1, p. 171-4, 1957.

A microcalorimeter incorporating thermistors was used to measure the luminescence efficiency of ZnS:Ag powders excited by 3650 Å radiation. Quantum efficiencies of 89-94% were obtained for hexagonal and cubic ZnS:Ag specimens, and 54.5% for a 50 ZnS--50 CdS:Ag specimen.

212. Gildart, L. and Ewald, A. W.  
Electron mobility and luminescence efficiency  
in cadmium sulfide. PHYS. REV. v. 83, p. 359-63,  
July 15, 1951.

The mobility of the photoelectrons produced in CdS by pulsed ultraviolet and X-ray excitation has been determined through measurements of the incident radiation, the luminescence radiation and the initial rates of rise and decay of the photocurrent. The mobility value as well as the efficiencies of the excitation and radiative recombination processes for the two types of excitation are obtained directly from these measurements by means of a general analysis which is independent of the details of the photoelectric mechanism. The following approximate numerical results are obtained: The electron mobility is  $30 \text{ cm}^2/\text{volt-sec}$ . 2% of the conduction electrons radiate red light quanta upon recombining. Each 0.5 Å X-ray quantum produces about 2 000 conduction electrons.

OPTICAL PROPERTIES

213. Gobrecht, H. and Bartschat, A.  
 On the optical and electrical properties of  
 single crystals of cadmium sulphide. Z. PHYS.  
 v. 136, n. 2, p. 224-33, 1953. (In German)

It is shown by measurements on single crystals of CdS that the lattice absorption edge must be at wavelengths less than 5025 Å.

214. Gobrecht, H. and Gumlich, H. E.  
 On the enhancement and quenching of the  
 sulphides by electric fields. Z. PHYS.  
 v. 156, n. 3, p. 436-55, 1959. (In German)

Previous work is surveyed. Results are reported for ZnS with a range of Mn activator concentrations, tested in the usual electro-luminescent cell. In general, the short wavelength end of the emission to X-rays or ultraviolet is diminished by an applied a.c. field, whereas the yellow emission is increased for preparations with certain Mn concentrations. Details are given of the effects of different field frequencies and different excitation intensities. The enhancement of quenching increase with field increase, but at less than a linear rate; presumably part of the energy lost from the "blue" centres is transferred to the "yellow" ones.

215. Golovin, B. M. et al  
 The photoelectric state in ZnS and two new  
 electrophotographic processes. FIZ. TVERDOGO  
 TELA v. 2, p. 1004-10, May 1960. (In Russian)

The photoelectric state and the luminescence in polycrystalline ZnS activated by copper and chlorine were studied, using ZnS powder dispersed in polystyrene and pressed into 1-mm-thick, 1-cm-wide tablets. The relation of photoelectric charge to time spent in darkness (dark depolarization) was investigated, and curves of dark polarization were plotted as a function of emission energy during the excitation.

OPTICAL PROPERTIES

216.                   Gobrecht, H. and Gumlich, H. E.  
On the enhancement and quenching of the  
luminescence of manganese-activated zinc sulphides  
by alternating electric fields. J. PHYS. RADIUM  
v. 17, n. 8-9, p. 754-7, Aug-Sep 1956. (In French)

According to the method of excitation, intensity of excitation, frequency of the applied field, and observed emission band, the alternating field can produce a quenching or an enhancing of luminescence in ZnS(Mn). These two processes seem to be independent.

217.                   Gobrecht, H., Nelkowski, H. and Hofmann, D.  
Investigations on cathode thermoluminescence.  
(Part)II. Z. PHYSIK v. 156, p. 657-66, 1959.  
(In German)

The temperature dependence of the cathode luminescence of various luminescent materials (3 zinc cadmium sulfides of various compositions, calcium silicate, and halophosphate) was investigated between 90 and 450°K. Glow curves were traced according to the cathode beam excitation. Distinct variations between the cooling and heating curves were found only in very weak cathode beam excitation. They are explained as the effect of the electrons stored in bond sites. This effect is not detectable at large excitation intensities, since the glow light increases less than proportionally with the excitation (measured in calcium silicate and zinc cadmium sulfide SF 305), which was reduced back to a saturation phenomenon in the bond site filling. The cooling and heating curves agree in all five luminescence materials within the measuring accuracy; the light emission is, in strong excitation, a definite function of the temperature characteristic for each phosphor.

218.                   Gool, W.v.  
Fluorescence and photoconductivity in Ag-

OPTICAL PROPERTIES

activated Zn-Cd sulphides. SEMICONDUCTORS  
AND PHOSPHORS. BRUNSWICK: VIEWEG p. 602-9,  
1958. (In German)

Some phosphors were made from CdS activated with Ag-Ga and Ag-Cl. These phosphors showed two fluorescence bands at low temperatures: 6200 and 7300 A. The 6200 A emission was only found when the activator concentration (Ag) was greater than the coactivator concentration (Cl or Ga). By making a series of mixed crystals (Zn, Cd)S it was shown that the 7300 A emission corresponds to the 4500 A emission in ZnS (sphalerite) and therefore to the normal silver centre (Ag<sup>+</sup> at a lattice site). The 6200 A emission in CdS is connected with 3950 A (sphalerite) or 3850 A (wurtzite) in ZnS. The experimental conditions necessary to obtain the short-wave emission (Ag > Ga) indicate that the short-wave fluorescence centre is formed by interstitial silver, by a sulphur vacancy or by an association containing at least one of these defects. It is also clear that the inversion of the normal band model proposed by Lambe and Klick (1955) may be possible for the short-wave centre (6200 A in CdS, 3950 A in ZnS); there are no indications, however, that the band model of the normal silver centre (7300 A in CdS, 4500 A in ZnS) ought to be changed.

219.

Gool, W.v.

Fluorescence and photoconduction of silver-  
activated cadmium sulphide. PHILIPS RES.  
v. 13, n. 2, p. 157-66, April 1958.

Several Ag-activated CdS phosphors are described, with Ga or Cl as coactivator. The fluorescence at low temperature shows two bands with maxima at 6200 A and 7300 A. High Ag concentration and low coactivator concentration promote the short-wave emission. Phosphors with equal concentrations of activator and coactivator show only the long-wave emission. Optimal photoconduction and low dark-current are only found with an activator-coactivator ratio slightly greater than one. A series of mixed crystals (Zn, Cd)S activated with Ag shows clearly the relation between 6200 A emission in CdS and a 3880 A emission in ZnS, and also between the 7300 A band in CdS and the normal blue Ag band at 4350 A in ZnS. The behaviour of the Ag bands in CdS is quite similar to those of Cu in ZnS. These results show that the conclusions drawn by Lambe and Klick regarding the position of the impurity level responsible for the normal blue Ag emission in ZnS:Ag. These results led to an improvement of the properties of a red colour-television phosphor.

OPTICAL PROPERTIES

220. Gool, W.v. and Cleiren, A. P.  
Self-activated and Cu-activated fluorescence  
of ZnS. PHILIPS RES. REP. v. 15, n. 3, p. 238-53,  
June 1960.

Two series of experiments on the fluorescence of ZnS are described. The first one, of which only a review of the experimental results is given, presents some additional data on the theory of ZnS activated with Cu, presented by Kröger and co-workers. In the second series a limited number of phosphors have been studied. In particular, the difference between the blue Cu emission and the blue self-activated emission of ZnS has been examined. The temperature dependence of the fluorescence bands and the influence of the coactivator on both mentioned fluorescences and the green copper fluorescence were determined. The results can be interpreted by assuming that the low-temperature fluorescence is dependent on the coactivator. The room-temperature emission bands can have a composite character, in such a way that in addition to the low-temperature emission band another band may be important. The results are to some extent uncertain, due to experimental difficulties. These are discussed and it is stressed that further careful experimental work may be more important for knowledge of the ZnS fluorescence than detailed calculations about some special model.

221. Gool, W.v., Cleiren, A. P. and Heijligers, H. J. M.  
Fluorescence of some activated ZnS phosphors.  
PHILIPS RES. REP. v. 15, n. 3, p. 254-74, June 1960.

Several series of ZnS phosphors were prepared in a  $H_2S$  atmosphere at 1150-1200°C. Activators used were Ag, Cu, Au and coactivators were Al, Sc, Ga, In. Phosphors were made with all combinations of activators and coactivators with one concentration. In other phosphors equal concentrations of selected pairs of activators and coactivators were studied at different levels. Some special series of phosphors were made in addition, and spectral distributions of all phosphors at room temperature and at -90°C are reported. The spectral distributions can be separated into parts of low and high photon energy.

OPTICAL PROPERTIES

222. Gottesman, J. and Ferguson, W. F. C.  
Optical properties of thin films of cadmium sulfide. J. OPT. SOC. AMER. v. 44, p. 368-70, 1954.

Thin evaporated films of CdS on glass were studied in the wavelength range 4000 to 7500 Å. Measurements of film thickness and reflectivity as a function of wavelength were used to determine the index of refraction and the extinction coefficient. Density measurements and ageing tests were also carried out. The effects on film properties of a variation of the rate of deposition were investigated.

223. Gribkov, V. I. and Zhevandrov, N. D.  
Polarization of luminescence of ZnS monocrystals. OPTIKA I SPEKTROSK. v. 8, n. 2, p. 275-6, Feb 1960. (In Russian)

Reports a study of the polarization of luminescence of ZnS monocrystals activated with copper. The azimuthal dependence and the maximum degree of polarization (20%) were found to be independent of the excitation wavelength (436, 405, 365 and 313 mμ). The polarization of luminescence was independent of the polarization of the exciting light due to migration of the excitation energy (an exciton or an electron-hole mechanism) across the crystal. The polarization was constant throughout the luminescence spectrum and afterglow had the same degree of polarization as the luminescence during excitation.

- 224 Grillot, E.  
Crystalline mineral substances with infrared luminescent emission. ACTA PHYS. HUNGAR. v. 5, n. 4, p. 445-63, 1956. (In French)

A review of the discovery and study of infrared luminescence in substances such as Cu<sub>2</sub>O, CdS, CdSe and HgS. An energy band scheme is proposed for cuprous oxide based on luminescence and semiconduction data including exciton levels recently found in experiment. Other energy schemes are given for the levels in ZnS and CdS activated by silver and copper.

OPTICAL PROPERTIES

225. Grillot, E.  
On the nature of the fluorescent emission of  
pure CdS at very low temperature. SEMICONDUCTORS  
AND PHOSPHORS. BRUNSWICK: VIEWEG p. 561-5, 1958.  
(In French)

Crystals of pure CdS were prepared by 6 different methods. 5 of the specimens exhibit green fluorescence at temperatures below 77°K, but the number of spectral bands at 20°K differs. Crystals prepared by sublimation show no green fluorescence at 77°K, but a blue banded fluorescence at 20°K. The green emission is attributed to lattice defects.

226. Grillot, E.  
Visible red photoluminescence of cadmium  
sulphide. C.R. ACAD. SCE., PARIS, v. 230,  
1159-61, March 20, 1950. (In French)

The preparation of samples of CdS(Ag) which show luminescence of wavelength as low as 6 150 Å is described.

227. Grillot, E.  
Fluorescence of the excitation in pure CdS.  
J. PHYS. RADIUM v. 17, n. 8-9, p. 822-3,  
Aug-Sep 1956. (In French)

228. Grillot, E.  
Comparative study of Ag and Cu luminescence  
centres in CdS and ZnS phosphors. J. PHYS. RADIUM  
v. 17, n. 8-9, p. 624-9, Aug-Sep 1956. (In French)

Two kinds of luminescent centres are observed in CdS(Ag) as in CdS(Cu) (red or infrared emissions). The distances between their energy levels and the

OPTICAL PROPERTIES

full band indicate an analogy of structure with the corresponding ones in ZnS. The substitutional position of the foreign atom and its monovalence in both cases of ZnS(Cu) are in agreement with the representation previously proposed by the author.

229. Bancie-Grillot, M. and Grillot, E.  
 Researches on the luminescence of cadmium  
 sulphide activated by silver. J. CHEM. PHYS.  
 v. 53, n. 6, p. 521-6, June 1956. (In French)

Silver activation is held to produce two types of emission centre with respective emission peaks at 0.73 and 0.78  $\mu$ . The first type of centre is reduced and the second type increased in efficiency by raising the firing temperature.

230. Grillot, E. and Bancie-Grillot, M.  
 Fluorescent emission ascribable to exciton  
 annihilation in pure CdS Crystals. J. PHYS.  
 CHEM. SOLIDS v. 8, p. 187-90, Jan 1959.

Rochester Semiconductors Conference Paper. The green emission of pure CdS at  $< 100^{\circ}\text{K}$  is variable in band structure and efficiency. Low temperature sublimation of CdS crystals affords a product not fluorescent at  $77^{\circ}\text{K}$  which at  $20^{\circ}\text{K}$  emits 9 lines in the blue, 6 of these being in a hydrogenoid series. At  $4^{\circ}\text{K}$  a more complex polarized line emission develops, with unusual Seeman effects. Absorption spectra of the crystals depend on the method of preparation. The hydrogenoid series is considered due to exciton annihilation in a nearly perfect lattice.

231. Grillot, E. and Freymann, R.  
 Phosphorescence and photodipolar effect.  
 WISS. Z. HOCHSCH. ELEKTROTECH. ILMENAU  
 v. 4, n. 1, p. 11-15, 1958. (In French)

A discussion is given of dielectric constant and loss changes in phosphors due to excitation. Results for variation in dielectric loss change with

OPTICAL PROPERTIES

applied field frequency and temperature are given for zinc and cadmium sulphides. Explanations are given in terms of the behaviour of trapped electrons.

232. Bansi-Griio, M. (Bancie-Grillot) et al  
 Studies of linear fluorescence and absorption  
 of pure cadmium sulphide crystals at the temper-  
 ature of 4.2°K. OPTIKA I SPEKTROSK. v. 6, n. 5,  
 p. 707-10, May 1959. (In Russian)

CdS monocrystals were produced by sublimation and their thicknesses were ~50  $\mu$  or less. A spectrograph of 4 A/mm dispersion was used to obtain the spectra at 4.2°K. The fluorescence spectrum of these crystals was linear and contained one new line (4868.2 A) in addition to those reported earlier (C.R. ACAD. SCI. (PARIS) v. 242, n. 14, April 4, 1956; Abstr. 4213 of 1957). As before, the fluorescence was mainly blue with very feeble emission at green wavelengths. The background between 4870 and 4942 A and the fluorescence lines were polarized with the electric vector at right-angles to the optical axis of the monocrystal, suggesting a common origin for all of them. The absorption spectrum in unpolarized light had three lines (4853.1, 4857.2, 4869.1 A) whose positions were very close to the three fluorescence lines at 4856.6, 486.14 and 4870.0 A. In the region where continuous absorption was somewhat weaker, the light which had passed through the crystal was completely polarized with the electric vector parallel to the optical axis of the crystal. The author's obtained also the fluorescence spectrum of a crystal which was not prepared by sublimation (the method of preparation is not given). This spectrum was characterized by a strong green band and a line structure in the blue region which was quite different from that observed in sublimated crystals; neither the green band nor the blue lines were polarized. See also the following abstract.

233. Bancie-Grillot, M. et al  
 Studies of the fluorescent emission lines and  
 luminescent absorption lines in crystals of pure  
 cadmium sulphide cooled to 4.2°K. C.R. ACAD. SCI. (PARIS)  
 v. 248, n. 1, p. 86-9, Jan 5, 1959. (In French)

Earlier data are improved using a spectrograph of much higher dispersion. A new fluorescent line is reported at  $\lambda = 4868.2$  A.

OPTICAL PROPERTIES

234. Gross, E. et al  
 Influence of mechanical treatments of pure cadmium sulphide crystals on their optical absorption spectra at low temperatures. C.R. ACAD. SCI. (PARIS) v. 250, n. 26, p. 4340-2, June 27, 1960. (In French)

The fine structure in the absorption edge of cadmium sulphide measured at low temperatures is destroyed by lapping and polishing of the crystals and absorption in the latter case is increased at longer wavelengths. The increase is attributed to dislocations and other defects produced by mechanical working.

235. Gross, E. F.  
 The effect of a magnetic field on the blue fluorescence and on the absorption lines of some pure cadmium sulphide crystals at the temperature 4.2°K. OPTIKA I SPEKTROSK. v. 6. n. 5, p. 710-12, May, 1959. (In Russian)

Continuation of the work described in the preceding abstract. A CdS monocrystal prepared by sublimation (dimensions 4 mm x 2 mm x 50-60  $\mu$ ) was placed between the poles of an electromagnet. A diffraction spectrograph with 1.7 A/mm dispersion was used to record the fluorescence spectrum of the crystal excited by the 3650 A line at 4.2°K. In a magnetic field of 28 000 Oe, oriented at right-angles to the optical axis of the crystal, the fluorescence lines at 4870, 4868 and 4861 A exhibited Zeeman splitting into doublets. The doublet components were polarized in the same way as the original lines, i.e. with the electric vector at right-angles to the optical axis of the crystal. No splitting was observed in magnetic field up to 28 000 Oe, oriented parallel to the optical axis of the crystal. The authors studied also the effect of magnetic fields on the absorption lines of sublimated CdS monocrystals. They found that the 4869.1 A line is broadened from 1.62 to 2.24 A by a field of 28 000 Oe (directed at right-angles to the optical axis of the crystal), indicating a possible Zeeman splitting into a doublet.

