

singularities which produce displacements of the form $u=c/r^2$ will scatter x-rays with the following effects: (1) an isotropic expansion of the lattice; (2) an artificial temperature factor; (3) no broadening of the Bragg reflections; (4) diffuse scattering surrounding the reciprocal lattice points.

While the lattice expansion and absence of line broadening have been widely observed in solid solutions, the artificial temperature factor has been observed only once and the diffuse scattering has not yet been observed in solid solutions. However, all four of the effects have been observed in certain neutron irradiated crystals, namely, boron carbide, diamond, silicon carbide, and magnesium oxide. The presence of the effects in these crystals is attributed to the defects produced during irradiation. The fact that the effects are readily

observed in irradiated crystals is due to the much greater "strength" of the defects produced by irradiation, *viz.*, interstitials, vacancies, and foreign atoms.

The qualitative agreement between the calculations of Huang and the observed x-ray effects leads to the conclusion that the representation of localized static defects as elastic singularities producing displacements of the form $u=c/r^2$ is a valid first-approximation model. However, it is suggested that it may be possible to work back from the observed diffuse scattering in irradiated crystals to obtain more precise information regarding the distortions around the defects.

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Luminescent Centers in ZnS:Cu:Cl Phosphors

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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 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.

INTRODUCTION

IN this paper we shall attempt to correlate the reported emissions in ZnS activated by copper with particular states of the activator, especially the valence of the activator and its position in the lattice.

The absorption of a quantum of ultraviolet radiation by the host crystal of ZnS is usually assumed to result in the formation of an electron and a hole. These may annihilate one another by giving up their energy to the lattice as phonons, or they may recombine at an impurity center with a characteristic emission. The electronic transitions are governed by interactions between the impurity and the lattice; it is to be expected, therefore, that the resulting emission would depend on the state of ionization of the center. Furthermore, the energy levels may well depend on the crystallographic phase of the host crystal, and on whether the impurity is incorporated interstitially or substitutionally.

Information regarding the nature of impurity centers in impurity activated phosphors has been obtained for several manganese-activated inorganic phosphors by means of static susceptibility measurements,¹ and for a

variety of phosphors by means of paramagnetic resonance.² In the case of ZnS:Cu, however, paramagnetic resonance measurements failed to yield any information because of the absence of an observable resonance absorption. The difficulties encountered in the resonance measurements, in being unable to distinguish between diamagnetism and a paramagnetism which results in a very broad absorption spectrum, are absent in the measurements of static susceptibility.

In the experiments to be described here, we have measured the emission spectra of a number of Cu-activated ZnS phosphors, prepared under various conditions, while at the same time, the phase has been determined from x-ray measurements. The state of ionization of the unexcited phosphors has been determined from measurements of the magnetic susceptibility as a function of temperature. Zinc sulfide is diamagnetic and, if the copper were introduced as Cu⁺, it would remain purely diamagnetic and its susceptibility would be substantially independent of temperature. On the other hand, the presence of Cu⁺⁺ or Cu⁰

¹ S. Larach and J. Turkevich, *Phys. Rev.* **89**, 1060 (1953). P. D. Johnson and F. E. Williams, *J. Chem. Phys.* **17**, 435 (1949).

² W. D. Hershberger and H. N. Leifer, *Phys. Rev.* **88**, 714 (1952).

would result in a temperature-dependent paramagnetic component in the susceptibility.

Five principal emissions of the ZnS:Cu:Cl system have been reported. The chemical and optical properties of this system have been the subject of much investigation.³ It is well established that the presence of chloride during the preparation of zinc sulfide results in a blue emission band under near-ultraviolet excitation, having its peak at approximately 4400 Å for the hexagonal phase and at 4600 Å for the cubic form.⁴ The addition of small quantities of copper together with chloride produces a strong green emission with peaks at 5200 Å and 5400 Å for the hexagonal and cubic forms respectively.⁵ At low copper concentrations,⁶ the blue and green peaks are both present, the higher concentrations of copper favoring the green emission, while at the same time diminishing the intensity of the blue. The green emission reaches its maximum intensity at 0.009 to 0.01 mole percent copper and at this concentration, the blue emission is virtually absent under ordinary conditions of excitation.

