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Interpretation of the Properties of Zinc Sulphide Phosphors

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The properties of pure and copper activated zinc sulfide phosphors are described, and an attempt is made to interpret these properties following the plan of a previous paper on alkali halide phosphors activated by thallium. It is pointed out, as has been done by previous workers, that the combination of photoconductivity and bimolecular decay law of phosphorescence implies that an ionization process accompanies the excitation of zinc sulfide phosphors. By applying the ideas of the quantum theory of solids, it is shown that this ionization process does not correspond to the freeing of an electron from the Zn^{++} or

S^{--} ions of the lattice. It is concluded that the pure ZnS phosphor probably contains neutral interstitial zinc atoms, and that these are responsible for the luminescence and photoconductivity. By analogous reasoning, it is concluded that the copper activated phosphor contains interstitial copper atoms. The relative stability of interstitial copper atoms and substitutional copper ions is discussed in terms of the Schottky-Wagner theory of deviations from stoichiometrical proportions. It is concluded that the interstitial copper atoms probably are in a metastable condition.

1. INTRODUCTION

IN a previous paper¹ on the luminescence of crystals the properties of alkali halides activated by thallium were discussed and interpreted in a tentative manner. It was found possible to relate the absorption and fluorescent spectra of these materials to the presence of monovalent thallium ions which are present in the lattice, substitutionally, replacing alkali metal ions. The weak phosphorescence which decays according to the laws of a monomolecular reaction was related to the properties of the small percentage of thallium ions which have other thallium ions as neighbors. In other words, these simple phosphors behave as though they consisted of a gas of monatomic thallium ions which contains a small percentage of diatomic thallium molecule ions. The fluorescent light is produced by an excitation process which is analogous to resonance excitation of the thallium ions. The phosphorescent light is produced by excitation of one of the thallium ions in a diatomic pair to a state above the resonance level. The valence electrons of the thallium ions should remain attached to the ion during all of these excitation processes, if the picture which is advanced is correct. Hence these phosphors should not become photo-conducting during excitation of phosphorescence. This seems to be in complete accordance with experimental work.

In the present paper the properties of zinc sulfide phosphors shall be discussed from a viewpoint similar to that used in the preceding paper. The experimental work relating to zinc sulfide, unlike that for the alkali halide phosphors,¹ is not summarized in any single series of papers. Many different investigators have contributed to present-day knowledge of these substances. We shall present a brief survey of the experimental conclusions in the next section, emphasizing only those experiments which are felt to be important for the present interpretation. This presentation will be followed by a tentative interpretation of the experimental work.

2. EXPERIMENTAL SURVEY OF THE LUMINESCENCE OF ZnS

Zinc sulfide exists in two crystallographic forms.² The low temperature form is known as zincblende or sphalerite and has a cubic lattice which is related to the structure of diamond. This form is obtained in ordinary precipitation methods of preparing zinc sulfide. The high temperature form, wurtzite, possesses a hexagonal structure in which the coordination number is four, just as in the cubic phase. The thermodynamical transition temperature for the phase change is not accurately known, but it is probably in the neighborhood of 400 or 500°C. The transi-

¹ J. Chem. Phys. **6**, 150 (1938).

² *Strukturberichte*.

tion proceeds very slowly at 660°C ³ and very rapidly at 900°C . The hexagonal form does not revert to the cubic form at a measurable rate at room temperature unless the material is ground or is placed under high nonhydrostatic pressure.⁴

We shall proceed upon the assumption that the ordinary luminescent varieties of ZnS have the high temperature hexagonal structure. All of the ZnS phosphors are produced by heat treatment at temperatures above the thermodynamical transition point and an at least partial transition to the hexagonal phase takes place. Cubic ZnS phosphors have been reported in the literature,⁵ but these materials were always a mixture of the two forms. It is the writer's opinion that the hexagonal form is responsible for the ordinary luminescence. It is conceivable that the cubic form could also be luminescent, but it seems unlikely that the type of changes which are needed in order to activate a crystal of ZnS can be brought about without causing the phase change as well. Theoretical reasons for this viewpoint will be discussed below.

A. Types of phosphors

We shall discuss the following two types of phosphors:

a. Pure ZnS. Pure zinc sulfide may be made⁶ active by appropriate heat treatment. A typical procedure is to heat the material at 900°C for one-half hour. The color of the luminescence of the pure salt is light blue, and it may be excited by any radiation in the near ultraviolet.

