

Electron Paramagnetic Resonance Studies of Luminescent Centers and Traps in Self-Activated ZnS Phosphors

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Electron paramagnetic resonance signals, *A* and *B* are found in self-activated ZnS phosphors. The center responsible for the *A* signal is the self-activated luminescent center which is an associate of a Zn ion vacancy and a co-activator atom at the nearest possible site and the center responsible for the *B* signal is a simple sulfur ion vacancy.

In hexagonal modification, two types of the centers are possible, one of which still retains an axial symmetry, while the symmetry of the other type is orthorhombic.

Also, described in this report are the effects of oxygen incorporated into ZnS by both the electron paramagnetic resonance and the thermoluminescence techniques. One of the effects is that the incorporation of oxygen leads to formation of self-activated luminescent centers whose co-activator ions are at the non-nearest possible sites.

1. Paramagnetic Resonance Detection of Signals, *A* and *B* in Cubic Form ZnS Phosphors

Two photosensitive electron paramagnetic resonance signals, *A* and *B* are found in self-activated ZnS phosphors at 77°K when illuminated with UV light as shown in Fig. 1¹⁾.

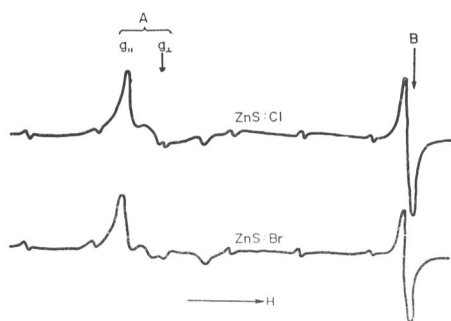


Fig. 1. EPR spectra of self-activated ZnS (10^{-1} KCl, 800°C, 3 hrs. in air) and ZnS (10^{-1} KBr, 800°C, 3 hrs. in air) under UV illumination at 77°K. Six equally spaced weak signals are due to Mn^{++} ion impurity, each spacing being approximately 68 gauss. $g_{||}=2.0530\pm0.0005$, and $g_{\perp}=2.0275\pm0.001$ for the *A* signal and $g=1.883\pm0.001$ for the *B* signal.

The *g* values of these two signals imply that the *A* signal is due to trapped holes, while *B* signal is due to trapped electrons.

1. Identification of the *A* center as the Self-Activated Luminescent Center

The *A* center was concluded to be the

self-activated luminescent center which is an associate of a zinc ion vacancy and a nearest coactivator atom on the following bases:

(a) The *A* center is a photosensitive hole trap.
(b) The signal *A* has an anisotropic *g* value.
(c) When KBr is used as a flux instead of KCl, the apparent line width of the signal *A* becomes much broader due to the difference of the average magnetic moments of the respective halogen nuclei.
(d) Within the limit of the experimental accuracy, the peak height intensity of the *A* signal is found to be proportional to the area of the glow curve of the corresponding sample. Introduction of impurities such as oxygen or Co^{++} which are known to provide deeper traps always results in an enhancement of the *A* signal.
(e) Prener and Weil have shown that the self-activated luminescent centers can be destroyed by refiring the sample in a reducing atmosphere²⁾. Refiring of our luminescent samples in a reducing atmosphere ($H_2/He=1/9$) always resulted in a reduction of both the *A* signal and the emission intensity.

2. Identification of the *B* Center as a Sulfur Vacancy

The *B* center was identified as a simple sulfur ion vacancy on the following bases:
(a) It is a photosensitive electron trap.
(b) The *g* value of the *B* signal is isotropic, and its deviation from the free electron value is found to be quite reasonable on a sulfur vacancy model.
(c) If the *B* center is a sulfur vacancy, the intensity of the *B* signal

is expected to increase when a sample is fired in a reducing atmosphere within the limit that the acceptor centers are not completely destroyed. This was indeed found to be the case.

2. Effect of Hexagonal Modification on the A and B Centers

When the crystal becomes hexagonal, all four sulfide ions surrounding a zinc vacancy are no longer equivalent. Thus in a hexagonal sample two kinds of A centers are expected, one with its halogen atom along the c -axis of the crystal and the other having its halogen atom in a direction other than the c -axis. The former center, which we shall designate as A_1 , still retains an axial symmetry, while the symmetry of the latter which we shall designate as A_2 is lowered to orthorhombic.

