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NEW THEORIES OF THE CHEMICAL NATURE OF LUMINESCENCE CENTRES IN ZINC SULPHIDE PHOSPHORS

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CONTENTS

I. Introduction 631
II. Activators and coactivators 632
1. Luminescence centres produced by activators 632
2. Association of activators and coactivators 635
III. Luminescence centres of "self-activated" phosphors 636
IV. Luminescence centres of copper- and silver--activated phosphors 639
V. "Indirect" activation and structure of the luminescence centres 643

I. INTRODUCTION

The chemistry of sulphide phosphors of the ZnS type is an important and very interesting area of solid state chemistry†. Because of their high luminescence efficiency under a variety of excitation conditions, and of the unusually wide range of their properties, crystal phosphors of this class have found extensive technical applications in television tubes, radar screens, oscilloscopes, electron--optical converters, X-ray screens, electroluminescent panels, electron microscopes, dosimeters and detectors of different types of radiation, etc. Cadmium sulphide crystals, which belong to the same class of materials, are among the most sensitive photoconductors.

The influence of very small traces of impurities on these two properties of crystalline sulphides — luminescence and photoconductivity — was recognised at the turn of the century. The efficiency with which the absorbed radiant energy is transformed into visible light (of spectral composition determined by the nature of an impurity, termed the activator) suggested that energy transfer takes place from the sites where energy is absorbed to the sites where the activator is located. This gave rise to the theory that the luminescence centres are special groupings where the act of light emission occurs. The ability of ZnS and CdS crystals to transmit the absorbed energy with high efficiency to the luminescence centres accounts for their high luminescence yield, their high photoconductivity, and the extreme sensitivity of phosphors of this class to a number of impurities, which can effect the optical properties of these phosphors even at a concentration of 10^{-6}–10^{-8} gramme per gramme of the sulphide.

Elucidation of the nature of the luminescence centres and of the relationship between the optical properties of phosphors and the structure of these centres, being one aspect of the more general problem of establishing the relation between the atomic–molecular structure and the properties of materials, is the key problem in luminescence and is of great importance in the general development of solid state chemistry and physics. Yet the first serious studies in this field began only towards the end of the 1940's, when research on the kinetics of luminescence and on the accompanying internal photoeffect provided, on the basis of the band model of solids, a fairly orderly picture of the physical effects involves in the luminescence of zinc sulphide luminous compositions. The work done in the last 15–20 years and still in progress has significantly changed our ideas on the nature of the luminescence centres and on the processes by which they are formed, and has made it clear that the solution of the problem lies in the domain of chemistry to a much greater extent than had originally been realised. Many difficulties still remain to be overcome, in particular those associated with the extreme sensitivity of the optical properties of zinc sulphide phosphors to various impurities present at a concentration level which defies analytical control with the required degree of precision, and also with our inadequate knowledge of the nature of structural defects and of the role played by these defects in the formation of sulphide phosphors. The situation is made worse by the abundant literature and by the close interplay of chemistry and physics: as a result, authors attempting to interpret their

† Luminescent crystals of zinc sulphide were prepared for the first time 100 years ago by Sidot, in Sainte-Clare Deville's laboratory.

results are often unaware of many relevant factors discussed in earlier publications. This causes a great deal of confusion and inconsistency in many of the papers devoted to the present problem. Hence, a review article discussing the work of all the main research schools and all the most important points of view would be very timely: such is the aim of the present paper, with the stipulation that we shall not attempt to consider all the questions which have a bearing on our problem. The reason for this is that zinc sulphide phosphors contain centres of two types. One type of centres, for example those produced by manganese or rare-earth ions, gives rise to luminescence as a result of electronic transitions within the activator ion itself ("direct activation"). The radiation from centres of the second type is not characteristic of the particular activator to the same extent. Thus, ZnS phosphors activated by impurities as diverse as Ag, Cu, Al, and Cl, can, under certain preparative conditions, produce blue radiation of very similar spectral composition. In this case we cannot ascribe the observed luminescence to electronic transitions within the ions (or atoms) of the activator. Centres of this second type are the most characteristic of zinc sulphide phosphors, the most important from a practical point of view, the most thoroughly investigated, and the least understood. The present paper is devoted to a discussion of centres of this type.

II. ACTIVATORS AND COACTIVATORS

1. Luminescence Centres Produced by Activators

Luminescence centres were originally thought to be rather coarse aggregates of many atoms, but in the early 1930's the suggestion was put forward, on the basis of several results, that the centres consist of single atoms (or ions) of the activator located at lattice or interstitial sites[1-4]. It has been commonly assumed, with Lennard[5], that only heavy metal atoms can act as activators. Since their energy levels are closely spaced[6], they emit radiation which is not absorbed by the phosphor matrix. The discovery[7] that zinc sulphide can emit bright blue luminescence in the absence of any deliberately added activators had a marked effect on the development of views on luminescence centres. This discovery was made possible by the improved methods of preparation of sulphide of a high degree of purity. An analogous phenomenon was observed with zinc oxide. Since it was assumed that only metals can serve as activators, the effect was interpreted as self-activation by the excess of zinc produced by thermal dissociation of the zinc oxide and sulphide[8], experimental confirmation being forthcoming in the case of ZnO. Arguing that ZnS should behave very much like ZnO, Seitz[2,9] suggested that free atoms of Zn give rise to luminescence centres by moving to interstitial sites, and that activation by silver and copper occurs by a similar mechanism. In favour of this point of view, Riehl and Ortmann[10] put forward some arguments based on earlier experiments by Tiede and Weiss[11], who had shown that, when a mixture of roasted ZnS and copper sulphide is heated, the diffusion of Cu, leading to the formation of luminescence centres, begins at a temperature as low as 330°. Adopting an ionic model for zinc sulphide, we can think of the material as an array of close-packed sulphur ions with half of the tetrahedral cavities occupied by zinc ions[12]. The presence of free tetrahedral cavities accounts, according to Riehl and Ortmann, for the diffusion of the activator deep into the lattice even at relatively low temperatures, the process being assisted by the fact that the activator enters the lattice in the form of atoms rather than ions. However, Riehl and Ortmann subsequently rejected[13] the last assumption. Bundel'[14] produced additional arguments in favour of the Schleede–Seitz–Riehl hypothesis. According to his observations, the quenching of luminescence produced by heating the phosphor in sulphur vapour occurs more readily the lower the dissociation pressure of the sulphide of the activator metal. This may be due to the fact that activation occurs when activator atoms formed by thermal decomposition of their sulphides are introduced into the crystal lattice[15]. Bundel' quotes as further evidence for this point of view the fact that luminescence quenching by vacuum heat-treatment occurs more readily in "self-activated" phosphors than in phosphors activated by copper or silver, in keeping with the greater volatility of Zn and Cd as compared with Ag and Cu[16]. Very similar views were put forward by Cherepnev[17-20], who considered that the activator may be present in zinc sulphide in a state involving different degrees of dispersion.

The model according to which luminescence centres are formed by free atoms of the activator was dominant until the end of the 1940's. However, several authors have doubted the correctness of the suggested "self-activation" of zinc sulphide by zinc in excess of stoichiometry when the material has been heat-treated in the presence of a flux and oxygen[21], and also the possibility that copper can exist in an atomic state in zinc sulphide[22] and that ZnS–Ag luminescence centres are created by atomic silver. (The latter assumption is inconsistent with the deleterious effect of a reducing atmosphere on ZnS–Ag[23].) A fundamental defect of the above model, stressed by a number of workers[21,24,25], is that it fails to explain a very remarkable feature of zinc sulphide phosphors — the favourable effect of halides, commonly used as fluxes, on their formation — which was noted long ago in the literature[5,26]. Whereas the flux used in the preparation of other phosphors serves only to lower the temperature to which the charge has to be heated, and often is not merely unnecessary but may even diminish the brightness of the luminescence[24], in the case of sulphides the use of halide fluxes (usually alkali or alkaline-earth metal chlorides) is essential to the achievement of efficient luminescence. Schlegel[27] pointed out that considerable quantities of $ZnCl_2$ are formed when ZnS is heated with NaCl, and, whilst ascribing this to reaction between the ZnS and NaCl, he nevertheless suggested that the role of the flux is to assist dissociation of the sulphide of the activator metal. Gugel'[28] stressed the importance of exchange reactions between ZnS and the chlorides of alkali and alkaline-earth metals, and suggested that these reactions assist diffusion of the activator into the crystal lattice of the sulphide by eroding the surface. The direct participation of chlorine in the formation of luminescence centres has also been considered[24,29]. An important function of the chloride, unrelated to its mineralising action, was convincingly demonstrated by Strange[24], who heated ZnS in evacuated quartz bulbs at 1000° for several hours, and found that the characteristic green luminescence of ZnS–Cu appeared in the presence of 0.001% CuS and an equivalent amount of NH_4Cl, but that the luminescence was weak or altogether absent in the presence of CuS alone (i.e. without NH_4Cl) or when the ZnS was heated without any intentional additive. A similar result was obtained with silver.

The role of halides in the formation of phosphors was examined in detail in a series of papers by Kröger[30-33], which marked the beginning of a new stage in the study of the nature of luminescence centres. Whereas the first stage of these researches, discussed above, was made possible by the development of effective methods for the purification of zinc sulphide from metallic activators, especially Cu, and luminescence "quenchers", such as Fe, Ni, Co, which led to the discovery of "self-activated" ZnS phosphors, the second stage began when attention was turned to the need to remove anionic impurities as well from the experimental material. In order to remove the chloride and oxygen present in commerial "phosphorescent grade" ZnS, Kröger subjected the material to a preliminary heat-treatment in a stream of H_2 or H_2S. Later workers[34-37] recommend deoxidation and dechlorination of ZnS by a two-stage treatment in hydrogen sulphide, first at a relatively low temperature (400°), and then at a more elevated temperature (900–1200°), because if the process is carried out with a high initial temperature the recrystallisation which occurs at the same time inhibits the removal of impurities from deep within the crystals. Another experimentally valuable innovation introduced by Kröger was to replace heating with a flux by heating in an atmosphere of HCl and H_2S. This permitted a more precise regulation of the preparation process and made it easier to interpret the results. The method has since found technical applications, particularly in the synthesis of electroluminescent materials[38,39].

