STRUCTURE OF A SILVER CENTRE IN ZINC SULPHIDE

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The results of investigations into the phenomena of absorption, emission, thermoluminescence and electron spin resonance of ZnS doped with Ag are given. Both the phosphor powders and the crystals were found to give an orange-yellow emission (maximum 1.93 eV at 300°K, 1.80 eV at 77°K), and thermoluminescence of the same colour. On excitation with 3650 Å light at 77°K, several electron spin resonance patterns appear simultaneously. The intensity of one of these patterns was in all experiments at least ten times higher than the sum of the intensities of the others. This pattern was studied in detail in the case of cubic ZnS crystals. It is evidently due to axial centres, $g_\parallel = 2.0072 \pm 0.0002$ and $g_\perp = 2.0024 \pm 0.0002$, with their axes in [111] directions. The centres have one unpaired electron, $S = \frac{1}{2}$. Hyperfine structure was observed, due to the presence of one Ag nucleus, $A_\perp^{Ag} = 0.1 \times 10^{-4} \mathrm{cm}^{-1}$. Further hyperfine structure, due to the interaction of the unpaired electron with the nuclear magnetic moments of Zn^{67}, was also observed. Three equivalent Zn sites are involved in the latter hyperfine structure, $A_\perp^{Zn} = A_\parallel^{Zn} = 0.8 \times 10^{-4} \mathrm{cm}^{-1}$.

These observations are explained by assuming that the axial centres consist of a sulphur vacancy with, on a nearest-neighbour zinc site, a silver atom.

There is some indication that these centres are responsible for the orange-yellow luminescence and that this emission follows the Lambe-Klick mechanism for fluorescence.

1. Introduction

Recently Kasai and Otomo [1], and Räuber, Schneider and Matossi [2], were able to give rather definite evidence for the structure of self-activated centres in ZnS by applying paramagnetic resonance techniques to the study of this problem.

A similar study was undertaken by us to elucidate the structure of the centres formed in II–VI compounds if Cu, Ag or Au are incorporated in these compounds in the absence of coactivating elements such as Al, Cl, *etc.* As might be expected, some of these centres were also found to be present in materials where coactivators had been added in such an amount that the concentration of the activator exceeded that of the coactivator.

This paper deals with results so far obtained for ZnS:Ag using paramagnetic resonance techniques in combination with hitherto more usual methods.

2. Instruments

The equipment for measuring emission and absorption spectra consisted of a Jarrell-Ash monochromator model 82-000 or a quartz double monochromator. Radiation detectors were: a photomultiplier type 7102 (RCA) or a lead sulphide cell for the near infrared, and a photomultiplier type 50 AVP (Philips) for the visible and near ultraviolet region. The electronic part of the equipment has been described previously [3].

Excitation spectra of the luminescence were measured with the aid of the Jarrell-Ash monochromator using an SP 1000 super-high-pressure mercury lamp. The energy of the monochromatic radiation incident on the specimen was kept constant by a servomechanism.

Thermoluminescence measurements were performed with an equipment similar to that described by Hoogenstraaten [4].

Paramagnetic resonance spectra were taken with a *Varian V*4500 electron spin resonance spectrometer operating at about 9225 Mc/s, using 100 kc/s magnetic field modulation. The microwave cavity was slotted to allow optical excitation of the samples. In most of the experiments the 3650 Å line of an SP500 Watt super-high-pressure mercury lamp (Philips) was selected for optical enhancement of the e.p.r. signals. Excitation spectra and quenching spectra of these signals were obtained with a high pressure Xenon lamp (Osram XB1001) and a Leiss monochromator. The spectral energy distribution of the light emerging from this equipment and incident on the samples was determined separately.

3. Samples

Phosphor powders were prepared by adding Ag_2S to prefired ZnS and firing at about 1150°C in highly purified H_2S. Cubic ZnS powders were obtained by refiring at 800°C. Impurities present in the initial ZnS (UCLAF)[1] were Si (20 ppm), Mg (10 ppm), Fe (0.5–1 ppm). Other impurities may have been present, but with concentrations below 1 ppm. Specially pure ZnS had been prepared in which all impurities were below 1 ppm.

Single crystals were obtained by vacuum sublimation of the activated powders at 1150°C. These crystals appeared to have roughly the same properties as the initial powders. In order to make them cubic they were refired in vacuum for about three days at 800°C. X-ray work showed them to be cubic with in many cases well-developed (111), (110) and (112) faces. The crystals showed stacking faults as have been discussed by others [2].