OPTICAL PROPERTIES

236. Gross, E. F. et al  
 Influence of a magnetic field on the blue  
 fluorescence lines and on the absorption  
 lines of certain pure cadmium sulfide crystals at a temperature of 4.2°K. OPTICS AND SPECTROSCOPY (ENGLISH TRANSLATION) v. 6, p. 462-3  
 May 1959.

Zeeman splitting into a doublet was detected in three fluorescence lines of cadmium sulfide crystals produced by sublimation in a high temperature gradient, at a temperature of 4.2°K in a magnetic field. This Zeeman splitting is not accompanied by a dimagnetic shift.

237. Gross, E. F., Kaplyanskii, and Novikov, B. V.  
 Structure of the spectral curve of the internal photoeffect in crystals of cadmium sulfide. ZHUR. TEKHN. FIZ. v. 26, p. 913-16, 1956.

A curve shows the spectral distribution for the photosensitivity of CdS for several orientations of the optical axis of the crystal relative to the light vector and beam direction at temps. of 4.2 and 77.3°K.

238. Gross, E. F. and Suslina, L. G.  
 Monocrystals of ZnS and the spectrum of their absorption edge at low temperatures. OPTIKA I SPEKTROSK. v. 6, n. 1, p. 115-17, Jan 1959.  
 (In Russian)

An monocrystals were produced by sublimation of very pure powder in an atmosphere of argon. The monocrystals were in the form of colourless plates of 25 x 5 mm area and their thickness varied from 0.1 mm to 0.1  $\mu$ . They were found to be uniaxial (hexagonal modification of ZnS) and their optical axes

OPTICAL PROPERTIES

lay in the plane of the crystals. Using crystals of various thicknesses the authors studied the absorption spectra in the region of 3300-3100 A. The structure of the long-wavelength edge of absorption was found to be clearly exhibited at liquid-helium temperature (4.2°K). Heating of crystals from 4.2 to 77°K and then to 20°C displaces the absorption lines towards longer wavelengths and makes them less distinct.

239. Gross, E. F. and Sobolev, V. V.  
Photoluminescence within the fundamental  
absorption edge of mixed CdSe-CdS crystals.  
DOKLADY AKAD. NAUK S.S.S.R. v. 133, p. 56-9,  
July 1, 1960. (In Russian)

The photoluminescence of large crystals of CdSe-Cds, monocrystals of CdSe, and large crystal layers of CdSe and CdS was investigated at the self-absorption edge. All specimens had hexagonal structure. The spectra were taken at 77.3 and 4.2°K with a spectrometer of 50 and 13 A/mm dispersion at 7000 A. At 4.2 to 77.3°K the emission spectra of mixed layers is dampened, the legibility of complex line emission is disturbed (at 77.3°K the mixed layer line emission appears on a band and only with 96% CdSe-4% does it retain a doublet structure); and, the intensity of short-wave lines is sharply reduced. As the temperature is increased from 4.2 to 77.3°K, the doublet and triplet components increase and long-wave components diminish.

240. Gross, E. F., Suslina, L. G., and Komarovskikh, K. F.  
Investigation of the absorption spectra of  
zinc sulphide crystals. OPTIKA I SPEKTROSK  
v. 8, n. 4, p. 516-20, 1960. (In Russian)

Polarization of the line structure of the absorption edge of hexagonal ZnS monocrystals was measured at 4.2 and 77°K, and the absorption spectra of sublimated polycrystalline ZnS films were recorded. The nature of polarization of the spectrum of ZnS monocrystals was similar to polarization observed in other uniaxial crystals with discrete structure of the absorption edge. Thin crystals ( $\sim 0.1 \mu$ ) were found to stick to the base and the consequent deformation produced displacement and broadening of the absorption lines. The positions and widths of the lines in the absorption spectra of polycrystalline ZnS films were close to the positions and widths of hexagonal ZnS monocrystals stuck to their bases; it follows that the films have hexagonal structure.

OPTICAL PROPERTIES

241. Gurvich, A. M.  
On variation of the optical properties of sulfide phosphors incident to elimination of the flux. BULL. ACAD. SCI. USSR - PHYS. SER. v. 23, n. 11, p. 1356, 1959.
242. Gurevich, D. V., Tolstoi<sup>"</sup>. N. A., Feofilov, P. P.  
Luminescence and photoconduction of cadmium sulphide. DOKL. AKAD. NAUK, SSSR v. 71, n. 1, p. 29-32, 1950. (In Russian)

Results are given of an investigation of the kinetics of luminescence and photoconduction in connection with previous work on the relaxation of photoconduction in semi-conductors. The investigation has been carried out on CdS monocrystals. It has been found from experiments that the momentary brightness of luminescence  $I \sim E/(1 + at)^{\alpha}$  where E is the intensity of the exciting light and  $a \sim \sqrt{E}$ , while the momentary value of photoconduction  $\Delta \sigma \sim E/(1 + bt)^{\beta}$  where  $b \sim \sqrt{E}$ . The magnitudes  $\alpha$  and  $\beta$  do not depend upon illumination. It has been calculated that the law of the decrease of the light sum of phosphorescence  $L(t) \sim \sqrt{E}/(1 + at)^{\alpha-1}$  coincides with the law of the decrease of photoconduction. It has been shown that  $\alpha - 1 = \beta$  and  $a = b$ . Hence, in the region of the "normal" stationary relationships, the kinetics of the light sum of phosphorescence are identical with the kinetics of photoconduction.

243. Hall, J. F., Jr.  
Optical properties of zinc sulfide and cadmium sulfide in the ultraviolet. J. OPT. SOC. AMER. v. 46, n. 12, p. 1013-15, 1956.

The index of refraction and the extinction coefficient of thin films of zinc sulphide and cadmium sulphide evaporated on quartz substrates were determined in the spectral range from the visible to 2100 A. The optical properties were calculated from reflectance and transmittance measurements made with a Beckman DK spectrophotometer equipped to measure specular reflectance.

OPTICAL PROPERTIES

The index of refraction and the extinction coefficient of zinc sulphide have maxima at 2300 Å and 2150 Å, respectively. There is a maximum of the extinction coefficient of cadmium sulphide at 2300 Å. The refractive index of cadmium sulphide has a maximum at 2500 Å and a subsidiary maximum at 5000 Å. There is a region of anomalous dispersion from 4000 Å to 5000 Å and a contribution to the absorption which are probably associated with the excitation of valence electrons into the conduction band.

244. Hall, Jr., J. F., and Ferguson, W. F. C.  
 Optical properties of cadmium sulfide and zinc  
 sulfide from 0.6 micron to 14 microns. J. OPT.  
 SOC. AMER. v. 45, n. 9, p. 714-18, 1955.

The index of refraction and the absorption of evaporated films of CdS and ZnS in the spectral region from 0.6 to 14  $\mu$  were determined from spectrophotometric reflectance and transmittance measurements. The index of refraction of CdS ranged from 2.52 at 0.6  $\mu$  to 2.26 at 14  $\mu$  and was independent of deposition rate. The index of ZnS varied from 2.34 at 0.6  $\mu$  to 2.15 at 14  $\mu$ , and was independent of deposition rate. The absorption coefficient of CdS depended upon the deposition rate from 0.6 to 6  $\mu$  and increased beyond 6  $\mu$  independently of deposition rate. The absorption coefficient of ZnS was approximately 0.001 in the region of investigation. Approximate formulae are given for calculating the index of refraction and absorption from the reflectance and transmittance when the absorption is small. A method is given for preparing the phosphors that yields films for which the index of refraction is independent of the deposition rate. The crystalline structure was investigated by means of X-ray diffraction.

245. Halperin, A., and Arbell, H.  
 Excitation spectra and temperature dependence  
 of the luminescence of ZnS single crystals.  
 PHYS. REV. v. 113, n. 5, p. 1216-21, 1959.

The luminescence of ZnS:Cl and ZnS:Cu:Cl crystals was measured for the temperature region 80-500°K and for different wavelengths of exciting light. The behaviour of the luminescence v. temperature curves differed from similar curves for powders reported in literature. Excitation spectra were also obtained for the green and blue luminescence bands. These were found to consist of a complexity of fine bands. Each of the bands was found not to shift when

OPTICAL PROPERTIES

varying the temperature of the crystal. The relative intensity of the bands near the absorption edge of the crystal, however, changed with temperature in such a way as to cause an apparent shift in the maximum of the excitation spectrum in this region.

246. Halperin, A., and Garlick, G. F. J.  
The absorption spectrum of excited crystals  
of cadmium sulphide. PROC. PHYS. SOC. B  
v. 68, Pt 10, p. 758-65, 1955.

Crystals of cadmium sulphide show new absorption bands when excited by visible light ( $0.546 \mu$ ). The bands extend from the excitation region out to  $1.4 \mu$  with a maximum intensity at  $0.78 \mu$ . The bands are stable in the dark at low temperatures but are thermally bleached on warming. They are also bleached by radiation of their own wavelength. Correlation is found between thermal bleaching characteristics and electrical conductivity characteristics. A model is proposed in which thermal bleaching and electrical conduction on warming result from the escape of trapped electrons, while optical bleaching frees positive holes which migrate to traps and recombine with trapped electrons.

247. Halsted, R. E.  
Photoluminescent modulation in nonuniformly  
excited ZnS phosphors. PHYS. REV. v. 99,  
p. 1897, 1955.

Experiments are described in which the photoluminescence of some ZnS phosphors was modulated by an alternating electric field applied parallel to the incident radiation. Modulation was observed with 2537 A excitation of ZnS:Ag,Cl and ZnS:Cu,Al and with 3650 A excitation of ZnCdS:Ag,Cl and ZnSSe:Cu,Cl phosphor powder samples. The experiments provide a simple demonstration of n-type photoconductivity and clarify the role of conduction electrons in the luminescent process.

OPTICAL PROPERTIES

248. Halsted, R. E., Apple, E. F., and Prener, J. S.  
Radiative energy transfer in ZnS. PHYS. REV.  
LETTERS v. 1, n. 4, p. 134-6, 1958.

Emission and diffuse reflectivity measurements on ZnS phosphors activated with Cu, Ag and Au were made under ultraviolet and infrared excitation. ZnS:Cu samples emitted in the infrared. The long-wavelength limit of the absorption band was typical for each activator.

249. Halsted, R. E., Apple, E. F., and Prener, J. S.  
Two-stage optical excitation in sulfide phosphors.  
PHYS. REV. LETTERS v. 2, n. 10, p. 420-1, 1959.

It is observed that photons of band gap energy (edge emission) can be continuously generated in ZnS and CdS phosphor powders at 80°K by photons with less energy. Results on a CdS powder, fired in a high-pressure sulphur atmosphere, are reported, showing the production of 2.4 eV photons by photons not exceeding 1.75 eV energy. A two-stage excitation process with transitions terminating in both conduction and valence bands, and the existence of type A and B impurity levels common to both classes of transition, are inferred.

250. Hamilton, D. R.  
Luminescence and conductivity of ZnS(Cu)  
single crystals. J. PHYS. RADIUM v. 17,  
n. 8-9, p. 797-800, 1956. (In French)

The luminescence and conductivity of a set of single crystals of ZnS activated by varying amounts of copper have been investigated. Considerable difficulties exist with the present models for temperature quenching. Conductivity measurements, although complicated by non-ohmic contacts, suggest the luminescence centres are the donors of photoelectrons. Lattice irregularities or Cu<sub>2</sub>S centres are believed to be predominant donors of semi-conduction electrons.

OPTICAL PROPERTIES

251. Heerden, P. J. van  
 Primary photocurrent in cadmium sulfide.  
 PHYS. REV. v. 106, n. 3, p. 468-73, 1957.

Experiments were performed on the photocurrent caused by short flashes of light and by individual  $\alpha$ -particles in high-resistivity cadmium sulphide crystals. It was shown that the photocurrent pulses could be described by the mechanism of the so-called primary photocurrent of both electrons and "holes". The energy lost by an  $\alpha$ -particle per electron-hole pair created was found to be 7.2 eV, which seems somewhat high. Efforts to correlate the primary photocurrent with the so-called edge luminescence were not successful.

252. Henderson, S. T., Ranby, P. W., and Halstead, M. B.  
 Activation of ZnS and (Zn,Cd)S phosphors by  
 gold and other elements. J. ELECTROCHEM. SOC.  
 v. 106, n. 1, p. 27-34, 1959.

A study has been made of the spectral emission characteristics of zinc and zinc-cadmium sulphide phosphors, activated by gold and excited by long wave ultraviolet at 25° and -120° C. The positions and heights of the Gaussian sub-bands constituting the emission were examined and compared with those derived from the series activated by copper, silver, and chloride ("self-activated"). Copper and gold produce the most similar phosphors, with 3 sub-bands each silver and chloride give 2 sub-bands, and resemble each other particularly in the effects associated with crystallographic change. Linear relations in the peak locations and an energy diagram are discussed. Other observations concern cathode-excitation, the effects of substituting selenium for sulphur, and a recently reported emission band of higher frequency.

253. Herforth, L., and Krumbiegel, J.  
 The effect of ultrasound on the conductivity  
 and fluorescence of zinc and cadmium sulphide  
 crystals. NOTE In NATURWISSENSCHAFTEN v. 42,  
 n. 2, p. 39, 1955. (In German)

Ultrasonic radiation causes the photoconductivity of excited ZnS and CdS crystals to fall to a constant value depending on the sound intensity (up to

OPTICAL PROPERTIES

0.8W/cm<sup>2</sup>). The effect is reversible. The fluorescence intensity in each case is unaffected even at the maximum sound intensity.

254. Herwelly, A.  
On the luminescence of phosphors in strong electric fields. ACTA PHYS. AUSTRIACA  
v. 5, p. 30-44, 1951, (In German)

An investigation of the luminescence in sulphide and other phosphors due to strong applied electric fields is made. For unidirectional fields the emission occurs only when putting on or taking off the field. The fields necessary range from 12000 V/cm for a Guntz ZnS phosphor to 200000 V/cm for most other phosphors. For high fields a small afterglow effect is observed. It is shown that the effect of the field in producing emission is still present when the phosphor is in vacuo.

255. Hoogenstraaten, W.  
The fluorescence of zinc sulfide. NED.  
TIJDSCHR. NATUURK v. 21, p. 150-9, 1955.  
(In Dutch)

A survey is given of the chemical and physical structure of the phosphors of the ZnS type. It is shown that the bimolecular reaction mechanism of the electronic processes in the phosphor is responsible for the non-linear properties of the fluorescence, the decay and other luminescence phenomena.

256. Hoogenstraaten, W.  
Electron traps in zinc sulphide phosphors.  
PHILIPS RES. REP. v. 13, n. 6, p. 515-693,  
1958.

An experimental study of electron traps in ZnS; Zn,CdS and ZnS,Se phosphors was made, largely by glow curve and related techniques. The relation of traps to phosphor constitution, particularly to impurity activators and

OPTICAL PROPERTIES

co-activators, was examined, including special effects of transition element impurities such as Ni and Co. The characteristic glow curve peaks of ZnS are explained in terms of lattice anion vacancies or of substitutional oxygen atoms in appropriate cases. Evidence is presented of slow luminescence decay in ZnS-Cu-Co phosphors at 77°K, which is not due to thermal activation of trapped electrons but to a tunnelling process. The theoretical section deals with the wave-functions and energy states for various luminescence and trapping centres in ZnS. Activator - co-activator pair theory is discussed and the paired centres are concluded to be unlikely in ZnS.

257.

Huldt, L., and Staflin, T.

Optical constants of evaporated films of  
zinc sulphide and germanium in the infra-red.

OPTICA ACTA v. 6, n. 1, p. 27-36, 1959.

The constants of vacuum evaporated films, several microns thick, were determined by three different methods in the region 2000-10000  $\text{cm}^{-1}$  (5-1  $\mu$ ). The refractive indices of both substances proved to be definitely higher than for the corresponding bulk material. If the films were evaporated with pure nitrogen as residual gas instead of air, the refractive index decreased considerably and reached, for ZnS, approximately the bulk value, whereas for Ge it still remained somewhat higher. The variations in the modes of determination seem to exclude the observed anomalies being due to complexity of the film structure.

258.

Ibuki, Sumiaki

Induced conductivity of CdS by  $\beta$ - and  $\gamma$ -rays.

J. PHYS. SOC. JAPAN v. 14, p. 1196-1204, 1959.

Properties of CdS crystals were investigated under irradiation by  $\beta$  rays from 10 mc of  $\text{Sr}^{90}$  or from an accelerator of the Van de Graaff type and  $\gamma$  rays from 1 c of  $\text{Cs}^{137}$  or from 200 c of  $\text{Co}^{60}$ . The ohmic contact of electrodes and the crystal uniformity were first inspected, and some properties concerning the induced conductivity of CdS crystals by  $\beta$  and  $\gamma$  rays were discussed in comparison with those observed when the crystals were irradiated by visible light. It was concluded that the sample crystals grown are uniform and that they have low trap density and high sensitivity for  $\beta$  or  $\gamma$  rays. It was also shown that the elementary phenomena of the induced conductivity

OPTICAL PROPERTIES

in the case of  $\beta$  or  $\gamma$  ray irradiation were quite similar to those in the case of visible-light irradiation, and that the number of electrons excited into the conduction band by a  $\beta$  particle was about one hundred times larger than that by a  $\gamma$  particle of 1.3 to 1.5 Mev.