With the addition of copper beyond 0.01%, the green emission diminishes in intensity and a blue emission reappears. This blue emission reaches its maximum intensity at 0.06% copper and diminishes at higher concentrations.^{6a,7} At a concentration of 0.3% copper, Bube⁵ has reported a new green emission, having a maximum at 5200 Å, but of a considerably broader band width. The foregoing emissions are all presumed to occur in the presence of an excess of chloride. Recently, Froehlich^{8,9} has described a broad red emission produced when copper is added to zinc sulfide and prepared in the absence of any additional impurity such as chloride. The peak wavelengths of all of the emissions and their optimum copper concentrations are summarized in Table I.

TABLE I. Impurity concentration and representative centers proposed in the literature for ZnS.

Impurity	Emission color	Wavelength at maximum Å	Proposed centers
Cl	blue I	4400	interstitial Zn ⁺ , Zn vacancies
Cu(0.01%):Cl	green I	5200	Cu ⁺ interstitial, or substitutional
Cu(0.06%):Cl	blue II	4400	Cu ₂ ⁺ Cl
Cu(0.3%):Cl	green II	5200	subt. Cu ⁺
Cu	red	6700	? Cu ⁺⁺

³ See for example H. W. Leverenz, *An Introduction to the Luminescence of Solids* (John Wiley and Sons, Inc., New York, 1950), Chap. 5.

⁴ F. A. Kroger and J. E. Hellingman, *J. Electrochem. Soc.* **93**, 156 (1948); also S. Rothschild, *Trans. Faraday Soc.* **42**, 635 (1946).

⁵ R. H. Bube, *Phys. Rev.* **80**, 655 (1950), see also Leverenz, reference 3, pp. 208, 209.

⁶ All concentrations are designated in molar percent.

^{6a} Kroger, Hellingman, and Smit, *Physica* **15**, 990 (1949).

⁷ F. A. Kroger and N. W. Smit, *Physica* **16**, 317 (1950).

⁸ H. Froehlich, *J. Opt. Soc. Am.* **42**, 982, (1952).

⁹ H. Froehlich, *J. Electrochem. Soc.* **100**, 496 (1953).

It has been stated that the green emission at low copper concentrations results from Cu⁺, and that the role of the chloride is to provide charge compensation in a lattice of Zn⁺⁺S⁼.¹⁰ The blue emission occurring when chloride alone is present, had formerly been attributed to Zn⁺ centers¹¹ but recently has been attributed to Zn⁺⁺ vacancies with an electron missing from one of the adjacent S⁼ ions.¹² The presence of Zn⁺ should be detectable in our experiment by its paramagnetic susceptibility.

The origin of the blue emission appearing at 0.06 mole percent copper is not well established. It has been suggested that this blue emission is due to a complex of the form [Cu₂⁺:Cl⁻].^{6,13} These centers should be paramagnetic owing to the presence of an unpaired electron spin. A similar lack of knowledge exists with regard to the red emission which appears when no chloride is present. Because of the absence of a charge compensating ion such as Cl⁻, one might be led to expect Cu⁺⁺ as the responsible center; hence these specimens may exhibit paramagnetic behavior.

EXPERIMENTAL PROCEDURES AND RESULTS

Preparation of the Specimens

Specimens were prepared by heating together pure precipitated zinc sulfide (R.C.A. LM476) to which requisite quantities of activator had been added. The copper activator was added as a solution of Cu(NO₃)₂. The components were mixed, dried, then thoroughly ground to insure proper mixing. Chloride was added as ammonium chloride, in large excess, usually 3%. The precise amount of chloride which remains in the lattice after firing is not certain; it is for this reason that the chloride concentrations are not included in the figures. Bube¹⁴ and Kroger¹⁵ have reported analyses for the chloride remaining; in general the chloride concentration increases with the amount of copper added. Without copper, however, a quantity of chloride is incorporated and produces the aforementioned blue emission. There is more certainty regarding the copper concentrations when chloride is present. Chemical analyses, and the continuous changes in physical properties with the copper concentration lead us to believe that, at least to 0.1% copper, all, or a substantial portion of the added copper is incorporated.

All chloride-free specimens were heated in an atmosphere of hydrogen sulfide and precautions were taken to exclude air. Chloride-containing specimens were fired in an atmosphere consisting of a mixture of hydrogen sulfide and ammonium chloride. The firing temperature and time depended on whether the hex-

¹⁰ F. A. Kroger and J. Dikhoff, *Physica* **16**, 297 (1950).