Kröger showed, in agreement with the results of Strange[24], that ZnS–Cu, ZnS–Ag, and ZnS s/a ("self-activated") phosphors are not formed in an atmosphere of H_2S when the system is free from chlorine. The normal luminescence appears on heating in a stream of gas containing HCl. The refinements in experimental technique mentioned above allowed these phenomena to be observed with satisfactory reproducibility. Kröger interpreted his results on the basis of the principle of charge compensation, well known from crystal chemistry and mineralogy[40,41] and successfully applied to the chemistry of semiconductors[42]. Essentially, this principle states that in the formation of substitutional solid solutions the sum of the charges on the substituent ions must be equal to the sum of the charges on the ions replaced. This principle is a simple corollary of the requirement that the electrical neutrality of the crystal must be preserved. If, for example, a Zn^{2+} ion is replaced by a Cu^{+} ion, the result is to create a defect with an effective charge of -1, which we propose to denote Cu'_{Zn}. This charge can be compensated by the simultaneous insertion of a Cl^- ion in an S^{2-} site, which produces a defect with an effective charge of +1 ($Cl_S^{\cdot}$). In the absence of chlorine, compensation can be achieved by the formation of an anion (sulphur) vacancy of effective charge +2 ($V_S^{\cdot\cdot}$) and therefore able to balance the charges of two Cu′ defects; however, Kröger regards the formation of solid solutions in which the compensation is of this type as thermodynamically the less probable. In the terminology of crystal chemistry[41], the formation of normal isomorphous mixed crystals ZnS.CuCl with heterovalent replacement (mixed crystals of a new kind, in Grimm's terminology) proceeds more readily than the formation of anomalous mixed crystals $ZnS.Cu_2S$ with addition or subtraction. ZnS and CuCl have the same atomic ratios of constituent elements and therefore have chemical formulae of the same type, similar atomic dimensions, and a similar bond type[43]. Hence, the two compounds are isomorphous, and are quite likely to form mixed crystals. This is confirmed by the fact that the concentrations of Cl and of Cu in the ZnS lattice increase in the same proportion[32,44,45]. Under these conditions the concentration of Cl can reach much higher values than when ZnS is heated in the presence of a copper-free chloride flux. An analogous situation exists in the case of silver activation. Formation of AgCl has been shown, by chemical analysis[46], to take place when sulphide phosphors are heated with silver and a chloride flux under normal conditions (in the air). It may also be imagined that charge compensation occurs by the simultaneous introduction of sulphide activator and zinc chloride[47]:

$$n\mathrm{ZnS} + \mathrm{Cu_2S} + \mathrm{ZnCl_2} \rightarrow \mathrm{Zn_{n+1}Cu_2S_{n+1}Cl_2}. \qquad (1)$$

The zinc chloride can be replaced by the sulphide of a tervalent metal[48], such as Al_2S_3:

$$n\mathrm{ZnS} + \mathrm{Cu_2S} + \mathrm{Al_2S_3} \rightarrow \mathrm{Zn_nCu_2Al_2S_{n+4}}. \qquad (2)$$

In this case charge compensation occurs through the formation of $Al^{\cdot}_{Zn}$ defects in equivalent amounts of Cu'_{Zn}. The activator and the tervalent metal are sometimes added to the charge in the form of a double sulphide, $CuAlS_2$, $CuInS_2$, $AgGaS_2$, etc.[49,50] The favourable effect of some tervalent metals on the formation of ZnS phosphors was recognised even before the work of Kröger[51], but application of the theory of charge compensation has made it possible to give a unified explanation of the effect of chloride and of tervalent metals, and furthermore has led to the development of a much wider range of luminescent systems of this type. The action of tervalent metals can be taken as proof[52] that Cu and Ag enter lattice sites, i.e. form substitutional solid solutions, in ZnS, since the effect could not occur if interstitial solid solutions were formed. From the fact that the spectral composition of the radiation from ZnS–Cu and ZnS–Ag phosphors is independent of the type of compensating ion it was concluded[33] that the activator and the compensating ion are located far from each other in the lattice, and that the luminescence centre does not contain the latter ion. Since halogens and tervalent metals merely assist penetration of the activator into the phosphor matrix but do not affect the luminescence spectrum, these substances have been termed "coactivators". We can see from the Periodic Table that activators, which include Au[53] and also P, Sb, and As[54-56] besides Cu and Ag, occupy a position to the left of the constituent elements of the phosphor in the neighbouring group, whereas the coactivators are found to the right of the main components[57] (Fig. 1). Under certain conditions, however, activators and coactivators can exchange roles[58,59].

As a rule, halides are more effective coactivators than are tervalent metal sulphides, in particular because the latter (especially Al_2S_3) are readily hydrolysed and oxidised.

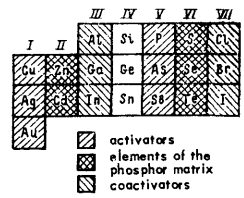


Fig. 1. Position of activators and coactivators of binary compounds of the ZnS type in the Periodic Table[57].

Indium dissolves in ZnS more easily than other Group III metals[60], and chemical analysis has shown[61] that this metal can enter the lattice. It has also been reported[60] that a higher concentration of Cu can be introduced into ZnS in the presence of In. Aluminium, on the other hand, goes into the ZnS lattice with difficulty in the absence of an activator[59]. Since aluminium salts are easily converted into Al_2O_3, which is transformed into the sulphide only to an insignificant extent[62] when heated in H_2S, the preparation of ZnS–Cu,Al and ZnS–Ag,Al requires special precautions[61] to enable a large proportion of the added Al to enter the lattice. The presence of the activator favours the dissolution of Al_2S_3, and therefore also makes possible its formation. In any case, the ability of aluminium to act as a coactivator has been demonstrated on many occasions[35,36,48,50,61,63]. Experiments in which Al is added to the charge in the formation of Al_2O_3 without an activator[64] give no grounds for refuting this statement. It is equally incorrect to ignore, as is often done, the fate of the partner of the impurity ion which replaces an ion of the main lattice, since we are dealing with the formation of a solid solution of the impurity compound, not of the free element.

When applying the principle of charge compensation, we have assumed that ZnS is an ionic crystal. In fact, however, the bond in zinc sulphide is more covalent than ionic[43,65,66]. But this does not alter the situation, since the principle of charge compensation can be replaced by the more general principle of valency compensation[67]. Consider the covalent model of a ZnS phosphor. The zinc atom has two valency electrons occupying a single s-shell ($4s^2$), and the sulphur atom has six valency electrons ($3s^2p^4$). In the crystal lattice every zinc atom is surrounded by four sulphur atoms, and every sulphur atom by four zinc atoms. The valency electrons are shared, as it were, between the zinc and the sulphur. As a result, four hybrid sp^3 orbitals appear in each atom[68], and form tetrahedral bonds where they overlap similar orbitals of neighbouring atoms. If an impurity atom is added to such a crystal, it tends to take up the electronic structure of the Zn and S atoms of which the host lattice is composed. If, for example, a sulphur atom with six valency electrons is replaced by a Cl atom, having seven valency electrons, one "excess" electron appears; this is very easily lost by the Cl atom, and enters the conduction band. The introduction of a Cu atom with one valency electron at the site of a Zn atom leads to the formation of a defect which, in contrast, tends to capture the one electron which it lacks. It is obvious that impurities of the Cl type will raise the electronic conductivity: in the study of semiconductors these impurities are called donors. Impurities similar to Cu decrease electron conduction or increase hole conduction: these are called acceptors. When both donors and acceptors are present together in the crystal, electrons tend to pass from the former to the latter. This process is accompanied by a gain in energy. As a result, the solubility of an acceptor impurity is increased by the simultaneous dissolution of a donor impurity. It is interesting to note that this phenomenon occurs also in elementary semiconductors. For example, the solubility of lithium in silicon is increased by the presence of boron[69]. Equal numbers of donors and acceptors produce what is known as a compensated semiconductor. The most effective ZnS–Ag,Cl and ZnS–Cu,Cl phosphors also appear to be compensated semiconductors[70]. If the number of acceptors is not equal to the number of donors, compensation can arise through sulphur vacancies in the case of an excess of acceptors, or through zinc vacancies in the case of an excess of donors[71,72]. However, after loss (or gain) of one electron the vacancy acquires a charge, which makes the loss (or gain) of a second electron more difficult. This is, obviously, one of the reasons why AgCl and CuCl dissolve in ZnS more readily than do Ag_2S and Cu_2S. The higher solubility is also partly due to the fact that the energy expenditure associated with the formation of vacancies is eliminated[47].

Studies of the influence of impurities on the dark conductivity and on the photoconductivity of zinc and cadmium sulphides have confirmed that activators (Ag and Cu) act as acceptors when they are introduced into the lattice, whereas coactivators (Cl, Ga, In, etc.) are donors[61,65,73–76]. This is one of the weightiest arguments[75] against the hypothesis that Ag and Cu enter the lattice as free atoms, since if that were the case they would give rise to donor defects[77]. It has been shown that ZnS, CdS, and (Zn,Cd)S phosphors are n-type semiconductors (i.e. their conductivity is due to electrons)[78,79], the conductivity increasing when cadmium and zinc chlorides are introduced into the lattice[73,76]. Activation with silver and copper does not convert the n-type conduction into p-type (positive-hole) conduction because of the high ionisation energy of the acceptor defects produced in the lattice of the sulphides[65], but there is a decrease in the n-type conduction, and this can be taken as evidence that Ag and Cu act as acceptors. Hence it is incorrect to assume, as is sometimes done[80,81], that the n-type conduction points to activation of ZnS by the free metals.

The hypothesis of activation by free metals is also inconsistent with experiments on the electrolytic activation of zinc sulphide with copper[63,82] and with the results of a study of the magnetic properties of ZnS phosphors. Measurements of the temperature variation of the magnetic susceptibility of ZnS–Cu phosphors[71] by a method sensitive to 0.0001% of a paramagnetic impurity have shown that copper enters the lattice in a diamagnetic state. This argues not only against the hypothesis of activation by free copper atoms, which have one unpaired s-electron, but also against an earlier suggestion[25] that the "green" copper centres are formed by a Cu^{2+} ion. We should also remember that CuS is unstable above 200°.