259.

Jaszczyn, P.

The effect of infrared radiation on the transfer of energy in ZnS:Mn. ACTA PHYS.

POLON. v. 18, n. 5, p. 427-38, 1959.

(In French)

Irradiation with infrared of ZnS:Mn powders under ultraviolet excitation at  $-190^{\circ}$  C caused a decrease in intensity of the blue band and enhanced the yellow band. Measurements of the dependence of this effect on the activator concentration, the thickness of the phosphor layer and the wavelength and intensity of the exciting and infrared radiations, indicated that the infrared radiation affected the energy transfer mechanism, by the freeing of holes from excited blue centres.

260.

Jaszczyn, P.

L'EXTINCTION ET LE RENFORCEMENT DE LA LUMINESCENCE DU ZnS-Mn PAR L'IRRADIATION INFRAROUGE. (Extinction and Reinforcement of Luminescence of ZnS (Mn) by Infrared Radiation). Polish Academy of Sciences. Inst. of Nuclear Research, Warsaw. Report No. 114/XIII, Oct 59, 14p.

Under the effect of infrared irradiation the blue luminescent band of ZnS(Mn) is extinguished and the orange band is reinforced. The effects are considerably smaller in the cubic crystals than in the hexagonal crystals. The introduction of cobalt to the phosphor reinforces the extinction of the blue emission and at the same time decreases the reinforcement of the orange emission.

OPTICAL PROPERTIES

The mechanism of the energy transfer causing the extinction and reinforcement are discussed, and an energy model for ZnS(Mn) is proposed. In the model proposed, only the processes which start by the photoionization of the blue centers are considered. The effect of different infrared wavelengths on the luminescence is determined. The spectrum of the stationary luminescence under infrared irradiation was studied in the temperature interval from 20 to -150°C. These investigations showed that the reinforcement of the orange band results from two actions of the radiation: the liberation of holes and the liberation of electrons.

261. Kallmann, H.  
RESEARCH OF FLUORESCENCE AND CONDUCTIVITY  
PHENOMENA. New York Univ., New York.  
Quarterly Progress Report No. 1, July 57,  
78p. (Contract DA-36-039-sc-73145).

Progress is reported in studies on energy transfer in liquid solutions under light and high energy excitation: energy transfer in plastics; the effect of externally applied dc and ac fields on the ac photoconductivity of ZnS and ZnCdS powder phosphors; and the effect of externally applied fields on the trap occupation distribution in ZnS and ZnCdS phosphors.

262. Kallman, H.  
RESEARCH ON SOLID STATE RADIATION-INDUCED  
PHENOMENA. New York Univ. New York. Quarterly  
Progress Report No. 2, Nov 58, 48p. (Contract  
DA 36-039 SC-75043).

Part I. Methods found successful in increasing the efficiency and extending the application of liquid scintillators are applied to scintillators prepared in polystyrene and in polymethylmethacrylate. It is found that concentration quenching does not occur in either and that the intermediate "solvent" method enhances energy transfer and overcomes quenching caused by the incorporation of specific impurities in both plastics. Efficient scintillators are prepared in both plastics. The best polystyrene scintillator prepared has a fluorescence efficiency approximately equal to that of the best liquid scintillators; the best polymethylmethacrylate scintillator has a fluorescence efficiency

OPTICAL PROPERTIES

Approximately 60% that of the best liquid scintillators. Part II. The conductivity and light emission of three ZnS phosphors are investigated at room and low (liquid nitrogen) temperature. The ZnS phosphor that is copper activated shows a marked decrease (by a factor of at least 100) in conductivity at liquid air temperature while the light emission decreases by a factor of 2. The rise time of the conductivity is about the same at liquid air as at room temperature. For the two ZnS phosphors that are silver activated, the conductivity does not change appreciable between room and liquid air temperature. The fluorescence increases at the lower temperature by a factor of 2 or 3 depending on the phosphor. The rise times are appreciably longer at low temperature than at room temperature. Part III. Measurements are reported on ZnS phosphors at liquid nitrogen temperature which compare the light emitted during a "glow curve" (G) with the deficiency area during the rise curve (D). For three different phosphors (Ag, Cu, or Mn as activators) the ratio  $G/D \geq 1$  for every case but one. For all 3 phosphors this ratio is greater when the excitation is band to band (short u.v. or  $\beta$ -rays) than with activator excitation. The fluorescent light emission is lower at room temperature than liquid nitrogen temperature for the Ag activated phosphor but the reverse is true for Cu or Mn activation. A short theoretical discussion is included in which the value of  $G/D$  is obtained from the kinetics of electron transitions, and, under certain conditions, it is shown that this ratio is the reciprocal of the phosphor efficiency.

263.

Kallman, H.

## FLUORESCENCE AND CONDUCTIVITY PHENOMENA.

New York Univ., New York. Quarterly Progress

Report No. 3. Apr 56, 73 p. (Contract DA -

36-039 sc-64526)

The process of light stimulation in ZnCdS phosphors is discussed. Experiments performed to indicate the reliability of present theory are reviewed. The photoconductivity of a number of ZnCdS phosphors has been measured. The data for two of these are plotted.

OPTICAL PROPERTIES

264. Kallmann, H.  
 RESEARCH ON SOLID STATE RADIATION-INDUCED  
 PHENOMENA. New York Univ., New York.  
 Interim Progress Report No. 5. June 1959,  
 20 p. (Contract DA-36-039-sc-75043)

Recent claims that the interaction leading to transfer of excitation energy from one molecule to another may be associated with a transition to the ground state without concomitant radiation are examined. Direct experimental evidence is presented which shows that such energy transfer interaction is not accompanied by special nonradiative transitions, and it is shown that this is to be expected on theoretical grounds. The anomalous behavior of the  $ZnCdS(Mn)$  phosphors under  $\beta$  excitation and infrared stimulation is reported. Stimulation data are available for the 0%, 10%, and 50%  $ZnCdS(Mn)$  phosphors. The 0% CdS phosphor was found to have a stimulation area 100 times larger than that of the respective deficiency areas, whereas for the 10% CdS phosphor it was 20 times larger. Although the 50% CdS phosphor has a negligible stimulation area, the  $\beta$  rise curve taken after stimulation indicated that the phosphor was de-excited. Excitation with  $\beta$  and concomitant infrared radiation is reported along with the dependence on the intensity of fluorescence with the wavelength of the emitted light. Excitation with the 4360 A mercury line is also presented for the 40% CdS phosphor. It was found that under direct solute with uv fluoranthene in PMMA does not show the decrease of fluorescence with increasing concentration which was reported for other solutes. PS/9,10-dimethoxyanthracene, behaves as a normal PS scintillator. Naphthalene is effective as intermediate "solvent" with this solute.

265. Kallmann, H.  
 RESEARCH ON SOLID STATE RADIATION-INDUCED  
 PHENOMENA. New York Univ., New York. Quarterly  
 Progress Report No. 7. Dec 1959, 36 p. (Contract  
 DA-36-039-SC-75043)

Quenchers of fluorescence in solutions under high energy excitation decrease the light output more by their decreasing of energy transfer than upon direct action upon the solute. In contrast to the energy transfer in an unquenched solution when a quencher is present there is a considerable dependence on the

OPTICAL PROPERTIES

solute. From theoretical considerations a straight line dependence on quencher concentration is expected for the inverse intensity if the solute effect is negligible. This behavior is found in the experiments. However, the quantitative prediction of quenching on solute concentration does not agree with the theory if a constant energy transfer parameter is assumed. It is found also that "naphthalene" solutions are somewhat less quenched than xylene solutions. The behavior of ZnS and CdS manganese activated phosphors was studied under the application of DC and AC fields with ultraviolet and x-ray excitation. In nearly all cases a DC field caused transient increases or decreases while the AC field produced permanent increases of light emission. The permanent light increase in the case of AC field and x-ray excitation was for the most part under 30%, although for one sample it was 100% and for another up to 600%. Equipment to measure the variation with temperature and concentration of the fluorescence of organic solutions is being built and calibrated. It is hoped that the manner in which the fluorescence varies with changing parameters will indicate the mechanism of energy transfer from solvent to solute. The equipment built so far comprises: electrometer circuitry; the multiplier phototube circuit; the vessels to contain the solutions; and part of the heating unit. A preliminary calibration has been made of the multiplier phototube response as it varies with light input.

266.

Kallmann, H. P.

Optical excitation of zinc and cadmium

sulphides. J. PHYS. RADIUM v. 17, n. 8-9,

p. 787-9, Aug-Sep 1956. (In French)

The conditions for stimulability of phosphors are investigated. The requirement of sufficient energy storage is fulfilled for practically all phosphors. The following model for stimuable phosphors is proposed: they must have special emission centres which enable the electrons to recombine rapidly with positive holes in radiative transitions. Infrared irradiation releases holes from activators; these holes are transferred to the recombination centres.

OPTICAL PROPERTIES

267. Kallmann, H. and Kramer, B.  
Induced conductivity and light emission in  
different luminescent type powders. PHYS.  
REV. v. 87, p. 91-107, July 1, 1952.

The currents induced in various (Zn : Cd)S luminescent type powders by ultra-violet radiation have been investigated as well as the quenching and stimulating effects due to infrared radiation. Similar experiments on the fluorescent emission have also been carried out. Currents induced in these powders by high-energy-particle radiation is also described. A model is proposed which contains two types of electron traps, deep traps and shallower traps (which are associated with the emission levels at the activator), and a coupling between the deep traps and the emission levels is assumed. Theoretical calculations based on this model are compared to the experimental results for stationary and nonstationary behavior. This comparison shows that in all (Zn : Cd)S powders investigated, traps exist from which so-called "direct transitions" to the activators occur with negligible contribution to the conductivity. These transitions may not be radiative, and they also occur in materials which exhibit no light-stimulation by infrared radiation.

268. Kallmann, H., Kramer, B. and Perlmutter, A.  
Infrared stimulation and quenching of photoconductivity  
in luminescent powders. PHYS. REV. v. 99, n. 2, p. 391--  
400, July 15, 1955.

A.C. measurements of impedance changes in (ZnCd)S fluorescent powders upon addition of infrared radiation (a) simultaneously with the exciting ultraviolet and (b) various periods after excitation by ultraviolet- or  $\gamma$ - radiation are described. A decrease (quenching) of conductivity is always observed in the steady state (a), but in case (b), a strong increase (stimulation) is often observed. The simultaneous quenching shows two maxima, one in the 7500 Å region, the other about 12500 Å, but the stimulation decreases monotonically with increasing wavelengths. These two effects (quenching and stimulation) are superimposed; quenching can most easily be observed at relatively high

OPTICAL PROPERTIES

conduction electron density, while stimulation is most easily observed long after excitation has ceased. The conductivity stimulation can be observed with most (ZnCd)S phosphors many days after cessation of excitation; thus these materials act as storage phosphors in which, however, the storage properties are observed by conductivity stimulation. Their light stimulability is often small. A specially activated Fonda-type storage phosphor with a very high light stimulability, however, shows only small conductivity stimulation. An explanation of this behaviour and the wavelength-dependence of the stimulation and quenching in terms of the action of infrared irradiation on trapped and valence-band electrons is given.

269.

Kallmann, H. and Sucov, E.

Energy storage in ZnS and ZnCDS phosphors.

PHYS. REV. v. 109, n. 5, p. 1473-8, March 1, 1958.

The deficiency area above a rise curve of fluorescence due to excitation by high-energy electrons is a measure of the total amount of energy stored in traps. In order to investigate the rate of decay of this energy, rise curves were taken for six phosphors of various luminescent properties and activation after various dark decay periods following excitation to equilibrium and after de-excitation by exposure to infrared light and heat. For all phosphors the trap concentration was found to be of the order of  $10^{17}/\text{cm}^3$  independent of the type of activator. In addition, the rates of decay of stored energy were determined and were found to be similar; from 20% to 60% of the energy remained in the phosphors after 1 week. This slow rate of decay is explained by predominant retrapping in traps of various depths. The areas under curves of phosphorescent emission were compared to the deficiency areas above rise curves taken immediately after the end of decay. For four of the phosphors these two areas are nearly equal to each other. One phosphor, especially activated with Ni and with practically no phosphorescence exhibited, however, a rate of energy decay similar to the phosphorescent phosphors. This means that the decay of stored electrons can take place radiatively and/or nonradiatively and that the rate for both processes is of the same order of magnitude. The areas under curves of visible light stimulated by infrared irradiation were compared with areas above rise curves taken immediately after the end of stimulation. If all stored electrons were released radiatively, these two areas would be equal. For only one phosphor (specially Pb activated ZnS) was this the case. All others exhibited only from 0.6% to 5% radiative recombinations. Thus the light sum under a stimulation curve does not give a true picture of the trap population.

OPTICAL PROPERTIES

270. Kallmann, H. and Warminsky, R.  
Excitation of luminescence in cadmium sulphide crystals by  $\alpha$ -particles and electrons. ANN. PNY. LPZ. (FOLGE 6) v. 4, n. 1-2, p. 57-60, 1948. (In German)

Studies were made of luminescence in large crystals of CdS due to  $\alpha$ - and  $\beta$ -particles. Ag-activated crystals have intense red emission (max. 7 500 Å) with high efficiency similar to that of ZnS-Ag (19%). Without Ag-activation luminescence is weak. Decay times for emission of CdS-Ag are about  $2 \times 10^{-4}$  sec (ZnS-Ag:  $< 10^{-5}$  sec). Internal reflection causes light to leave crystals at edges. Strongly luminescent crystals exhibit good photoconductivity.

271. Keller, S. P. and Pettit, G. D.  
Optical properties of activated and unactivated hexagonal ZnS single crystals. PHYS. REV. v. 115, n. 3, p. 526-36, Aug 1, 1959.

For previous work, see Abstr. 7972 (1958). Single crystals of hexagonal ZnS, unactivated and activated with Cu, Al, or Mn, were 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 m $\mu$ . 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 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.

OPTICAL PROPERTIES

272. Klick, C. C.

Luminescence and photoconductivity in  
cadmium sulfide at the absorption edge.

Phys. Rev. v. 89, p. 274-7, Jan 1, 1953.

Measurements of optical transmission, photoconductive response, luminescent edge emission and excitation spectrum for edge emission have been made on single crystal specimens of CdS at 77°K and 4°K. At the lowest temperature there is an energy gap of more than 0.1 eV between the absorption edge and the onset of emission. Coupled with information from the emission spectrum and the i.r. properties of CdS, this observation suggests that edge emission in this material may occur at a special centre and not be characteristic of the pure lattice.

273. Kobayashi, A. and Kawaji, S.

Adsorption and photoexcited adsorption  
of zinc sulfide. J. CHEM. PHYS. v. 24, n. 4,  
p. 907-9, April, 1956.

The ZnS was a phosphor activated with Cu and it was illuminated in the fundamental absorption band of the crystal (3650 Å). The specific surface was  $0.3 \text{ m}^2\text{g}^{-1}$  and the initial heat of adsorption (calc. from the adsorption isotherms at 50° and 100°) was  $\Delta H = 8 \text{ kcal}$ ;  $\Delta H$  was, as expected, equal to the maximum change of the work function (calc. from contact potentials) with adsorption. The adsorption was enhanced by heating in vacuo, more at 100° than at 50°. The photoexcited adsorption is attributed to two factors (a) an increase of reversible adsorption capacity due to pair creation and (b) irreversible photochemical reaction between adsorbed oxygen and defects in the crystal.

274. Koppelman, G. and Krebs, K.

The influence of dispersion on the optical determination  
of the thickness of thin films. Z. PHYS. v. 145, n. 4,  
p. 486-95, 1956. (In Russian)

The dispersion in reflectivity measurements of vacuum-evaporated ZnS films was determined and the effect of the dispersion on the thickness determination

OPTICAL PROPERTIES

was investigated theoretically and experimentally. The results are expected to hold in general for any thin film showing interference.

275. Kotera, Y. and Naraoka, K.  
The Gudden-Pohl effect of ZnS:Cu. J.  
ELECTROCHEM SOC. v. 106, n. 12, p. 1066,  
Dec 1959.

Measurement of the Gudden-Pohl effect and thermoluminescence of ZnS:Cu showed that in the cubic phase, the effect decreased with increasing temperature between 20 and 120 C, and no glow peak occurred in this range, while in hexagonal ZnS the effect had a maximum at 70°C, and a glow peak occurred at 55°C.