¹¹ J. T. Randall, *Trans. Faraday Soc.* **8** (1939).

¹² F. A. Kroger and H. J. Vink, *J. Chem. Phys.* **22**, 250 (1954).

¹³ F. A. Kroger, *Brit. J. Appl. Phys.*, Supplement No. 4, 58-62 (1955).

¹⁴ R. H. Bube, *J. Chem. Phys.* **19**, 985 (1951).

¹⁵ F. A. Kroger and J. E. Hellingman, *J. Electrochem. Soc.* **95**, 68 (1949).

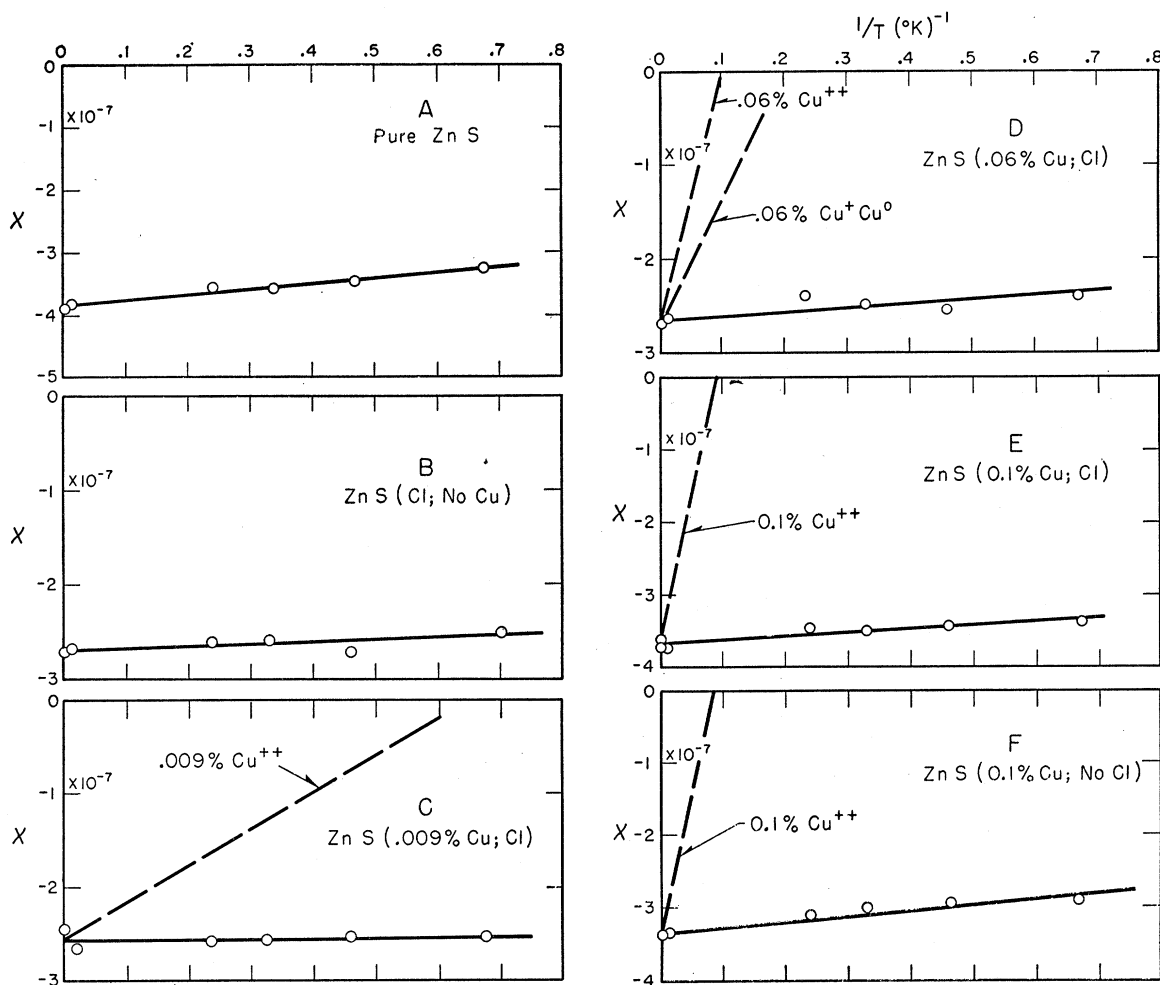


FIG. 1. Temperature dependence of the susceptibility of ZnS with various concentrations of copper and chloride. Emission bands corresponding to the compositions shown are: B, "blue I"; C, "green I"; D, "blue II"; F, red.