As we mentioned above, the fact that the nature of the coactivator does not affect the spectral positions of the green band of ZnS–Cu and the blue band of ZnS–Ag phosphors has been interpreted as a consequence of the spatial separation of activator and coactivator. This means that the phosphor contains, as a rule, at least two kinds of defects, which are not related to one another. On an energy diagram (or band diagram) these defects are represented by two kinds of level in the forbidden gap: levels close to the conduction band, formed by the coactivator, and levels located above the valency band, formed by the activator (Fig. 2a). It follows from the above arguments that in an unexcited phosphor, which is a compensated semiconductor, the electrons reside mostly on the activator levels, whose distance from the conduction band determines to a first approximation the luminescence spectrum. On excitation the electrons pass into the conduction band, and may be captured by the coactivator levels, from which they are freed by thermal vibrations. Different coactivators can be expected to give rise to levels (electron traps) at different depths below the conduction band. The application of the so-called thermal glow method, which enables trap depths to be measured, has demonstrated the correctness of this hypothesis: it was found that the depth

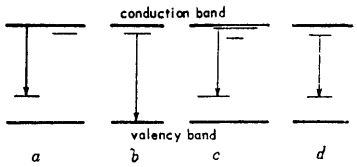


Fig.2. Energy-level models of the centres (explained in the text). The arrows denote electronic transitions.

of the electron traps is indeed determined by the nature of the coactivator and is independent of the nature of the activator [83-85]. In this way, Blokhintsev's hypothesis [86] of the spatial separation of luminescence centres and traps was verified, and furthermore the nature of the defects which may be responsible for the appearance of the trapping levels was established. The fact that the depth of the latter is independent of the activator does not in any way imply that the thermoluminescence and the afterglow are also independent of the activator, for the activator takes an active part in the luminescence process. Thus, in the case of a phosphor with two activators the thermal glow curves for the bands corresponding to these activators are not identical, since as the temperature is raised the probability of electron emission from the valency band to the activator levels increases, producing shorter-wavelength radiation. Under these conditions, holes migrate to the luminescence centres formed by the second activator, and are captured by them. Hence, the contribution of the long-wavelength band to the thermoluminescence spectrum increases with increase in temperature. The dependence of the afterglow on the nature of the activator can be explained in a similar way. It is also clear that the intensity of the thermoluminescence is related not only to the concentration of the trapping centres but also to that of the luminescence centres, since the radiation intensity I is proportional to the product of the concentration n of electrons freed from the traps and the concentration p_t of holes localised at luminescence centres: $I = \beta n p_t$, where β is the coefficient of recombination. Neglect of these principles leads to groundless conclusions [87,88] as to the relation between electron traps and luminescence centres.

Thus, we can now point to a whole series of proofs that chlorine and other coactivators actually enter the sulphide lattice at the same time as the activators. The fact that a coactivator must be present for activation by copper or silver to occur, established by the work of Strange, Kröger, and Schleede [89], was later confirmed in experiments with evaporated films [90] and single crystals [76]. It should be noted that the majority of workers (including the originators — Schleede [89,91] and Riehl and Ortmann [13] — of the hypothesis that the sulphides are activated by free atoms) now believe that the blue silver band and the green copper band are due to Ag^+ and Cu^+ ions located at lattice sites. (When referring to ions, here and subsequently, we have in mind the fact that the activators enter the lattice as compounds rather than as free atoms.) We must point out, however, that the mere fact that an impurity such as Cl must be present to cause luminescence to appear in the band of any particular activator cannot be taken as proof that this impurity is a coactivator, since cases are known in which the role of the impurity is to sensitise the luminescence [92-94], i.e. to form centres which absorb the energy of the exciting radiation and later transfer it to the activator centres.

2. Association of Activators and Coactivators

It has been suggested [30,95] that, at the normal temperature of formation of ZnS phosphors (800–1200°), the coulombic interaction of the activator and coactivator ions will favour their association, whereas the tendency of the system to maximise its entropy will act in the opposite sense. According to Prener and Williams [57,72,96], the relatively high impurity concentration (10^{-4} g-atom $mole^{-1}$) and the relatively low dielectric constant of ZnS should cause the tendency to association of the activator and coactivator to predominate, forming donor–acceptor pairs. These pairs of activator and coactivator atoms, associated as second or third nearest neighbours, are identified with the luminescence centres. Thus, Prener and Williams ascribe to the coactivator even more active a role than does Kröger, since they assume that it forms part of the luminescence centre by contributing an excited level close to the conduction band (Fig. 2*c*). This must increase the probability of capture of a conduction electron by the luminescence centre [57,97]. The suggestion that the luminescence centre of ZnS–Cu phosphors includes an excited level close to the conduction band is supported by the observation [98] that at low enough temperatures the photoconductivity of ZnS–Cu single crystals irradiated with light corresponding to the characteristic absorption band of the Cu centres vanishes, whereas the luminescence persists. However, the excited level is not necessarily associated with the presence of a coactivator. Prener and Williams quote [72] as an experimental proof of their theory the fact that the luminescence of ZnS is unaffected by the transmutation of ^{65}Zn atoms (obtained from ^{64}Zn by irradiating the sample with a neutron flux) to ^{65}Cu atoms, despite the fact that in this case the Cu appears at lattice sites and the lattice contains randomly distributed Cl ions. However, this could be ascribed, rather than to absence of associated Cu–Cl pairs, to the fact that luminescence centres are formed by univalent copper, whereas the nuclear reaction yields bivalent copper at the lattice sites [99]. Thus, the Prener–Williams hypothesis can hardly be said to be substantiated for systems such as ZnS–Cu,Cl and ZnS–Ag,Cl, whose radiation has a spectral composition independent of the nature of the coactivator [48,61,90]. It is true that Williams [100] explains this by postulating electronic transitions from the excited donor level — or even from the bottom of the conduction band — to the main acceptor level, and states (in contrast to his earlier hypothesis) that the activator and coactivator atoms are situated at an appreciable distance from each other — no nearer than seventh-nearest neighbours — in systems of this kind. But when modified in this way the views of Williams are hardly different from the generally accepted views. We should note that the postulated direct participation of the coactivator in the makeup of the green luminescence centres of ZnS–Cu phosphors and the blue luminescence centres of ZnS–Ag phosphors conflicts with reports in the literature that phosphors can be prepared without valency compensation by a coactivator [63,101] if the preparative conditions are such that Ag^+ and Cu^+ ions can reside at lattice sites.

Moreover, studies of ZnS phosphors containing Group III elements as coactivators have revealed luminescence bands which can in fact be ascribed to associated centres. Kröger had established that the luminescence spectrum of these phosphors sometimes exhibits long-wavelength bands in addition to the normal luminescence bands due to the activator [48]. Since these additional bands, which lie in the orange–red region of the spectrum, shift towards longer

wavelengths with increase in the depth of the electron trap formed by the coactivator, the suggestion was put forward[83] that these bands are due to the recombination of free holes with electrons trapped at coactivator centres (Fig. 2*b*). Thus, the latter act as luminescence centres as well as trapping centres. However, an experimental determination of the depth of the traps has shown that the radiation associated with this process should lie on the short-wavelength side (rather than on the long-wavelength side) of the luminescence bands due to silver and copper[84]. For this reason, Hoogenstraaten[84] proposed that an electron trapped at a coactivator centre recombines with a hole in a localised level above the valency band ("holding state") rather than in the valency band itself. The observed dependence of the spectral position of the long-wavelength band on the nature of the activator has led to the conclusion[49] that this level is bound to the activator and that the corresponding luminescence centre is therefore the result of association of the activator and the coactivator. This is confirmed by the fact that the proportion of long-wavelength radiation in the spectrum increases when the concentration of activator and coactivator (taken in equimolar amounts) is raised. Bands in the orange–red appear only when coactivators whose concentration in the ZnS phase can reach quite high values are used (e.g. Ga, In, Sc). Aluminium, which enters ZnS with difficulty, does not give this effect.

An attempt was made[49] to interpret the nature of centres responsible for the long-wavelength radiation in terms of the above-mentioned theory of Prener and Williams, developed on the basis of concepts[102] similar to those used in the theory of strong electrolytes. Assuming that in this case the radiative transition occurs from the ground level of the donor to the ground level of the acceptor (Fig. 2*d*), Apple and Williams calculated that the centre responsible for this radiation must consist of atoms of the activator and coactivator associated as fourth–sixth nearest neighbours[49,100], when overlapping of the ground state of the acceptor and the ground state of the donor sets in. With larger separations of the activator and coactivator atoms this overlapping does not occur, and the spectrum of the radiation shows only the normal activator band. However, the smaller the distance between the activator and the coactivator atom, the nearer their levels move towards the corresponding bands. Therefore, once the long-wavelength radiation appears, it can be expected to shift towards shorter wavelengths when the concentration of activator and coactivator is raised still further, and to disappear completely when the association becomes very close, owing to the fact that the ground levels of the donor and the acceptor have penetrated into their corresponding energy bands. van Gool[61] found that the long-wavelength band probably consists of several sub-bands, but that an increase in the concentration of activator and coactivator causes a shift towards longer rather than shorter wavelengths. Nevertheless, there can be no doubt as to the associated nature of the luminescence centre in this case. The location of the excited level within the forbidden gap is confirmed by the fact that the long-wavelength band has a lower thermal stability than the short-wavelength band, which would be impossible if the transition took place from the bottom of the conduction band. It should be noted that a long-wavelength emission with similar properties has been observed also in the absence of the main activator (Ag, Cu), for example when In [103,104] or Ga [105] impurities are added to ZnS. The luminescence centre responsible for this effect could also result from some kind of association — most probably that of $Ga^{\cdot}$ (or $In^{\cdot}$) with $V_{Zn}Ga'$ (or $V_{Zn}In'$). [105]

Thus, the hypothesis that a coactivator enters the lattice at the same time as the activator during the preparation of sulphide phosphors, and that this gives rise to a normal substitutional solid solution, provides an explanation of a large number of phenomena encountered in the preparation and in the study of ZnS phosphors. Nevertheless, a great deal still remains to be explained. This is because, in addition to the normal solid solutions with heterovalent substitution, which include the most effective and technically important cathodo-, röntgeno-, radio-, and photo-luminescent materials, solid solutions involving vacancies or interstices are also formed. A particularly difficult problem was that of interpreting the nature of the blue luminescence centre in self-activated (s/a) ZnS, and also the blue and the red luminescence of ZnS–Cu phosphors. Most objections to the views on the role of coactivators discussed above have been raised in connection with these particular problems. We shall consider these objections in the following sections.