276. Kozina, G. S. and Poskacheva, L. P.  
Total luminance of luminescence of  
fields. OPTIKA I SPEKTROSK v. 8, n. 2,  
p. 214-17, Feb 1960. (In Russian)

Reports measurements of the total luminance of electro-luminescence of green (ZnS:Cu) and yellow (ZnS:Cu:Mn) phosphors excited with unipolar sinusoids and square pulses. Luminance of the yellow phosphors in pulsating fields ( $B_p$ ) was found to be several times greater than their luminance in two-directional (ordinary a.c.) fields ( $B_{ac}$ ), and these high values of  $B_p$  were accompanied by large currents through the samples. The difference between  $B_p$  and  $B_{ac}$  was considerably reduced with rise of frequency. Luminance of the green phosphors in pulsating fields was slightly smaller than in two-directional fields. The difference between the behaviour of the yellow and green phosphors is due to the fact that the former luminesce in d.c. fields and are consequently affected by the d.c. component of the pulsating field.

OPTICAL PROPERTIES

277.

Kramer V.

ELECTRON MICROSCOPE AND ELECTRON DIFFRACTION

STUDY OF ZINC SULFIDE OPTICAL COATINGS. Pitman-

Dunn Laboratories Group, Frankford Arsenal

Philadelphia 37, Pa. Report NR-652, June 57,

7 p.

Electron microscope studies of optical coatings of zinc sulfide show a relatively structureless surface on "soft" coatings, and a structure which progressively increases in bubblelike elevations and in the presence of tiny crystals as the coating is hardened. Electron diffraction studies show that a phase change takes place during the aging process. The softer coatings are hexagonal in structure while the "hard" films are face-centered cubic.

278.

Kröger, F. A.

Some optical and electrical measurements

on blue fluorescent ZnS-Cl single Crystals.

PHYSICA v. 22, n. 8, p. 637-43, Aug 1956.

For hexagonal ZnS-Cl single crystals, measurements of the intensity of luminescence, photoconductivity, Hall effect, thermoluminescence and the thermooconductivity have been carried out. Analysis of the experimental results provides the following data: (a) the electron mobility at room temperature  $\mu_c \cong 120 \text{ cm}^2\text{V}^{-1} \text{ sec}^{-1}$ ; the mobility decreases with increasing temperature, (b) the depth of traps formed by  $\text{Cl}^-$  is  $\epsilon_{\text{Cl}^-} = 0.24 \pm 0.02 \text{ eV}$ , (c) the frequency of escape from  $\text{Cl}^-$  traps  $s = 7 \times 10^4 \text{ sec}^{-1}$ , (d) the capture cross-section of the  $\text{Cl}^-$  traps is  $\sigma \cong 3 \times 10^{-21} \text{ cm}^2$ , (e) recombination levels ("killers") are situated  $\sim 0.7 \text{ eV}$  below the conduction band.

OPTICAL PROPERTIES

279.

Kröger, F. A. and Vink, H. J.

The origin of the fluorescence in self-activated

ZnS, CdS, and ZnO. J. CHEM. PHYS. v. 22, p. 250

-2, Feb 1954.

It is proposed that the luminescent centre in "self-activated" ZnS consists of a cation vacancy whose nearest surroundings have lost one electron. Such a centre is consistent with the fact that at low firing temperatures, the appearance of the blue fluorescence of self-activated ZnS depends upon the presence of "promoter ions" (monovalent anions or trivalent cations) whereas, if the firing temperature be sufficiently high, some blue fluorescence is obtained without the presence of such promoter ions. The luminescence of reduced ZnS, CdS and ZnO is also discussed, and is attributed to anion vacancies that have trapped one electron.

280.

Kröger, F. A., Vink, H. J. and Van Den Boomgaard, J.

Controlled conductivity in CdS single crystals.

Z. PHYS. CHEM. (LEIPZIG) v. 203, n. 1-2, 1-72,

May 1954.

The electrical and optical properties of single crystals of pure CdS or of CdS containing Ga, In, Sb, Cl or Ag are found to depend markedly on the composition of the atmosphere in which they are prepared. Crystals exposed to an oxidizing atmosphere (e.g. sulphur vapour) are insulators or semiconductors and show photoconductivity; those exposed to a reducing atmosphere show quasimetallic conductivity. In crystals containing Ga or Cl the concentrations of the charge carriers are equal to the respective concentrations of the foreign ions. Bands appear in the yellow region of the absorption spectrum of oxidized but not of reduced crystals. The theory of defect structures is extended to calculate the dependence of the concentration of defects (donors, traps, acceptors) on the concentration and nature of the impurities and the reducing power of the atmosphere. Satisfactory agreement with experiment is found.

OPTICAL PROPERTIES

281.

Kuwabara, G.

The optical and electrical properties of cadmium sulphide films. J. PHYS. SOC. JAPAN v. 9, p. 97-102, Jan-Feb 1954.

The optical and electrical properties of evaporated CdS film were measured. The optical properties are similar to those of the single crystal, that is, the absorption edge lies at 2.4 eV; the photosensitivity peaks near the edge; with temperature decrease, the adsorption edge and photosensitivity maximum shift towards shorter wavelength; while the electrical properties show wide variation from sample to sample and by heat treatment. The photoresponse shows large dependence on the temperature and is closely related to the dark conductivity. By baking in air the conductivity at room temperature decreases a great deal and the activation energy increases. By baking in a reducing atmosphere, the conductivity, the activation energy and photoresponse almost regain their initial values. In this process, the adsorption or desorption of oxygen on the surfaces of microcrystals plays an important role. The bi-molecular recombination argument for the interpretation of spectral sensitivity curves seems inadequate.

282.

Kuwabara, G.

Optical properties of cadmium sulfide in glass. J. PHYS. SOC. JAPAN v. 9, n. 6, p. 992-6, Nov-Dec 1954.

The optical properties of glasses containing CdS were measured for a few specimens after different heat treatment. The absorption edge shifts towards longer wavelengths as the reheating progresses. However, its shape and temperature-dependence are similar to those of the single crystal. The maximum wavelengths of luminescent and excitation spectra also shift with the absorption edge and a linear relation exists between those wave-numbers. From these results, it may be inferred that the optical properties of these glasses are due to CdS crystals, and their changes show that the energy gap between the filled and the conduction band in the crystals decreases with reheating; this is probably caused by the change in the lattice constants of the crystal.

OPTICAL PROPERTIES

283.                   Kuwabara, G. and Isiguro, K.  
                       Optical constants of ZnS films.  
                       J. PHYS. SOC. JAPAN v. 7, p. 72-4,  
                       Jan-Feb 1952.

These were determined by photometric and interferometric methods for the wavelength between 400 m $\mu$  and 1000 m $\mu$ . The results obtained by both methods agree within experimental error, and the density of the film calculated by Lorenz-Loreng formula is c. 0.98 of that of the bulk ZnS.

284.                   Kynev, K. D.  
                       On low-temperature activation of precipitated  
                       zinc sulphide by copper. OPTIKA I SPEKTROSK.  
                       v. 3, n. 6, p. 652-4, Dec 1957. (In Russian)

It was found possible to prepare ZnS:Cu phosphors, with a feasonable luminescent intensity, at temperatures not exceeding 100°C. ZnS was precipitated from a 3N solution of zinc carbonate on addition of a 3N solution of sodium sulphide and on vigorous shaking. The suspension thus produced was covered with a solution of copper sulphate containing  $2 \times 10^{-4}$  g/m. of Cu. After a second shaking the suspension was activated by heating at 100°C for 10 min. It was found that emission of ZnS:Cu phosphors prepared at 100°C was 100 times weaker than the emission of ZnS:Cu prepared at high temperatures and ZnS:Cu activated at 100°C exhibited no afterglow. See also following abstract.

285.                   Kynev, K. D.  
                       The structural sensitivity of luminescence  
                       of the ZnS:Cu phosphor prepared at low temperatures.  
                       OPTIKA I SPEKTROSK. v. 3, n. 6, p. 655-7,  
                       Dec 1957. (In Russian)

Deals with the effects of variation in the chemical conditions of preparation of ZnS:Cu at 100°C on its luminescence. Preparation of the samples followed essentially the technique described in the preceeding abstract. The spectral distribution and intensity of luminescence were recorded and it was found that

OPTICAL PROPERTIES

changes in the chemical conditions of preparation produce changes in luminescent centres, which are crystalline structural defects. This affects strongly the intensity and spectral distribution of luminescence. The results obtained suggest that the Cu activator centres are localized at the phosphor surface.

286. Kynev, S.  
Peculiarities of the kinetics of photo-  
dielectric losses in (ZnS,CdS):Cu crystal  
phosphors in powder form. C.R. ACAD. BULG. SCI.  
v. 9, n. 2, p. 5-8, April-June 1956. (In Russian)

It was found that the photodielectric-loss v. excitation-light curve for these phosphors shows a distinct maximum. When such a phosphor is excited by a high light intensity and then placed in darkness, the losses first increase for a short period and then decrease. Other graphs show the dependence of the kinetics of photodielectric losses on the intensity and wavelength of the exciting light and on temperature.

287. Laboratoire d'Infra Rouge Technique et Applique (France)  
CONSTRUCTION OF AN INFRA RED SOURCE OF HIGH  
LUMINANCE. Final technical rept. 1 June-30 Sep 60,  
17 p. (Contract DA 91-591-EUC-1130)

Work was devoted to the spectroscopic study of cadmium sulphide, either pure or activated with silver or indium, and mercury sulphide. Besides the red radiation already known from ultra-violet irradiation experiments, a green light of unknown origin was observed, its wavelength being close to that characteristic of the absorption limit of cadmium sulphide. This radiation has no appreciable inertia and is therefore of interest for optical telecommunication. It appears to compete with the red or infra-red radiation in which we are interested, and it probably plays a part in the destruction of powders by bombardment. An investigation of this phenomenon is therefore important, especially since an effect of similar origin is observed in case of mercury sulphide. The first results of this research are given, together with some theoretical observations aimed at its interpretation.

OPTICAL PROPERTIES

288.. Lambe, J.

Cadmium sulfide with silver activator.

PHYS. REV. v. 100, n. 6, p. 1586-8, Dec 15, 1955.

Further experimental evidence is presented in connection with a model which has been proposed by Lambe and Klick for CdS(Ag). In this model it is assumed that the silver activator gives rise to a level which is approximately 0.4 eV below the conduction band, and that luminescence occurs when an electron in such an activator level recombines with a free hole. It is shown that irradiation in the 1 micron infrared region stimulates luminescence by generating free holes, while also causing well known quenching effects in photocurrent. It is also shown that 3 micron irradiation gives rise to photoconduction by exciting electrons from the activator levels into the conduction band. The proposed model indicates that irradiation in the 3 micron region should quench luminescence by removing electrons from activator levels, and this is found experimentally. These experiments further substantiate the proposed model for CdS(Ag).

289. Lambe, J. J., Klick, C. C. and Dexter, D. L.

Nature of edge emission in cadmium sulfide.

PHYS. REV. v. 103, n. 6, p. 1715-20, Sep 15, 1956.

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

290. Lambe, J. and Klick, C.

Model for luminescence and photoconductivity in the sulfides. PHYS. REV. v. 98, n. 4, p. 909-914, 1955.

A model for sulfides activated by monovalent metals is discussed which differs in several important respects from that usually employed. Because of the net negative charge of the lattice volume surrounding the activator there is a large

OPTICAL PROPERTIES

cross section for trapping of holes which may be accompanied by release of a large amount of energy. This is presumed to be the transition leading to luminescence. A subsequent trapping of an electron returns the center to its original condition. For the electron trapping there is no Coulomb field and both the capture cross section and energy released would be expected to be small compared with the case of hole trapping. On the basis of this model, there is a simple explanation of the fast luminescence decay associated with hole capture and the slow conductivity decay associated with that of free electrons. Other well-known phenomena in the sulfides are examined on the basis of this model. In addition, predictions of this model concerning the infrared photoconductivity and infrared stimulation of luminescence have been verified by experiment on silver-activated cadmium sulfide.

291. Lashkar'ov, V. Ye., Fedorus, H. A. and Sheinkman, M. K.

Photo-carrier diffusion in CdS single crystals.

UKRAYIN. FIZ. ZH. v. 2, n. 4, p. 374-5, 1957.

(In Ukrainian)

292. Lashkar'ov, V. Ye. et al

Investigation of reasons for decrease of

the photosensitivity of CdS single crystals

in their absorption range. UKRAYIN. FIZ. ZH.

v. 2, n. 3, p. 261-73, 1957. (In Ukrainian)

Measurements were made of the variation with  $\lambda$  of photocurrent, photocurrent efficiency, mobility and lifetime of photocarriers, reflection and transmission coefficients of the CdS single crystal. The effects observed are considered to be explainable upon a hypothesis of non-photoactive exciton annihilation at the crystal surface when absorbing strongly-absorbed light.

OPTICAL PROPERTIES

293. Lavron, A. V.  
On the formation and characteristics of some ZnS  
luminophors. BULL. ACAD. SCI. USSR-PHYS. SER.  
v. 23, n. 11, p. 1337, Nov 1959.
294. Lempicki, A.  
Polarization of luminescence in ZnS and CdS  
single crystals. J. ELECTROCHEM SOC. v. 107,  
n. 5, p. 404-9, May 1960.

The fluorescent emission from hexagonal ZnS and CdS single crystals is found to be polarized preferentially perpendicular to the c axis for both polarized and unpolarized excitation. Cubic ZnS crystals emit unpolarized radiation. The results are analysed in terms of a simple dipole theory which is shown to be inadequate for the description of luminescent centres in these materials. Preliminary observations on the polarization of fluorescence of ZnO crystals are reported.

295. Lempicki, A.  
Polarization of fluorescence in ZnS and CdS  
single crystals. PHYS. REV. LETTERS v. 2,  
n. 4, p. 155-7, Feb 15, 1959.

The polarization was measured of impurity fluorescence of ZnS:Cu or Mn and CdS crystals, excited with natural or plane polarized 3650 A radiation. The fluorescence is polarized preferentially perpendicular to the c axis. The degree of polarization depends on the crystal structure, perfection and impurity activation. Simple dipole theories cannot account for the observations (see following abstract).

OPTICAL PROPERTIES

296. Jean-Pierre Leroux and Pierre Thureau.  
 A pyrometric application of the photoluminescence of zinc-cadmium sulfide activated by manganese and gold. COMPT. REND. v. 248, p. 3424-6, June 15, 1959.  
 (In French)

A change in the color of the photoluminescent emission of mixed Zn and Cd sulfides activated by Au and Mn under the influence of temperature is used for pyrometry. A thermosensitive parameter is explained on the basis of spectral deformation.

297. Leverenz, H. W.  
 Luminescence in electronically active solids.  
 J. PHYS. RADIUM v. 17, n. 8-9, p. 612-15, Aug-Sep 1956. (In French)

There are three basic electronic activities in phosphors and other electronically active solids. These activities are (1) orientation of spin, (2) excitation leading to radiation, (3) unilateral displacement. Atomic interaction provides, through chemical synthesis, effective means for modifying, controlling and combining these activities. Research in this field has made many physical phenomena tractable and useful, and has afforded greater understanding of the fundamental natures of solids and of luminescence.

298. Levshin, V. L. and Orlov, B. M.  
 Investigation of the energy of thermal phosphors.  
 OPTIKA I SPEKTROSK. v. 7, n. 4, p. 530-6, Oct 1959.  
 (In Russian)

Deals with stimulation of the optical flash in ZnS:Cu:Pb phosphors by infrared light of  $\sim 1 \mu$  wavelength. It was found that to liberate electrons from localization levels it is necessary to activate them thermally first. The energy of thermal activation depended on the nature of the localization levels and was independent of the wavelength of the stimulating light.

OPTICAL PROPERTIES

299. Levshin, V. L. and Rebane, V. N.  
 A comparative study of light-sum storage  
 and temperature quenching in a ZnS:Ag  
 phosphor excited with  $\beta$ -rays and light.  
 OPTIKA I SPEKTROSK. v. 7, n. 2, p. 236-40,  
 Aug 1959. (In Russian)

Reports a study of thermoluminescence and temperature quenching of ZnS:Ag:MgCl<sub>2</sub> excited by means of light (3650 Å) and  $\beta$ -rays from P<sup>32</sup>, Tl<sup>204</sup> and S<sup>35</sup>. For both types of excitation the same system of local levels (indicated by thermoluminescence peaks) was obtained. Peculiarities of  $\beta$ -excitation exhibited both in thermoluminescence and in temperature quenching were found to be entirely due to its low intensity: a 5.7 millicurie P<sup>32</sup> source delivered energy to the phosphor surface at the rate of about  $10^{13}$  eV cm<sup>-3</sup> sec<sup>-1</sup>, which was the equivalent of a 0.003  $\mu$ W cm<sup>-2</sup> light beam.

300. Levshin, V. L. and Ryzhikov, B. D.  
 Formation and action of localization levels  
 in ZnS:Mn phosphors. OPTIKA I SPEKTROSK. v. 4,  
 n. 3, p. 358-64, 1958. (In Russian)

Trapping level measurements were made with ZnS phosphors containing Mn up to 0.1 g/g. Blue emission was obtained up to a Mn concentration of 0.001 g/g. orange emission occurred for concentrations between 0.0002 and 0.03 g/g. Thermal glow curves are given for various Mn concentrations and various wavelengths of exciting light. The change of absorption of ZnS with Mn concentration was measured. The relation between trap depth and probability of excitation is discussed. At low concentrations Mn ions occupy positions close to defects, at higher concentrations Mn ions replace Zn ions at lattice sites.

