

PARAMAGNETIC RESONANCE DETECTION OF LUMINESCENT CENTERS AND TRAPS
 IN SELF-ACTIVATED ZnS PHOSPHORS

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The atomic nature of the luminescent center in self-activated ZnS phosphors has been the subject of many papers.¹⁻⁴ Kröger and Vink¹ have proposed that the self-activated centers are Zn⁺⁺ ion vacancies that have lost one electron from their nearest surrounding S⁻ ions. Magnetic susceptibility measurements by Bowers and Melamed,² however, revealed that the self-activated center is diamagnetic, whereas the model proposed by Kröger and Vink should be paramagnetic. Prener and Williams³ then suggested a model in which the centers in question are Zn⁺⁺ ion vacancies with one of their charge-compensating ions (Cl⁻, Br⁻, I⁻, Al⁺⁺⁺, or Ga⁺⁺⁺) associated at the nearest possible sites in the ZnS lattice. More recently Prener and Weil⁴ supported the latter model by showing experimentally that the emission peak of the self-activated luminescence depends on whether a group III-B or group VII-B element is used as a coactivator. The existence of various traps for excited electrons or holes in luminescent ZnS phosphors including the self-activated type are also well known,⁵ though here again the problems concerning the exact nature of some of these traps are still unsettled. If the self-activated ZnS phosphor is truly diamagnetic in its unexcited state, then the presence of such traps implies that the phosphor should become paramagnetic when enough electrons are transferred from the luminescent centers into these traps as is often done in thermoluminescence experiments. The following is the preliminary report of our electron paramagnetic resonance (EPR) detection of such excited states frozen at the liquid nitrogen temperature.

The polycrystalline samples of self-activated ZnS phosphors were prepared by firing the luminescent grade ZnS powder using various alkali halides (NaCl, NaBr, KCl, and KBr) as flux at 800°C for 3 hours. A comparatively low firing temperature was employed in order to ensure the formation of cubic crystals. The x-ray analysis did prove that they were all cubic, and all of them exhibit a single emission band peaking around 4640 Å characteristic of the self-activated emission.

In parallel with the result of Bowers and Mel-

amed, none of these samples give an EPR signal in the dark, either at room temperature or at 77°K, except six equally spaced weak lines due to a trace of Mn⁺⁺ impurity. At room temperature, simultaneous illumination of the sample with 3650 Å ultraviolet radiation produced no change in the observed spectra. At liquid nitrogen temperature, however, the simultaneous ultraviolet illumination gave rise to two additional signals A and B in every sample. Figure 1 shows such spectra obtained with ZnS(NaCl) and ZnS(NaBr), respectively. Changing the cation of the flux from Na⁺ to K⁺ has no effect upon the spectra.

The shape of the signal B is more or less symmetric, and is little affected when the halide ion in the flux is changed. The *g* value of the signal B is 1.883 ± 0.001 . The fact that its *g* value is less than 2 implies that the signal B is associated with un-ionized donors, namely filled traps.⁶

The shape of the signal A is just what one would expect for a polycrystalline sample having an anisotropic *g* value.⁷ Also, as can be seen from the figure, when Cl⁻ in the flux is replaced by Br⁻, the apparent linewidth becomes much broader. In either case the *g* values observed on the signal A are

$$g_{\perp} = 2.052 \pm 0.001,$$

$$g_{\parallel} = 2.027 \pm 0.005.$$

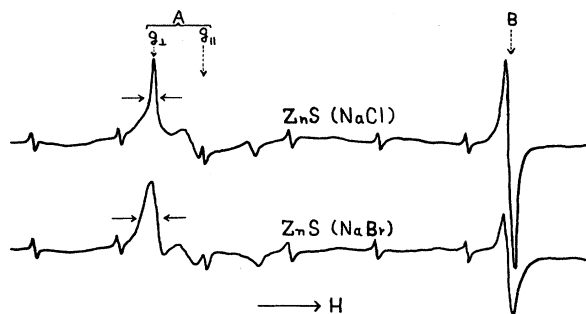


FIG. 1. EPR spectra of self-activated ZnS phosphors under ultraviolet illumination at 77°K. Six equally spaced weak signals are due to Mn⁺⁺ ion impurity, each spacing being approximately 68 gauss.