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[1] UCLAF = Usine Chimique des Laboratoires Français, Paris.

4. Electron spin resonance

When heated to 200°C and afterwards observed in the dark, both at 300°K and 77°K, none of our samples showed resonances, except for a weak pattern due to a trace of Mn^{2+}.

Excitation with light centred around 3650 Å gave no resonances at 300°K, but several resonance patterns appeared at 77°K both in powders and single crystals. The pattern with highest intensity, which we shall discuss here, has g-values slightly above $g = 2.0023$, the free electron value.
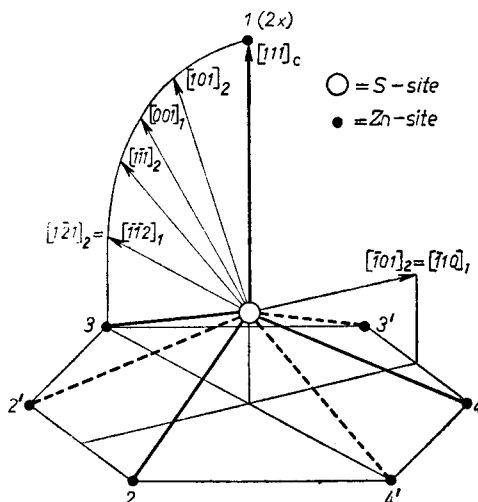

Fig. 1. Illustration of the "microscopic" twinning of cubic ZnS single crystals

The angular dependence of this pattern was investigated for cubic ZnS single crystals containing about 10^{-4} gramatom Ag and 10^{-6} gramatom Fe per mole ZnS. It was found that the previously mentioned stacking faults give rise to "microscopic" twinning of the crystals in such a way that a series of regularly stacked layers is followed by another series of regularly stacked layers rotated as a whole by 60° about a common [111] axis [2], and so on. This is equivalent to saying that for each tetrahedron in these cubic single crystals there is another one which has been rotated by 60° about the $[111]_c$ axis. This is illustrated in Fig. 1 where, also, the planes $(111)_c$, $(\bar{1}\bar{1}2)_1 = (1\bar{2}1)_2$ and $(\bar{1}10)_1 = (\bar{1}01)_2$ are indicated in which the magnetic field H was rotated. Taking account of the "microscopic" twinning of the crystal, both the angular dependence of the lines belonging to the pattern and their relative intensities can be explained by assuming that the centres under consideration

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[2] This common [111] axis was in most cases the growth axis of the crystal and will be denoted by $[111]_c$. Indices 1 and 2 will be used to distinguish between the two "parts" of the crystal.

a. have one unpaired spin ($S = \frac{1}{2}$) and

b. are axial with their axes in the [111] directions of the cubic crystal with

c. $g_{\parallel} = 2.0072 \pm 0.0002$ and $g_{\perp} = 2.0024 \pm 0.0002$.

Fig. 2 shows that there is good agreement between the calculated and experimentally determined line positions. At higher magnetic fields, each of these lines is split into two equally intense lines by the interaction of the unpaired electron with the nuclear magnetic moment of one Ag nucleus ($I = \frac{1}{2}$ for both isotopes Ag^{107} and Ag^{109}) [5]. This is clearly seen in Fig. 3 where the
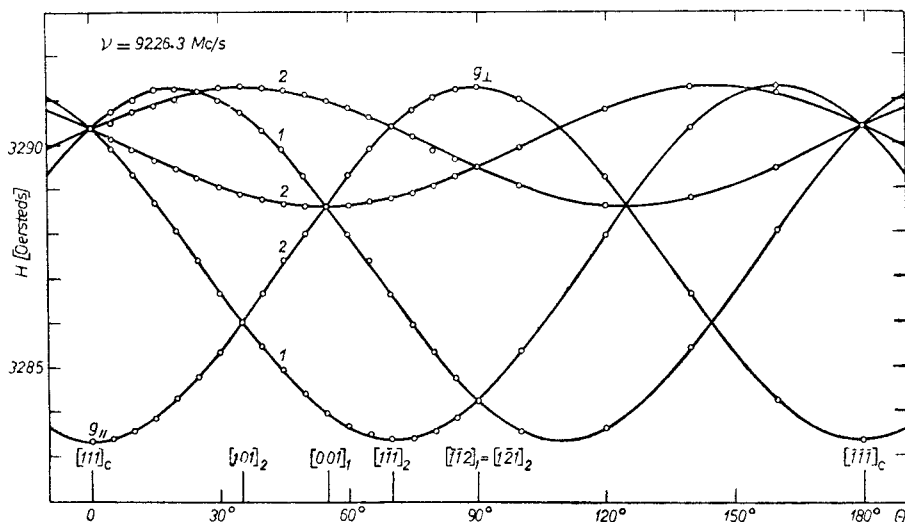
Fig. 2. Angular dependence of the electron spin resonance pattern of the centre, and intensities of the various groups of lines for rotation of the magnetic field H in the $(\bar{1}10)_1 = (\bar{1}01)_2$ plane. The circles denote experimentally determined line positions; the full lines are calculated