OPTICAL PROPERTIES

301. Levshin, V. L. and Tunitskaya, V. F.  
Thermoluminescence and localization levels  
of ZnS:Mn phosphors. OPTIKA I SPEKTROSK.  
v. 8, n. 5, p. 663-71, May 1960. (In Russian)

The structure, population and thermal de-excitation (thermoluminescence) of capture levels in ZnS:Mn crystals (with  $10^{-6}$  to  $10^{-2}$  gMn/gZnS) of sphalerite structure were studied in a wide range of temperatures using exciting light of various wavelengths and intensities. The effect of increasing the manganese concentration on the spectrum of levels was also studied.

302. Levshin, V. L. and Tunitskaya, V. F.  
The nature and kinetics of radiation processes  
in ZnS-Mn phosphors during excitation. OPTICS  
& SPECTROSCOPY USSR v. 9, n. 2, p. 118, Aug 1960.

303. Link, R. and Seiwert, R.  
The temperature dependence of the luminescence  
of CdS crystals. I: Crystals without foreign  
activators. Z. PHYS. CHEM. (LEIPZIG) v. 212,  
n. 5-6, p. 295-318, 1959. (In German)

The purest available crystals were tested between  $-200$  and  $+200^{\circ}\text{C}$  under 3650 A excitation, with measurement of intensities near the band peaks (5150, 5800, and 7100 A) and spectrophotometry of the whole visible emission. All crystals gave a green band with maximum intensity at the lowest temperature reached. The crystals were classified according to the behaviour of the red emission, which showed three types of temperature dependence: a maximum at  $-50^{\circ}\text{C}$ , or at  $-200^{\circ}\text{C}$ , or two maxima at  $-200^{\circ}$  and  $0^{\circ}\text{C}$ . The maximum of the orange band was  $-150^{\circ}\text{C}$ . Plots of the measurements are given, and the data discussed at length without a decision on the types of luminescent transition involved, through a tentative band diagram is included. It is possible that the orange band arises from traces of impurity, while the red emission may depend on a partial conversion of the original green band by self-absorption.

OPTICAL PROPERTIES

304. Litvinova, P. S.  
 Temperature variation of absorption in  
 sulphide phosphors. OPTIKA I SPEKTROSK  
 v. 1, n. 3, p. 427-32, 1956. (In Russian)

The experimental part of the work consisted in measuring the emission and absorption, and their variation with temperature. Curves are given for ZnS:Zn, ZnS:Cu, ZnS:Mn, also ZnS:Cu:Fe and ZnS:Cu:Co. It is concluded from the curves given that temperature extinction of luminescence is associated with growth of absorption in the extinction region.

305. Ludwig, W., and Seiwert, R.  
 The temperature dependence of the luminescence  
 intensity of various activated CdS crystals.  
 Z. PHYS. CHEM. (LEIPZIG) v. 207, n. 3-4,  
 p. 250-72, 1957. (In German)

The temperature dependence of luminescence was measured over the range - 180 to +120°C using 3650 Å excitation. Maxima were shown in the intensity/temperature curves for emission in the 6000-9500 Å region. For "pure" crystals the intensity remained essentially constant over a wide temperature range. The results are explained by use of the Klasens-Schön energy-band model of crystal phosphors.

306. Margolin, S. D., and Fakidov, I. G.  
 Application of CdS photoresistance in  
 combination with phosphors as the detector  
 of cobalt 60 gamma rays. DOKLADY AKAD.  
 NAUK S.S.S.R. v. 105, p. 976-7, 1955.  
 (In Russian)

The photoresistance of a CdS monocrystal was tested in a scintillation counter with naphthalene, toluene, cesium iodide, and sodium iodide, and Co<sup>60</sup> isotope with 0.6g-equivalent of radium as a gamma radiation source. The tables show

OPTICAL PROPERTIES

CdS photoresistance without the phosphors and with various phosphor combinations. The highest sensitivity was observed in the presence of sodium iodide. The results of the study showed that CdS can be used as an effective detector of  $\gamma$  rays.

307. Markovskii, L. Y., and Smirnova, R. I.  
Chemical aspects of the formation of ZnS-selenide phosphors. BULL. ACAD. SCI. - USSR - PHYS. SER. v. 23, n. 11, p. 1327, 1959.

308. Meijer, G.  
Infrared fluorescence of copper-activated zinc sulphide phosphors. J. PHYS. CHEM. SOLIDS v. 7, n. 2-3, p. 153-8, 1958.

An infrared fluorescence was observed for ZnS:Cu, Al and ZnS:Cu, Ga at 1.57  $\mu$  and 1.72  $\mu$ . This emission appeared to be excited at low temperatures by radiation of 1.38  $\mu$  and between 0.5  $\mu$  and 0.8  $\mu$ , provided that the phosphor was excited by 3650 A. The infrared quenching of the visible fluorescence and an infrared stimulation of the visible phosphorescence show a spectrum analogous to the infrared excitation spectrum, and seem to be connected with the same transitions.

309. Meijer, G., and Avinor, M.  
Excitation spectra of vanadium-activated phosphors. PHILIPS RES. REP. v. 15, n. 3, p. 225-37, 1960.

Excitation spectra were measured for the 2  $\mu$  fluorescence band. The emission is excited by absorption in two composite bands due to vanadium at 1.1 and 1.6 eV, by absorption in an auxiliary impurity centre, such as copper or silver, if present, and by fundamental excitation.

OPTICAL PROPERTIES

310. Melamed, N. T.  
Energy transfer in ZnS:Cu:In phosphors.  
J. PHYS. CHEM. SOLIDS v. 9, n. 2,  
p. 149-52, 1959.

Transport of energy between luminescence centres has been observed in ZnS:Cu:In phosphors at room temperature and at 77°K. The results support a photoconductive transfer mechanism. Energy transfer at low temperatures can be interpreted as resulting from a process in which a given wavelength is capable of putting an electron into an impurity level from the valence band, as well as exciting it from the same impurity level to the conduction band.

311. Miyazawa, H., Maeda, H., and Tomishima, H.  
Lattice scattering mobility of electrons in  
cadmium sulphide. J. PHYS. SOC. JAPAN v. 14,  
n. 1, p. 41-7, 1959.

The Hall mobility of electrons was measured between 90° and 400°K for dark-conducting CdS:Ga, CdS:Cl and CdS:Cd single crystals. The lattice scattering mobility after correction is well given by equation  $\mu_L = A \{ \exp(\theta/T) - 1 \}^{-1}$  with  $A = 92.5 \pm 15 \text{ cm}^2(\text{V sec})$  and  $\theta = 370^\circ + 30^\circ\text{K}$ . There are thus about  $10^{17} \sim 10^{18}$  uncontrollable deep-lying centres per unit volume in the crystals, which permanently capture the conduction electrons and act as scatterers. The value of the characteristic temperature seems to be reasonable as compared with the one ( $\theta = 250 \sim 300^\circ\text{K}$ ) previously obtained by Kroger et al. (Abstr. 3752 of 1955) from the infrared absorption band ( $\theta = 335^\circ\text{K}$ ) and the fine structure data in the edge emission ( $\theta = 460^\circ\text{K}$ ).

312. Moore, C. W.  
SILVER ACTIVATION OF ZINC SULFIDE SINGLE  
CRYSTALS FOR SCINTILLATION COUNTING. Air  
Force Inst. of Tech., Wright-Patterson Air  
Force Base, Ohio. Master's thesis. Rept.  
no. GNE 59-11, Mar 59, 47p. ASTIA AD-215-508

Development of large single crystals has opened the possibility of using zinc sulfide single crystals as scintillators. Silver is the best activator, for

OPTICAL PROPERTIES

it produces the highest intensity of luminescence of any known activator. Charge compensation is brought about by additional silver ions in interstitial positions, by sulfur vacancies, or by use of co-activators. The silver activator may be introduced into the lattice by surrounding the crystals with a mixture of zinc sulfide and silver sulfide powder and heating in an argon atmosphere at 800-1000°C for 2 hours. The activated crystals produce blue luminescence with wavelength of approximately 4560 Å when excited with ultraviolet light. The intensity of the emission is greater for activated crystals than for unactivated crystals, and it is of different wavelength. Intensity decreases with increasing activation temperature. At 77.4°K two emission bands appear at 4440 Å and 5600 Å, but the total emission appears less than at room temperature. When the crystals are used in a photomultiplier scintillation counter large pulses are produced by alpha particles which may be counted by the electronic circuit.

313. Nakamura, K.  
Effects of infrared on emission of ZnS:Cu  
phosphors. Note In J. PHYS. SOC. JAPAN  
v. 10, n. 8, p. 715-16, 1955.
314. Neumark, G., Fajans, J., and Frankl, D. R.  
Thermoluminescence measurements on ZnS  
phosphors in vacuo. Letter In J. CHEM.  
PHYS. v. 23, n. 8, p. 1553, 1955.

Although photoconductivity in ZnS and CdS is affected by surface traps due to adsorbed gases no effect is found in thermoluminescence curves.

OPTICAL PROPERTIES

315. Niekisch, E. A.  
 Determination of trap distribution by modulated light measurements on single crystals of photoconducting cadmium sulphide. Note In Z. NATURFORSCH v. 9a, n. 7-8, p. 700-1, 1954.  
 (In German)

The effective mobility of conduction electrons depends on the trapping states, and measurements of this with weakly modulated periodic excitation provide a means of determining the trap distribution.

316. Nine, H. D.  
 Photosensitive ultrasonic attenuation in CdS.  
PHYS. REV. LETTERS v. 4, n. 7, p. 359-61, 1960.

The attenuation of compressional waves (10 to 200 Mc/s) propagated along the c-axis was observed to be affected by the intensity and wavelength of light incident on the crystal.

317. Nymm, U. Kh.  
 Photoelectric phenomena in luminescence powders of ZnS-Cu(Ni, Fe, Co) and ZnS-Cds-Cu.  
IZVEST. AKAD. NAUK. S.S.S.R., SER. FIZ. v. 23, p. 1286-9, 1959. (In Russian)

The photoelectric phenomena in ZnS-CdS-Cu phosphors containing 45, 35, 25, 18, 8, and 0% CdS and ZnS-Cu (Ni, Fe, Co, ZnO) phosphors were investigated by a condenser method. The spectral and temperature relations were derived as functions of photoelectric response. The luminescence excitation spectrum and the curves of thermal de-excitation were measured for ZnS-CdS phosphors.

OPTICAL PROPERTIES

318. Osada, K.  
Thermoluminescence of zinc sulfide phosphors.  
J. PHYS. SOC. JAPAN v. 15, p. 145-9, 1960.

The glow curves of the thermoluminescence of some zinc sulfide phosphors are measured for two different exponential heating rates by means of an oscilloscope, and the values of the depth and frequency factor of their traps are obtained by the Booth method. The value of the frequency factor is not constant for all traps, but becomes larger as the depth increases. Equations are developed which permit the analysis of the glow curves for the exponential heating rate.

319. Pedrotti, L. S., and Reynolds, D. C.  
Change in structure of blue and green  
fluorescence in cadmium sulfide at low  
temperatures. PHYS. REV. v. 119, n. 6,  
p. 1897-8, 1960.

The two fundamental fluorescences observed in CdS crystals subjected to ultraviolet excitation at low temperatures are classified according to wavelength. Photographs of the two fluorescences at  $4.2^{\circ}$  and  $77^{\circ}$  K are given, and their structures are compared. Experimental evidence on the change in structure of the green emission near 5130 Å between  $4.2^{\circ}$  K and  $77^{\circ}$  K is presented and used to confirm an explanation for the apparent "green" shift in CdS proposed by Thomas and Hopfield.

320. Piper, W. W.  
Some electrical and optical properties of  
synthetic single crystals of zinc sulfide.  
PHYS. REV. v. 92, p.23-7, 1953.

The fundamental optical absorption edge and the temperature dependence of electrical conductivity of synthetic single crystals of hexagonal zinc sulphide have been measured, as well as the photoconductivity near the absorption edge. The fundamental absorption coefficient is  $1 \text{ mm}^{-1}$  at a photon energy of  $3.58 \pm 0.02$  eV and increases exponentially by a factor of ten every 0.07 eV up to  $10^3 \text{ mm}^{-1}$ . The logarithm of the electric resistivity varies linearly as a function

OPTICAL PROPERTIES

of the inverse absolute temperature with a slope of  $(3.77 \pm 0.1)eV/2k$ . A peak in the spectral variation of photoconductivity has been observed at the optical absorption edge.

321. Piper, W. W., Johnson, P. D., and Marple, D. T. F.  
 Temperature dependence of the optical band  
 gap in ZnS. J. PHYS. CHEM. SOLIDS v. 8,  
 p. 457-61, 484-5, 1959.

Hexagonal ZnS crystals were grown from the vapour phase, and curves are given of the absorption coefficient v. photon energy for light polarized perpendicular or parallel to the c-axis. Peaks occur in the absorption at 3107, 3155, 3179 and 3202 Å at 4°K. The temperature shift does not alter the curve shape up to 5000 cm<sup>-1</sup> and is independent of the direction of polarization. The shifts of the position of the 3179 Å line, and of frequencies corresponding to definite values of the absorption coefficient in the continuous band, have been compared with calculations based on the sum of the lattice dilatation effect and the electron-phonon interaction (with  $m^*/m_0 = 3.3$  for electrons and holes). Previous measurements at room temperature and above agreed with the calculation, but the new determinations do not agree between 150° and 20°K. This may be due to electron scattering by piezoelectric acoustical modes in the crystal.

322. Piper, W. W., Marple, D. T. F., and Johnson, P. D.  
 Optical properties of hexagonal ZnS single  
 crystals. PHYS. REV. v. 110, n. 2, p. 323-6,  
 1958.

The optical transmission of hexagonal zinc sulphide crystals was measured in the spectral range from 0.32 to 15 μ.

OPTICAL PROPERTIES

323.

Prener, J. S., and Weil, D. J.

The luminescent center in self-activated

ZnS phosphors. J. ELECTROCHEM. SOC.

v. 106, p. 409-114, 1959.

A model for the ground state of the self-activated luminescent center in ZnS phosphors proposed by Prener and Williams in 1956 has been confirmed experimentally. It is shown that a Zn vacancy is involved in the blue luminescence and that the spectrum depends on whether the required coactivator can occupy a Zn or S site near the vacancy. The calculated energy levels of the center using a simple model are in qualitative agreement with the observed spectra.

324.

Radelt, H.

The temperature dependence of the absorption

edge in CdS single crystals. Z. NATURFORSCH

v. 15a, n. 3, p. 260-70, 1960. (In German)

Continuation of previous experimental work in which the temperature range is extended downwards to 20°K. At the low temperature end, the rate of change of optical energy gap with temperature ( $d\Delta E/dT$  in eV/deg K) is reduced to  $-2.0 \times 10^{-4}$  from the value of  $-5.8 \times 10^{-4}$ , characteristic of the temperature range 120-650°K.

325.

Ramazanov, P. E.

Photoelectric effects in ZnS-Cu, Fe phosphors.

IZVEST. AKAD. NAUK. S.S.S.R., SER. FIZ. v. 23,

p. 1290-3, 1959. (In Russian)

The temperature dependence of photoelectric effects at various frequencies is correlated with the theoretical dependence in thermal ion displacement polarization. Fe(Cu,  $10^{-4}$ ; Fe,  $10^{-5}$ ) specimens were investigated and the temperature functions  $\Delta t g \phi$  and  $\Delta C/C_t$  (where  $C_t$  is the condenser dark space) were taken at 90.2kHz, 2.94 MHz, and 9.69 MHz at equilibrium excitation and at various stages of phosphorescence damping.

OPTICAL PROPERTIES

326. Beames, J. P.  
Cathodoluminescence of evaporated zinc sulfide-manganese films. Reprint from 'Sixth National Symposium on Vacuum Technology Transactions'. Pergamon Press, 1960.

The cathodoluminescence of thin evaporated ZnS-Mn films has been investigated by varying both the Mn concentration and the postheat time.

327. Rebane, K. S.  
Quenching of the luminescence of ZnS:Cu phosphor by infrared light. BULL. ACAD. SCI. USSR-PHYS. SER. v. 23, n. 11, p. 1287, 1959.

328. Rebane, K. S. K.  
On deep trapping states in ZnS phosphors. OPTIKA I SPEKTROSK v. 4, n. 2, p. 211-16, 1958. (In Russian)

Deep traps in ZnS activated by various impurities were studied ZnS:Cu:MgCl<sub>2</sub>, ZnS:ZnO:Cu, ZnS:Cu:Te and ZnS:Cu:Ni. Slow rise of fluorescence with time under weak excitation at room temperature and after previous heating procedures revealed deep traps emptied at 110 and 190°C. The first group can be found in thermoluminescence for some phosphors. 800 m $\mu$  light empties the "190°C" traps. Visible light down to 485 m $\mu$  stimulates the phosphorescence with a maximum at 563 m $\mu$ .

OPTICAL PROPERTIES

329.

Rebane, K. -S. K.