agonal or cubic phase was desired. For the hexagonal specimens reported on here, the firing was for 30 minutes at 1150°C. The red-emitting specimens were fired for considerably longer periods at the above temperature as well as at higher temperatures, in an attempt to produce the hexagonal form, but the products were mixtures of cubic and hexagonal phases.

Measurement of the Magnetic Susceptibility

The susceptibility of the powder specimens has been measured from 300°K down to 1.5°K using the Gouy method. A Gulbransen type microbalance capable of measuring a force of 1 μ g with a 3-g load has been used to measure the force on the specimen.^{16,17} Because of the sensitivity of the balance and the wide temperature range covered, it is possible to separate the temperature-dependent paramagnetism which would correspond to 0.0001% molar Cu⁺⁺ in ZnS.

¹⁶ E. A. Gulbransen, Rev. Sci. Instr. 15, 201 (1944).

¹⁷ R. Bowers and E. A. Long, Rev. Sci. Instr. 26, 337 (1955).

The phosphors to be measured were placed in thin-walled quartz tubes; they were evacuated to 10⁻⁶ mm and heated to 300°C for one hour in the vacuum in order to remove paramagnetic oxygen. The tubes were then filled with just less than one atmosphere of pure helium before sealing to ensure thermal equilibrium during the measurements.

The actual susceptibility measured is that of the phosphor and quartz container. The susceptibility of the quartz glass has been measured from 300°K to 1.5°K and has been found to be suitable for our work because its variation with temperature is very small.

The correction due to the quartz container was often as high as 30%, as calculated from a measured average cross-sectional area of the container. However, the quartz tubing was not uniform and the correction itself could not be calculated to better than about 30%. We did not consider it worthwhile to devote much attention to an accurate evaluation of this almost temperature-independent correction in the case of

each specimen, since we were primarily interested in temperature-dependent terms in the susceptibility. The density of the powder in the tubes was determined gravimetrically, assuming the powder to be uniformly packed. Lack of corrections for the nonuniformity of the quartz tubing and the nonuniform density of the powders may account for the differences in the observed absolute values of the susceptibilities.

The technique has been checked by measuring the susceptibility of a known paramagnetic phosphor, ZnS, activated with 0.1% Mn²⁺. The temperature-dependent paramagnetism was observed to obey Curie's law and could be calculated as arising from 0.093% Mn²⁺. This is in good agreement with the chemical analysis of 0.095% Mn. The quantitative agreement shows that there is temperature equilibrium between the powder and the low temperature bath.

The phosphors chosen for measurement were, wherever possible, ones which had the optimum impurity content for each of the reported emissions. The results for these phosphors are shown in Fig. 1.

Results

The measured susceptibility for pure ZnS, Fig. 1A, exhibits a small temperature-dependent component. The origin of this component is not certain, but may be due in part to surface paramagnetism or crystalline defects¹⁸ in the particles, whose diameters are estimated to range between 0.1 and 10 microns. The temperature dependence may also be explained by the presence of one part per million of a strongly paramagnetic impurity, although there is no evidence that such a high concentration of impurities exists in the pure material.

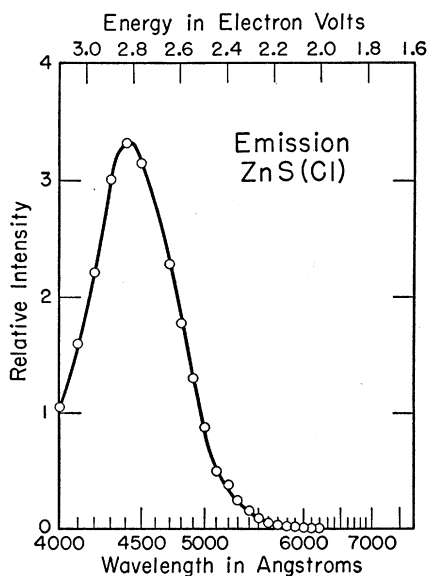


FIG. 2. Emission spectrum of ZnS containing chloride but no copper; designated in text as "blue I".