The increased complexity of the A signal shown in Fig. 2 (a) can be understood easily if we assume that the observed signal is a superposition of the two spectra arising from the A_1 and A_2 centers respectively, the latter of which may possess an orthorhombic g tensor. Because of the identity of the symmetry, the g tensor of the A_1 center is expected to be quite similar to that of the A center in a cubic crystal. A shape function (a weighted distribution function of a poly-

crystalline sample) thus expected for the A_2 signal is given in Fig. 2(b). The g tensor of an axially symmetric center may be characterized by the relations $g_1 = g_{\parallel}$ and $g_2 = g_3 = g_{\perp}$. Now judging from the predominant role played by the halide ion in the structure of the A center, the value of g_1 of the A_2 center should be very close to that of the A_1 center. Then the only effect of the orthorhombic symmetry of the A_2 center that may be manifested is a splitting of $g_{\perp}$ into g_2 and g_3 . Furthermore if such a splitting does take place, the method of calculation carried out in the preceding section predicts

$$g_2 - g_1 = g_1 - g_3 \quad (1)$$

where g_1 is the value observed on the A_1 center. The shape function of the A_2 center thus expected is fitted to the observed spectrum as shown in Fig. 2(b)³. Our final assignments of the g values of the A_1 and A_2 centers are summarized in Table I together with the result obtained with a cubic sample.

Table I. Observed g values of the A centers.

Crystal modification	center	g_1^*	g_2^*	g_3^*
cubic	A	2.0530 (± 0.0005)	2.0275 (± 0.001)	
hexagonal	A_1	2.0597 (± 0.001)	2.0282 (± 0.001)	
	A_2	2.0597 (± 0.001)	2.0403 (± 0.001)	2.0185 (± 0.001)

* For A (cubic) and A_1 centers $g_1 = g_{\parallel}$ and $g_2 = g_3 = g_{\perp}$.

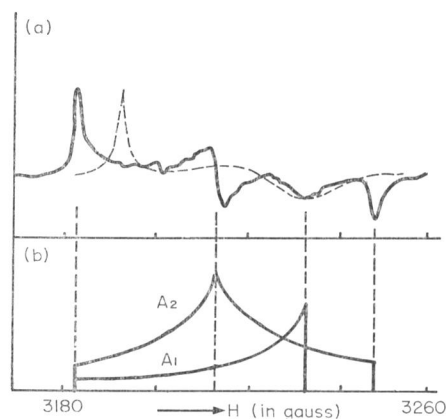


Fig. 2. (a) EPR spectrum of the A signal region obtained with ZnS (10^{-1} KCl, 1150°C , 2 hrs. in He) at 77°K under a steady UV illumination. The dotted line is the spectrum obtained with a cubic sample.

(b) The shape functions expected for the A_1 and A_2 centers respectively. The A_1 center has an axial symmetry while the symmetry of the A_2 center is orthorhombic.

As can be seen from this table, the relation given in Eq. (1) is well satisfied. Statistically the ratio of the number of the A_1 centers to that of the A_2 centers should be 1 to 3. Though no definite conclusion can be drawn with regard to the intensity ratio from such a powder pattern, the signal corresponding to the A_1 center is definitely weaker than that of the A_2 center.

The most striking change that occurs to the B signal when the crystal becomes hexagonal is its weakening and sometimes its disappearance. The signal is barely observable when samples are fired in a reducing atmosphere, and it is completely gone when fired in air. When observed, its shape is broad ($H_{\text{peak-to-peak}} = 6$ gauss) and

fairly symmetric. The measured g value is slightly closer to the free spin value than the case of a cubic crystal, that is

$$g=1.888\pm0.001.$$

The decrease of the number of the B centers in a hexagonal sample may be ascribed to the occupancy of the sulfur vacancy sites by the halide ions. The diffusion of the halide ions is believed to be more facilitated in the hexagonal crystal because of (1) the increased interatomic distance and (2) much higher temperature of firing necessary for the preparation of the hexagonal form.

3. Effect of Oxygen

Oxygen incorporated in ZnS phosphors is known to produce various effects upon the phosphors. It has been found that Cu and Ag activators can be incorporated into ZnS without charge compensating coactivators if oxide is present.⁴⁾ Introduction of oxygen into the ZnS lattice should affect the lattice dimensions thus bringing about a change in the emission spectrum. Oxygen is also known to introduce at least three traps in ZnS phosphors⁵⁾. Many of the reported results, however, are obscure and the interpretations are speculative. Reported in the following are the results of investigating the particular effects of incorporated oxygen upon the EPR spectra and the glow curves.

1. Effect on the A Center

In a cubic sample, the only effect found on the A center is that samples fired in air always exhibit a much brighter self-activated emission and therefore a stronger A signal than those fired in an inert atmosphere. No significant change in the line shape nor in the g value was detected.