III. LUMINESCENCE CENTRES OF "SELF-ACTIVATED" PHOSPHORS

In an attempt to produce a unified theory of the nature of the luminescence centres in s/a ZnS, ZnS–Ag, and ZnS–Cu phosphors, Kröger suggested[30] that the blue luminescence centre of s/a ZnS consists of a Zn^{+} ion whose deficiency of one positive charge is compensated by the simultaneous introduction of a Cl^{-} ion, so that in effect an s/a ZnS phosphor is a solid solution of the subchloride ZnCl in zinc sulphide. Generally speaking, subchlorides of this type are known. They are formed, for example, when the metal is dissolved in a melt of its normal chloride. Thus, Kröger's original hypothesis is equivalent to assuming that zinc in excess of stoichiometric (or, at least, partly reduced zinc) is involved in the formation of the luminescence centres. Subsequently, however, relying on the results of Bube[106–108], who had observed a blue luminescence in what he assumed to be pure ZnS which had been heated to a high enough temperature, and also noting that in the ionic model Zn^{+} is indistinguishable from a free electron in the conduction band, Kröger[109] changed his point of view and suggested that the blue luminescence centre in s/a ZnS is a cation vacancy (in this case, a zinc vacancy V'_{Zn}) with one electron missing from its immediate surroundings. Such a centre, however, should be paramagnetic, which conflicts with the results of magnetic susceptibility[71] and electron spin resonance (e.s.r.) measurements[110] on s/a ZnS phosphors. A model of the centre which satisfies these results was put forward by Prener and Williams[111], who suggested that the defect responsible for the formation of the centre is a zinc vacancy immediately adjacent to a donor impurity, e.g. $V_{Zn}Cl'_{S}$. This defect behaves very much like Ag'_{Zn} and Cu'_{Zn}. We should note that the association of a vacancy with an oppositely charged impurity defect is regarded as very important in the theory of the ionic conductivity of crystals[112].

Riehl and Ortmann's discovery[113] that no visible luminescence at room temperature is produced when ZnS is heated with NaCl in the complete absence of traces of oxygen revealed a new difficulty. This observation was confirmed by several other workers[36,76,114–116]. Similar statements on the role of oxygen are to be found also in earlier papers[117]. Although some authors[59,114] state that it is sufficient to introduce oxygen in combined form, e.g. as

ZnO, others[36,91,101,118] have been unable to obtain a blue luminescence when ZnO, moisture, and other oxygen compounds are present in the system. In this connection it is relevant to record a number of statements[113,115] that minute traces of free oxygen in the nitrogen or argon are sufficient to cause the characteristic blue luminescence when a ZnS(NaCl) charge is heated in a stream of these gases. Hence it is desirable to carry out these experiments under static conditions.

To explain these results it was initially suggested[114,118] that oxygen atoms are involved in the structure of the luminescence centres. However, this hypothesis conflicts with the fact that bright phosphors can be prepared from deoxygenated ZnS in HCl medium[30,115,119], and especially with the fact that a similar luminescence can be produced by introducing elements of Group III into the ZnS using an H_2S atmosphere[101]. In an attempt to make these two sets of data mutually compatible, and adopting the hypothesis that the luminescence centres are produced by V_{Zn} vacancies, Riehl and Sizmann[120] suggested that the Zn^{2+} ion tends to take up a position adjacent to the O^{2-} ion, which is smaller than the S^{2-} ion. In doing so, it can move into an interstitial site, i.e. into a normally empty tetrahedron, and this process gives rise to a V_{Zn} vacancy. However, this contradicts the above results (including those of Riehl and Ortmann[118]), according to which the presence of zinc oxide alone is insufficient to give rise to luminescence. Thus the situation concerning the nature of the luminescence centres in s/a ZnS was very confusing[121]. However, shortly afterwards, a way was found to correlate the results of Kröger[30,101] with those of Riehl and Ortmann: this was to make a combined study of the effect of preparative conditions on the luminescence and on the chemical reactions taking place in the system[46,67,91,122]. It was found that direct reaction between ZnS and NaCl with formation of $ZnCl_2$, whose possibility had been suggested previously[27,28], leads to such a large increase in the free energy of the system as to be negligible in practice[46,105]. In the presence of oxygen, on the other hand, we have the so-called "chlorinating roast"[113,123], which can be described by the overall equation

$$ZnS + 2NaCl + 2O_2 = ZnCl_2 + Na_2SO_4. \quad (3)$$

If we assume that the blue luminescence of s/a ZnS results from the dissolution of $ZnCl_2$ in ZnS, the role of oxygen is clearly to make reaction (3) possible. Hence, no oxygen is needed to bring about the blue luminescence in the cases where $ZnCl_2$ can be formed even in the absence of oxygen, e.g. when ZnS is heated in the presence of HCl or with fluxes such as $MgCl_2$.[124] The ability of $ZnCl_2$ to activate ZnS with formation of a typical s/a ZnS phosphor has been demonstrated by direct experiment[36,125]. The failure of $ZnCl_2$ to give good phosphors when used as a flux[113] has been ascribed to its volatility (b.p. 733°) and also to the fact that it is a poor mineraliser[126]. Hence it is necessary, in order to prepare efficient phosphors, to heat the material with $ZnCl_2$ either in a closed vessel[36,91] or with a flux, such as NaCl, which promotes crystal growth and also inhibits the volatilisation of $ZnCl_2$ by complex formation with the latter[46].

The effect of ZnO dissolved in ZnS is to give rise to luminescence quenching rather than to the formation of luminescence centres[36]. This, evidently, is the reason for the frequently reported[7,127,128] sharp drop in the brightness of luminescence of an s/a ZnS phosphor prepared in the air after transition from sphalerite to wurtzite, in which ZnO has a much higher solubility[39,101,113] because it, too, has the wurtzite structure. In this case it is possible to raise the intensity of the luminescence by restricting the access of oxygen[26,125] or by using chlorinating agents able to form $ZnCl_2$ without the participation of oxygen[115,124,125]. According to Riehl[120] we can envisage the formation of deep oxygen traps which act as quenching centres. However, since oxygen also causes the luminescence band to shift to longer wavelengths, it is conceivable that the oxygen becomes associated with the defect responsible for the luminescence, forming a new centre with a lower recombination coefficient[36].

For steric reasons, the Cl^- ions are unlikely to reside in interstitial sites. Hence they are most likely to replace sulphur ions in lattice sites, and in order to satisfy the principle of valency compensation the appropriate number of V_{Zn} vacancies must appear when $ZnCl_2$ is dissolved in ZnS:

$$n\,ZnS + ZnCl_2 \rightarrow Zn_{n+1}V_{Zn}S_nCl_2. \quad (4)$$

In a system of this type three main kinds of defect — $Cl_S^{\cdot}$, $V_{Zn}Cl_S^{\cdot}$, and V_{Zn}'' — can arise. As already mentioned, it has been suggested[111] that the acceptor defect $V_{Zn}Cl_S^{\cdot}$ is the one responsible for the formation of the blue luminescence centres. An analogous situation should arise when activation is by sulphides of tervalent metals, because these, too, should generate zinc vacancies when dissolved in ZnS. The association of V_{Zn}'' with a tervalent metal ion which has entered the lattice gives a centre similar to $V_{Zn}Cl_S^{\cdot}$, but in this case the ion associated with V_{Zn}'', e.g. $Al_{Zn}^{\cdot}$, will occupy a Zn site rather than an S site. Thus we can expect some difference in the spectral composition of the luminescence between s/a ZnS phosphors prepared by doping with halides and those containing tervalent metals. It has been shown experimentally[35,61] that this difference actually exists.

Thus, the "self-activated" ZnS phosphor is in fact activated by halogens or tervalent metals, i.e. by impurities which act as coactivators in ZnS–Cu and ZnS–Ag phosphors. A similar state of affairs exists in the case of CdS, which, like ZnS, does not show luminescence (and does not change its electrical conductivity) when heated with NaCl in the absence of free oxygen[36,76,91,115]. Nevertheless, CdS is activated by cadmium chloride[36,91], whose formation under ordinary conditions of heat-treatment in air has been demonstrated by chemical analysis[46].

It must be stressed that the concentration of luminescence centres in ZnS–Cl and CdS–Cl phosphors, and even more so the intensity of luminescence, do not necessarily vary in parallel with the concentration of Cl in the sulphide phase, although in some cases such parallelism has been observed[31,125]. We must remember firstly that some of the Cl may not be at lattice sites but on internal surfaces of the crystallites[64,129], secondly that only Cl associated with V_{Zn} gives rise to luminescence centres (the extent of association depending on the temperature of heat-treatment and on other preparative conditions), and lastly that the luminescence yield is determined not by the concentration of luminescence centres but by the ratio between this concentration and the concentration of quenching centres, the latter also being a function of the preparative conditions[125]. Therefore the reported[106–108,129] lack of agreement between the concentration of Cl determined by chemical analysis and the luminescence intensity cannot be used as an argument to refute the above ideas. The fact that the sulphide phase contains, in addition to Cl, cations originating from the flux (or from its interaction with ZnS and atmospheric

oxygen[67]) does not provide grounds for doubting[64] that Cl enters the lattice at lattice sites, as many workers have confirmed (see Section II).

In recent years many new data in keeping with the Prener–Williams model have been reported[110,130,131]. The development of a method for growing single crystals of ZnS from the melt has made it possible to use Feofilov's polarisation method[132] to study the nature of the luminescence centres in crystals belonging to the cubic system. Shionoya and coworkers[130,133] have shown that the observed anisotropy of the luminescence and its dependence on the properties of the exciting radiation are consistent with the hypothesis that the luminescence centre in a ZnS–Cl crystal has a characteristic C_{3v} symmetry, as should be the case with a $V_{Zn}Cl'$ centre. The e.s.r. method gave similar results[110,134-136]. When the crystal is excited at 77°K with ultraviolet radiation, ionisation of the luminescence centres and electron capture by the traps takes place. As a result, both defects become paramagnetic, and give a signal from whose characteristics we can derive information on the symmetry of the corresponding centre and on whether the signal is the result of electron capture or hole capture. A parallel study of the magnitude of the signals and of the luminescence intensity can identify which of the two signals corresponds to the luminescence centre. An analysis of the results obtained for ZnS–Cl and ZnS–Al phosphors has shown that the Prener–Williams model is consistent with the e.s.r. measurements.

