

## Paramagnetic Resonance Spectrum of Some Doubly Activated Phosphors

W. Low

*Department of Physics, The Hebrew University, Jerusalem, Israel*

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The paramagnetic resonance spectra of four different infrared stimulable strontium sulfide phosphors have been investigated. The hyperfine spectrum in SrS:Eu,Sm phosphor confirms the existence of divalent europium. The quantum efficiency in this phosphor is less than 1 photon per 10 europium activators. The ground state of europium is split by  $0.18 \text{ cm}^{-1}$  because of spin-orbit coupling in a cubic field. The manganese spectrum in a solid solution of strontium sulfide and selenide is discussed.

### INTRODUCTION

THE processes involved in fluorescence and phosphorescence of inorganic phosphors are at present imperfectly understood. Most of these phosphors contain paramagnetic activators, which form luminescent centers or traps. These paramagnetic ions are in a definite valence state and may lose or gain electrons in these processes. In many cases the valency of these activators is not known with certainty or can only be inferred with difficulty from chemical or spectroscopic evidence. Often there are auxiliary activators present in the phosphor. These may have been incorporated without knowledge or design into the lattice of the host material, and owe their origin to the impurity of the chemical substances of which the phosphor is made. Moreover, there is at present no direct way of measuring the number of activators taking part in these processes.

Paramagnetic resonance is an ideal method for studying the valence state of paramagnetic impurities, as each ion of different valence state has a separate spectrum. It gives, moreover, information as to the number of paramagnetic ions per unit cell and an indication of their location in a single crystal. Unfortunately it is very difficult to grow single-crystal phosphors. In general, phosphorescent substances are available only in powdered form.

As the paramagnetic spectrum is a function of the orientation of the crystalline electric field with respect to the external magnetic field, the resonance lines are very much broadened due to the random orientation of the crystallites. Only in a few cases, where the spectrum shows little anisotropy, is information easily obtained. This fact limits the impurities which can be studied in this manner to a restricted group, in the main to divalent manganese, divalent europium, and trivalent gadolinium. These paramagnetic ions have an  $S$  ground state; their spectra are centered around  $g=2.00$  ( $g$  is the gyromagnetic ratio of the electron spin) and can be studied at room temperature.

This paper reports some new results on powdered phosphors which contain divalent europium or divalent manganese. These strontium sulfide phosphors are activated by two impurities, a dominant activator, presumably the luminescent center, and the auxiliary

activator, probably the electron trap. The crystal structure of strontium sulfide is of cubic symmetry,<sup>1</sup> and, therefore, no undue complications caused by low-order symmetries of the crystalline field were anticipated in the interpretation of the spectrum.

The paramagnetic spectrum of divalent manganese has been intensively studied. The ground state is  ${}^6S_{5/2}$ . Experiments of Bleaney and Ingram<sup>2</sup> on manganese salts and the interpretation of the spectrum by Abragam and Pryce<sup>3</sup> have shown that the six-fold degeneracy is removed mainly because of the noncubic portion of the field in the salts studied. A very pronounced hyperfine structure due to the magnetic moment of Mn<sup>55</sup> has been found. This has been explained as arising from an unpaired electron because of configurational interaction in which a  $3s$  electron is promoted to the  $4s$  state.

Schneider and England<sup>4</sup> and Hershberger and Leifer<sup>5</sup> have investigated ZnS phosphors activated with manganese. They find that hexagonal ZnS gives a complicated spectrum, while cubic ZnS shows only the central six lines so characteristic of the hyperfine structure spectrum of manganese. In the phosphor discussed here, the crystal host consisted of a solid solution of cubic strontium sulfide and strontium selenide. It was interesting to find out to what extent the diamagnetic neighbors influence the hyperfine structure.

Divalent europium has a half-filled  $4f$  shell and, therefore, a ground state of  ${}^8S_{7/2}$ . In a cubic field the ground state is split into a twofold degenerate level, followed by a fourfold, and then again by a twofold degenerate level. The ratio of the separation of the levels is 5:3. A theory of the splitting of the energy levels in the presence of an external field for various directions of the crystalline axes with respect to this field has been developed by DeBoer and van Lieshout<sup>6</sup>

<sup>1</sup> R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, New York, 1948).

<sup>2</sup> B. Bleaney and D. J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

<sup>3</sup> A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

<sup>4</sup> E. E. Schneider and T. S. England, Physica **17**, 221 (1951).

<sup>5</sup> W. D. Hershberger and H. N. Leifer, Phys. Rev. **88**, 714 (1952).

<sup>6</sup> J. DeBoer and R. Van Lieshout, Physica **15**, 568, (1949).

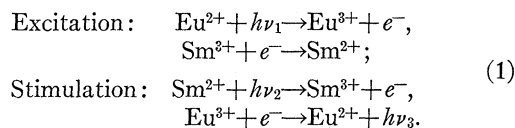
for trivalent gadolinium in a cubic field. This theory should also apply to divalent europium. A hyperfine spectrum resulting from the magnetic moments of the two isotopes of europium was found by Bleaney and Low<sup>7</sup> while investigating one of these phosphors. This paper is not concerned with the nuclear information derived from this spectrum but mainly with the implications of the spectrum as far as these phosphors are concerned.