resonance pattern is shown for H in the $(\bar{1}10)_1 = (\bar{1}01)_2$ plane at $\theta = 40°$ (compare also Fig. 2). The line denoted by 3, which is due to a single [111] direction and for that reason is not sensitive to some slight misorientation of the crystal, shows this splitting reasonably well. The same splitting is hardly resolved for line 1, which is also related to a single [111] direction. This is due to the angular dependence of the line width. The line widths at higher magnetic fields are seen to be smaller than at lower fields. Apart from the hyperfine structure (h.f.s.) due to Ag, a further structure was observed around each main line. The pattern for $H//[111]_c$, in which only two main lines are present (compare Fig. 2), showed that this is due to hyperfine interaction with Zn^{67} ($I = 5/2$, natural abundance 4.11%) [5]. Six equally-spaced weak lines around each main line were seen. Two of these weak lines were resolved on either side, whereas the inner two were superimposed upon the main lines. The intensity of each of these six weak lines, as determined for various direc-

tions of the magnetic field, was found to be $(2.14 \pm 0.28)\%$ of the main line. This means that three equivalent Zn-sites are involved in this hyperfine interaction, the calculated intensity ratio then being 2.16% [3]. The weak outrider lines, indicated by crosses in Fig. 3, form part of this Zn^{67} hyperfine interaction. The hyperfine structure constants deduced from the experiments are $A_\perp^{Ag}$ $=0.1 \times 10^{-4}$ cm^{-1}, $A_\perp^{Zn} = A_\parallel^{Zn} = (0.8 \pm 0.05)10^{-4}$ cm^{-1}.
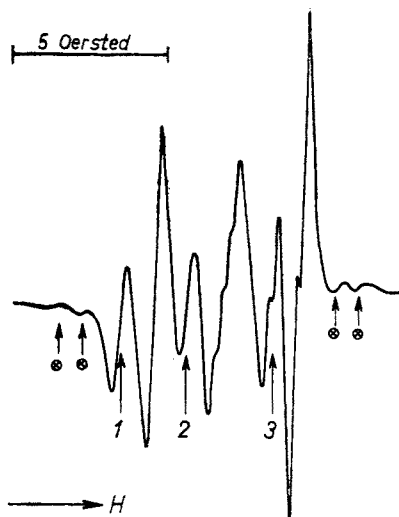
Fig. 3. Derivative of the absorption for H in the $(\bar{1}10)_1 = (\bar{1}01)_2$ plane, $\theta = 40$; (cf. Fig. 2). Lines 1 and 2 have intensities one, line 2 is an isotropic resonance $g = 2.0046 \pm 0.0002$, due to a not yet identified photosensitive centre. The outrider lines indicated by crosses are h. f. s. lines due to interaction of the unpaired electron with the magnetic moment of Zn^{67}

The spin resonance results are easily interpreted by assuming that the centre is an associate of a sulphur vacancy V_S and an Ag-atom on a nearest-neighbour Zn site [4]. It can be denoted by $[Ag_{Zn}V_S]^\times$. Prener and Williams [6] have speculated on the existence of such a centre in ZnS. According to these authors, it constitutes a singly ionizable donor. Our interpretation is that the centre is singly ionized before irradiation. The centre $[Ag_{Zn}V_S]^\circ$ has one excess positive charge with respect to the lattice, is nonparamagnetic and is compensated by acceptor centres, the structure of which is being investigated. The main process caused by 3650 Å irradiation at 77°K is excitation of electrons from filled acceptors into the conduction band, Hall measurements having

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[3] $\dfrac{3 \times (0.9589)^2 \times 0.0411}{(0.9589)^3} \times \dfrac{1}{6} \times 100\% = 2.16\%$.