The views described here have found numerous supporters. It must be stressed, however, that the chemical nature of the blue luminescence centres in s/a ZnS phosphors is one of the points of greatest disagreement. In particular, many workers restate outdated opinions that self-activation is actually present in this case, some[15,137-142] following Schleede's original views[6] in regarding the luminescence centres as formed by a stoichiometric excess of Zn or Cd, while others[143,144] adopt the opposite view, and suggest, following Bube[107,108], that the luminescence centres are formed by zinc vacancies. Schleede himself[91] gave convincing arguments against activation by excess zinc or cadmium, and abandoned his original point of view (though more gradually than did Kröger): he found that, after being heated in a sealed tube, ZnS gives a bright luminescence if $ZnCl_2$ is present as well as an excess of sulphur, whereas the characteristic luminescence of "self-activated" phosphors does not appear if the Zn or Cd is in excess. Other workers[36,127,139] also obtained negative results in their attempts to induce luminescence by an excess of Zn or Cd. The lack of luminescence of ZnS heat-treated in hydrogen[15,30,118,125] is evidence of the same kind. According to a number of reports[35,36,61], no luminescence is obtained also on heating ZnS and CdS prepared by precipitation and completely free from chlorine, whether or not an excess of sulphur is present. Work on the preparation of ZnS films by synthesis from the ultrapure elements[145] has confirmed that departures from the stoichiometric composition cannot give rise to the blue luminescence. These observations cannot be ascribed to imperfections in the crystal structure, because, as already pointed out, addition of a mineraliser such as NaCl does not induce luminescence in the complete absence of oxygen[113-115,146]. Furthermore, a hydrogen atmosphere, which inhibits the development of luminescence, favours the recrystallisation of ZnS.[22] Lastly, the most perfect single crystals of ZnS and CdS, prepared by sublimation of the precipitated sulphides, very often do not show luminescence[76]. The relative instability of s/a ZnS and s/a CdS when heated in a vacuum[14], on which Riehl and Ortmann have cast doubt[118], can be explained by the volatility of $ZnCl_2$ and $CdCl_2$. In the light of these results, there are no grounds for attempting to explain the "gap" in the luminescence intensity in the series of s/a ZnS–CdS(hex.) phosphors at 5–10% CdS by postulating the displacement of the emission band due to excess zinc by the cadmium band[14,138], especially since a similar "gap" (though less marked) is found also in the series of ZnS. .CdS(hex.) phosphors activated by Ag, Cu, and Au.[53,147].

The luminescence of sulphides not containing deliberately added activators is usually due either to the presence of activating impurities (in particular Cl) in the sulphide source material or to impurity pick-up from the walls of quartz crucibles[148,149]. Technical "phosphorescent" ZnS and CdS usually contain an appreciable amount ($\geq 0.005\%$) of chloride[36,76,113,135,150], which is readily coprecipitated with sulphides[151,152] or derived from absorption of HCl, a common constituent of the atmosphere in chemical laboratories and workshops. Both the importance[21] and the difficulty[153] of removing chlorine have long been stressed in the literature. Even when the material is synthesised from the elements it is necessary to guard against the presence of activating impurities, in particular In, Ga, and Al.[154]

Thus, there is still no convincing experimental proof of the hypothesis that the blue luminescence of ZnS or the corresponding red luminescence of CdS can be ascribed exclusively to structural defects, and the term "self-activated" is retained for phosphors of this type largely on grounds of tradition.

The green luminescence displayed by ZnS under certain conditions of heating in the absence of deliberately added metal activators[23,91,155-157] has attracted less attention. It is observed most often when the sulphide is slightly oxidised. Leverenz, noting the similarity between this luminescence and the green emission of ZnS–Cu, suggested that the true activator in all cases of luminescence of this type is oxygen, the only function of the copper being to promote the oxidation of ZnS.[23] This hypothesis, however, does not account for the observed activation by copper in the absence of oxygen[32]. Bundel'[155] also suggested that oxygen can act as an activator, but he did not identify the oxygen centres with those responsible for the green luminescence of ZnS–Cu. An important aspect of this problem is the fact that this effect is shown only by free oxygen in amounts insufficient to cause extensive oxidation of ZnS. We may therefore assume that the activating effect of oxygen shows itself in the initial stages of its reaction with ZnS. The suggestion has been put forward[36] that this initial stage consists in addition of oxygen to ZnS with formation of a defect of effective charge -2, i.e. a cation vacancy adjacent to an oxygen atom in an anion site:

$$n\mathrm{ZnS} + {}^1/_2\mathrm{O}_2 \rightarrow \mathrm{Zn}_n\mathrm{V}_{\mathrm{Zn}}\mathrm{OS}_n. \qquad (5)$$

Other workers also have assumed that oxygen reacts with zinc in the first instance[22,158]. Kröger holds the opposite opinion[101]. He explains[159] the green luminescence band of a preparation heated in zinc vapour, not in terms of zinc vacancies, V_{Zn}, but, on the contrary, by the presence of an excess of zinc in the lattice, thus resorting to the oldest explanation[2,8] of the blue band of s/a ZnS phosphors. Other authors[36,91,139], however, failed to confirm these observations. Browne[156], referring to experiments by Hamilton on the heat-treatment of CdS in sulphur vapour, considers that the green band of ZnS and

the corresponding band of CdS are due to cation vacancies. Kulp[160] expressed a similar opinion with respect to CdS. However, the preparation by this method of ZnS with green luminescence has not been confirmed[36,61,116]. It is obvious that further experimental work with careful control over copper and oxygen impurities is needed to solve the problem of the true nature of the green luminescence centres, since this luminescence has been observed also in sublimed phosphors[143,145] and in single crystals[150,161].

Many workers[15,116,145,162,163] have reported also the appearance of an orange and a red luminescence in ZnS free from deliberately added metal activators‡. The only suggestion put forward to explain this phenomenon is that an excess of sulphur can induce luminescence[116].

In addition to the bands situated on the long-wavelength side of the blue band of s/a ZnS phosphors, and of the corresponding red band of s/a CdS, short-wavelength bands have also been reported[59,164-167], in particular a band having λ_{max} = 380–390 nm with ZnS [59] and 580 nm with CdS,[98,166] observed on excitation of the phosphors at low temperatures. Kröger[164] ascribed this band in ZnS to the Na^+ cation of the flux, assumed to form a luminescence centre analogous to Cu'_{Zn} and Ag'_{Zn}. However, as shown by Rothschild[59], the same band can be obtained also in the absence of Na^+. The condition for the predominance of this band in the spectrum is that the concentration of Cl or other halogen in the ZnS phase shall be low enough. This is achieved, for instance, by heat-treatment in an atmosphere which almost suppresses the chlorinating roast[59,105]. However, this luminescence band also disappears when the "coactivators" are completely removed. According to Rothschild, the role of luminescence centres in this case is played by the "coactivator" ions, which replace sulphur ions in the lattice: these are defects which give rise to electron traps. We may suppose that a decrease in the concentration of Cl causes the ratio $[Cl_S]/[V_{Zn}Cl_S^{\bullet}]$ to increase, owing to dissociation of $V_{Zn}Cl_S^{\bullet}$. This, besides lowering the probability of electron emission from the trap when the temperatures fall, increases the probability of radiative recombination of a trapped electron with a free hole in the valency band. This is evidently a specific case of the scheme (Fig. 2*b*) proposed by Klasens to explain the long-wavelength emission of phosphors containing tervalent metals as coactivators (see above). Consequently, there is no sharp boundary between trapping centres and luminescence centres[168], and the coactivators are in fact activators in this case as with the blue self-activated luminescence, because they determine the spectral composition of the radiation. It has been suggested[169,170] that sulphur vacancies may also be a cause of the luminescence at 380–390 nm. However, direct experiments with sulphides which had been dechlorinated in hydrogen sulphide failed to confirm this suggestion[105]. The effect of heat-treatment in zinc vapour on sulphides containing chlorine, which is to increase the contribution of the short-wavelength band to the emission spectrum[170], can be explained by a shift towards the right-hand side in the equilibrium

$$V_{Zn}Cl' \rightleftarrows V''_{Zn} + Cl,$$

caused by the interaction of V''_{Zn} with $V_S^{\bullet}$ formed under these conditions of heat-treatment. This results from the fact that the product of the concentrations of V''_{Zn} and $V_S^{\bullet}$ must be constant. The role of excess zinc may also be to influence the occupancy of the Cl levels by electrons.

Perhaps the only radiation which cannot be eliminated by even the most thorough purification of the sulphides is the so-called "edge-emission"[171-173], observed mostly at low temperature and consisting of a series of narrow bands close to the edge of the absorption band of the main lattice. Most of the work on this type of luminescence has been done on cadmium sulphide. Essentially, there are at least two "edge emissions", lying in the green and the blue regions of the spectrum in the case of CdS. Kröger[171] ascribed the green radiation to interband transitions in the undisturbed lattice. However, this interpretation had to be abandoned for two reasons: firstly, the energy of the quanta corresponding to the green radiation is less than the width of the forbidden gap[172,174], and secondly the green luminescence is strongly affected (even in the absence of emission bands in the visible and infrared regions) by the preparative conditions, the most perfect single crystals with the smallest number of structural defects being free from this luminescence[36,175-177]. There are reports[76,91,141,178-180] that the green band can occasionally be observed in the photoluminescence spectrum of CdS single crystals and powders even at room temperature, particularly in the case of activation by metallic indium[105], and that an excess of cadmium enhances the effect[91,181]. On the other hand, it is stated[142] that single crystals showing green luminescence have a high resistance, whereas an excess of cadmium in the lattice should raise the electrical conductivity. Some workers[182,183] have ascribed the green luminescence to an excess of sulphur. The view that the defects responsible for the green luminescence are pairs of vacancies of the two kinds ($V_{Zn}V_S$) has become increasingly popular in recent years[97,184]. The fact that a strong green luminescence is occasionally observed at room temperature suggests that the defects responsible for this effect are located at special sites in the crystals, most probably at the surface[105] or at dislocations[185]. Several observations[186,187] may indicate that even the short-wavelength component of the edge emission is ultimately produced by structural defects, possibly localised just below the crystal surface[187]. Thus, only the edge radiation can with sufficient justification be linked with centres produced by self-activation.

IV. LUMINESCENCE CENTRES OF COPPER- AND SILVER-ACTIVATED PHOSPHORS

The theoretical concepts discussed in Section II provide a satisfactory description of the structure of one luminescence centre in the ZnS–Cu phosphor. In fact, the nature of this phosphor is far more complex. In the visible region of the spectrum alone, four emission bands — blue, green, yellow, and red — have been observed[25,188]. Three emission bands have been found in the infrared region[156].

