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# Magnetic Properties of Zinc Sulfide and Cadmium Sulfide Phosphors*

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Measurements of magnetic susceptibility were made of various preparations of zinc sulfide and cadmium sulfide by the Gouy method, from 77°K to 300°K. The materials differed in crystalline state and modification, type and content of impurities, methods of preparation, and neutron radiation treatment. No temperature-dependent paramagnetism was found for either the zinc sulfides or the cadmium sulfides. The diamagnetism was dependent on the variables cited above.

Uncrystallized zinc sulfide obtained by precipitation had a specific diamagnetic susceptibility of $-0.36\times10^{-6}$, while that of cadmium sulfide was $-0.268\times10^{-6}$. On crystallization, the susceptibility values obtained depended on whether air, nitrogen or hydrogen-sulfide atmospheres were used during the crystallization, and whether chloride or aluminum ion "flux" was used. Only small differences were found in the susceptibilities of the cubic and of the hexagonal forms of zinc sulfide.

It has been postulated that $Cl^{-1}$ or $Al^{+3}$ aided in the luminescence of zinc sulfide phosphors by allowing the formation of monovalent zinc, through charge compensation. It would be expected that this monovalent zinc would give rise to a temperature-dependent paramagnetic species. No such paramagnetism was found. Instead, the diamagnetism increases, suggesting that the role of the $Cl^{-1}$ and $Al^{+3}$ ions is to perturb the lattice. The radial extent of such a perturbed volume in a zinc sulfide phosphor, optimally activated with Ag or Cu, is calculated as approximately 50 A. The luminescence center in such phosphors is identified with the metallic activator surrounded by the perturbed volume.

High-intensity neutron bombardment of a zinc sulfide:Cu phosphor causes a marked increase in the value of the diamagnetic susceptibility.

## INTRODUCTION

THE present investigation of magnetic properties of phosphors is part of a general program on the physico-chemical properties of inorganic luminescent materials. Although the luminescence properties of zinc sulfide phosphors have long been known and described, very little work has been reported on the magnetic properties of zinc or cadmium sulfides. Rupp[1] and Sibaiya and Venkataramiah[2] have reported on the magnetic properties of some sulfide-dominated phosphors, Zimens and Hedvall[3] have investigated magnetic susceptibility as a function of crystal structure of zinc sulfide, and Pacault[4] has investigated the susceptibilities of colloidal dispersions of several sulfides.

In the present investigation, the purity, crystal modification, and synthesis procedures were carefully controlled, and the effect of charge-compensating-agents ("fluxes") and activators on the magnetic properties were determined. In this fashion, it was hoped to gain further insight into the role of sulfide-phosphor-constituents.

## EXPERIMENTAL METHODS

### Magnetic

The Gouy equipment, described in a previous article,[5] was modified for the present study, in order to obtain greater sensitivity. An Ainsworth Type FDI microbalance, capable of being read to two micrograms was used on a vibration-proof mounting. The sample tubes consisted of precision-bore Pyrex, 1.25 mm i.d.±0.01 mm, enabling density determinations to be carried out with a high degree of accuracy.

Figure 1 shows a circuit designed to measure and control the magnet current, as well as to protect the magnet from surge voltages. The power was obtained from a motor-generator, exclusively used with the magnet. The current was controlled by a pair of high-capacity, water-cooled rheostats, R7, R8, and was measured by the *IR* drop across a 0.0045-ohm resistor, R2. In order to provide surge protection for the magnet, a fuse delay-line was provided, F1-F4, R3-R5, in conjunction with a 1000 VDC capacitor, C1, and a General Electric Thyrite across the magnet coils. The magnet was calibrated with Mohr salt,[6] the field strength being obtained as a function of millivolts developed across the 0.0045-ohm resistor.

The simplified Gouy equation requires that the field be a maximum at one end of the sample, and negligible

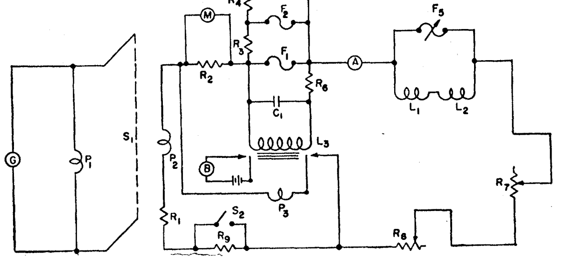

FIG. 1. Electromagnet control, measuring, and protective circuit.