*b. Copper-activated ZnS.*⁷ This is the oldest and most commonly known variety of luminescent zinc sulfide. The luminescent light is brilliant green and is excited by radiation in the blue and near ultraviolet. The peak of this excitation band lies at a longer wave-length than the peak for the excitation of pure ZnS. The fraction of copper which is required to activate this luminescence is about 10^{-5} .

Zinc sulfide may be activated by introducing many foreign atoms other than copper. Examples

of such substances are silver and manganese. We shall not deal explicitly with these cases because the experimental facts relating to them are not sufficient to furnish a complete picture. It is highly probable that the type of explanation which we shall develop in order to explain the foregoing two cases will apply *in toto* to a large number of these other cases.

B. Characteristic absorption of ZnS

Qualitative experiments carried on in this laboratory show that the peaks of the characteristic absorption bands of ZnS lie well below 2500\AA . This was proved by studying the transmission of films of zinc sulfide several microns thick which were evaporated on quartz. The tails of these peaks extend into the near ultraviolet. Since the relatively small peaks of the bands which stimulate luminescence lie entirely in the near ultraviolet, it is natural to assume that they arise from a process which is different from that of the fundamental peaks. This fact, which is similar to the facts for alkali halide phosphors, was appreciated by Lenard⁸ very early in the study of zinc sulfide phosphors. To explain it, he assumed that a small number of irregularly placed atoms rather than the typical atoms of the bulk material are responsible for luminescence. In lieu of exact knowledge of the electronic structure of these active regions he referred to them as centers. We shall use this word in the same sense, accepting Lenard's viewpoint that the two peaks have different origin. Just as in the case of the alkali halide phosphors, a part of the object of this paper is to provide an interpretation of the structure of the center in the two cases which were discussed in A.

C. Decay characteristics of phosphorescence

Experimental measurements of the decay characteristics of zinc sulfide activated by copper seem to indicate that the emitted light is entirely phosphorescent⁹ at room temperature. We have checked this in some cases at liquid-air temperatures by showing that the intensity of emitted light is zero when a specimen is first exposed to

³ Experiments by Dr. N. T. Gordon and this laboratory.

⁴ Guntz, *Ann. d. Chemie* **5**, 157 (1926) et seq. Lenard, *Handbuch der Experimental Physik*, Vol. 23, p. 267.

⁵ Tiede and Schleede, *Chem. Ber.* **53**, 1721 (1920).

⁶ Schleede, *Zeits. f. angew. Chemie* **48**, 277 (1935). Riehl, *Ann. d. Physik* **29**, 636 (1937).

⁷ Discovered by Sidot, *Comptes rendus* **63**, 188 (1866).

⁸ Lenard and Tomaschek, *Handbuch der Experimental Physik*, Vol. 13 (1928), pp. 1 and 2.

⁹ Perkins and Kaufmann, *Pub. No. ST38*, R.C.A. Res. and Dev. Lab. Riehl and Ortmann, *Ann. d. Physik* **29**, 556 (1937).

3650Å radiation. The emission becomes appreciable only after several seconds of exposure.

The decay of intensity in copper activated material is given¹⁰ fairly closely by the equation

$$(I(0)/I(t))^{\frac{1}{2}} = \alpha t + 1, \quad (1)$$

where $I(t)$ is the intensity at time t and α is a constant which is temperature dependent, decreasing with decreasing temperature. This decay law implies that the number of excited centers which are left after time t if there are N_0 at time $t=0$ is given approximately by the equation

$$N = N_0/(\alpha t + 1). \quad (2)$$

Deviations from (1) are observed at small values of t .

Equation (2) is characteristic of a bimolecular reaction, that is, of a reaction in which two perfect gases A and B combine to form AB . This type of decay law is to be distinguished from the exponential type observed in the alkali halide phosphors.

The decay characteristics of pure zinc sulfide phosphors have not been measured quantitatively, but they show the same temperature-dependent characteristics as the copper activated phosphors. We shall assume that the law (1) is valid in this case too.

D. Photoconductivity

The photoconductivity of zinc sulfide activated by copper was investigated by Gudden and Pohl¹¹ in 1920. They found that the absorption peaks for stimulating luminescence and photoconductivity are practically identical. The pure sulfide phosphor does not seem to have been¹² investigated for photoconductivity, but it should be photoconducting if our assumption that there is a one-to-one correspondence between the properties of the two types is correct.