Much of the work has been concerned with the origin of the green and blue emission bands. As a rule, an increase in the copper content initially enhances the green luminescence at the expense of the blue luminescence of "self-activated" ZnS, but subsequently the blue luminescence again predominates over the green[17,25,32], and the phosphor begins to develop a grey colour. This has led a number of authors[19,71,115,189] to suggest that the copper is simply precipitated from the ZnS lattice as a separate phase,

‡ We are not concerned here with the yellow and red fluorescence often observed in precipitated ZnS and in ZnS which has been heated below the normal temperature of formation of the crystal phosphor.

with restoration of the ability of the "self-activation" centres to emit radiation. According to several workers [190-193], however, this hypothesis conflicts with observed differences between the properties of the bands in question. The blue copper band, when it can be clearly resolved from the green band by suitable preparative or excitation conditions, occurs at significantly shorter wavelengths, and is appreciably narrower, than the blue self-activated band [45,190,192]. On decreasing the temperature the Cu band shifts to shorter wavelengths, and the self-activated band to longer wavelengths [45,61,193,194]. Phosphors with a strongly developed blue Cu band, unlike the self-activated phosphors, have a sharp characteristic absorption band [32,193,195,196] and a corresponding blue luminescence excitation band [197,198]. It must be noted that, with phosphors prepared by conventional techniques in air, the blue and the green bands are poorly resolved in the luminescence spectrum at room temperature. This evidently accounts for discrepancies [189,193,198,199] between various measurements of absorption and excitation spectra. Hence the following facts provide more convincing evidence of a difference in chemical nature between the defects responsible for the formation of "blue" luminescence centres in ZnS–Cu and in s/a ZnS phosphors: (1) when ZnS–Cu(NaCl) is heated in hydrogen a strong blue luminescence appears, whereas when a copper-free charge is heated under otherwise identical conditions no luminescence is obtained [192], because the chlorinating roast of the ZnS is suppressed; (2) introduction of Cu into s/a ZnS phosphors at relatively low temperatures (290–550°) enables the gradual displacement of the self-activated band by the blue Cu band to be monitored [193].

Another question which has been the subject of lively discussion is the mechanism of the enhancement by oxygen, established by many workers [101,200-203], of the formation of the "green" luminescence centres. Grillot and Bancie-Grillot [128,200-202] assumed that the difference between the "green" and the "blue" centres is determined essentially by their environment: if they consist of sulphur ions exclusively a blue luminescence centre is formed, whereas if an oxygen ion is present in the immediate vicinity of the Cu^+ a green luminescence centre is formed. These views are not very different from those of Konstantinova-Schlezinger [204-206], who considers the luminescence centre to be a complex (quasi-molecule) formed by an activator ion with the anions surrounding it. Grillot's explanation conflicts, however, with the fact that ZnS–Cu phosphors showing a strong green luminescence can be prepared from deoxidised ZnS even in an atmosphere which contains no oxygen, such as dry HCl. [32,116] Grillot's more recent suggestion [207] that a V_S vacancy (rather than an oxygen ion) is the neighbour of Cu^+ which can alter the nature of the centre is also unable to explain these facts, particularly since a hydrogen atmosphere, which should favour the formation of V_S, leads to enhanced blue, not green, luminescence in ZnS–Cu. [25,192] Kröger [208] points out that, when NaCl is used as a flux, only the blue luminescence is produced in the absence of oxygen, and suggest that oxygen can somehow assist the separation of Cl from Na. The mechanism of this effect of oxygen has subsequently been clarified [67,124] by thermodynamic calculations: CuCl is not formed by the direct interaction of Cu_2S and NaCl, since the process would involve a large increase in the free energy of the system, but in the presence of oxygen CuCl can be formed by a chlorinating roast similar to reaction (3). This explanation is of limited application, however, since cases are known in which oxygen assists the formation of "green" centres even in the absence of chloride fluxes [101]. Kröger points out that oxygen has a similar effect on the formation of ZnS–Ag phosphors, which he explains on the basis of the principle of volume compensation [101], assuming that the small volume of the O^{2-} ion (as compared with S^{2-}) favours the entry into lattice sites of Cu^+ ions, which are larger than Zn^{2+}. Unlike Cl^-, the oxygen ion appears as a nearest neighbour of Cu^+, but this causes only a slight shift of the green band of the Cu^+ centre to longer wavelengths, rather than converting a blue centre into a green centre, as postulated by Grillot. The same principle was later used to explain the favourable effect of $MgCl_2$ on the formation of ZnS phosphors [124]. It is possible, on the other hand, that the true mechanism of the reported effect of ZnO, which is specially evident in the case of ZnS(hex.)–Cu, consists in the formation of additional structural defects of the dislocation type, which assist diffusion into the bulk of the lattice [36]. To some extent, this could also be the role played by chlorinating agents.

When Cu_2S is dissolved in ZnS containing ZnO, valency compensation is achieved (at least partly, if chloride is present) by sulphur vacancies, which give rise to trapping centres. Furthermore, the higher electronegativity of oxygen as compared with sulphur should cause the zinc atoms situated next to oxygen atoms to become trapping centres. Hence we can expect a sharp change in the nature of the thermal glow curves if the phosphor is prepared in the presence of oxygen. Experiments have shown [84,85] that this effect actually occurs.

Many investigations have been devoted to determining the nature of the Cu blue luminescence centres. The fact that the blue luminescence appears at high copper concentrations suggests that the centres are associated. Riehl and Ortmann arrived at this conclusion from their experiments on the introduction of copper at a relatively low temperature (450°) into s/a ZnS or ZnS–Cu phosphors which had been previously heated at a high temperature [209]. Since the blue luminescence band appears only after the copper concentration exceeds a definite limit, they suggest that this limiting concentration is determined by the concentration of point defects generated in the previous high-temperature treatment ("acceptors"), and able to take up copper with formation of "green" centres. This model recalls Smekal's early views [210]. Noting, in common with other workers, that chlorides promote the appearance of green luminescence and raise the limiting concentration of copper, Riehl and Ortmann ascribe the effect to the desulphurising action of chlorides, leading to the formation of V_S vacancies, which, as originally suggested [118,203], are associated with a neutral Zn atom located at a regular lattice site. Replacement of the Zn atom by a Cu atom produces a "green" centre. If the concentration of copper exceeds the concentration of $Zn_{Zn}V_S$ defects, the excess of copper goes into interstitial sites with formation of blue luminescence centres $Cu_i Cu_{Zn} V_S$, where the subscript i denotes an atom in an interstice. Subsequently [13], taking into account the results of magnetic susceptibility measurements on ZnS–Cu phosphors, Riehl and Ortmann modified their views and admitted that the whole of the copper is present in the lattice as Cu^+, the blue luminescence centre being formed by the association of Cu_i^+ with a "green" centre, i.e. a Cu^+ ion at a lattice site. However, they retained their assumption regarding the desulphurising action of chlorides, and ascribed to the resulting sulphur vacancies the function of charge compensation. Having observed that heating even at temperatures of the order of 100–200° converted green centres into blue centres, which did not require charge compensation according to their

new model, they were faced with the problem of explaining the fate of the sulphur vacancies during this conversion. This led them to yet another hypothesis [13,211], according to which charge compensation is ensured by interstitial Zn_i^{2+} ions during formation of the "green" centres. The conversion of "green" centres into "blue" centres involves exchange of places between Cu^+ and Zn_i^{2+} ions, accompanied by the formation of $Cu_i^+Cu_{Zn}^+$ associations. This idea has found the support of other authors [191,212-214], despite the fact that it became necessary, for example, to postulate blocking of interstices [212] by Zn_i^{2+} ions to explain the failure of some ZnS–Cu phosphors to accept additional quantities of copper at low temperature with formation of "blue" centres. (It may be recalled that the number of free tetrahedral cavities is equal to the number of lattice sites occupied by zinc ions.) We could list a number of phenomena which cannot be explained satisfactorily within the limits of Riehl and Ortmann's theory. This applies primarily to the role of chlorides. Their suggested desulphurising action still lacks convincing experimental proof [215,216], and is inconsistent with the results of a thermodynamic analysis [119]. The exact role of this factor is also obscure if charge compensation is achieved by interstitial Zn_i^{2+} ions. Furthermore, as has already been pointed out, an atmosphere of H_2, known to assist desulphurisation, favours the formation of "blue" rather than "green" centres [25,192]. Also unexplained is the appearance of red luminescence in ZnS–Cu phosphors prepared in the absence of coactivators and oxygen [148,188]. In their more recent papers [13,211,217,218] Riehl and Ortmann admit the possibility of charge compensation by chlorine, and also of reactions of type (6) (see below), but they have not yet modified their model accordingly.

In an attempt to reconcile the assumption of associated blue luminescence centres with the fact that these centres are not formed when ZnS–Cu is heated in H_2S in the absence of coactivators, Kröger [219] concluded that phosphors showing blue luminescence are produced by dissolution of the subchloride Cu_2Cl in ZnS. To make the idea more concrete, he put forward a model according to which the "blue" centre arises as a result of association between a Cu^+ ion at a lattice site and a neutral Cu atom in an interstitial site. In support of his model, Kröger quotes the results of a chemical analysis which shows that the concentration of Cu in phosphors with a blue luminescence band is double the Cl concentration, and also some approximate thermodynamic calculations in agreement with experiment. It was found, however, that an atmosphere of sulphur vapour favours the appearance of blue luminescence [91,190], which makes the presence of free atoms seem unlikely, particularly in view of the diamagnetic nature of the centres [71]. A more accurate chemical analysis, allowing for the fact that part of the copper is on the surface of the crystals [45], showed that $[Cu]:[Cl] < 2$, and in many cases approaches unity. A kinetic study of the formation of ZnS–Cu phosphors on heating in a chloride flux in the presence of air showed that the appearance of a blue luminescence band is preceded, as a rule, by the green luminescence: this led to the hypothesis [67,124] that the formation of "blue" centres is a secondary process occurring in the ZnS phase after dissolution of CuCl and consisting in an atomic rearrangement leading to the association of two Cu^+ ions in adjacent cation sites of the lattice. This process can be envisaged as a preliminary to the formation of Cu_2S as a separate phase, as shown by the equation [67,192]

$$2\,(CuCl) + ZnS \rightleftarrows (ZnCl_2) + (Cu_2S), \qquad (6)$$

(where the symbols in brackets denote species dissolved in the ZnS phase), resembling the reaction between AgCl and ZnS which occurs on the surface of ZnS–Ag phosphors [46]. The fact that HCl must be present for blue luminescence to appear on heating in H_2S [32] is explained, on this model, by the solubility of CuCl in ZnS being greater than that of Cu_2S; thus, since the $ZnCl_2$ formed by reaction (6) remains in the lattice, Tomlinson's analytical results [45] are readily explained. When ZnS–Cu is heated in H_2, a treatment which gives rise to sulphur vacancies, entry of Cu_2S occurs by the scheme

$$Zn_nS_{n-1}V_S + Cu_2S \rightarrow Zn_{n-1}Cu_2S_nV_S + Zn, \qquad (7)$$

similar to the one proposed earlier by Riehl and Ortmann for the formation of "green" centres.