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* This article is based upon a dissertation submitted by Simon Larach in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University.

[1] E. Rupp, Ann. Physik **78**, 505 (1925).

[2] L. Sibaiya and H. S. Venkataramiah, Current Sci. **9**, 224 (1940).

[3] K. E. Zimens and J. A. Hedvall, Svensk, Kem. Tidskr. **53**, 12 (1941); Trans. Chalmers Univ. Tech. **9**, 3 (1942).

[4] A. Pacault, J. Chim. Phys. **49**, 585 (1952).

[5] S. Larach and J. Turkevich, Phys. Rev. **89**, 1060 (1953).

[6] L. C. Jackson, Trans. Roy. Soc. (London) **A224**, 1 (1923).

at the other end. Field strength as a function of vertical distance was determined, and is shown in Fig. 2. As the squares of the field strengths are involved, it is seen that samples longer than 11 cm can be treated as having negligible field at the upper end.

Magnetic susceptibilities were determined from the weight change of the sample as a function of the field. In making measurements, the characteristics of the material were obtained by measuring the magnetic properties of the glass sample tube and of the tube filled with material.

## Chemical

### *Phosphor Syntheses*

Techniques for the preparation of sulfide phosphors have been given by Leverenz.[7] The precipitated, luminescence-pure zinc sulfide[8] that was used, showed no spectroscopically-detectable "poison" impurities, such as Fe, Co, Ni, or activator impurities, such as Ag, Cu, Mn.

The phosphors were synthesized from the base material by adding appropriate solutions of activator and flux materials in triple-distilled water. The mixtures were stirred well, dried at 110°C, and transferred to silica containers, for crystallization from 800°C to 1200°C in temperature-controlled, Vycor tube furnaces. Where an inert atmosphere was desired during crystallization, purified nitrogen was used. After crystallization, the preparations were washed free of water-soluble chlorides and were dried.

## EXPERIMENTAL RESULTS

The results of the magnetic measurements are given below, and are summarized in Table I. Figure 3 is an example of a typical run.

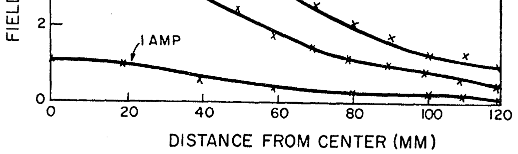

FIG. 2. Field strength as a function of vertical distance, for various magnet currents.

## Diamagnetism of Zinc Sulfide Phosphors

*Precipitated zinc sulfide.*—The specific diamagnetic susceptibility of zinc sulfide (precipitated and dried) was determined as $-0.36\times10^{-6}$. Other investigators[1,3,4] have reported $-0.28\times10^{-6}$, $-0.42\times10^{-6}$, and $-0.33\times10^{-6}$, the last value being for a colloidal dispersion.

*Effect of crystal modification and synthesis procedures.*—On crystallization in a nitrogen atmosphere, the susceptibility dropped, being $(-0.262\pm0.009)\times10^{-6}$ for cubic-ZnS, and $(-0.290\pm0.003)\times10^{-6}$ for the hexagonal modification.[9] The values of the susceptibility were temperature independent in the range of 77°K–300°K.

If however the crystallization was carried out in a reactive atmosphere, the susceptibility increased. Thus, hexagonal-ZnS, crystallized in an atmosphere of hydrogen sulfide, had a specific diamagnetic susceptibility of $(-0.387\pm0.005)\times10^{-6}$. Cubic-ZnS, crystallized in air in a closed container, or essentially in an $SO_2$ atmosphere, had a specific diamagnetic susceptibility of $(-0.373\pm0.004)\times10^{-6}$.

TABLE I. Summary of sulfide magnetic properties.

| Material | Crystal modification | Crystallization atmosphere | $-\chi\times10^6$ |
|---|---|---|---|
| ZnS(pptd.) | cubic[a] | ... | 0.36 |
| ZnS | cubic | $N_2$ | 0.262 |
| ZnS | hexagonal | $N_2$ | 0.290 |
| ZnS | cubic | air | 0.373 |
| ZnS | hexagonal | $H_2S$ | 0.387 |
| ZnS:NaCl | cubic | air | 0.402 |
| ZnS:Ag:NaCl | cubic | air | 0.406 |
| ZnS:Al(0.01) | cubic | $H_2S$ | 0.357 |
| ZnS:Al(0.1) | cubic | $H_2S$ | 0.409 |
| CdS(pptd.) | [b] | ... | 0.268 |
| CdS(650°C) | [b] | $N_2$ | 0.254 |
| CdS(900°C) | [b] | $N_2$ | 0.158 |
| CdS:Cl | ... | $N_2$ | 0.253 |

[a] The precipitated (pptd.) zinc sulfide was found to be cubic, and of very poor crystallinity.