[4] The centres will be denoted in the manner proposed by F. A. Kröger and H. J. Vink, *Solid State Physics*, 3, Editors F. Seitz and D. Turnbull, *Academic Press Inc.*, New York, pp. 307—435 (1956).

shown the phtoconductivity to be caused by electrons. These electrons are subsequently trapped at the $[Ag_{Zn}V_S]^\circ$ centres transferring them to $[Ag_{Zn}V_S]^\times$ (Fig. 4). The latter centres are responsible for the pattern mentioned above.

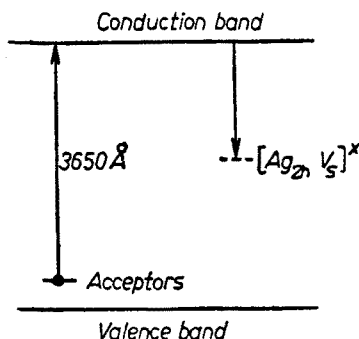Fig. 4. The process of charge transfer caused by 3650 Å excitation at 77°K

5. The relationship between the $[Ag_{Zn}V_S]^\circ$ centre and orange emission

Both the powders and the crystals showed the orange-yellow emission reported by Aven and Potter [8]. The emission for a cubic ZnS single crystal is shown in Fig. 5. At 300°K the maximum was at 1.93 eV, (Aven and Potter's value 1.97 eV), whereas at 77°K the maximum was shifted to 1.80 eV. A second emission maximum was found in the near infrared 1.39 eV at 77°K, not resolved at 300°K.

In this section, a summary will be given of the evidence indicating that the centre already described is in all probability responsible for the orange emission and that this emission follows the Lambe-Klick mechanism for fluorescence [9]. The corresponding processes will be indicated in Fig. 6.

The cubic single crystals contained, apart from the Ag added intentionally, a small amount of Fe (1 ppm). Now Fe is known to provide a deep hole trap [10]. On excitation with light centred around 3650 Å at 77°K resonance is also observed of Fe_{Zn}°. After this excitation the crystals showed an orange afterglow at 77°K. At the same time, changes in the intensity of the resonances are observed, Fig. 7. The signals due to the $[Ag_{Zn}V_S]^\times$ centres decreased, whereas a simultaneous increase in the Fe_{Zn}° signals was observed in the first minutes. (Over longer periods the Fe_{Zn}° signals decreased again, probably due to tunnelling processes). These observations can be explained by assuming that holes are excited thermally from shallow acceptors A_1 into the valence band, process 1 in Fig. 6. These holes can either recombine with electrons trapped at $[Ag_{Zn}V_S]^\times$ centres causing the emission of orange light, process 2 in Fig. 6, or they can be retrapped by $Fe_{Zn}^\times$ centres enhancing the Fe_{Zn}° concentration, process 3 in Fig. 6.
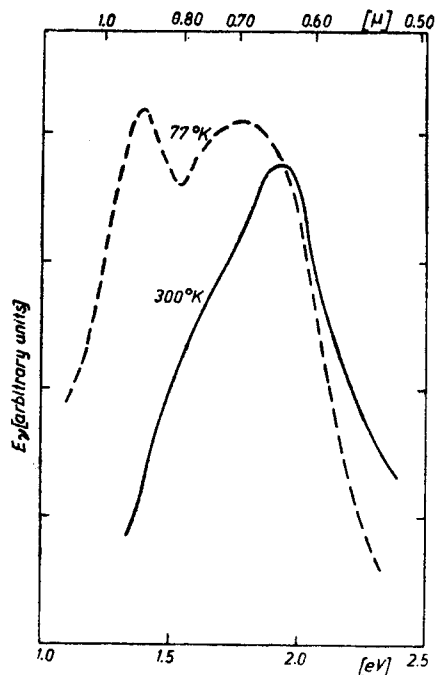
Fig. 5. Emission of a cubic ZnS single crystal doped with Ag