Later researches [192,193] showed that conversion of the "green" centres in ZnS–Cu,Cl phosphors into "blue" centres usually occurs at relatively low temperatures (below 250°). The favourable effect of quenching on the green luminescence and of slow cooling on the blue luminescence had been pointed out earlier by Rothschild [25]. Some authors [220-222] regarded the increase in the blue luminescence at the expense of the green as an irreversible process ("aging" of the phosphor), but it has been shown [13,192,223,224] that heating at 250–300° restores the green luminescence. According to Riehl and his coworkers [13,211], who heated the phosphor in a vacuum, this conversion of blue into green luminescence is irreversible unless it is carried out in a closed, evenly heated space. However, experiments with ZnS–Cu, Cl phosphors prepared with a chloride flux in air have indicated [192] complete reversibility of the interconversion of "green" and "blue" centres even when the process is carried out in an open vessel at atmospheric pressure. If we assume that the reaction can be described by Eqn. (6) or that it somehow involves the association of Cu^+ ions into pairs and the dissociation of these pairs, we are faced with the problem of suggesting how the necessary movement of ions in the lattice can occur so readily below the Tammann temperature. Riehl's hypothesis of the diffusion of Cu^+ ions through interstices is no real answer, because, as was stated above, it does not explain why diffusion occurs in some cases and not in others. The suggestion that dislocations play an important part in these processes is more reasonable [192,198]. There has been a growing realisation in recent years that many phenomena observed in crystal phosphors [144,225-229] are controlled by the presence of dislocations. The diffusion of activators in ZnS at low temperatures is probably one of these phenomena. This is confirmed by the observation [230] that single crystals with a high dislocation density can take up abnormally large amounts of Cu. Riehl and Ortmann point out [190] that in diffusion experiments of this type the "blue" centres behave as intermediate states, since prolonged heating results in conversion of the "blue" centres into "green" centres. Wendel [212] drew attention to the fact that often the appearance of blue luminescence goes hand in hand with the electroluminescent properties of the phosphors, and attempted to relate both phenomena to the presence of Cu^+ in interstices, despite the numerous reported instances of blue luminescence not accompanied by electroluminescence [193]. However, all these observations help to establish an interrelation between the various sets of phenomena: one possible explanation is based on the assumption that dislocations play an important part both in the formation of "blue" centres and in the erection of the barriers needed for electroluminescence. Kinetic studies of the conversion of "green" centres into "blue" centres [231] support the suggestion that the process consists in the "expulsion" of Cu^+ ions to remote regions of the dislocation field, where Cu'_{Zn}–Cu'_{Zn} dimer formation takes place as indicated by Eqn. (6). These

dimers can be regarded as an intermediate state between single Cu^+ ions and more or less coarse agglomerations of these ions around dislocations, known as "Cottrell atmospheres" (since ZnS and Cu_2S are not isomorphous, the latter tends to appear in regions where the lattice is disturbed[232,233]). The segregation of Cu^+ ions around dislocations under certain conditions gives rise to the barriers to which the electroluminescent properties of ZnS–Cu phosphors are attributed. Thus, both the formation of "blue" centres, arising from defects of the Cu'_{Zn}–Cu'_{Zn} type, and the electroluminescent properties result from the process which precedes the precipitation of copper from the ZnS lattice as a separate Cu_2S phase. This hypothesis is consistent with the fund of experimental data obtained in the investigation of electroluminescent materials[193,212,225,234]. The study of phenomena such as the diffusion of activators and in particular the low-temperature interconversion of luminescence centres has shown a need for a wider application of the new concepts, which are now relegated to a separate branch of science — the chemistry of the defect solid state.

In addition to the views considered above, there are others on the nature of the Cu centres giving rise to blue luminescence. According to Curie[235,236] it is the "green", not the "blue", centres which have an associated structure comprising both activator and coactivator ions. But the association of Cu^+ and Cl^- should be enhanced by increasing the concentration of Cu^+, leading to conversion from blue to green luminescence, which is at variance with the facts. Nor is this hypothesis consistent with the fact that the spectral position of the green luminescence band is independent of the nature of the coactivator[237].

It has been suggested[45,156] that the blue and the green luminescence bands belong to a single centre having two levels, the difference between phosphors with blue and with green luminescence arising, according to Browne[156], from differences in the occupancies of these levels. An attempt was made to interpret the infrared luminescence of ZnS–Cu phosphors from this point of view. Essentially, Browne identifies the "blue" and the "green" centres of "self-activated" phosphors with those of copper-activated phosphors, and ascribes a decisive role to the zinc vacancies. We have already listed the arguments against identifying in this way centres of different kinds. In general, this seems an unlikely standpoint from which to attempt to explain the great variety of facts relating to the influence of preparative conditions on the optical properties of phosphors.

Some complications arise from the fact that the blue Cu band is again displaced by the green band as the concentration of copper is increased[32]. This happens under conditions which give a fairly high solubility of Cu in ZnS.[198] Several workers[32,45,71] point out that the green bands corresponding to a low ("green-I") and to a high ("green-II") concentration of copper have the same shape and occupy the same position in the spectrum. The slight differences observed by other authors[106,236] may be due to incomplete resolution of the blue and the green band, to the formation of a Cu_2S filter on the surface of the phosphor, to the faster conversion of wurtzite into sphalerite when the phosphor is cooled in the presence of high concentrations of copper[238], and to the influence of ZnO in the ZnS lattice on the position of the maximum and on the half-width of the band. There is some evidence[198] that the excitation spectra of the green-I and the green-II bands are identical, although even this question involves divergence of opinion[199], no doubt resulting from the influence of preparative conditions. Studies of the temperature dependence of the luminescence suggest[32,45,52,71] that the appearance of a green-II band in place of the blue luminescence band is caused by a fall in the temperature of incipient quenching of both bands under the influence of an increase in the concentration of quenching centres: as a result, the blue luminescence band ceases to be observable at room temperature. The quenching centres can be more or less coarse aggregates of Cu^+ ions[124,222], whose formation within the ZnS phase becomes possible only at high enough concentrations of dissolved Cu. Thus, the green-II band does not appear when the Cu is introduced by diffusion at 450°,[239] or when ZnS–Cu is heated in H_2 or ZnS–Cu, Al is heated in H_2S.[198] Hence there are grounds for regarding the green-I and the green-II bands as identical, produced by the same luminescence centres, in spite of the fact that some anomalies[198] in the behaviour of phosphors showing a green-II band are still unexplained.

According to Froelich[188,240] and others[61,63,148,241-243], it is possible to prepare a ZnS–Cu phosphor with a red luminescence band (λ_{max} = 670–720 nm) in an atmosphere of H_2S at relatively high Cu concentrations (optimum 0.1%[188]), when the system has been rigorously freed from coactivators and oxygen. It has been suggested that the "red" centres, like the "blue" luminescence centres, are formed by the association of two Cu atoms[148,188]. Froelich believes that, in the absence of coactivators which stabilise the Cu in the Cu^+ state, the copper is more readily reduced to neutral copper atoms, which can then form red luminescence centres by becoming associated with Cu^+. However, this hypothesis is inconsistent with the lack of paramagnetic properties of the "red" centres[71]. Aven and Potter[148] have suggested that Cu^+ is oxidised to Cu^{2+} under the influence of the S_2 produced by the dissociation of H_2S. Two Cu^{2+} ions at neighbouring cation sites undergo charge transfer and form a $Cu'Cu^{\cdot}$ red luminescence centre. This hypothesis is not consistent with the fact that phosphors having a red luminescence band are not formed in an atmosphere of sulphur vapour. van Gool and Shionoya ascribe the decisive role to another product of the dissociation of H_2S — hydrogen — since they believe that hydrogen can penetrate ZnS[241] or form sulphur vacancies[242], whose association with Cu^+ gives rise to red luminescence centres. This hypothesis, however, conflicts with their own experimental finding that no red luminescence is produced by heating in H_2, and also with reports of red luminescence in phosphors heated in CS_2[188,244] in the absence of H_2. Furthermore, a $Cu_{Zn}V_S^{\circ}$ centre should be compensated by a Cu'_{Zn} centre giving green emission, but this has not been observed. Bowers and Melamed[71], having found a blue and a red luminescence band in the same sample, made the suggestion that the Cu^+ is displaced into interstitial sites, the resulting cation vacancy acting as the blue luminescence centre, whilst the Cu^+ ion accounts for the red emission. However, other workers have shown[148,241,242] that the appearance of red luminescence is by no means invariably accompanied by the blue luminescence band.

Presland et al.[245] obtained ZnS–Cu phosphors with yellow and red luminescence by rapidly cooling (quenching) the phosphor after heat-treatment in hydrogen sulphide or argon. The effect was not inhibited by the presence of a chloride flux. A subsequent low-temperature heat-treatment at first increased the relative contribution of the red band to the spectrum, and then produced the usual blue and green luminescence. These workers[245] suggested that the excess of Cu remaining in the ZnS lattice after quenching perturbs the levels of the "blue" and "green" centres, con-

verting them into "yellow" and "red" centres respectively. The possibility of producing ZnS–Cu phosphors with a yellow (λ_{max} = 590 nm) and a red luminescence in the presence of Cl has been mentioned also by Vlasenko [90] and Kazankin [193]. It has recently been shown [231] that a ZnS(hex.)–Cu phosphor with strong yellow and red bands in its luminescence spectrum can be prepared also in the presence of oxygen by heating the phosphor at 145–150° for 10–30 min after it has been heated in the air with a chloride flux and quenched. In contrast to the findings of Presland et al., the "quenched" phosphor had a green luminescence, which became yellow and then red only after low-temperature baking. The same result was obtained [246] in a study of "quenched" phosphors prepared in a medium of HCl + H_2S. An interpretation of these observations is [231] that, in the absence of coactivators and oxygen, and if the heating conditions do not favour the formation of sulphur vacancies, one-half of the Cu^+ ions remain in interstitial sites when Cu_2S is dissolved in ZnS. The tendency of Cu_2S to be precipitated as a separate phase induces a tendency for the interstitial Cu_i^+ ions to combine with Cu_{Zn}^+ ions located at lattice sites. At high enough copper concentrations (~ 0.1%) this process occurs even in the presence of coactivators and oxygen, but the latter promote the transfer of Cu^+ ions to lattice sites during cooling. However, if the phosphor is "quenched" and then baked at a low temperature, it is possible to freeze the intermediate state corresponding to the formation of Cu_i^+–Cu_{Zn}^+ associations; these are evidently responsible for the formation of luminescence centres, the "yellow" and the "blue" centres corresponding to different extents of association.