¹⁰ Antonow-Romanowsky, *Physik. Zeits. Sowjetunion* **7**, 366 (1935).

¹¹ Cf. Gudden, *Photoelectric Phenomena* (Springer, 1928).

¹² Gudden and Pohl [*Zeits. f. Physik* **2**, 181 (1920)] report finding photoconductivity in "impurity free" zinc sulfide. They do not describe the luminescent properties of this material. Incidentally they report conductivity in the manganese activated phosphor.

3. INTERPRETATION OF THE PROPERTIES OF THE PHOSPHORS

The key to the interpretation of the zinc sulfide phosphors evidently is the coexistence of photoconductivity and phosphorescence with the bimolecular decay law. These facts indicate that the absorption process results in ionization of the center and that the phosphorescence is a consequence of the subsequent recombination of the electrons with the ionized centers. This view has been expressed in a number of papers¹³ and will not be amplified further in this one. The fundamental problem is: What is ionized during the absorption of light? We shall attempt to answer this question first for the pure sulfide phosphor and then for the copper activated substance. Before doing this, however, we shall discuss the probable origin of the fundamental peaks in pure zinc sulfide.

A. The fundamental absorption bands of zinc sulfide

The Madelung potential at a negative ion in the wurtzite lattice is¹⁴

$$V_M = 1.64(Ze/r), \quad (3)$$

where Z is the valence of the positive ions and r is the distance between nearest unlike ions. The value of V_M for positive ions is the negative of this. Using this and data concerning the ions Zn^{++} and S^{--} we may determine the relative energy of electrons in the lattice.

The electron affinity of S^{--} as determined from the Born cycle is about -90 kcal. or about -4 ev. Lozier¹⁵ has found that this characteristic instability of divalent negative ions is due entirely to the second electron in the case of O^{--} . The affinity of the first electron is 2.2 ± 0.2 ev. Since the affinities of the halogens decrease with increasing atomic number, we shall assume that the affinity for the first electron in sulfur is less than that for oxygen and shall select a value of 1 ev. The affinity for the second is then about -5 ev. The energy of S^{--} relative to that of S^- is shown on the right-hand side of Fig. 1 as

¹³ Cf. reference 11. Also Blochinzew, *Physik. Zeits. Sowjetunion* **586** (1937), and Reimann, *Nature* **140**, 501 (1937).

¹⁴ Hund, *Zeits. f. Physik* **34**, 833 (1925). Gross, *Zeits. f. Krist.* **76**, 565 (1931).

¹⁵ Lozier, *Phys. Rev.* **46**, 268 (1934).

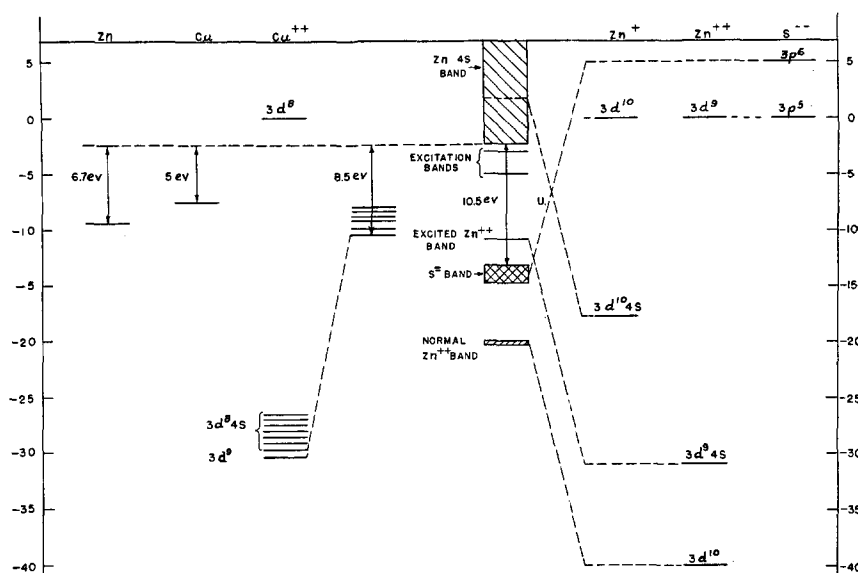


FIG. 1. Behavior of atomic and ionic energy levels before and after formation of zinc sulfide lattice.

the position of a $3p^6$ configuration relative to a $3p^5$.