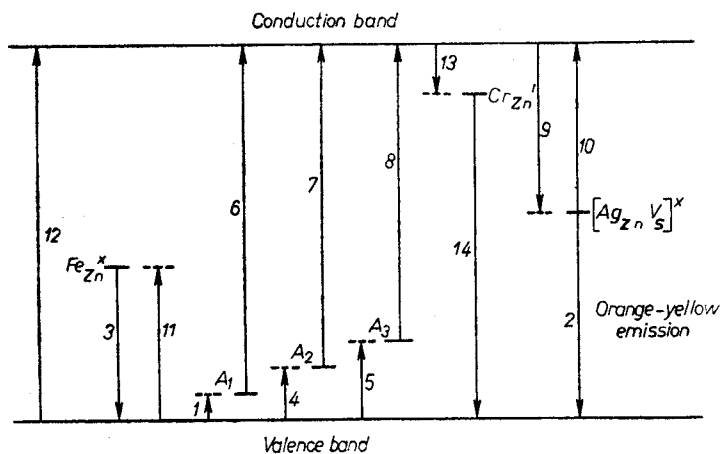Fig. 6. In illustration of the phenomena discussed in Section 5

The excitation spectrum of the $[Ag_{Zn}V_S]^{\times}$ resonance and that of the orange emission are shown in Fig. 8 for cubic single crystals at $77°$K. The excitation spectrum of the resonance shows peaks at 3.55 and 3.4 eV and a shoulder at about 3.27 eV. The spectrum is explained by assuming that electrons are excited from filled acceptors A_1, A_2 and A_3 into the conduction band, processes 6, 7 and 8 in Fig. 6, and are subsequently trapped at $[Ag_{Zn}V_S]^{\circ}$ centres, pro-

cess 9 in Fig. 6. The excitation spectrum of the orange emission sets in at about 3.4 eV, has a peak at 3.6 eV and extends into the edge. This observation is in accordance with the mechanism proposed for the orange emission, appreciable excitation of this fluorescence being expected only for process 6 combined with the thermal process 1, and for process 12.

Before irradiation the crystals showed absorption within the edge in the same wavelength range where the $[Ag_{Zn}V_S]^{\times}$ resonance is excited. Irradiation of the crystals with ultraviolet light centred around 3650 Å at 77°K gave rise to a change in the absorption spectrum. This is shown in Fig. 9. This change
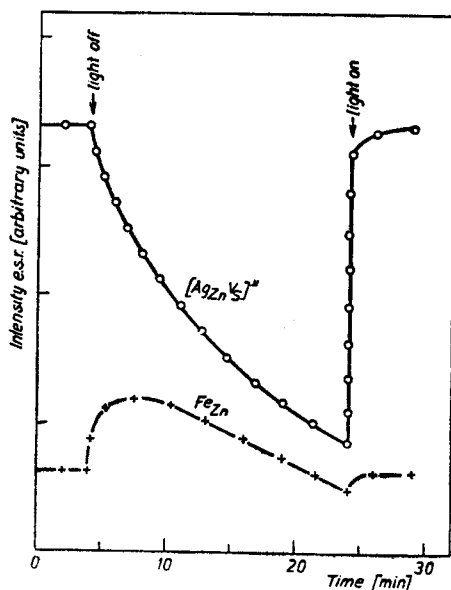

Fig. 7. Changes in the resonance intensities at 77°K after excitation with 3650 Å light