[b] W. O. Milligan, J. Phys. Chem. **38**, 798 (1934), has reported the existence of cubic and hexagonal forms of cadmium sulfide, depending on synthesis procedure. X-ray findings (unpublished) by Dr. J. A. Amick have confirmed this. Precipitated cadmium sulfide was found to be 30 percent cubic and 70 percent hexagonal. Co-crystallization with chloride yields materials with very high hexagonal content, which upon grinding, revert partially to the cubic modification. The materials were prepared by Dr. S. M. Thomsen of the RCA Laboratories.

*Effect of "fluxes."*—The use of chloride or aluminum ions as "fluxes" also increased the susceptibility. Cubic-ZnS was air-crystallized with two percent, by weight, of NaCl. The residual chloride was removed by washing, and the material was dried. The incorporated chloride for similar materials has been found to be approximately 130 microgram-atoms per mole of phosphor.[10] The specific diamagnetic susceptibility of this material was $(-0.402\pm0.017)\times10^{-6}$, an appreciable increase over the material with no chloride.

That the incorporated halide is responsible for the increased diamagnetic susceptibility rather than the

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[7] H. W. Leverenz, *Introduction to Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950).

[8] Obtained as LM476, from the RCA Victor Division, Lancaster, Pennsylvania.

[9] W. Voigt and S. Kinoshita, Ann. phys. **24**, 492 (1907), obtained a value of $-0.264\times10^{-6}$ for a crystal of sphalerite (cubic-ZnS).

[10] R. H. Bube, J. Chem. Phys. **20**, 708 (1952).

activator is shown by the fact that additional incorporation of a metallic activator ion (silver) had no further effect. Thus, cubic-ZnS, air-co-crystallized with chloride and with 0.01 percent by weight of Ag, had a specific diamagnetic susceptibility of $(-0.406\pm0.008)\times10^{-6}$.

Trivalent charge-compensating additives have been reported by Kröger and Dikhoff[11] and by Bube and Larach.[12] To test the effect of such trivalent additives, the magnetic properties were determined of zinc sulfide: Al materials, crystallized in hydrogen sulfide. The specific diamagnetic susceptibility for the material to which 0.01 percent by weight of alumium ion had been added was $(-0.357\pm0.008)\times10^{-6}$, and for the material with 0.1 percent aluminum $(-0.409\pm0.003)\times10^{-6}$.

*Neutron-irradiated* ZnS.—Zinc sulfide: Cu, irradiated for approximately 32 hours in the Brookhaven National Laboratory nuclear reactor, had the extremely high diamagnetism of $-0.59\times10^{-6}$.

## Diamagnetism of Cadmium Sulfide

*Uncrystallized* CdS.—The specific diamagnetic susceptibility for precipitated, and dried CdS was found to be $-0.268\times10^{-6}$. Pacault,[4] working with colloidal dispersions has reported a value of $-0.394\times10^{-6}$.

*Crystallized* CdS.—Cadmium sulfide was fired at 650°C in an atmosphere of purified nitrogen. The resulting material was electrically insulating ($\sim10^{10}$ ohm cm), and its specific diamagnetic susceptibility was $(-0.254\pm0.015)\times10^{-6}$, again temperature-independent in the range of 77°–300°K.

A sample of CdS, fired at 900°C in a nitrogen atmosphere, was electrically conducting ($\sim10^4$ ohm cm). The specific susceptibility was $(-0.158\pm0.003)\times10^{-6}$. This decrease in diamagnetism is not associated with a temperature dependence of susceptibility, in the range of 77°K to 300°K.

CdS, with incorporated chloride, fired at 900°C in a nitrogen atmosphere, was conducting, and had a specific diamagnetic susceptibility of $(-0.253\pm0.004)\times10^{-6}$.