¹⁸ P. W. Selwood, *Magnetochemistry* (Interscience Publishers, Inc., New York, 1953), p. 253.

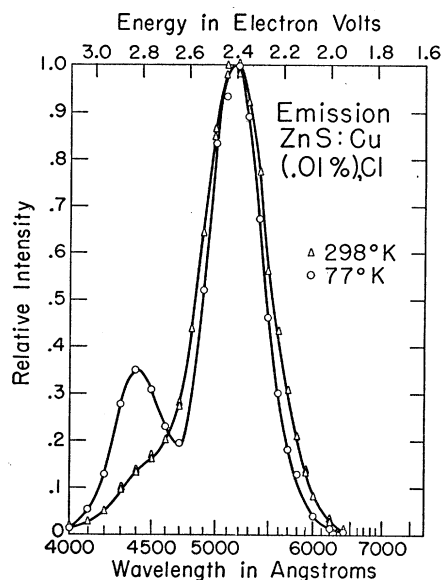


FIG. 3. Emission spectrum of ZnS containing chloride and 0.01% copper; referred to in text as "green I".

For our present purpose, however, we are concerned only with increases in the temperature dependence of the susceptibility as the result of deliberate addition of impurities.

Figure 1B shows the susceptibility of ZnS prepared with the addition of chloride but without copper. The susceptibility is slightly less temperature dependent than even the pure zinc sulfide.

The addition of copper with chloride up to 0.1% copper produced no detectable change in the temperature dependence of the susceptibility compared with the pure zinc sulfide. This is illustrated in Figs. 1C, D, and E for samples with increasing copper concentration. In each of these figures, the dotted line represents the expected slope of the added copper had it been present as Cu²⁺ or Cu⁰Cu⁺.

Figure 1F shows the temperature dependence of the susceptibility for a specimen containing 0.1% copper prepared without chloride, and exhibiting a red emission. As in the previous specimens, no change in the original susceptibility is observed.

We conclude, therefore, that neither the addition of copper or chloride, nor the addition of copper together with chloride in concentrations necessary to produce the reported emissions, results in any observable increase in the temperature dependence of the susceptibility of zinc sulfide. Hence, the impurities are present in forms which are diamagnetic.

Emission Spectra

Emission spectra were obtained by means of a Beckman spectrophotometer with a 931A photomultiplier replacing the Beckman light source. The calibration included the sensitivity of the phototube and the

transmission of the spectrophotometer. All emission curves are reported on a relative-intensity basis. For the emission spectra, the phosphors were normally excited by 3650 Å radiation from an A-H4 mercury lamp containing a Corning 5860 filter. The spectrophotometer band width at which the measurements were taken was kept at a minimum and, except where otherwise indicated, the half-intensity band width is 40 Å.

Results

Pure, unactivated zinc sulfide exhibits an ultraviolet emission but no visible emission.¹⁹ The blue emission resulting from the addition of chloride is shown in Fig. 2.

Figure 3 shows the emission spectrum of ZnS:Cu(0.01%):Cl. At room temperature the predominant emission is due to the 5200 Å band, with almost no contribution from the 4400 Å band. At 77°K the blue band is considerably enhanced, as can be expected from the Schoen-Klasens²⁰ theory of hole migration.

The emission of ZnS:Cu(0.065):Cl, the optimum concentration for the blue II emission, is shown in Fig. 4. A difference in the shape of the emission spectrum of the blue band in the copper-containing specimen and the blue band of ZnS:Cl is seen in the more rapid decrease in the intensity of the former on the short-wavelength side of the band. The approximate shape of the absorption band introduced by copper in the tail of the lattice absorption band has been obtained by

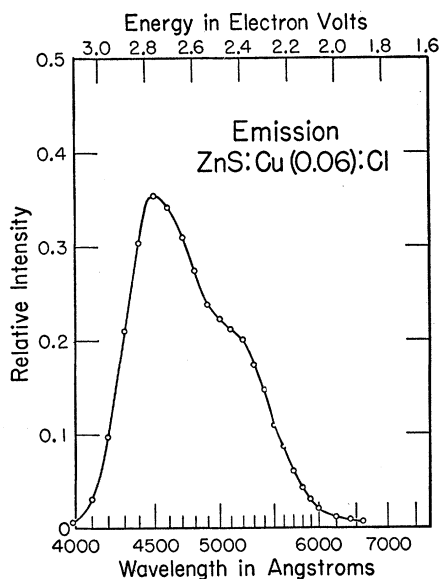


FIG. 4. Emission spectrum of ZnS containing chloride and 0.06% copper, referred to in text as "blue II". A small green I component of emission is present.