An investigation of the dependence of the luminescence characteristic of ZnS phosphors on the intensity of exciting light. TRUDY INST. FIZ. I ASTRON, AKAD, NAUK ESTON.

S.S.R. n. 8, p. 105-33, 1958. (In Russian)

It is shown that under the influence of infrared light the region of nonlinear dependence of luminescence on excitation intensity shifts toward higher excitation intensities. It is not possible to quench luminescence completely by means of infrared light. It was found that upon increasing excitation intensity the light sum value increases at first and then begins to decrease. Changes in excitation intensity are accompanied by changes in the rapidity of rise process and the decay law. The law of temperature quenching for that part of luminescence which cannot be quenched by infrared light differs from the law of temperature quenching for the remainder of the luminescence. Existing theories of non-linearity were examined on the basis of the data obtained. It is shown that the theory based on the model with two classes of recombination centers, representing only electronic and hole processes, is generally capable of explaining satisfactorily the phenomenon of non-linearity. Experimental data obtained in this work indicate that this model does not take into account all the essential processes occurring in the phosphor. The hypothesis is suggested that sensitized processes exist in the phosphor and the possibility is shown of accounting for experimental data by assuming that sensitized processes occur in ZnS phosphors alongside hole and electronic processes.

330.

Rebane, K. -S.

The influence of the concentration of copper on some spectral properties of ZnS-Cu, Cl phosphors. TRUDY INST. FIZ. I ASTRON., AKAD. NAUK ESTON. S.S.R. n. 11, p. 197-8, 1960.

(In Russian)

The influence of Cu concentration in ZrS-Cu phosphors on the emission and excitation spectra was studied in specimens with Cu  $10^{-2}$ g/g with blue and green bands.

OPTICAL PROPERTIES

331. Reynolds, D. C.  
 Temperature dependence of edge emission  
 in cadmium sulfide. PHYS. REV. v. 118,  
 n. 2, p. 478-9, 1960.

The temperature dependence of the blue and the green emission was investigated from 77° to 300°K. The blue emission shifts to longer wavelengths as the temperature is increased above 77°K with a temperature coefficient of  $4.9 \times 10^{-4}$  eV/°C. The intensity of the green emission falls off exponentially above 77°K with very little shift in the spectral position of the green peaks.

332. Riehl, N., and Ortmann, H.  
 The structure of light centers in activated  
 zinc sulfide phosphors. ANN. PHYSIK v. 4,  
 p. 3-14, 1959. (In German)

The transformation of blue luminescent Cu centers into green luminescent centers (and the reverse transformation) was studied. It is shown that the transformation can occur at 200°C with easily observable velocity. The transformation leads to the standardization of a fixed equilibrium ratio, characteristic for each temperature, for the concentration of the green luminescent centers up to that of the blue luminescent centers. In the temperature range from 20 to 300°C the equilibrium is displaced with increasing temperature in favor of the green luminescent centers. (Reagents capable of desulfurizing the surface of the crystal work in the same direction.) Sufficiently rapid cooling back to room temperature can freeze an equilibrium characteristic for a higher temperature. The reverse transformation green → blue occurs even at room temperature with a finite observable velocity. From this and from the highest value found for the activation energy it is seen that the green → blue transformation is bound to no incorporation or exhaustion of S<sup>2-</sup> or Cl<sup>-</sup> ions. It can be treated only as a diffusion of Cu<sup>+</sup> or Zn<sup>2+</sup> ions in the interstices. As a model proposal for the blue luminescent Cu centers it is shown that there is a Cu<sup>+</sup> ion in the interstices in addition to a Cu<sup>+</sup> ion on a lattice position.

OPTICAL PROPERTIES

333. Riehl, N. and Sizmann, R.  
The influence of oxygen on ZnS and CdS  
phosphors. Z. NATURFORSCH. v. 14a, n. 4,  
p. 394-403, April 1959. (In German)

The presence of oxygen in the preparation of ZnS and CdS phosphors has a marked influence on their luminescent properties. It is shown that oxygen substitutes sulphur on the sulphide crystal lattice. Interpretations are suggested for the maximum in the "glow curves" between 100°C and 500°C, and also for the nature of the colour centres in "activation-free" ZnS and CdS phosphors.

334. Ril, N. and Ortman, G.  
Injection of activators into ZnS phosphors  
by diffusion. ZHUR. OBSHCHEL' KHIM. v. 25,  
p. 1693-1700, Sep 1955. (In Russian)

Diffusion and migration of copper activators in ZnS crystals, and ZnS spectral luminescence under various temperatures were studied.

335. Antonov-Romanovskii, V. V. and Vinokurov, L. A.  
On the lowering of the luminescence yield of phosphors  
is intense excitation. SOVIET PHYS. v. 2, p. 711-13,  
July 1956. (In English) ZHUR. EKSPL.'I TEORET. FIZ.  
v. 29, p. 830-3, Dec 1955. (In Russian)

It is shown that the lowering of the luminescent output of ZnS-Cu and ZnS-Cu, Co phosphors with intense excitation is conditioned to a considerable degree by the illuminating action of the exciting light and by the fact that the recombination of optical electrons or "holes" results in radiationless transitions. The same causes result in the fact that the total illumination, as determined from the curve of increasing illumination, turns out to be considerably smaller than the total illumination as determined from the curve of the extinction process.

OPTICAL PROPERTIES

336. Antonov-Romanovskii, V. V. and Vinokurov, L. A.  
 Nature of the losses of luminescence of  
 the phosphor ZnS-Cu, Co in the region where the  
 output is independent of the intensity of the  
 exciting light. OPTIKA I SPEKTRSK. v. 1, n. 1,  
 p. 66-70, 1956. (In Russian)

It was shown by the authors and M. N. Alentsev (DOKL. AKAD. NAUK SSSR v. 94, n. 6, p. 1133, 1954) that the quantum output of luminescence of the phosphor ZnS-Cu depends upon the intensity,  $E$ , of the exciting light. Output is constant only for medium values of  $E$  and outside this plateau region output falls for both increasing and decreasing values of  $E$ . In the present paper it is shown that the basic cause of lowering of luminescent output of the phosphor ZnS-Cu with introduction of the killer Co are the non-radiative transitions associated with the movement of "holes" in the filled zone.

337. Rood, J. L.  
 Evaporated zinc sulfide films. J. OPT.  
 SOC. AMER. v. 41, p. 201-2, March 1951.

A study was made of evaporated ZnS films on glass, including method of preparation, optical properties and ageing effects. The influence of rate of evaporation and pressure during evaporation was noted. Thicknesses and indexes of refraction of the films were determined from measurements of reflected intensity as a function of wavelength. ZnS films are quite soft just after preparation but become harder if aged in a dry atmosphere.

338. Rothschild, S. and Eaton, G. K.  
 The influence of fluxes on the colour of  
 luminescent sulphides of zinc and cadmium.  
 J. PHYS. RADIUM v. 17, n. 8-9, p. 630-2,  
 Aug-Sep 1956. (In French)

The spectral distribution of the reflectivity of luminescent sulphides depends on the composition of fluxes (dimension of particles, and perhaps presence

OPTICAL PROPERTIES

of solid solutions of barium sulphide, strontium sulphide or other sulphides in the lattice).

339. Rusanova, A. I.  
X-ray luminescence of zinc sulfide luminophors.  
IZVEST. AKAD. NAUK S.S.S.R. SER. FIZ. v. 15,  
p. 754-61, 1951. (In Russian)

Luminescence spectra at 950 to 1150°C of ZnS phosphors activated with Zn, Ag, Mn, Cu, or Fe and excited by x rays or ultraviolet light are presented and discussed.

340. Ryvkin, S. M. and Konovalenko, B. M.  
Dependence of the induced conductivity in  
cadmium sulfide on the energy of exciting  
electrons. SOVIET PHYS. -SOLID STATE v. 1,  
p. 1606-9, May 1960.

In a study of the dependence of the electron-induced conductivity in CdS monocrystals on the energy of incident electrons, it was found that with increase of the electron energy the induced conductivity reached saturation.

341. Saddy, J.  
The decay of phosphorescence in zinc sulphide.  
J. PHYS. RADIUM v. 20, n. 11, p. 890-6, Nov  
1959. (In French)

The distribution of electron traps was studied using the law of decay of phosphorescence as a function of time. The brightness was measured over a long interval of time, and accurate analyses made of decay law exponentials. The trap distribution so determined is well represented by a Gaussian group. The decay law results from it by making an integral of the depth of the group,

OPTICAL PROPERTIES

as a whole. That integral may be represented, in practice, by an analysis of a suitable sum of exponential functions. The best analysis makes use of exponentials representing the successive contribution of traps of equidistant depth, taken from within the group.

342.

Schnürer, E.

SOLID STATE PHYSICS AND THE PHYSICS OF LUMINESCENT

MATERIAL. Session of the Physics Society in the

German Democratic Republic from 20 Oct to 24 Oct 1957,

in Erfurt.) Berlin (East), Akademie-Verlag, 1958.

322 p.

The relative photosensitivities of CdS crystals in light, x-ray, and gamma excitation were compared. The dependence of the photoelectric current on the voltage and intensity of the gamma irradiation, as well as the photoelectric current behavior in supplementary gamma or light excitation, was obtained. The pulse-height distribution occurring in the connection of the cells as crystal counters was studied.

343.

Schön, M.

Kinetics of emission of sulphide phosphors with

several activators. ANN. PHYS. LPZ. (FOLGE 6)

v. 3, p. 333-42, 1948. (In German)

In crystal phosphors with several activators the intensity of a given emission band is not  $\propto$  the corresponding activator but depends on the intensity and wavelength of the exciting light and on the temperature. The fluorescence and afterglow are also different. This is explained as follows: the emission follows from the recombination of electrons excited into the conduction band with the ionized activator so that the rate of recombination depends on the intensity of excitation and on its spectral distribution. By short-wave excitation the deeper lying levels of the activator are relatively more favored than the higher levels would be in the case of a thermal equilibrium, which is only established slowly by interaction of the activators with the valency band electrons. The rate of establishment of this equilibrium runs parallel with that of the recombination process and is strongly temperature dependent.

OPTICAL PROPERTIES

Reaction equations for phosphors with two activators are set down and solved. The effect of killers is related to similar causes. The interaction effects of activator with valency band influences phosphorescence, which is weakened or lost if only deeplying activator terms are excited. Some quantitative observations are made on the term scheme of ZnS phosphors.

344.

Schön, M.

Photoconduction and luminescence in crystals  
of the ZnS group. PHYSICA v. 20, n. 11, p. 930-  
49, Nov 1954. (In German)

Reaction equations for excitation of a ZnS-type phosphor are developed assuming simple emission centres with energy levels below and trapping centres with levels above the Fermi limit. Solutions for variation of luminescence and photocurrent with excitation intensity are given for the stationary state. Kinetics of "build up" and decay are also treated.

345.

Schulman, J. H. and Klick, C. C.

Luminescent centers in sulfide phosphors.  
PHYS. REV. v. 104, n. 2, p. 548, Oct 15, 1956.

The conclusion of Prener and Williams from studies of  $\text{Cu}^{65}$  formed in ZnS from  $\text{Zn}^{65}$  by K-electron capture is that an isolated copper impurity at a Zn lattice site does not constitute a luminescence centre. It is shown that this is not so since  $\text{Cu}^{2+}$  is formed whereas  $\text{Cu}^+$  is needed for the luminescence centre.

346.

Schwager, E. A. and Fischer, A.

A note on the problem of "self activation" in  
ZnS. Z. PHYS. v. 149, n. 3, p. 345-6, 1957.  
(In German)

The "self-activated" fluorescence of zinc sulphide phosphors is attributed to a change in the equilibrium conditions for Schottky defects dependent on preparation conditions.

OPTICAL PROPERTIES

347. Seiwert, R.  
 The decay of the luminescence of crystal phosphors of the ZnS type. ABHANDL. DTSCH. AKAD. WISS. BERLIN, KL. MATH. PHYS. TECH. n. 8, 22 p., 1956. (In German)

The Riehl-Schon energy band model for phosphors is used to derive decay curves for ZnS phosphors. Activator centres at one level above the valence band and traps at one depth below the conduction band are assumed. In the first treatment radiationless transitions are neglected but are later introduced together with assumption of distributed trapping levels. The agreement and differences between various theories of decay are also discussed.

348. Shionoya, S.  
 Thermoluminescence of zinc sulfide phosphors doubly activated with copper and manganese. J. CHEM. PHYS. v. 23, n. 10, p. 1976-7, Oct. 1955.

Glow curves of ZnS-Cu-Mn phosphors are explained by deep traps due to Cu (0.21 and 0.23 eV) and a shallow trap due to Mn (0.15 eV).

349. Shinoya, S. and Amano, K.  
 Sensitization of the luminescence of manganese incorporated in zinc sulfide phosphors. J. CHEM. PHYS. v. 25, n. 2, p. 380-1, Aug 1956.

The effect of additions of Pb, Ag or Bi on the luminescence ZnS. mn phosphors. From the response to varying excitation wavelength Pb acted as a sensitizer, Ag and Bi did not. This is advanced as evidence for a resonance transfer mechanism of sensitization.

OPTICAL PROPERTIES

350. Shneider, A. D.  
 Quenching of photoconductivity in HgS.  
 ZH. TEKH. FIZ. v. 26, n. 7, p. 1433-6,  
 1956. (In Russian) Translation In SOVIET  
 PHYSICS-TECH SERIES 6, p. 1400-2, 1957.

The photoconductive peak was found to occur at  $0.63 \mu$  at room temperature. No infrared quenching was observed at this temperature but an increasing amount occurred as the temperature was lowered. Low temperature results on HgS were similar to the room temperature observations on CdS by the same author (see preceding abstract).

351. Shui, Ju-tung et al  
 Effects of infrared light in post illumination  
 excitation of ZnS-Cu Sm. WU LI HSUEH PAO v. 15,  
 p. 550-8, Oct 1959. (In Chinese)

The influence of excitation intensity and infrared light on the damping curve, parameter  $\alpha$ , luminosity J, in ZnS-Cu-Sm phosphors was investigated. The variations of  $\alpha$  and J following day-light excitation at various conditions are analyzed. The mechanism of damping parameter changes induced by infrared light was determined.

352. Sihvonen, Y. T., Boyd, D. R. and Woelke, C. D.  
 Some properties of green and red-green luminescing  
 CdS. PHYS. REV. v. 113, n. 4, p. 965-8, Feb 15, 1959.

A series of electro-optical experiments at room temperature were made with two types of high-purity single crystals of CdS. Those of type A, believed to have near-perfect stoichiometry, luminesce green ( $5145 \text{ \AA}$ ) under  $3650 \text{ \AA}$  ultra-violet irradiation, have low dark conductivity ( $2.5 \times 10^{-11} \text{ mho cm}^{-1}$  at  $300^\circ\text{K}$ ), exhibit no photopeak, and have a relatively short carrier lifetime (about 4 microseconds or less). Those of type B, believed to have a sulphur deficiency, luminesce first strongly red ( $\approx 7200 \text{ \AA}$ ), then strongly green ( $>5145 \text{ \AA}$ ) as the exciting radiation is increased in intensity. Simultaneously both emissions

OPTICAL PROPERTIES

shift toward longer wavelengths. Also, as the red emission intensity begins to saturate, the intensity-rate change of conductivity abruptly changes. It is suggested that red luminescence is the result of a free hole capture by one of the electrons residing in a sulphur vacancy. This trapping sensitizes the crystal but at the expense of increasing carrier lifetime to millisecond magnitudes. Furthermore, some of these vacancies ( $\sim 0.4$  eV below the conduction band) act as donors to increase dark conductivity (about  $10^{-9}$  mho  $\text{cm}^{-1}$  at 300°K.

353. Smidt, D.

The decay of luminescence of Ag activated Zn sulfide phosphors after excitation by single alpha particles and electrons. ANN. PHYSIK v. 15, p. 325-36, March 1955. (In German)

354. Smith, A. W. and Turkevich, J.

A study of the electron traps in zinc sulfide phosphor. PHYS REV. v. 87, p. 306-8, July 15, 1952.

The thermoluminescence characteristics of a hexagonal ZnS phosphor, Cu-activated, were measured as a function of the wavelength of the exciting light. The glow curve had maxima at 120, 220 and 280°K. It was found that the heights of these maxima at saturation varied with the wavelength of the exciting light, reaching the greatest values at  $4\ 270\ \text{\AA}$  for the 120°K maximum,  $4\ 400\ \text{\AA}$  for the 220°K maximum, and  $4\ 500\ \text{\AA}$  for the 280°K maximum. When the sample was irradiated with  $4\ 400\ \text{\AA}$  light for a definite time interval and then irradiated with monochromatic radiation of either shorter or longer wavelength for another time interval, it was found that the subsequently measured glow curve showed a decrease in the heights of the maxima from that with  $4\ 400\ \text{\AA}$  light alone. Since the glow curve can be interpreted as a process of emptying electrons from traps, the above results are interpreted to mean that light which is capable of filling the traps is also capable of stimulating electrons out of the traps. There is a long wavelength limit beyond which irradiation does not affect electrons present in traps. It is 0.7 micron for the trap represented by the 280°K maximum.