## DISCUSSION

### Effect of Crystallization

The value of the diamagnetic susceptibility of uncrystallized zinc sulfide found in the present investigation falls within the range of values previously reported by others.[1,3,4] The effect reported by Rupp[1] of a decrease in the diamagnetic susceptibility on crystallizing zinc sulfide has been corroborated. It has been found, however, that this effect occurs only when zinc sulfide is (1) pure, and (2) when it is crystallized under inert atmosphere conditions. This decrease in the absolute value of the diamagnetic susceptibility has no temperature coefficient, and consequently, the crystallization process does not involve the formation of atomic or molecular species having normal temperature-dependent paramagnetism. The decrease in susceptibility must be ascribed to an actual decrease of diamagnetism, either on the surface or in the volume of the material. If this decrease in diamagnetism is ascribed to changes of bulk properties, defects of the order of 30 percent would have to be postulated, a value inconsistent with the constancy of position of the x-ray lines and their becoming sharper on crystallization, as shown in Table II.[13] For this reason, the decrease in diamagnetism is ascribed to a decrease in the surface, where the electrons must have a greater orbital radius and diamagnetism than in the bulk. This point of view is consistent with the high surface recombination effects often observed in semiconductors.

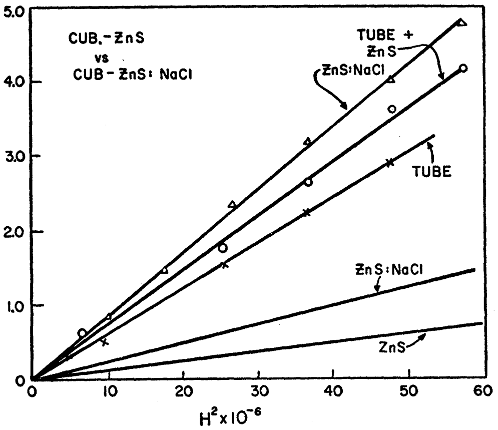

FIG. 3. Force on the sample as a function of the square of the field strength, for (a) cubic-ZnS, and (b) cubic-ZnS with chloride flux.

On the other hand, crystallization in a reactive atmosphere, such as air or $H_2S$, causes a slight increase in the diamagnetism. To account for this effect, it must be assumed that the decrease of surface diamagnetism is more than compensated for by the formation of Schottky defects, produced by the diffusion of zinc atoms from the interior to the surface layer of oxygen or sulfur, deposited by the reactive atmosphere. Since the half-width of the x-ray lines is not broadened, the defects are probably less than 1 percent, indicating that the diamagnetic contribution of these Schottky defects is very great.

Cadmium sulfide, like zinc sulfide, shows a decrease in the absolute value of diamagnetism on crystallization at a temperature of 900°C. No temperature-dependence of susceptibility was observed, and the susceptibility decrease is ascribed to a diminution of the surface area. It should be noted that this decrease in diamagnetism is associated with conversion of the cadmium sulfide from an insulator to a conductor, an effect which may be associated with the destruction of surface recombination sites.

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[11] F. A. Kröger and J. Dikhoff, Physics 16, 297 (1950).

[12] R. H. Bube and S. Larach, J. Chem. Phys. 21, 5 (1953).

[13] X-ray data were obtained by Dr. J. A. Amick of the RCA Laboratories, with a Philips Norelco x-ray diffractometer.

TABLE II. X-ray data for several zinc sulfide materials.

| Form of material | Crystallization<br>Temp | <br>Atmos | Crystal modification | Half-width of peak (*hkl*) | Intensity of peak (*hkl*) | $a_0$ | $c_0$ |
|---|---|---|---|---|---|---|---|
| Precipitated | ... | ... | cubic[a] | 0.55°(331)<br>0.7°(422) | | 5.404 | |
| Crystallized | 800°C | $N_2$ | cubic[a] | 0.37°(331)<br>0.4°(422) | | 5.411 | |
| Crystallized | 1200°C | $N_2$ | hexagonal | 0.275°(203)<br>0.325°(210) | 13.25(203)<br>6.5(210)<br>6.0(211) | 3.822 | 6.257 |
| Crystallized | 1200°C | $H_2S$ | hexagonal | 0.25°(203)<br>0.325°(210) | 13.5(203)<br>6.5(210)<br>5.5(211) | 3.821 | 6.255 |

[a] The precipitated material was less crystalline than the 800°-$N_2$ material. The $\alpha_1$ and $\alpha_2$ peaks could not be resolved for the precipitated ZnS, but were resolvable for the 800°-$N_2$-crystallized ZnS.