The situation, however, is found to be quite different for the case of hexagonal samples. For this case, the intensity of the A signal is increased by the presence of oxygen, but in addition at least two different kinds of A centers are found to appear when oxygen is incorporated. A solid line in Fig. 3 shows the EPR spectrum of the A signal obtained with oxygen containing ZnS (10^{-1} KCl, 2×10^{-2} ZnSO₄, 1150°C, 2 hrs. in air). One must pay attention to the fact that these new centers arise only after a substantial amount of oxygen ($\sim 1\%$) has been added, and also to the fact that the g values of the new centers are not

greatly different from those of sample containing no oxygen (dotted line). These results suggest that the new centers are formed as a result of a change in some macroscopic properties of ZnS that has been brought about by the incorporation of oxygen, and are not directly connected with oxygen itself. The most plausible interpretation is that the new centers are A centers whose halide ions are associated to the respective zinc ion vacancies at one of the non-nearest neighbor sites.

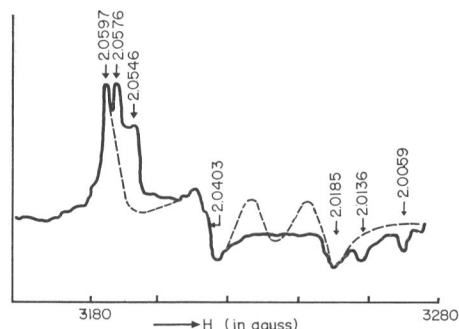


Fig. 3. EPR spectrum of the A signal region obtained with oxygen containing ZnS (10^{-1} KCl, 2×10^{-2} ZnSO₄, 1150°C, 2 hrs. in air). The dotted line is the spectrum obtained with ZnS containing no oxygen (10^{-1} KCl, 1150°C, 2 hrs. in He).

In hexagonal ZnS, the distance between a given zinc ion vacancy and its first nearest sulfide ion is $2.36\text{\AA}$, while the distance between the vacancy and its first nearest zinc ion is $3.85\text{\AA}$. As for sulfide ions which are at the second nearest sites from the vacancy, there are nine of them at the distance of $4.52\text{\AA}$ and only one at $3.93\text{\AA}$. Prenner and Weil²⁾ calculated the binding energy of a hole trapped by the potential of $-2e$ (ascribed to the zinc ion vacancy) and $+e$ (ascribed to the associated coactivator ion) separated by a distance of R in a medium of dielectric constant 8 (the dielectric constant of ZnS). They were thus able to explain the difference of $80\text{\AA}$ observed between the peak values of the self-activated emission of ZnS coactivated with halogen ($R=2.36\text{\AA}$) and ZnS coactivated with Al ($R=3.85\text{\AA}$). Interpretation of the result of their calculation leads us to predict that the emission peak of the centers whose halide ions are at the second nearest sites (taking the dominant type, $R=4.52\text{\AA}$) should be shifted to the longer wave length side by as

much as 200Å from the peak value of the *A* centers whose halide ions are at the first nearest sites. The emission spectrum of sample containing oxygen is indeed shifting toward the longer wave length side. The amount by which it shifts is in semiquantitative agreement with the value quoted above and the relative amounts of various *A* centers as inferred in the EPR spectra of Fig. 3. No such large shift in the emission peak is observed when oxygen is introduced into a cubic sample.

2. Effect upon the Glow Curve

Two effects of oxygen upon the glow curves are shown in Fig. 4. One of them is a growth of a new and deeper trap at around 220°K, and the other is a gradual shift of the peak position of the original glow curve to lower temperature. In the absence of oxygen, the peak of the original curve is at 170°K, but it moves to as low as 130°K when 2% of ZnSO₄ is introduced.

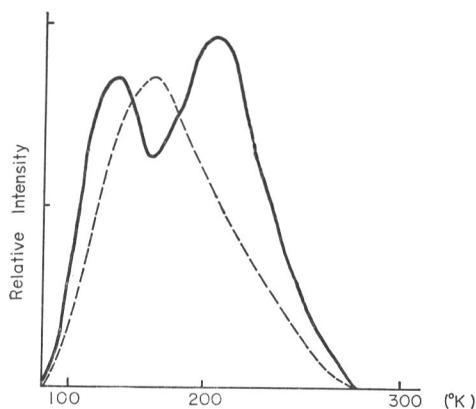


Fig. 4. Solid line shows a glow curve obtained with oxygen containing ZnS (10^{-1} KCl, 2×10^{-2} ZnSO₄, 1150°C, 2 hrs. in air). Dotted line is a glow curve obtained with ZnS containing no oxygen. A sample refired from the oxygen containing ZnS in a reducing atmosphere also shows the similar glow curve to that of dotted line.