OPTICAL PROPERTIES

355. Smith, A. W. and Turkevich, J.  
Effect of neutron bombardment on a zinc  
sulfide phosphor. PHYS. REV. v. 94, p. 857-  
65, May 15, 1954.

An investigation has been made of the effect of neutron irradiation on the following properties of a copper-activated zinc sulfide phosphor: luminescence efficiency under ultraviolet and x-ray excitation, infrared quenching of luminescence, temperature dependence of luminescence efficiency, thermoluminescence, rise time of luminescence, and dependence of the rise time of luminescence on the previous history of the sample. In addition, the analogous changes in the dielectric constant of the phosphor on illumination were measured for samples damaged to a varying degree by neutrons. It was shown that neutron damage can be removed by annealing at high temperature.

356. Snyder, D. D. and Bleil, C. E.  
On the mechanism for carrier excitation in CdS.  
J. APPL. PHYS. v. 30, n. 6, p. 736-9, May 1959.

Induced conductivity in CdS crystals produced by electron bombardment (cathodoconductivity) and the associated X-ray production were studied employing electrons in the 30 to 60 keV range. The conductivity induced solely by these X-rays was studied. Using classical X-ray theory, the production and absorption of X-rays in the experimental crystals were calculated. Some confirmatory data are presented. From calculated excitation rates and observed conductivities the X-rays produced by impinging electrons are shown to be sufficient to explain the effects observed in cathodoconductivity, and may be significant in cathodoluminescence.

357. Socra, T. Y. and Serdyule V. V.  
A new band in the absorption spectrum of  
polycrystalline layers of CdS. ACAD. SCI  
USSR. OPTICS & SPECTROSCOPY v. 9, n. 3, p. 210,  
Sep 1960.

OPTICAL PROPERTIES

358.                   Soo, Lee Sang  
Ageing effect in evaporated films of zinc  
sulphide. PROC. PHYS. SOC. v. 74, p. 641-3,  
Nov. 1959.

Changes in the phase retardation of light transmitted by approximately  $\lambda/4$  ZnS films of order  $1^{\circ}$  were found over periods of a few days.

359.                   Soudek, I.  
The dependence of the decay of luminescence  
on the surface concentration of the sample.  
CZECH. J. PHYS. v. 8, n. 3, p. 332-5, 1958.  
(In Russian)

The decay of luminescence was measured of zinc-cadmium sulphide films of varying thickness after ultraviolet excitation. The films were sprayed on to a layer of nitrocellulose lacquer on a glass plate. The phosphor contained 49% ZnS, 51% CdS,  $10^{-4}$  Ag as an activator and of the order of  $10^{-6}$  Cu as an impurity. The surface concentration of the phosphor was determined by weighing the sample, washed from the glass. The average thickness was calculated from the density of the phosphor. Two of the films were not continuous. There is a slight difference between the initial intensities of the thicker films, only a thinner distribution of the crystals causing a more marked decrease. The time dependence of the logarithm of the intensity of decay was plotted. The relative (and to a certain extent also the absolute) difference between the values of the various curves increases with time. Qualitatively the same dependences were observed on zinc-cadmium sulphides activated by copper. The results of these measurements can be interpreted as follows: a certain interaction between the crystals supports the intensity of decay and this interaction decreases with increasing distance between the crystals. This interaction can be either optical or electronic; the fact that the distance between the crystals in continuous films is of the same order as the mean free path of the electron in air speaks for electronic interaction.

OPTICAL PROPERTIES

360.

Soudek, I.

The study of the photodielectric luminescence properties of ZnS and CdS. CZECHOSLOV. J. PHYS. v. 9, p. 590-6, 1959. (In German)

The spectral dependence of the photodielectric luminescence properties of various compositions of ZnS and CdS shows that a Cu impurity develops a phase with greater polarizability, which results in a change in the actual component of the dielectric constant. The copper concentration can be limited, in that it is not important in the luminescence emissions. The infrared loss maxima correspond to levels established by other authors and methods. The maximum excitation spectra of the attendant lines of the absorption margin range are connected with the maximum variation of the actual components of the dielectric constant.

361.

Soudek, I.

Influence of temperature on the spectral composition of the zinc sulphide luminescence. BRIT. J. APPL. PHYS. v. 11, n. 7, p. 289-92, 1960.

The temperature dependence of the spectral composition has been presented by a new method which shows better the relative changes of the form of the emission band. On the main emission band of some zinc and zinc-cadmium sulphides, between the liquid air temperature and the temperature break-point, certain effects have been observed; these are that (a) below 180°K the short wave side of the emission band of all phosphors grows faster than the long wave side with increasing temperature, (b) that in the neighbourhood of 220°K, the intensity of the whole band has a minimum for all copper-activated and copper-contaminated phosphors, and that (c), above 220°K some phosphors behave inversely as (a). These effects can be explained by the existence of two temperature-dependent processes having inverse influence on the form of the emission band, one being similar to the hole-migration process and the other being in connection with the thermal liberation of trapped electrons.

OPTICAL PROPERTIES

362. Soudek, I.  
Study of the photodielectric phenomenon in  
luminescing zinc cadmium sulphides. CZECH.  
J. PHYS. v. 9, n. 5, p. 590-6, 1959.  
(In German)

Powder layers of ZnS and ZnCdS without binder were used to measure the spectral distribution of excitation, of luminescence, and of the alteration under irradiation of the real component of the dielectric constant  $\epsilon'$  and of the dielectric loss. A trace of Cu insufficient to evoke its characteristic luminescence in the phosphors can cause an alteration in  $\epsilon'$ . The spectral maximum of  $\Delta\epsilon'$  agrees with the excitation maximum.

363. Soudek, I.  
Temperature dependence of the photoluminescence  
intensity of zinc-cadmium sulphide. CZECH. J.  
PHYS. v. 7, n. 1, p. 109, 1957. (In Russian)

The photoluminescence intensity, studied in the range  $10^{\circ}$ - $370^{\circ}$ C, is found to vary non-monotonically with temperature, and to display hysteresis. Although the non-monotonic nature of the variation and the change in colour with temperature can be explained by the existence of two types of luminescence centre, this does not account for the hysteresis. The latter is explained by the occurrence of red centres at higher temperatures, and the increase in their concentration with temperature; since a definite time is required for formation and annihilation of these centres, their concentration at a given temperature is greater when the temperature is decreasing. Another possibility is that quenching of red centres occurs at a lower temperature than that for formation.

OPTICAL PROPERTIES

364.

Soudek, I.

The temperature dependence of the  
photoluminescence of silver-activated

zinc-cadmium sulphides. CZECH. J.

PHYS. v. 8, n. 1, p. 66-80, 1958.

(In German)

Five samples of ZnS or ZnCdS were excited by long wavelength u.v. and their light output measured at a single wavelength in each experiment during temperature cycles to about 200°C. Some heating and cooling curves coincided, but often on cooling the original output was regained more slowly. This hysteresis effect was attributed to traces of copper in the phosphors. Excessive heating produced permanent losses in the fluorescence. The temperature dependence varied for different emission wavelengths in the same phosphor, showing the presence of subsidiary bands. The non-linear response to altered irradiation intensity was also studied.

365.

Steinberger, I. T., Low, W., and Alexander, E.

Influence of alternating electric fields on  
the light emission of some phosphors. PHYS.

REV. v. 99, p. 1217-22, 1955.

The influence of an alternating electric field on the fluorescence and phosphorescence of various ZnS and ZnS:CdS phosphors was investigated. The light pulses and the average brightness of the luminescence were measured simultaneously. The wave pattern during fluorescence consists of two different pulses per cycle. The two pulses differ in their respective amplitudes, time dependence, and shape. The pulses corresponding to positive polarity of the illuminated electrode show a similar behavior for all phosphors. The second pulse differs for the various phosphors. Voltage dependence of the amplitudes and light sums per cycle were found to be different for the two pulses. These two pulses must be due to two different processes and suggest surface effects.

OPTICAL PROPERTIES

366.                   Stöckmann, F.  
                           On the physics of crystal phosphors. II.  
                           NATURWISSENSCHAFTEN v. 39, p. 246-54,  
                           1952. (In German)

The review of luminescence, conductivity and related effects in phosphors is continued. Topics include the quantitative treatment of phosphorescence, relation between phosphorescence and fluorescence, thermoluminescence and the energy spectrum of trapping states. Phosphors considered include alkali and silver halides and Zn, Cd and alkaline earth sulphides. Sixty-three references are given to past and modern work in the field.

367.                   Svechnikov, S. V.  
                           Properties of cadmium sulphide photocells  
                           irradiated by  $\gamma$ - and  $\beta$ -rays. ZH. TEKH. FIZ.  
                           v. 26, n. 8, p. 1646-50, 1956. (In Russian)

Three types of photocells were studied: thin single crystal, thick single crystal and polycrystalline layer. The sensitivities to  $\beta$ - and  $\gamma$ -radiation are plotted as a function of energy of radiation and of voltage applied to cell.  $\text{Co}^{60}$ ,  $\text{P}^{32}$  and  $\text{Ir}^{192}$  were used as sources. Thin specimens were found to be more sensitive to soft radiation and thick specimens to hard. The growth and decay time constants of the photocurrent were of the order of tens or hundreds of seconds. Comparisons are made with the author's X-ray observations.

368.                   Svernikov, S. V.  
                           Comparison of CdS (monocrystal) and CdS  
                           (polycrystal) photoresistance in the x-ray  
                           region. ZHUR. TEKH. FIZ. v. 27, p. 656-62,  
                           1957. (In Russian)

Dosimetric properties of CdS monocrystals and CdS compressed powder polycrystals in x radiation are evaluated.

OPTICAL PROPERTIES

369. Svechnikov, S. V.  
 Properties of monocrystalline photo-resistivities  
 of cadmium sulphide when excited by Röntgen  
 rays. ZH. TEKH. FIZ. v. 22, n. 8, p. 1305-14,  
 1952. (In Russian)

The photo-resistivities of monocrystals of cadmium sulphide possess great sensitivities in the region of hard ionizing radiation. With properly chosen illumination it is possible to increase the sensitivity of the crystal in the ionizing radiation by 1.5 to 2 times. The photo-resistivity of cadmium sulphide can be successfully utilized on alternating as well as constant currents.

370. Thomas, D. G., Hopfield, J. J., and Power, M.  
 Excitons and the absorption edge of cadmium  
 sulfide. PHYS. REV. v. 119, n. 2, p. 570-4,  
 1960.

The absorption coefficient between 10 and  $300\text{ cm}^{-1}$  was measured for crystals of CdS in polarized light between 20 and  $300^{\circ}\text{K}$ , at wavelengths near 5000 Å. Analysis of the results at various temperatures near  $70^{\circ}\text{K}$  shows that the absorption is in agreement with that calculated for a process involving the simultaneous creation of an exciton and the absorption of a phonon, both particles having a small wave vector. This agreement is strong evidence that the conduction band minimum and the valence band maximum in CdS both occur at the centre of the Brillouin zone.

371. Thomas, D. G., and Hopfield, J. J.  
 Exciton spectrum of cadmium sulfide. PHYS.  
 REV. v. 116, p. 573-82, 1959.

The reflectance and fluorescent spectra of hexagonal CdS crystals were measured at  $77^{\circ}$  and  $4.2^{\circ}\text{K}$  using polarized light in the region of 5000 Å. Structure not previously reported was found in the reflectivity curves which leads to the identification of three exciton series. These can be understood in terms of the splitting of the valence band into three levels at  $k = 0$ .

OPTICAL PROPERTIES

The observation of excited exciton states and the polarization properties of the excitons make possible: (1) The determination of two of the three exciton binding energies, (2) the determination of the energy splittings of the three valence bands, (3) the verification of the symmetry assignments of the valence and conduction bands, and (4) correlation of the work of others with the present work, showing that the definite intrinsic effects are consistent both with our observations and our interpretations. The fluorescent experiments strongly suggest that the radiative decay of excitons occurs not directly, but from localized impurity exciton states in agreement with theory.

372. Thureau, P., and Leroux, J. P.

A pyrometric application of the photoluminescence  
of ZnS:Cu excited by ultraviolet radiation  
(366 m  $\mu$ ) modulated at a frequency of 100 c/s.

C. R. ACAD. SCI. (PARIS) v. 250, n. 26,  
p. 4301-3, 1960. (In French)

The emission of a ZnS:Cu phosphor under a Wood's glass lamp is modulated at 100 c/s, and the relation between the degree of modulation and the mean level of emission varies with the intensity of excitation, the layer thickness, and the temperature. From oscilloscope measurements of the emission and a family of curves drawn for different values of the first two parameters, the temperature of the sample may be determined.

373. Trapeznikova, Z. A.

Some optical properties of new luminophors  
activated by elements of the rare earth group.

POSTEPY FIZ. v. 9, p. 211-20, 1958. (In Polish)

Observation of luminophors activated by Nd, Pr, Sm, Dy, Eu, and Tm shows the appearance of absorptions of a linear character in the visible spectrum. By the application of radiation with a wave length corresponding to these lines a weak luminescence was induced (also of a linear type) in ZnS-Er at room and low temperatures and in ZnS-Dy and ZnS at liquid nitrogen temperature. The strong luminescence of luminophors activated by lanthanides is not connected with any absorption of light by these activators. The influence of oxygen on the luminescence and excitation spectra of Zn-Sm was observed in

OPTICAL PROPERTIES

the spectrum of ZnS and Sm ( $1.9 \times 10^{-4}$  g-atom Sm/mol ZnS) dried at  $300^{\circ}\text{C}$  in a stream of N purified of oxygen and then heated in a stream of N at  $1150^{\circ}\text{C}$ . The ZnS-Sm luminescence spectrum produced by radiation of wave length  $\lambda = 365 \text{ m}\mu$  consists of three lines: red, orange, and green; red is most intense. Introduction of ZnO causes the appearance of an additional wide green strip. It is concluded that with ZnO introduction ( $2.4 \times 10^{-2}$  mole ZnO/mole ZnS) the number of primary centers of luminescence in which the Sm ion was surrounded by S ions decreases and the number of centers where O replaced S increases. Introduction of other anions, such as selenium, to ZnS also causes changes in the luminescence spectrum.

374.

Trapeznikova, Z. A.

Luminescence centers in phosphors of zinc sulfides activated by samarium. IZVEST.

AKAD. NAUK. S.S.S.R., SER. FIZ. v. 23,

p. 1319-25, 1959. (In Russian)

The formation of luminescence centers in the case when the introduction of an activator is followed by the formation of anion and cation vacancies was investigated. Newly formed vacancies may appear near the activator ions, creating new luminescence centers. Also, an increased luminescence can be achieved by activator-ion pairing as a function of activator concentration. It was found that samarium can simultaneously form three or more types of luminescence centers with variant electron and vacancy captures depending on the samarium concentration and the preparation method.

375.

Trofimenko, A. P., Fedorus, G. A., Razmadze, A. K.

Some peculiarities of heat stimulated conductivity in CdS single crystals. FIZ.

TVERDOGO TELA v. 2, p. 1141-7, 1960.

(In Russian)

The temperature dependence of the electron-capture cross section of CdS(S) monocrystals was determined, and the trap saturation magnitude was experimentally verified at the thermally stimulated conductivity maximum. The photosensitivity was correlated with the regions under the thermal stimulation conductivity curves. The effects of etching and glow discharge treatment on thermally stimulated conductivity were determined.

OPTICAL PROPERTIES

376. Tolstoi, N. A.  
Luminescence flashes in zinc sulfide  
crystals and the two-stage excitation  
mechanism. SOVIET PHYS. (DOKLADY) v. 1,  
p. 698-700, 1956.

Investigations in the area of luminescence flashing have shown this phenomenon to be much more universal than was anticipated. It can be used as the basis for a new method of investigating local phosphor levels. The processes revealed by the investigations are used in the construction of a theory of phosphorescence in sulfide phosphors.

377. Tolstoi, N. A.  
Flash outburst [of luminescence] of the phosphor  
ZnS-Ni. OPTIKA I SPEKTROSK v. 1, n. 2,  
p. 271-2, 1956. (In Russian)

The author and P.P. Feofilov drew attention to this kind of burst of luminescence in 1949. The present paper describes some results obtained with ZnS-Ni provided by A.A. Bundel', which gives strong bursts of illumination in the long-wave band far exceeding in intensity those of ZnS-Mn. Contents of Ni employed were  $10^{-7}$ ,  $10^{-6}$ ,  $5 \times 10^{-6}$ ,  $10^{-5}$  g/g. Afterglow persistence exceeded 24 hours at room temperature. It is suggested that the bursts of luminescence of this type may be a much more widespread phenomenon than it has appeared up to now.