## Cubic and Hexagonal Zinc Sulfide

Zinc sulfide exists in two well-known crystal modifications, cubic (sphalerite) and hexagonal (wurzite), the transition temperature from the cubic to the hexagonal form being about 1020°C.

Very little work has been reported on the susceptibilities of these two crystalline forms of zinc sulfide. Zimens and Hedvall[3] have given the values of $-0.38\times10^{-6}$ for the cubic form, and $-0.40\times10^{-6}$ for the hexagonal form. However, their hexagonal zinc sulfide was a phosphor containing traces of copper, and synthesis procedures were not given.

In the present investigation, pure zinc sulfide was used, and crystallizations were carried out in an atmosphere of pure nitrogen. The phosphors were not ground, since the hexagonal modification can revert to the cubic form on grinding.[14,15] A value of $(-0.262\pm0.009)\times10^{-6}$ was obtained for the specific susceptibility of cubic zinc sulfide, and $(-0.290\pm0.003)\times10^{-6}$ for the hexagonal form.[16]

## Chloride and Aluminum "Fluxes"

Zinc sulfide phosphors are usually prepared with the addition of an alkali halide, commonly referred to as a "flux." The proportion added is rarely critical. The functions of a flux have been thought to be mainly: (1) to provide a fluid phase for solvation and transport of ingredients, and (2) to increase surface reactivity and atomic mobility to facilitate crystal growth.[17] Recent investigators have assigned a greater role to halide than that of a mere chemical flux, by postulating that the presence of halide affects the luminescence properties of zinc sulfide phosphors by causing changes in the internal structure of the crystal.[12,18] Smith[19] has suggested that the halide is incorporated into the crystal and causes crystal defects, and Kröger and Hellingman[20,21] have reported a correlation between proportion of chloride incorporated and emission intensity. Kröger's recent theory assumes that the luminescence center involves monovalent zinc, whose formation is permitted by the incorporation of a halide anion, or by a trivalent cation, aluminum.

Cubic zinc sulfide, air-fired with chloride, was found to have a specific susceptibility of $-0.402\times10^{-6}$, compared to $-0.373\times10^{-6}$ for the material prepared without chloride. The specific susceptibility of ZnS:Al is apparently dependent on the concentration of aluminum, going from $-0.357\times10^{-6}$ for 0.01 percent Al, to $-0.409\times10^{-6}$ for 0.1 percent Al.

No temperature dependence of susceptibility was found to 77°K, indicating the absence of a temperature-dependent paramagnetic species which could be attributed to monovalent zinc. The detection limit of the equipment for such a paramagnetic species is about 0.01 percent. Not only is a paramagnetic species absent, but the absolute value of diamagnetism is *increased* by the flux incorporation. As with zinc sulfide, the incorporation of chloride in cadmium sulfide acts to increase the diamagnetism.

A large *increase* in the absolute value of the diamagnetism is obtained when either chloride or aluminum ions are used as "fluxes." This increase, above that related to crystallization in an active atmosphere, is evidently due to the incorporation of the flux ions, with consequent perturbation of the lattice. The extent of the perturbation is discussed in a later paragraph.

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[14] A. Schleede and H. Gantzckow, Z. Physik **15**, 184 (1923).

[15] J. S. Van Wieringen, Physica **19**, 397 (1953).

[16] The value given by Zimens and Hedvall for their cubic form $(-0.38\times10^{-6})$ corresponds to that obtained in the present investigation for air-crystallized cubic material $(-0.37\times10^{-6})$, indicating that their material was probably air-fired. Similarly, the Zimens and Hedvall value for hexagonal zinc sulfide (phosphor) is the same as obtained in the present investigation for phosphors crystallized with chloride flux, as is usually the case with copper-activated phosphors.

[17] Reference 7, p. 78.

[18] S. Rothchild, Trans. Faraday Soc. **42**, 635 (1946).

[19] A. L. Smith, J. Electrochem. Soc. **96**, 75 (1949).

[20] F. A. Kröger and J. E. Hellingman, J. Electrochem. Soc. **93**, 156 (1948); **95**, 68 (1949).