¹⁹ F. A. Kroger, *Physica* 7, 1 (1940).

²⁰ M. E. Wise and H. A. Klasens, *J. Opt. Soc. Am.* 38, 226 (1948); Klasens, Ramsden, and Quantie, *J. Opt. Soc. Am.* 38, 60 (1948); H. A. Klasens, *Nature* 158, 306 (1946); M. Schoen, *Z. Physik* 119, 463 (1942).

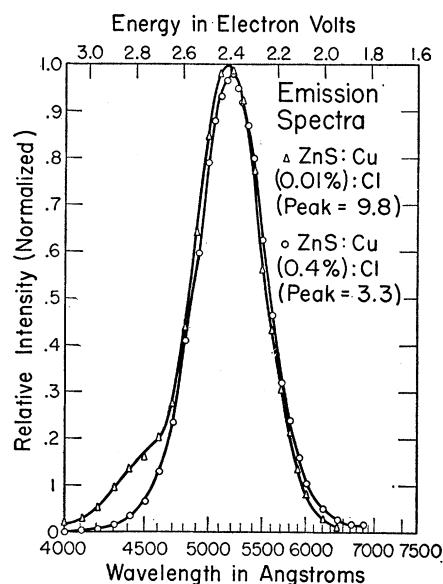


FIG. 5. Comparison of the green emission bands obtained with low and with high copper concentrations. These are designated in the text as "green I" and "green II".

Gisolf.²¹ The difference in the shape of the blue emission spectra of ZnS:Cl and ZnS:Cu(0.06):Cl can, at least in part, be attributed to absorption of the short-wavelength side of the blue emission by the copper absorption band. An apparent displacement of the peak of the blue emission of Fig. 4 towards longer wavelengths is due to the superposition of the green emission.²²

Figure 5 shows on a normalized ordinate scale the room-temperature emission of ZnS:Cu(0.4%):Cl, corresponding to the band we have designated as green II, and for comparison the emission of ZnS:Cl(0.01):Cl. Except for the presence of a small amount of blue I in the 0.01% copper specimen no differences are observed which can be attributed to a broadening of the emission at high copper concentrations.

Figure 6 shows the room-temperature emission of ZnS:Cu(0.01) prepared without chloride. The broad red emission has its maximum at 6700 Å. Also present is a blue emission similar to the blue emission present in zinc sulfide prepared with chloride, but without copper. The presence of the blue emission together with the red emission has been verified for all of our specimens ranging in copper concentration from 0.0001% Cu to 1% Cu. In some specimens, only the red emission appears at room temperature; the presence of blue centers can readily be established, however, by cooling the specimen to 77°K.

DISCUSSION

There has been considerable speculation regarding the number of different emission centers and their

²¹ Gisolf, De Groot, and Kroger, *Physica* 8, 805 (1941).

²² J. M. Vanderbilt and C. Henrich, *Appl. Spectroscopy* 7, 171 (1953).

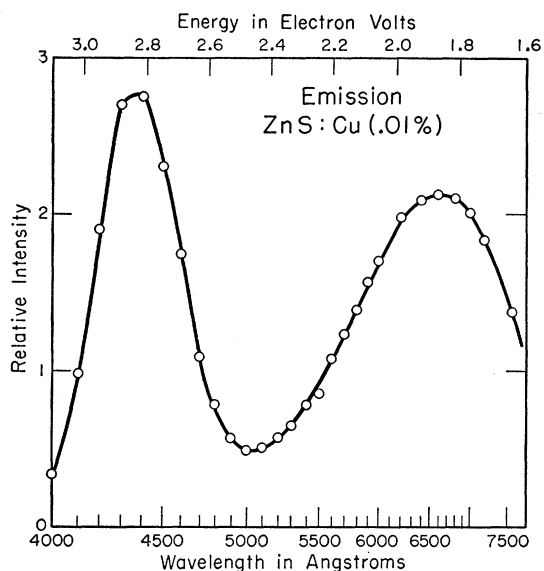


FIG. 6. Emission spectrum of ZnS containing 0.01% copper but no chloride, showing the long-wavelength red emission with its associated blue emission. The intensity of the blue emission in this specimen is greater than in many similar specimens.