It should be noted that the mean g value is greater than the free spin value, implying that the signal A is caused by a hole, an empty acceptor.

Both signals A and B are found to decay when the illumination is stopped. The rate of the decay is quite slow at 77°K except for the first few minutes immediately after stopping the excitation. Approximately half of the original intensity can be still detected after 5 hours, so long as the sample is kept in the dark at 77°K . The rapid initial decay may be what is responsible for the glow peak observed near liquid nitrogen temperature in the thermoluminescence experiments.^{5,8,9} The subsequent slow but steady decay is probably due to the tunneling process discussed by Hoogenstraaten.⁵

Among many defects which can act as electron traps in the ZnS phosphors, the Co^{++} ion is known to provide one of the deepest traps.⁵ Consequently if our previously stated analysis concerning the nature of the signals A and B is correct, the introduction of Co^{++} ions into these phosphors should result in a strong enhancement of the signal A and weakening of the signal B . This was indeed found to be the case. Introduction of 10^{-6} (mole ratio) CoCl_2 increased the intensity of the signal A by a factor of five while making the signal B appear only as a trace. Figure 2 shows the spectrum obtained with $\text{ZnS}(\text{KCl})$ containing 10^{-5}Co^{++} . A strong broad resonance at the left is due to Co^{++} ions. The g value of this Co^{++} resonance is 2.248 ± 0.005 .¹⁰ In Fig. 1 one also notices a weak negative dip near the $g=2.00$ position, the center of the six Mn^{++} hyperfine components. This signal, however, cannot be incorporated into the signal A , since it does not grow upon the introduction of Co^{++} ions. The nature of this signal is still unknown.

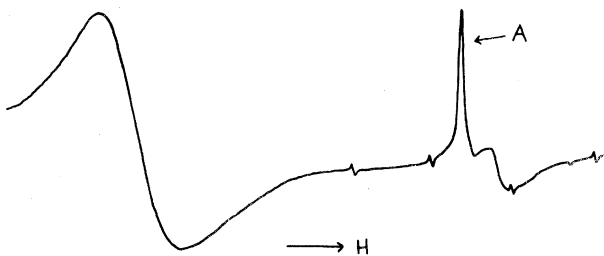


FIG. 2. EPR spectrum obtained with $\text{ZnS}:10^{-5}\text{Co}(\text{KCl})$ under ultraviolet illumination at 77°K . A strong broad resonance at the left is due to the Co^{++} ion. Note the enhancement on signal A . The amplifier gain used for this record was about $1/3$ of that used for the records in Fig. 1.

If the defect responsible for the signal A is a simple Zn^{++} ion vacancy surrounded by four S^{--} ions at the tetrahedral corners, the observed anisotropy in the g value and the dependency of the line shape upon the halide ion in the flux are both difficult to explain. We, therefore, believe that the signal A is caused by the defect proposed by Prener and Williams.³ The Zn^{++} ion vacancy surrounded by three S^{--} ions and one halide ion at the tetrahedral corners could well account for the above-mentioned features of this signal. Also since there is no significant change in the g value when Cl^- in the flux is replaced by Br^- , we must attribute the observed difference in the line shape to the difference in the nuclear magnetic moments of the respective halogen nuclei. A careful study of the spectra revealed that the ratio of the apparent linewidth of the signal A (the width shown by the arrows in Fig. 1) of $\text{ZnS}(\text{NaCl})$ to that of $\text{ZnS}(\text{NaBr})$ is 1:2.8, in close agreement with the ratio of the average magnetic moments of the respective halogen nuclei. The nature of the defect responsible for the signal B is less certain. The chloride flux always produces more of this signal than the bromide, though there is no significant change in the line shape, nor in the g value. The sulfur vacancies produced by some chemical reaction involving the alkali halide flux are probably responsible for this signal.

The EPR spectrometer used for this work is a Varian 100-kc spectrometer, model V-4500, and the frequency of the microwave is about 9.2 kMc/sec.

A more detailed and fuller account of this work will be published in the future together with the work on a single crystal which is now in progress.

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