[21] More recently, F. A. Kröger and H. J. Vink [J. Chem. Phys. **22**, 250 (1954)] have proposed that the luminescent center in "self-activated" ZnS phosphors is associated with a cation vacancy whose environment has lost an electron.

Thus, in cadmium sulfide, as in zinc sulfide, the incorporation of chloride has a large effect on the crystal diamagnetism, presumably due to the large perturbation introduced by the chloride. As CdS:Cl is practically nonluminescent in the visible region of the spectrum, it might be expected that (1) an infrared emission band may occur,[22] or (2) conductivity, and possibly other electronic properties would be affected.

## Composition and Extent of the Luminescence Center

The existence of large activator centers in phosphors has been postulated by various investigators. Lenard[23] proposed that the luminescence center consisted of an impurity atom linked with a number of host atoms. This view was further developed by Ewles,[24,25] who first attempted to explain luminescence efficiency as a function of activator concentration.

The diamagnetic data obtained in the present investigation of magnetic properties of solids can be used to calculate the size of a luminescence center in zinc sulfide.

The diamagnetism of zinc sulfide is increased from $-0.373\times10^{-6}$ to $-0.402\times10^{-6}$ when chloride is incorporated into the solid during crystallization, and to $-0.406\times10^{-6}$ when 0.01 percent Ag is also incorporated. From the susceptibility change and the amount of chloride which is incorporated, the radius of the electron orbit can be calculated from the well-known formula

$$\chi=\frac{-Ne^2}{6mc^2}\sum\langle r^2\rangle_{\text{Av}},$$

where $N$ is the number of atoms, $e$, $m$, and $c$ have their usual meanings, and $\langle r^2\rangle_{\text{Av}}$ is the mean square radius of the electron orbit. In the present case, the radius of the orbit is calculated as being approximately 50 A.

Mott and Gurney[26] and Mott[27] have pictured a foreign atom in a crystal as being in a continuum having a high dielectric constant, and having an associated electron traveling in a large orbit over a considerable number of lattice atoms. Simpson[28] has calculated for electrons trapped in defects, that the associated wave function may spread over several lattice spacings.

It is seen therefore, that the function of the halide in zinc sulfide is to perturb the lattice. The diameter of the perturbation sphere, extending over 26 zinc atoms, is approximately 100 A, compared to 115 A, for the chloride-to-chloride distance for a given chloride proportion calculated for zinc sulfide assuming random distribution. Leverenz[29] has calculated the average silver-to-silver distance for the optimum proportion of silver in cubic zinc sulfide as being 83 A. This would indicate that the optimum proportion of silver is obtained when one, and only one, silver lies within the perturbation volume produced by a given chloride atom.

The luminescence center in optimally activated (Ag or Cu) and fluxed zinc sulfide phosphors can thus be associated with a metallic activator ion with its immediate environment, and situated in a perturbed volume. This perturbed volume encompasses about $2\times10^4$ zinc atoms.

## CONCLUSIONS

The role of chloride (flux) in zinc sulfide phosphors is to perturb the sulfide lattice. The luminescence center in activated and fluxed zinc sulfide consists of a metallic activator ion and its environment, situated in a perturbed volume of the crystal.

No evidence was found for the existence of a paramagnetic species, such as monovalent zinc, in phosphors to which halide or aluminum charge-compensating-agents had been added.

The diamagnetic susceptibilities of zinc sulfide as a function of impurity, crystal modification, and synthesis procedure were determined. Only small differences were found to exist in the susceptibilities of the cubic and hexagonal forms of zinc sulfide.

The effects of crystallization and chloride incorporation in cadmium sulfide were found to be similar to zinc sulfide.

An anomalously high diamagnetic susceptibility was found in a ZnS:Cu phosphor which had previously undergone neutron bombardment.

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[22] An infrared emission band has recently been reported for CdS:Cu by Garlick and Dumbleton, Proc. Phys. Soc. (London) **B67**, 442 (1954).

[23] P. Lenard, *Handbuch der Physik* (Verlag Julius Springer, Berlin, Germany, 1926), Vol. 23, p. 569.

[24] J. Ewles, Proc. Roy. Soc. (London) **A129**, 509 (1930).

[25] J. Ewles, J. Electrochem. Soc. **100**, 392 (1953).

[26] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1948), second edition, p. 84.

[27] N. F. Mott, Proc. Inst. Elec. Eng. (London) **96**, 254 (1949).

[28] J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949).

[29] Reference 7, p. 480.