The energy of the various states of Zn^{++} relative to the ground state of Zn^{++} (d^9 configuration) is shown in the second column from the right in Fig. 1. The energy required to ionize Zn^{++} is 40 ev. Hence the normal state of Zn^{++} is placed at -40 ev in this diagram. The first excited state of Zn^{++} (corresponding to $3d^9 4s$) is about 9 ev relative to the lowest state.

The lowest state of Zn^+ relative to $3d^{10}$ is given in the third column from the right in Fig. 1. We shall use this in estimating the energy required to transfer an electron from the sulfur ion to the zinc ion.

The dotted lines in Fig. 1 show the way in which the electronic energy changes as ions are brought together to form the wurtzite lattice. The energy of electrons on negative ions is decreased by an amount (3), Z being 2 in the present case. The energy of electrons on positive ions is increased by the same amount. In addition to this displacement, the levels broaden into bands in accordance with the band theory of solids. We can estimate the broadening only roughly. By analogy with the negative ion band¹⁶ in the alkali halides we may expect the S^{--} level

to broaden by several ev. The broadening of the $4s$ level of Zn^+ can be estimated roughly from the broadening of the $4s$ level in metallic copper which was investigated by Fuchs,¹⁷ since the broadening is determined mainly by the interatomic distance. In this way the writer has decided that the lower edge of the $4s$ band is about 4 ev below the energy determined by adding the Madelung energy to the $3d^{10} 4s$ level of atomic zinc. The relative positions of the various bands and levels in zinc sulfide are shown in the fourth column from the right of Fig. 1. The highest band is the $4s$ band and about 10.5 ev below it is the p^6 band of the sulfur ion electrons. Below this is the band of the outer electrons of Zn^{++} . The line 9 ev above this is the first excited level of the Zn^{++} ion. It is assumed that this excitation energy does not change appreciably in going from the free ion to the solid. The lines immediately under the $4s$ band correspond to the excitation bands of the sulfur ion. In the atomic picture of solids these levels correspond to transfer of electrons from the S^{--} ions to the nearest neighboring Zn^{++} in a way such as that described in reference 1. We have computed roughly the position of these levels in the manner employed by von Hippel,¹⁸ which is

¹⁶ Shockley, Phys. Rev. **50**, 754 (1936). Ewing and Seitz, Phys. Rev. **50**, 760 (1936).

¹⁷ Fuchs, Proc. Roy. Soc. **151**, 585 (1935).

¹⁸ von Hippel, Zeits. f. Physik **101**, 680 (1936).

based on an earlier method of Gudden and Pohl. The lowest of these excitation levels which is analogous to a p^5S state of S^{--} turns out to be about 7 ev above the $S^{--} p^6$ band. This should be the first excited state of the ideal crystal of zinc sulfide if the rough computational methods employed here are approximately correct. The transition to the $4s$ or conduction band requires about 11 ev. Hence the excitation bands should lie between about 1800Å and 1100Å, according to this picture. Since the first excited state of Zn^{++} is 9 ev above the d^{10} ground state, we may expect that the bands corresponding to excitation of Zn^{++} and of S^{--} will overlap.

Let us suppose that some Zn^{++} ions are replaced by Cu^{++} ions. The position of the normal state of Cu^{++} relative to that of Cu^{+++} ($3d^8$) is shown in the third column from the left of Fig. 1.¹⁹ As cupric ions are brought into the lattice in Zn^{++} positions, the energy of a valence electron on the Cu^{++} ion is raised to the positions shown in the fourth column from the left in Fig. 1. The ground level of the ion is roughly 8 ev below the conduction band of the solid, implying that photoconductivity would be observed only in the far ultraviolet if copper ions could enter the zinc sulfide lattice only substitutionally, replacing Zn^{++} ions. Incidentally, it should be observed that the color of pure cupric salts may be ascribed to the closeness of the $3d^9$ and $3d^8 4s$ configurations.

To summarize, we may say that the observed positions of the fundamental absorption peaks of zinc sulfide can be explained semiquantitatively in terms of simple energy-level diagrams of the type used in alkali halide lattices. There is no reason for expecting photoconductivity for near ultraviolet quanta in the ideal zinc sulfide lattice or in a zinc sulfide lattice in which some of the zinc ions are replaced by cupric ions.