OPTICAL PROPERTIES

378. Tolstoi, N. A.  
 A flash-like burst of luminescence in zinc sulphide phosphors, and the two-step mechanism of its stimulation. DOKL. AKAD. NAUK. S.S.S.R. v. 111, n. 3, p. 582-4, 1956. (In Russian)

Many ZnS phosphors after prolonged exposure to constant 365 m $\mu$  excitation luminesce with intensity  $I_0$ , but after excitation is stopped for time  $t$  and then restored show a burst of luminescence of intensity  $I > I_0$ .  $I/I_0$  has a maximum value, almost independent of excitation intensity, for  $t = t_{max}$ . The value of  $1/t_{max}$  is found to vary as  $\exp(-1/T)$ .  $I/I_0$  can be as much as 6 [for ZnS(Ni)]. The effect is interpreted in terms of serially operative trapping centres, electrons being excited to the luminescent centres (L) via source and flash-generating centres (S and F). On interruption of excitation electrons from S fall to F, filling the latter above the previous (constant excitation) level, so that subsequent excitation can transfer a larger-than-steady-state number of electrons to L. Infrared background radiation was found to affect the process in a manner consistent with this mechanism. Similar effects have been observed in Cd<sub>2</sub>P<sub>2</sub>O<sub>7</sub>(Mn + Pb) and TlCl phosphors.

379. Tolstoi, N. A.  
 A relationship between the blue and red emission bands in the ZnS:Co phosphor.  
 OPTIKA I SPEKTROSK v. 3, n. 1, p. 73-5, 1957. (In Russian)

Preliminary results are reported on the relationship between the steady-state emissions of the blue (Zn) and red (Co) bands of the ZnS:Co phosphor containing 5 p.p.m. by weight of Co. As temperature is increased from -20° to +120°C the blue emission intensity falls and the red emission becomes stronger. This is due to transfer of electrons or holes from short-wavelength centres (first localization levels) to other, energetically lower, localized states (second localization) which are located at the long-wavelength centres of emission; the rate of this transfer increases with temperature.

OPTICAL PROPERTIES

380. Tolstoi, N. A., and Ryskin, A. I.  
 Superlinearity in the luminescence and  
 photoconductivity phenomena and the  
 Rose-Bube theory. OPTIKA I SPEKTROSK  
 v. 8, n. 2, p. 272-4, 1960. (In Russian)

An experimental study of the superlinear dependence of luminescence and photoconductivity of CdS on the excitation intensity did not confirm the theory of Rose and Bube (Abstr. 2886 of 1956 and J. Phys. Chem. Solids, Vol. 1, 234, 1957), but the results were in good agreement with the main ideas of the two-step theory of Lashkarev and Fedorus (1952) and Tolstoi (Abstr. 5015 of 1956), which assumes a rise of the quantum yield of electrons transferred to the conduction band with the excitation intensity.

381. Tomlinson, T. B.  
 Luminescence in ZnS : Cu, Cl single crystals.  
 J. ELECTRONICS v. 2, n. 3, p. 293-300, 1956.

The impurity responsible for the green and blue bands in "spectrographically pure" single crystals of zinc sulphide is proved to be copper, in conjunction with chlorine. The crystal growth process tends to exclude chlorine so that introduction of copper results in luminescence typical of a low chlorine content, i.e. there is no green-2 band and the electroluminescence is blue at room temperature. The diffusion rate of chlorine is found to be much less than that of copper so that attempts to introduce both copper and chlorine into the crystals were unsuccessful. The provision of copper during crystal growth permits the retention of a greater chlorine content. This gives both the green-2 band and green electroluminescence.

382. Tomlinson, T. B.  
 Luminescence in ZnS : Cu, Cl phosphors at  
 high Cu concentration. J. ELECTRONICS v. 2,  
 n. 2, p. 166-78, 1956.

ZnS phosphors prepared with a varied Cl content and with 0.3% added Cu, have been analysed for both Cu and Cl. There is found to be a close

OPTICAL PROPERTIES

interdependence between the incorporated Cu and Cl, and the ratio of Cu : Cl in gram atoms per mole, is near to unity over a wide range of concentrations. This implies that there is only one copper centre, viz.  $\text{Cu}^+$ . Spectral distribution curves of emission show that the ratio of the intensities of the blue and green-2 emission bands is a function of temperature as well as of the Cl concentration. The spectral distribution of the electroluminescence is similarly temperature dependent. A close comparison of the spectral emission distributions of the "copper-blue" and "self-blue (Zn)" bands in ZnS phosphors at various temperatures shows that there are distinct differences between them. They are not identical as other authors have recently suggested. The origin of the blue and green luminescence bands due to Cu activator is discussed.

383. Trapeznikova, Z. A.  
Luminescence centers in samarium activated  
ZnS phosphors. BULL. ACAD. SCI. U.S.S.R. -  
PHYS. SER. v. 23, n. 11, p. 1306, 1959.
384. Trapeznikova, Z. A., and Shchaenko, V. V.  
Some optical properties of the new zinc  
sulfide phosphors, activated by rare  
earth elements. DOKLADY AKAD. NAUK.  
S.S.S.R. v. 106, p. 230-2, 1956. (In Russian)

Rare-earth-activated zinc sulfides have been obtained by adding some fusing agent and the coactivators. Experiments with annealing in atmospheres of  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and  $\text{N}_2$ , and in vacuum produced the following systems: ZnS-Nd, ZnS-Pr, ZnS-Sm, ZnS-Dy, ZnS-Er, ZnS-Tm, and ZnS-Eu. Variations in the spectra of activated ZnS phosphors in relation to the annealing atmosphere indicate that various luminescent centers are formed under different atmospheric conditions. The experiments established that the luminescence of the trivalent rare earth ions of these phosphors results from the transition energy which is absorbed by the substances and from special centers absorbing in the narrow range of  $\sim 333 \text{ m}\mu$ .

OPTICAL PROPERTIES

385. Trapeznikova, Z. A.  
 On the interaction of "blue" and "samarium"  
 centres in the ZnS:Sm(Cl) phosphor. OPTIKA  
 I SPEKTROSK v. 6, n. 4, p. 512-16, 1959.  
 (In Russian).

Reports studies of the dependence of the intensity of luminescence due to "blue" and activator centres on the intensity of excitation in ZnS:Sm and ZnS:Sm(Cl) and of the temperature dependence of the luminescence spectra of these phosphors. An interpretation of the results obtained is given and a mechanism of energy transfer between "blue" and "samarium" centres is suggested.

386. Vasil'eva, E. G., and Fridman, S. A.  
 Use of thermography for investigating ZnS.  
 BULL. ACAD. SCI. U.S.S.R.-PHYS. SER. v. 23,  
 n. 11, p. 1333, 1959.

387. Veith, W., and W rick, G.  
 An effect of light on semiconductors: a  
 variation in the contact potential difference.  
 C. R. ACAD. SCI. (PARIS) v. 233, p. 1097-9,  
 1951. (In French)

A method of preparing a highly sensitive CdS layer and operating it in vacuo is described. It is found that a formula will describe with sufficient accuracy the variation of the difference of the contact potential between a reference metal and a semiconductor when the latter is illuminated and then obscured. This difference increases with the ambient temperature. The curves obtained with the semiconductor illuminated and then dark are strictly parallel up to saturation point.

OPTICAL PROPERTIES

388. Vergunas, F. I.  
 Law of attenuation of afterglow of ZnS  
 phosphors close to and in the region of  
 temperature extinction. OPTIKA I SPEKTROSK  
 v. 1, n. 3, p. 416-26, 1956. (In Russian)

To account for the observed behaviour of the afterglow of ZnS phosphors in the temperature extinction region after the exciting light has been cut-off the author assumes that the kinetics of extinction change from monomolecular to bimolecular type.

389. Vergunas, F. I., and Lukontsever, Yu. L.  
 Determination of the absolute values of the  
 parameter  $\gamma$ , equal to the ration of probabilities  
 of localization and recombination, for the ZnS-Cu  
 phosphor. OPTIKA I SPEKTROSK v. 5, n. 2, p. 156-61,  
 1958. (In Russian). English summary: PBl41047T-5,  
 obtainable from Office of Technical Services, U.S.  
 Dept. of Commerce, Washington, D.C., U.S.A.

The ratio of the probabilities of trapping and recombination  $\gamma$  is derived for phosphors with one depth of trapping levels and one type of emission centres. Experimental confirmation was obtained with a ZnS:Cu phosphor, that as the temperature increased,  $\gamma$  first increased and then tended to zero as thermal quenching occurred.

390. Vinokurov, L. A., and Fok, M. V.  
 Quenching of the phosphors ZnS-Cu, Co and  
 ZnS-Cu, Ni by infrared light. OPTIKA I  
 SPEKTROSK v. 1, n. 2, p. 248-54, 1956. (In Russian)

Since the decay of the afterglow of these phosphors under the action of infrared light is hyperbolic instead of exponential the quenching action of the infrared

OPTICAL PROPERTIES

must be external. A theoretical formula is derived for the variation of brightness of the phosphor with respect to the intensity of the exciting light. An explanation is offered for the killer action of Co and Ni in these phosphors.

391. Vinokurov, L. A., and Fok, M. V.  
The simultaneous action of light and electric fields on phosphors. OPTIKA I  
SPEKTROSK v. 7, n. 2, p. 241-3, 1959.  
(In Russian)

The effects of light and electric fields were found to be non-additive: in some cases the luminescence brightness due to simultaneous excitation was higher and in other cases it was lower than the sum of the brightnesses of both types of luminescence. In two ZnS:Cu,Al phosphors the maximum observed non-additivity amounted to about 10%. The authors show that the exact additivity can be obtained when  $A/B = \text{const.}$ , where A and B are the number of acts of ionization of luminescence centres per unit volume and per unit time due to light and due to electric field respectively.

392. Vlasenko, N. A.  
The effect of temperature on photoluminescence of the sublimated phosphor ZnS:Mn. OPTIKA I  
SPEKTROSK v. 8, n. 6, p. 847-54, 1960.  
(In Russian)

The effect of temperature on the absorption and luminescence spectra of the sublimated phosphor ZnS:Mn was investigated between 100° and 550°K and the temperature dependence of the relative quantum yield of luminescence was obtained for samples with amounts of Mn from 0.05 to 5%. The results obtained were used to reduce the mechanism of excitation of luminescence centres, the nature of luminescent and radiation less transitions and the kinetics of concentration quenching.

OPTICAL PROPERTIES

393. Vlasenko, N. A.  
Investigation of the fundamental absorption  
spectrum of zinc sulphide. OPTIKA I SPEKTROSK  
v. 7, n. 4, p. 511-17, 1959. (In Russian)

The fundamental absorption spectrum (in the spectral region 220-600 m $\mu$ ) of zinc sulphide films produced by vacuum deposition at  $5 \times 10^{-5}$  mm Hg was investigated. The spectrum had a maximum at 325 m $\mu$  and a region of strong absorption at long wavelengths, extending to 550 m $\mu$ ; the latter was absent in the spectrum of ZnS crystals and it disappeared in the case of films when the latter were heat-treated in sulphur vapours or in vacuum. The 325 m $\mu$  band represents formation of the first excited state of the lattice by transition of electrons from negative ions to the nearest positive ions. The long-wavelength absorption is due to lattice defects such as dislocations or grain boundaries, or it may be related to localization of the excited state of the lattice at the defects. The temperature dependence of the form of the absorption spectrum of ZnS was obtained between 110 and 500°K.

394. Waibel, E.  
On the excitation efficiency for red and  
green luminescence of cadmium sulphide  
crystals. ANN. PHYS. (LEIPZIG) v. 17,  
n. 6-8, p. 389-400, 1956. (In German)

The quantum yield of fluorescence is measured for intense Hg line excitation between 0.365  $\mu$  and 0.578  $\mu$  wavelengths and for micro and single crystal specimens. Transmission and reflection spectra for the latter yield the absorption coefficient. At 90°K for the green emission a quantum efficiency of 0.2 is found and for the red emission a value of 0.4 is obtained.

OPTICAL PROPERTIES

395. Waibel, E., and Seiwert, R.  
The quantum yield of the red luminescence  
of cadmium sulphide at room temperature  
and for excitation with u.v. light. J.  
PHYS. CHEM. (LEIPZIG) v. 205, n. 5,  
p. 266-84, 1956.

A discussion of the measuring technique for determination of the quantum yield of luminescence is given. A value of 0.2 is obtained for the maximum efficiency of a CdS phosphor excited by 3650 Å radiation.

396. Warncke, J., and Neuert, H.  
Differences in fluorescence decay of ZnS(Ag)  
for particles of different ionization thicknesses.  
NATURWISSENSCHAFTEN v. 47, p. 11, 1960.  
(In German)

The pulse discrimination effect in ZnS(Ag) was studied using Po  $\alpha$  particles, (D,D) protons, and secondary electrons. The pulses thus obtained produced voltage pulses in relation to the fluorescence decay process from which current pulses were obtained by graphic differentiation according to work-time constant considerations. These current pulses were then analyzed from exponential decay components. By selection of the proper time constants a direct particle discrimination is possible.

397. Warschauer, D. M., and Reynolds, D. C.  
Edge and impurity emission in cadmium sulfide.  
PHYS. REV. LETTERS v. 3, n. 8, p. 370-2, 1959.

The variation of the edge and impurity emission of a copper doped crystal was examined as a function of the angle of polarization. The edge emission reaches a peak for the electric vector perpendicular to the c-axis, whereas the impurity emission is a maximum for the electric vector along the c-axis. A band structure of CdS is proposed to account for these results.

OPTICAL PROPERTIES

398. Warschauer, D. M., and Reynolds, D. C.  
Mechanically-excited emission in cadmium  
sulfide. J. PHYS. CHEM. SOLIDS v. 13, n. 3-4,  
p. 251-6, 1960.

The phenomenon of radiative emission obtained by mechanical excitation of optically or thermally stimulated cadmium sulphide is described and discussed in terms of the recently proposed band structure of the material and the existence of trapping levels in the forbidden-gap region.

399. Williams, F. E.  
Nature of luminescent centers in alkali  
halide and zinc sulfide phosphors. J. OPT.  
SOC. AMER. v. 47, n. 10, p. 869-76, 1957.

The present state of understanding of the luminescent centres in alkali halide and zinc sulphide phosphors is reviewed. These two classes of phosphors complement each other: the first is ionic; the second, primarily covalent. The energy levels of luminescent centres in alkali halides are approximated by states of the free impurity ion perturbed by crystalline interactions, whereas the levels of luminescent centres in zinc sulphide phosphors are suitably approximated by states of the crystal band structure perturbed by impurities. The theory of the excitation and emission spectra of thallium-activated potassium chloride is reviewed and extended to the problem of oscillator strengths for luminescent transitions.

400. Wlérick, G., and Prégermain, F.  
Study of the physical properties of  
thin-layer photo-elements of cadmium  
sulphide. J. PHYS. RADIUM v. 15, n. 11,  
p. 757-64, 1954. (In French)

OPTICAL PROPERTIES

401. Zhukova, N. V.  
Investigation of storage and origin  
of the localized electron levels in zinc  
sulfide phosphors. DOKLADY AKAD. NAUK  
S.S.S.R. v. 103, p. 1001-4, 1955.  
(In Russian)

The origin of local levels and the storage of accumulated phosphorescence on levels of various depths as well as the thermal release of phosphorescence are studied using the thermal method for phosphorescence of phosphors. Samples of ZnS-Cu phosphors, prepared by the author, were calcined in a closed quartz crucible furnace for 15 min. in 1100° temp. Excitation was induced for 10 min. by a section of mercury spectrum from a wave of  $\lambda$  366 to  $\lambda$  436  $\mu$ .

402. Zhukova, N. V.  
Investigation of the origin of levels of  
electron localization in zinc sulphide  
phosphors. ZH. ÉKSPER. TEOR. FIZ. v. 29,  
n. 5(11), p. 680-92, 1955. (In Russian)  
English translation In: SOVIET PHYSICS JETP  
(NEW YORK) v. 2, n. 4, p. 608-19, 1956.

The role of copper and oxygen in the formation of three bands of localization levels of electrons in ZnS(Cu) phosphor is clarified by the method of temperature controlled luminescence. The action of iron, nickel and cobalt on the separate maxima of the temperature controlled luminescence curve is examined. It is found that Fe and Ni in small concentrations may sharply increase the intensity of luminescence.

OPTICAL PROPERTIES

403.

Zyryanov, G. K.

Variation of the cadmium sulfide contact potential during illumination. ZH. TEKH.

FIZ. v. 28, n. 12, p. 2657-68, 1958.

(In Russian). English translation In:

SOVIET PHYSICS-TECHNICAL PHYSICS (NEW

YORK) v. 3, n. 12, p. 2429-38, 1958.

The photoshift method (displacement of the V-I curves) was used with simultaneous measurement of the electron current due to scattering and reflection from the CdS surface layer. It was found that reflection of slow electrons with energies from 1 to 10 eV at the semiconducting layer did not increase monotonically, but displayed minima and maxima at given electron velocities. The minima are presumably due to inelastic collisions between the electrons and their subsequent transition from the filled band to the conduction band (in this way it is possible to measure the width of the forbidden zone). The time and spectral relationships of the photoshift are similar to the corresponding photoconductivity curves. The dependence of the photoelectric shift on the intensity of illumination is logarithmic. It is demonstrated that the experimental data can be described by the known photo-e.m.f. formula without the necessity for an adsorbed gas film at the CdS surface, as postulated by Wlerick. Evaluation of the coefficients in the experimental formula gives a "quantum yield" in excess of  $10^3$ . The possibility of explaining the results on the basis of diffusion theory is investigated.