Because of oxygen's smaller atomic size coupled with its stronger electronegativity in comparison with sulfur, the zinc ions surrounding an incorporated oxygen atom are pulled in closer to the core atom. A cluster of tightly bound cations thus formed is expected to behave as an electron trap

itself, but what seems more important is the fact that it leaves behind a void space. When the concentration of such clusters is as high as 1% (in mole ratio), the hitherto difficult diffusion of negative ions should become an easier matter. The presence of oxygen thus leads to closer association of positively charged electron traps such as halide ions or sulfur vacancies and the negatively charged *A* centers. The apparent trap depth of such traps then becomes shallower owing to the increased degree of overlapping between the excited states of the trap and the luminescent centers as can be seen in Fig. 5. The new

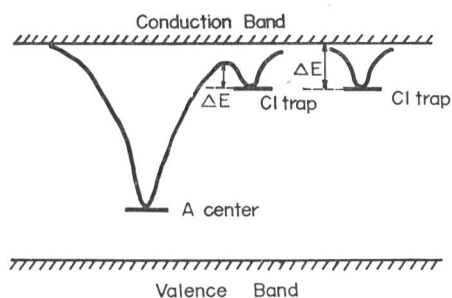


Fig. 5. The apparent trap depth, ΔE , of a trap becomes shallower with increasing degree of its association with a luminescent center.

trap with its glow peak at 220°K is not likely a trap formed by oxygen itself for the two following reasons: (1) Hoogenstraaten⁵⁾ has found that the intensity of the 320°K glow peak in ZnS (Cu, Cl) is proportional to the amount of oxygen incorporated. (2) It is clear from our infrared quenching experiments that the trap at 220°K may still bear a residual positive charge even after it has captured an electron. This is quite unlikely for a trap produced by a neutral impurity such as oxygen.

References

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DISCUSSION

Matumura, O.: Concerning to the *B*-signal, I remember that in the case of CdS, Prof. C. Kikuchi of the University of Michigan has found a signal at a position of $g \approx 1.8$ at 4.2°K, and he attributed this signal to an electron trapped at Cl^- . According to his considerations, the signal shape is little influenced by the nuclear moments of halogen ions. The situation seems to be similar to the present case. I would like to know the reason why you did not take the Cl-trap model.

Otomo, Y.: We consider four reasons as follows:

(1) From our calculation of Δg by LCAO molecular orbital treatment, we think our model is reasonable.

(2) We did not observe any effect of halogen upon the g value and line shape when the halogen ion was changed.

(3) When we use III Group elements (Al, Ga, In) as coactivator atoms instead of halogen atoms, formation of S-vacancy may be impossible. Actually we did not observe *B* signal in ZnS (Al, Ga, In) phosphors.

(4) When we applied the quenching light (I. R.), the reduction of the *B* signal was quite less compared with that of the *A* signal.

Mitchell, J. W.: Were the emission spectra after ultra-violet stimulation of the self-activated zinc sulfide phosphors which you used for these electron paramagnetic resonance studies determined independently?

Otomo, Y.: Yes, we did.

PROCEEDINGS OF THE INTERNATIONAL CONFERENCE ON CRYSTAL LATTICE DEFECTS, 1962, CONFERENCE JOURNAL OF THE PHYSICAL SOCIETY OF JAPAN VOL. 18, SUPPLEMENT II, 1963

Associated Defects Showing Luminescences in Zinc Sulfide

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The purpose of the paper is to show that in ZnS the association of native lattice defects with impurities introduced intentionally creates luminescence centers composed of two localized levels. The red emitting copper center and the blue emitting self-activated center are dealt with. The basic characteristics for these centers, including the ESR absorption under the ultraviolet excitation in the case of the self-activated center, were measured.

The temperature dependence of the half-width as well as the temperature shift of the peak energy for the emission and excitation spectra are reasonably understood, if the configurational coordinate model for the localized center is applied. It may be concluded that the copper red center is formed by the association of the substitutionally introduced copper with the sulfur vacancy, while the self-activated center by the association of zinc vacancy with the coactivator of VIIb elements at a nearest sulfur site.

1. Introduction

In ZnS crystal, luminescences due to various types of electronic transition are observable because of lattice defects and impurities. This paper presents some experimental facts which may lead to the conclusion that the association of native lattice defects with impurities in-

tentionally introduced creates luminescence centers of which both the ground and excited states are localized within the forbidden band of the host crystal. Two kinds of luminescence center, the red emitting copper center and the blue emitting self-activated center, are dealt with. It will be shown that in ZnS