constitution, in zinc sulfide activated by copper and by chloride. Our results indicate that only three emissions are to be distinguished out of the five reported: a blue emission produced by chloride alone, a green emission due to the simultaneous addition of copper and chloride, and a red emission due to the presence of copper without chloride. Emission spectra obtained for the blue-emission specimens with high copper concentration (0.06 molar percent) were similar to those obtained with specimens prepared with only chloride. At very high (0.34%) copper concentrations, no broad green emission was observed. The green emission retained its shape to the highest concentrations to which we went; the only noticeable changes were in relative intensity. This latter observation confirms Kroger's²³ view that no new emission appears at the higher copper concentrations.

The susceptibility measurements obtained on all of the specimens described above indicate that the concentration of paramagnetic centers introduced by copper or chloride was, in each case, less than 0.001 molar percent. Thus, it is not likely that, in the ground state, any configuration of copper other than Cu^+ is present, as opposed to centers of the type Cu_2^+ , Cu^{++} , or Cu^0 . If any of the latter are present, their concentrations are too low to be correlated with the observed emissions.

On the basis of the above results, several conclusions can be drawn as to the probable nature of the luminescent centers. We shall discuss these results first assuming an ionic model, and then indicate how they may be interpreted using an energy band model.

Regarding the blue emission, the two most obvious possibilities are that this emission occurs at a Cl^- site, or in the region of a zinc vacancy. (The possibility of Zn^+ being responsible for the blue emission is ruled out because such a center would be paramagnetic.) Since the same blue emission can be produced by a variety of impurities other than Cl^- , such as Br^- , I^- , Al^{+++} , Sc^{+++} ,⁶ all of which would produce Zn vacancies, as well as by heating the pure material to a sufficiently high temperature,⁵ the evidence favors Kroger's recent contention¹² that Zn vacancies are responsible for this emission. It is, however, in disagreement with Kroger's picture of a blue center as that of a zinc vacancy with one electron missing from an adjacent sulfur ion, inasmuch as the missing electron would produce a paramagnetic center.

The situation regarding the green and red emissions is somewhat less apparent. Because of the difference in charge between Zn^{++} and Cu^+ , the incorporation of Cu^+ substitutionally in a lattice such as ZnS requires the simultaneous incorporation of a monovalent negative ion, such as Cl^- , Br^- , or I^- , or a tripositive ion, such as Al^{+++} , or sulfur vacancies. Since one of these impurities must be present with copper in order to produce the green emission, we conclude that in this case the copper is present substitutionally. Furthermore, since the emission is the same for any one of the above impurities, direct association between them and the copper can be ruled out, and the green emission must arise from the copper in a substitutional site having a normal or nearly normal zinc and sulfur environment, a conclusion in agreement with Kroger. This being the case, the red emission can arise from copper in a substitutional site whose environment differs from a normal substitutional position, or from interstitial copper. In the former case, since charge compensating ions are absent, sulfur vacancies would be required. For interstitial Cu^+ however, zinc vacancies are necessary. Since we have always observed a blue emission associated with the red emission, similar to the blue emission obtained in $\text{ZnS}:\text{Cl}$, we conclude that zinc vacancies are produced, and that therefore the red emission due to copper without chloride results from interstitial copper ions.

Because it is believed that zinc sulfide is at least partially non-ionic in character,²⁴ we should like to show that similar results can be obtained on a semiconductor model. Using the band approximation, we may describe the system as follows: We replace a neutral zinc atom in sulfide with a neutral copper atom. Since the neutral copper atom contains only one 4s electron, there will be a deficiency of one electron per copper atom, and positive holes will appear in the valence band. In semiconductor terminology, copper will act as an acceptor impurity. At high temperatures, with the acceptors ionized, the copper atoms will each have one additional

²³ F. A. Kroger, *J. Chem. Phys.* **20**, 345 (1952).