B. Luminescence of pure zinc sulfide

A clue concerning the nature of pure luminescent zinc sulfide is provided by the investigations of Wagner,²⁰ Baumbach, Fritsch and

their co-workers on the electron conductivity of zinc oxide. This oxide has the same crystal structure as the luminescent form of zinc sulfide. Experiments of the same type carried out on zinc sulfide would obviously be preferable for our purposes, but it seems safe to assume that the two materials have analogous properties. As a matter of fact, experiments carried on in this laboratory indicate that zinc oxide has luminescent properties which are qualitatively identical with these of zinc sulfide.

Zinc oxide is a typical semiconductor. Specimens which have been heated in a vacuum for a considerable length of time exhibit at room temperature an appreciable electronic conductivity which decreases with decreasing temperature. At room temperature and at lower temperatures the temperature dependence is described approximately by the equation

$$\sigma = Ae^{-\epsilon/kT}, \quad (4)$$

where σ is the conductivity, A is practically constant, and ϵ is a constant which varies between 1 and 0.01 ev, depending upon the specimen and type of heat treatment it has received. In general, ϵ is smaller the longer the specimen has been heated in a vacuum.

Hall effect and thermoelectric measurements show that this conductivity is principally electronic and that the carriers are negative charges; that is, the sign of the Hall coefficient is the same as in bismuth. In addition, there is a very small positive ion transport number. This indicates that the zinc ions are considerably more mobile than are the oxygen ions.

The conductivity of conducting zinc oxide is dependent upon the vapor pressure of oxygen with which a specimen is at equilibrium during its high temperature heat treatment. Generally speaking, the higher the vapor pressure of oxygen the lower is the room temperature conductivity. The room temperature conductivity of some specimens has been reduced by as much as one million by heating at 1000°C in one hundred atmospheres of oxygen for several days. Large changes of this type are usually due to changes in both A and ϵ in (4). The first constant decreases and the second increases with oxygen pressure. The dependence of A on oxygen pressure, p_{O_2} , is

¹⁹ I am indebted to Professor A. G. Shenstone for the estimate of the ionization energy of Cu^{++} which is used in this diagram.

²⁰ Wagner, *Zeits. f. physik. Chemie* **B22**, 181 (1933) et seq. Wagner and Baumbach, *Zeits. f. physik. Chemie* **22**, 199 (1933). Fritsch, *Ann. d. Physik* **22**, 375 (1935).

described roughly by the equation

$$A = Cp_{O_2}^{1/4.3}, \quad (5)$$

where C is a constant.

From this dependence of A and the sign of the Hall effect, Wagner²⁰ concludes that the composition of conducting zinc oxide deviates from strict stoichiometric proportions and that there is an excess of zinc. One of the results of heating an ideal specimen in a vacuum at high temperatures is the driving off of oxygen which leaves the crystal with an excess of zinc. The system presumably reaches equilibrium when a fraction of about 10^{-4} of the oxygen atoms have left. Since the crystal remains electrostatically uncharged, the oxygen which leaves must be neutral. The electrons which are left behind are normally bound in some way but may be freed thermally and may then conduct a current. The decrease of A with oxygen vapor pressure is explicable if heating the specimen in a vapor pressure of oxygen shifts the equilibrium fraction of excess zinc. Wagner and Schottky^{20, 21} have given this process a reasonable interpretation in terms of principles of statistical mechanics. Thus the relation (5) may be explained semi-quantitatively in terms of the laws of mass action, as they are ordinarily applied to gaseous reactions.

In what physical form is the excess zinc present? According to Wagner there are two ways in which we may have deviations from ideal stoichiometric ratios. First, this may occur by having oxygen ions missing from ordinary oxygen sites. In this case the electrons left behind will occupy these sites at low temperatures. Second, the deviations may occur by having the excess zinc ions present in the lattice interstitially. The excess electrons will accompany these vacant ions at low temperature, essentially giving us interstitial zinc atoms. As in the other case, these zinc ions may be ionized thermally. The observed positive ion transport number strongly supports the second picture, since it indicates that the negative ions are practically unable to move through the lattice. Apparently we may conclude that the oxygen atoms leave the surface of the

specimen when it is heated in a vacuum and that the zinc atoms which remain diffuse into the interstices of the lattice. This procedure is partly reversed when the oxygen vapor pressure is increased. Crystals which have the zincblende and wurtzite structures are very porous because of the low coordination number and leave ample room for interstitial atoms and ions.