An analysis of the published data reveals a large measure of similarity in the physicochemical behaviour of ZnS–Cu and ZnS–Ag phosphors, although some of the phenomena are less easy to observe in the case of ZnS–Ag. This is clearly because the large size of Ag^+ makes it difficult to achieve sufficiently high concentrations of activator and the formation of associations in the ZnS phase. At high Ag concentrations and low amounts of coactivator, a short-wavelength band is observed (λ_{max} = 620 nm in CdS and 380–395 nm in ZnS). [247–251] Although a band close to this one has also been observed in phosphors not containing Ag, and has given rise to the suggestion [169] that the emission is due in both cases to sulphur vacancies, the slight difference in the position of the two maxima [98], and especially the effect of baking on the spectrum of the CdS–Ag phosphor with a short-wavelength luminescence band [231,248], indicate that the centres responsible for this band may be similar to the "blue" centres in ZnS–Cu phosphors. Heat-treatment of ZnS–Ag in H_2S in the absence of coactivators and oxygen gave [148,252,253] an orange luminescence band (λ_{max} = 620–640 nm), evidently similar to the red band in ZnS–Cu. The effect of the nature of the activator on the spectral composition of the luminescence of these phosphors, and also the disappearance of these bands at low concentrations of Cu or Ag, suggest a causal relationship between luminescence centres and activator. Although e.s.r. measurements point to the presence of defects of the type $Ag_{Zn}^{\cdot}V_S^{\cdot}$ in these phosphors [252], there is no convincing proof that these are the defects responsible for the luminescence centres. There are some isolated reports [53,254,255] of a weak greenish-blue band (λ_{max} = 480–495 nm) in the luminescence spectrum of ZnS–Ag phosphors, recently confirmed by the work on "quenched" phosphors, in whose spectrum this band is most clearly visible [231]. The similarity in physicochemical behaviour (disintegration of the centres on low-temperature baking) suggests that the "green–blue" Ag centres and the "yellow" Cu centres are alike. The corresponding centres in CdS–Ag give a band with λ_{max} = = 780 nm. [256,257] In the light of what has been said in this and in the previous Sections, we can conclude that, notwithstanding statements to the contrary [97], the luminescence centres formed by silver usually give radiation of shorter wavelength than the corresponding "copper" centres (see Table).

TABLE. *Defects most likely to be responsible for the formation of the luminescence centres in various ZnS phosphors. (The maxima of the corresponding emission bands are shown in brackets).*

Wavelength scale, nm		400	450	500	550	600	650	700
Spectral region		ultraviolet	violet	blue	green	yellow	orange	red
Phosphor	ZnS-Cl	$Cl_S^{\cdot}$ (380-390)	$V_{Zn}Cl_S^{\cdot}$ (450-465)	$V_{Zn}O_S^{\cdot\cdot}$ (510-520)				
	ZnS-Ag	$Ag_{Zn}^{\prime}$–$Ag_{Zn}^{\prime}$ (380-395)	$Ag_{Zn}^{\prime}$ (435-450)	$Ag_{Zn}^{\cdot}$–$Ag_i^{\cdot}$ (480-495)			$Ag_{Zn}^{\prime}$–$Ag_i^{\cdot}$ (620-640)	
	ZnS-Cu		$Cu_{Zn}^{\prime}$–$Cu_{Zn}^{\prime}$ (440-450)	$Cu_{Zn}^{\prime}$ (515-530)	$Cu_{Zn}^{\prime}$–$Cu_i^{\cdot}$ (570-590)			$Cu_{Zn}^{\prime}$–$Cu_i^{\cdot}$ (670-720)

V. "INDIRECT" ACTIVATION AND STRUCTURE OF THE LUMINESCENCE CENTRES

It should be evident from the previous Sections that attempts to explain the great variety of properties of the sulphide phosphors on the assumption of a unique state of the activators in the sulphide lattice (atoms in interstices, ions with an effective charge of -1 at lattice sites, etc.) have proved fruitless. It is also clear that luminescence bands having similar positions in the spectrum are often due to centres produced by defects of different chemical origin, and attempts to attribute them to one and the same centre are groundless. It appears that the wealth of properties of zinc sulphide phosphors depends on the fact that defects, formed by a large number of different impurities and by their combinations with one another and with structural defects, can give rise to luminescence centres, which is not the case with other classes of phosphors. The fundamental cause of this phenomenon is a question that theory must answer.

In the preceding pages we have discussed the chemical nature of the defects responsible for the formation of luminescence centres. But there is another side to the problem under discussion; does the electronic transition responsible for the act of emission occur in the impurity atom (or ion), or does it occur in its immediate vicinity, consisting of atoms of the host material? To solve this problem we must first of all note that the luminescence centres become ionised during the excitation of luminescence. This is shown by the bimolecular nature of the luminescence of ZnS phosphors [258], and by the internal photoeffect which accompanies the luminescence. It was the need to adopt a model which would give a relatively small (about 3 eV) excitation energy for the luminescence centres which caused Seitz [2] to put forward his original hypothesis that the phosphors are activated by free atoms which have penetrated to interstitial sites in the lattice. However, this hypothesis soon came into conflict with the facts, and was displaced by new concepts, according to which the blue luminescence centres in ZnS–Ag and the green luminescence centres in ZnS–Cu are formed by Ag^+ and Cu^+ ions occupying sites of the host lattice. But this

made it necessary to deny that the activator species themselves become ionised, because not only are the ionisation energies of Ag^+ and Cu^+ an order of magnitude higher than those of the corresponding luminescence centres, but they are in the reverse order to the relative quantum energies of the emitted radiation actually found[83,85]. Starting from an ionic model of a crystal phosphor, Klasens[83] suggested that the electronic transitions responsible for the act of emission take place between ions of the main compound. The deficiency of positive charge at a site occupied by a univalent activator assists the removal of electrons from neighbouring S^{2-} ions, and this gives rise to a localised level above the valency band. Even earlier, Leverenz[23] had explained the gradual shift in position of the luminescence band of (Zn, Cd)S phosphors on increasing the concentration of CdS by suggesting that the radiation is emitted by the sulphur atom. Klasens claims support for these views in the fact that replacement of S by Se leads not only to a shift in the luminescence band to longer wavelengths, arising from the smaller width of the forbidden gap, but also to the appearance of a new luminescence band[14,83], which can be ascribed to a perturbed selenide ion. In conformity with the lower electronegativity of Se as compared with S, this band occurs at a longer wavelength than does the corresponding band in the ZnS phosphor. In a similar way the trapping centres can be considered to be Zn^{2+} ions perturbed by neighbouring atoms of the coactivator or by V_S. In agreement with this theory, replacement of Zn^{2+} by Cd^{2+} leads to the appearance of a new trapping level. The small differences in spectral position of the luminescence bands associated with centres of different chemical nature argue in favour of the hypothesis that the electronic processes giving rise to luminescence occur in structural elements of the host lattice. We are now discussing the so-called "indirect activation"[259], which leads to the formation of localised levels which are not characteristic of specific activators.

In the electrostatic approximation the level of S^{2-} adjacent to a defect of charge -1 should lie at a height of $\epsilon = e^2/Kd = 0.74$ eV, where e is the electronic charge, $K = 8.3$ the dielectric constant of ZnS, and $d = 2.35$ Å the interionic distance. Attempts have been made to explain the dependence of the energy level of the centre on the nature of the activator in terms of the polarising effect of the latter, but no rigorous and universally applicable quantitative theory has yet emerged[85]. This has produced a tendency to abandon the ideas of Klasens[47,61]. Thus, Kröger[47] considers that holes localised on excited centres must spend part of their time in the electron shell of an impurity. This point of view is essentially similar to the above-mentioned ideas of Konstantinova-Shlezinger[204], who regards the centres as quasi-molecules. One development of the tendency to explain all the various properties of ZnS phosphors in terms of a single model was Broser's attempt[98] to construct a hydrogen-like model of the luminescence centre. However, the identification of the particular structural elements of the crystal phosphor in which the radiative electronic transitions take place remains an open question.

The experimental material discussed in the preceding Sections provides several illustrations of the similarity between the emission spectra of phosphors containing luminescence centres of entirely different chemical, electrical, and structural nature. This argues in favour of the assumption that the luminescence is caused by electronic transitions in the host material. However, any theory based on this hypothesis must take cognisance of the fact that the bond in ZnS and CdS is predominantly covalent. Therefore the valency electrons taking part in transitions belong not just to sulphur atoms but to both S and Zn (or Cd) atoms. This means that a molecular model of the luminescence centre is a better approximation than an ionic or an atomic model for phosphors of this class. Observations which suggest that molecularly disperse sulphides can luminesce in approximately the region of the spectrum where most of the luminescence bands of normal crystalline sulphide phosphors appear lead to the same conclusion. Thus, according to Weyl[260] and Vargin[261], the yellow luminescence of glasses coloured with cadmium sulphide is due to molecularly disperse CdS, as shown in particular by the absence of a crystalline phase in the glasses with the brightest emission. Gurvich[262,263] found that the dissolution of small amounts of CdS and ZnS in melts of $CdCl_2$, $CdBr_2$, and mixtures of these salts with $ZnCl_2$ produces phosphors having a strong luminescence; this can be explained by electronic transitions in molecules of CdS and ZnS held in the gap between the layers of atoms of the cadmium and zinc halides, which form a layered structure. Several other luminescent systems have been prepared whose ability to emit light can be ascribed to activation by CdS molecules distributed in the bulk or on the surface of the phosphor substrate[260,264,265]. Atoms of Cd (Zn) and S can interact, of course, not only among themselves but also with other neighbouring atoms, but the bond between Cd (Zn) and S is so different in character from all other bonds that we can speak of the formation of CdS and ZnS molecules: this difference accounts for the fact that these molecules are energetically isolated, a necessary condition for the development of luminescence. In a sulphide crystal the bonds between S and Cd (or Zn) atoms adjacent to a defect in the crystal lattice are different, owing to the perturbation caused by the defect, from the bonds in the unperturbed regions of the crystal, and thus we can again use the term molecules or quasi-molecules, formed by the atoms of the sulphide nearest to a defect. Electronic transitions in quasi-molecules of this type, responsible for the act of emission, could be likened to transitions in isolated molecules in a vapour (unfortunately, very little is known about the properties of these molecules[266]) or in solution, for example in the solid solutions discussed above. Since the S–Zn bond is strongly polarised[65,66], the cloud of valency electrons being mainly around the S atom, replacement of Zn by Cd does not have such a marked effect on the luminescence as has replacement of S by Se. This is the case both in normal crystalline sulphide phosphors[83] and in halides activated by sulphides[263]. The relative closeness of a quantum of the characteristic radiation of the majority of centres to the width of the forbidden gap in the sulphide, and the very important close interaction between the electronic processes taking part in the luminescence centres and in the lattice of the host material, are natural consequences of the fact that the phosphor matrix and the luminescence centres are composed of atoms of the same elements. Thus, the capacity for luminescence is embedded, as it were, in the sulphides themselves.

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