was measured under constant excitation from 0.5 to 2.9 eV and just after excitation above 2.9 eV. In the same figure, we have plotted the changes in intensity of the Fe_{Zn}° and $[Ag_{Zn}V_S]^{\times}$ resonances induced by shining equal numbers of photons of various wavelengths upon an excited crystal. Starting from the lower energies, the first series of processes consists in the optical excitation of holes from empty acceptor levels A_1, A_2 and A_3 into the valence band, processes 1, 4 and 5 in Fig. 6. These holes can either be retrapped by $Fe_{Zn}^{\times}$ centres, giving rise to an enhancement of the Fe_{Zn}° resonance, process 3 in Fig. 6, or recombine with $[Ag_{Zn}V_S]^{\times}$ centres, giving rise to a decrease of the $[Ag_{Zn}V_S]^{\times}$ resonance and stimulated orange emission, process 2 in Fig. 6. This infrared stimulation of orange emission was observed. At about 1.3 eV a second series of processes begins to overlap on the first, viz. excitation of electrons from the $[Ag_{Zn}V_S]^{\times}$ centres into the conduction band, process 10 in Fig. 6. These electrons may recombine either with holes
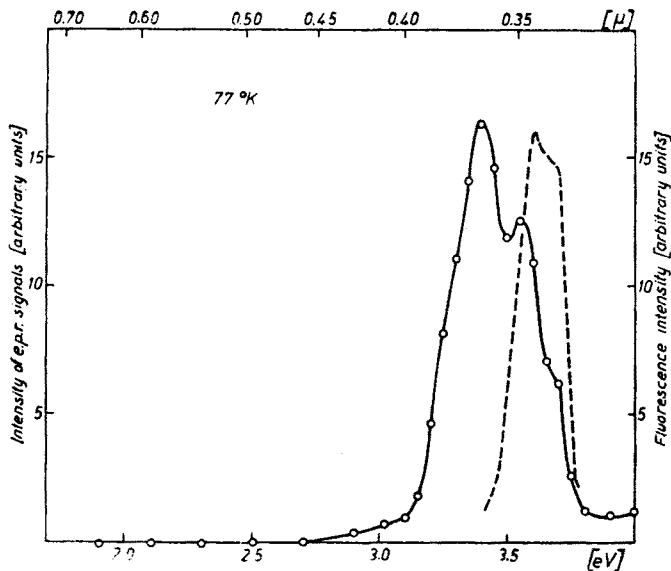
Fig. 8. Excitation spectrum of the $[Ag_{Zn}V_S]^\times$ resonance and excitation spectrum of the orange emission for cubic ZnS·Ag single crystals at 77°K. ○–○–○ excitation spectrum e. s. r., – – – excitation spectrum of fluorescence
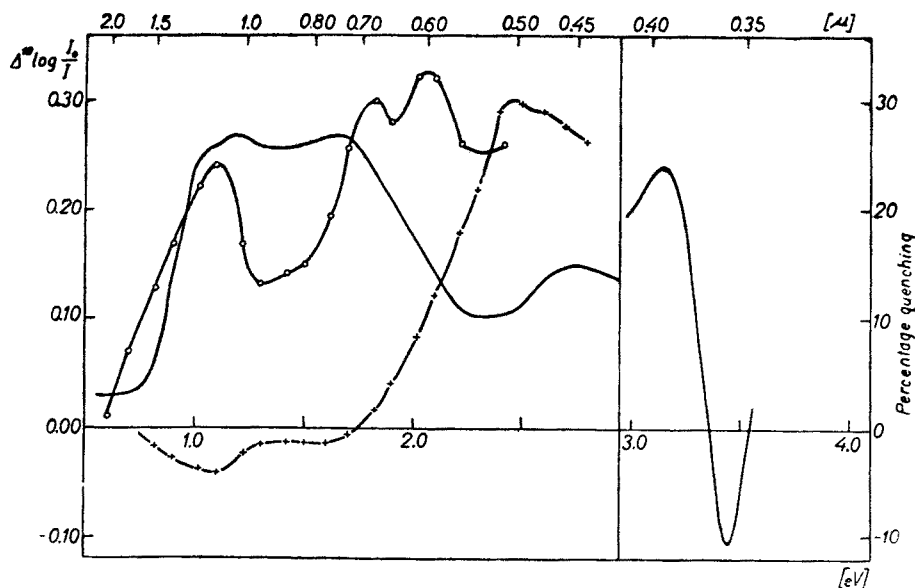

Fig. 9. Changes induced in the absorption spectrum of cubic ZnS:Ag single crystals by excitation with 3650 Å light at 77°K. Quenching and/or stimulation spectra of the $[Ag_{Zn}V_S]^\times$ resonance and the Fe_{Zn}° resonance. —— optical absorption, ○–○–○ quenching e. s. r. of $[Ag_{Zn}V_S]^\times$, +–+–+ quenching e. s. r. of Fe_{Zn}°

in the valence band, with empty acceptors A_1, A_2 and A_3, or with $Fe_{Zn}°$ centres. The maximum of this second process at 1.83 eV and the maximum of the orange emission at 1·80 eV add up to the band gap energy of 3.65 eV. At still higher energies holes are excited from $Fe_{Zn}°$ centres into the valence band, *etc.* Both the $Fe_{Zn}°$ resonance and the $[Ag_{Zn}V_S]^×$ resonance will be quenched strongly by this process. The decrease in absorption around 3.4 eV (see Fig. 9) is due to the decrease in number of filled acceptors by the process of charge transfer.

The colour of the thermoluminescence was in all experiments orange. Powder samples of purely hexagonal ZnS: Ag have a main glow peak at about 140° K. In samples in which a few per cent of the cubic phase were present a second glow peak was observed at lower temperatures. However, glow curves of purely cubic ZnS: Ag powder samples are not yet available.

A more extended account of the relation between the $[Ag_{Zn}V_S]°$ centre and similar centres in Cu- or Au-activated ZnS and the orange emissions found in these materials and the mechanism of this fluorescence will be given in a forthcoming publication.

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