The dependence of ϵ in (4) on oxygen vapor pressure indicates that the interstitial zinc atoms are not bound equally tightly and that the looser ones which leave the lattice most easily have smaller values of ϵ . A similar conclusion has been drawn for the case of Cu_2O by Engelhard.²²

If we now assume that zinc oxide and zinc sulfide have analogous properties, we may explain the luminescence of pure zinc sulfide in the following way. The pure zinc sulfide which is formed by precipitation from solution has practically ideal structure and practically no excess of zinc atoms. Sulfur evaporates from these crystals when they are heated in a vacuum and the excess zinc atoms diffuse into the lattice. These atoms may be optically as well as thermally ionized. The recombination of an interstitial zinc ion and an electron gives rise to phosphorescence. The recombination should approximately obey an equation of the type (1).

Since the most efficient wave-lengths for exciting pure zinc sulfide lie in the ultraviolet and the emitted radiation lies in the blue, one might at first sight be inclined to say that the thermal activation energy for ionizing the interstitial atoms in zinc sulfide is so large that no semi-conductivity may be expected at ordinary temperatures. This conclusion may be in error for the following reasons, aside from the Franck-Condon principle and the fact that ϵ in (4) must be less than half the optical excitation energy because of the bimolecular character of ionization. As we said above, the dependence of ϵ on oxygen vapor pressure in the case of ZnO indicates that all interstitial zinc atoms are not bound in the same way. Hence it is possible that (a) either most of the centers have a larger value of ϵ than those which ordinarily are responsible for conduction, or (b) the centers which have largest ϵ 's have the largest cross section for optical ionization. Either

²¹ Schottky and Wagner, *Zeits. f. physik. Chemie* **B11**, 163 (1931). A survey of these computational methods may be found in the review article by Nix and Shockley, *Rev. Mod. Phys.* **10**, 1 (1938).

²² Engelhard, *Ann. d. Physik* **17**, 501 (1933).

or both of these possibilities may account for the coexistence of visible luminescence and a low value of ϵ in the same crystal.

C. Luminescence of copper activated zinc sulfide

The close similarity of the luminescent behavior of zinc sulfide activated by copper and pure zinc sulfide suggests that a similar mechanism is responsible for the luminescence in both cases. In view of B , we may postulate that the copper activated sulfide contains interstitial copper atoms. These are ionized by the light which stimulates both phosphorescence and photoconductivity, and the phosphorescent light is produced by the recombination of these ions and electrons.

What can be said about the energy required to ionize either interstitial zinc or copper atoms? The position of the normal states of free copper and zinc atoms relative to the levels of zinc sulfide are illustrated in the first and second columns from the left in Fig. 1. These diagrams show that the energies required to remove an electron from these atoms and place the electron in the conduction band are approximately 6.7 and 5 ev, respectively. The fact that the optical excitation energies of the phosphors are considerably less than these values indicates that the atoms are appreciably perturbed by being brought into the lattice.

One of the important questions which remain to be answered is the following: Why do the activating copper atoms enter interstitial rather than substitutional positions? If the copper atoms would prefer substitutional positions in the true equilibrium state, we must assume that interstitial diffusion takes place much more rapidly than substitution, in which case the copper activated phosphor is in a metastable state. However, it is not necessarily true that the copper atoms would prefer substitutional positions. This may be shown by the following schematic computation, which is patterned after the theory of Schottky and Wagner,²¹ on deviations from ideal stoichiometric relations.