²⁴ Y. K. Syrkin and M. E. Dyatkina, *Structure of Molecules* (Butterworths Scientific Publications, London, 1950), p. 340.

electron, and will thus be diamagnetic; the system as a whole will be paramagnetic, however, due to the presence of free holes. At sufficiently low temperatures, the holes will be associated with the copper atoms, and the system will remain paramagnetic. Similarly, we assume that the replacement of sulfur by chlorine will produce donor centers. In this case also the system will be paramagnetic, whether or not the centers are ionized.

If we now introduce equal numbers of donor and acceptor centers by adding equal amounts of copper and chlorine, the ZnS will remain intrinsic; the donor electrons produced by chlorine will have annihilated the holes produced by copper, and the system will be diamagnetic at low temperatures. It is thus noted that in this situation, copper will have one more electron, and chlorine one less electron than in the neutral atomic configurations.

It can be shown in a quantitative fashion²⁵ that in many semiconductors the number of acceptor levels will always very nearly equal the number of donor levels. The condition for this is that the energy gap be large with respect to the energy necessary to produce a defect such as a vacancy. If one adds only a donor impurity to such a semiconductor, for example, it is energetically economical for the system to produce an equivalent number of *physical* acceptor centers by means of the appropriate kind of vacancies. This is the situation presumed to exist in the cases discussed here. It is to be expected, therefore, that if copper and chlorine are both present in the preparation, they will both be assimilated, in any relative proportion which will produce nearly equal numbers of donor and acceptor states.

The above description, involving the simultaneous presence of copper and chlorine, is the situation we believe to exist when the green emission is observed. The need for chlorine or a similar donor impurity, together with the copper, to produce this emission leads us to conclude that the copper is substitutional. The absence of any appreciable difference between the green emission produced with any other donor such as bromine or iodine indicates that the emission is associated mainly with the copper impurity.

As was indicated earlier, if substitutional chlorine donor atoms are introduced by themselves they will result in the production of acceptor levels; in the absence of a second impurity, the acceptor levels can be provided by vacancies. That the blue emission is a property of the acceptor states and not of the chlorine impurity is indicated by the fact that the same blue emission occurs with either bromine or iodine.¹⁰

Although direct evidence is lacking concerning the

defect responsible for these acceptor levels, arguments similar to those used for copper lead us to assign them to zinc vacancies. This choice finds support in (a) analogy with other semiconductors, notably PbS and PbSe, in which Pb vacancies behave as acceptors, and (b) the observation that the blue emission can be produced by heating impurity-free ZnS to a sufficiently high temperature. In order to account for the diamagnetism when chlorine is present, each zinc vacancy must produce two acceptor levels each of which is occupied in the luminescent ground state by an electron.

The same blue emission which is produced by chlorine is observed in the specimens having a red emission, and containing only copper impurities. In these red specimens, therefore, the copper behaves as a donor. Since we believe substitutional copper to be an electron acceptor, we attribute the donor character of the copper in these specimens to interstitial copper atoms.

As in the case of substitutional copper, the interstitial copper, if introduced without vacancies would be paramagnetic due to the one $4s$ electron. Because of the simultaneous presence of acceptor levels in the form of zinc vacancies, the copper atoms are ionized, and the system remains diamagnetic.

The semiconductor description leads us to certain conclusions which were similar to those obtained on an ionic model: the green emission is attributed to substitutional copper, the red emission to interstitial copper, and the blue emission to zinc vacancies. There are differences, however, in the detailed description of these centers. On the ionic model we would describe both the interstitial and substitutional copper as Cu^+ . This implies that in their optically unexcited states interstitial and substitutional copper impurities are alike in that they each have one electron less than the neutral atom. On the semiconductor model, the two are quite different; the substitutional copper has gained an electron while the interstitial has lost one. Other differences also result from the different assumptions made in the two descriptions. Charge compensation in the ionic model is replaced by an equality of donors and acceptors. By means of the latter principle, we would not expect to find copper present in ZnS as Cu^{++} , whereas Cu^{++} should be possible on the basis of charge compensation alone, and should require no coactivation nor vacancy.

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²⁵ R. L. Longini, Bull. Am. Phys. Soc. 30, No. 3, 36 (1955).