Let us consider a zinc sulfide crystal in which there are N lattice sites for zinc ions and let us add to this m copper atoms where $m \ll N$. We shall assume that n of these enter substitutional positions and $m-n$ enter interstitial ones,

replacing zinc atoms which then appear in interstitial positions. We shall let ϵ_{Cu} and ϵ_{Zn} be the cohesive energies of the interstitial copper and zinc atoms and shall let $\Delta\epsilon_{\text{sub}}$ be the energy required to interchange a free copper ion and a bound zinc ion which is in a zinc site. This energy is composed of two terms: (1) The difference in cohesion of a copper ion and a zinc ion in a zinc site, and (2) the energy of 0.65 ev required to remove two valence electrons from a neutral copper atom and to place them on a zinc ion. The copper sulfide lattice is considerably different from the zinc sulfide lattice and its cohesive energy, referred to monatomic copper, is about 0.92 ev per molecule more stable than the ZnS lattice, referred to monatomic zinc. Mayer²³ has shown in the case of some monovalent halides that the relative stability of different lattice types is of the order of 1 ev per molecule. Hence we may conclude that $\Delta\epsilon_{\text{sub}}$ is probably positive and of the order of magnitude 1 ev.

We shall assume that the entropy which is gained by substituting n copper ions for n zinc ions is the mixing entropy

$$k \log \frac{N!}{n!(N-n)!} \cong -kn \log \frac{n}{N}.$$

The entropy of $m-n$ interstitial atoms will lie between the value

$$-k(m-n) \log (m-n)/\rho,$$

associated with the possible permutations among ρ interstitial sites, and the value

$$-k(m-n) \log (m-n)/C + 5/2k$$

for a perfect gas. Here

$$C = (2V/h^3)(2\pi\mu kT),$$

where V is the volume of the crystal and μ is the mass of the atoms. Fortunately both of these expressions lead to practically the same equilibrium value of n since the sum of the number of interstitial zinc and copper atoms is constant. The total relative free energy ΔA of the crystal is

$$\begin{aligned} \Delta A = & (m-n)\epsilon_{\text{Cu}} + n\epsilon_{\text{Zn}} + n\Delta\epsilon_{\text{sub}} \\ & + kT[n \log (n/N) + (m-n) \log (m-n) \\ & + n \log n] + \alpha, \end{aligned}$$

²³ Mayer, J. Chem. Phys. **1**, 327 (1933).

where α is independent of n . This is a minimum when

$$\frac{n^2}{(m-n)N} = \exp(\epsilon_{\text{Cu}} - \epsilon_{\text{Zn}} - \Delta\epsilon_{\text{sub}})/kT.$$

The energy term $\epsilon_{\text{Cu}} - \epsilon_{\text{Zn}} - \Delta\epsilon_{\text{sub}}$ is the energy required to interchange an interstitial zinc atom and a substituted copper ion. We have estimated $\Delta\epsilon_{\text{sub}}$ roughly above, but it does not seem feasible to attempt an estimate of $\epsilon_{\text{Cu}} - \epsilon_{\text{Zn}}$. The condition which must be satisfied if n is to be small compared to m is that

$$\exp -(\Delta\epsilon_{\text{sub}} + \epsilon_{\text{Zn}} - \epsilon_{\text{Cu}})/kT$$

be small compared to m/N , which we shall take to be of the order of 10^{-4} . For $T \sim 1200\text{K}$, the temperature at which phosphors are ordinarily activated, this implies that the energy which is required to interchange an interstitial copper atom and a zinc ion must be greater than 2 ev. If this condition is satisfied most of the copper atoms will remain in interstitial positions. If it is not quite satisfied all interstitial copper atoms eventually should be replaced by zinc atoms, assuming $m/N \sim 10^{-4}$. In this case the copper activated luminescence should be replaced by the luminescence of the pure sulfide in the course of extended heating at high temperature.

Guntz⁴ has pointed out that copper activated

zinc sulfide which has been made nonluminescent by extensive nonhydrostatic pressing becomes light brown in color as a result of the pressing. This color, he estimates, is the same as that one would obtain by making a mechanical mixture of pure zinc sulfide and an amount of cupric sulfide which is chemically equivalent to the amount of copper present in the phosphor. This suggests that the copper is not present in the cupric form in the luminous material and that it reverts to this form when thermodynamical equilibrium is attained by pressing.

4. CONCLUSION AND SUMMARY

In conclusion it may be pointed out that the alkali halide phosphors and the zinc sulfide phosphors probably furnish the standard types for classifying most other phosphors. As yet it is not possible to say definitely to which class belong substances such as Zn_2SiO_4 (willemite) and CaWO_3 , but it is hoped that experiments which will permit such a classification will be carried out in the near future.

A summary of the contents of this paper can be found in the abstract.

In conclusion I wish to thank Dr. N. T. Gordon and Mr. F. Quinlan for their collaboration in connection with some of the experiments described in this work.