#### PROPERTIES OF THE PHOSPHORS INVESTIGATED

The phosphors for which the paramagnetic resonance spectra were examined are all infrared-stimulable. They all have two or more rare earth activators. They are SrS:Eu,Sm (Std. VI); SrS:Eu,Sm (B 1); SrS:Ce,Sm (Std. VII); and one experimental phosphor similar to B 1 but containing in addition Mn (and a little gadolinium). The dominant activators (Eu, Ce . . .) constituted less than one part per ten thousand per mole of strontium sulfide, and the auxiliary activator (Sm) about 5–10 times this amount.

Considerable experimental work has been done on the optical,<sup>8–11</sup> photoconductive,<sup>12,13</sup> and electroluminescent<sup>14</sup> properties of these phosphors. Their optical characteristics can best be explained by a concrete example of Std. VI. This phosphor can be excited by blue or ultraviolet light. It stores the energy, and on subsequent illumination by infrared radiation it emits visible light. The usual explanation of the mechanism of infrared stimulability is illustrated in Fig. 1. Blue light ( $h\nu_1$ ) excites the luminescent center, which is the dominant activator, in our example divalent europium is ionized and loses an electron to the conduction band. The electron is captured by a low-lying trap, the auxiliary activator (trivalent samarium). The energy level of samarium is only 1.25 eV below the conduction band, and infrared light ( $h\nu_2$ ) can, therefore, ionize the auxiliary activator. The electron is captured by a trivalent europium ion and emits visible light ( $h\nu_3$ ).

These events can be written as chemical reactions as follows:



<sup>7</sup> B. Bleaney and W. Low, Proc. Phys. Soc. (London) **68**, 55 (1955).

<sup>8</sup> Urbach, Pearlman, and Hemmendinger, J. Opt. Soc. Am. **36**, 373 (1946).

<sup>9</sup> G. Fonda and F. Seitz, *Preparations and Characteristics of Solid Luminescent Materials* (John Wiley and Sons Inc., New York, 1948).

<sup>10</sup> P. Brauer, Z. Naturforsch. **1**, 70 (1946); **2a**, 238 (1947).

<sup>11</sup> F. Stockmann, Naturwiss. **10**, 226 (1952).

<sup>12</sup> Low, Braun, and Steinberger, J. Opt. Soc. Am. **44**, 88 (1954).

<sup>13</sup> J. J. Dropkin, "Photoconduction in Phosphors" Polytechnic Institute of Brooklyn, 1954 (unpublished).

<sup>14</sup> Low, Steinberger, and Braun, J. Opt. Soc. Am. **44**, 504 (1954). (A full report is in preparation.)

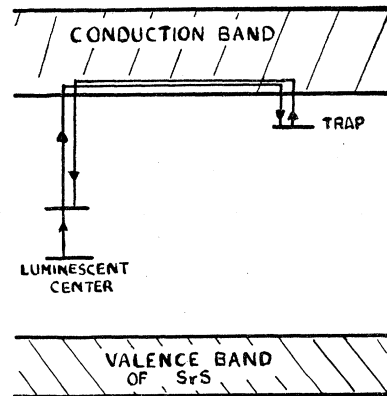


FIG. 1. Schematic picture of energy bands and levels in an infrared storage phosphor.

In the case of Std. VII the cerium changes valencies from a trivalent to a quadrivalent state.

This picture accounts for the fact that the wavelength of the emitted light ( $h\nu_3$ ) differs for the various phosphors, whereas the peak stimulation frequency is substantially the same for all these phosphors. The emitted light is a characteristic of the dominant activator, whereas the stimulation frequency is a function of the auxiliary activator Sm, common to all these phosphors.

To substantiate this picture it would be necessary to show that the activators are in the unexcited state in their proper valencies and that these valencies change on excitation. There is some evidence<sup>9</sup> that there is trivalent samarium in the unexcited phosphor. The evidence that europium is in the divalent state is not so conclusive. No characteristic line spectrum,<sup>15</sup> so peculiar to trivalent europium, has been found.

#### EXPERIMENTAL RESULTS

All measurements were made at 3 cm, and a range of 0–6000 gauss was scanned, at room, liquid oxygen, and liquid hydrogen temperatures. The apparatus was the standard 3-cm setup used at the Clarendon Laboratory.<sup>2</sup> In the case of Std. VI, the influence of ultraviolet light on the paramagnetic spectrum was investigated. This was done by removing the sample from the cavity, placing it in a wide glass vessel, and exposing it to very strong ultraviolet light for half an hour. The glass vessel was shaken off and on to make sure that as many grains as possible were exposed to the radiation. The signal to noise ratio was compared before and after excitation. While the results were not entirely reproducible, because of instability of the oscillator, and because the cavity was not always filled to the same level, one can conservatively estimate that changes of 10 percent would have been observable.

*Std. VI.*—Three phosphors of slightly different europium-to-samarium ratio and of different phosphor

<sup>15</sup> R. Tomaschek, *Ergeb. exakt. Naturw.* **20**, 268 (1942).

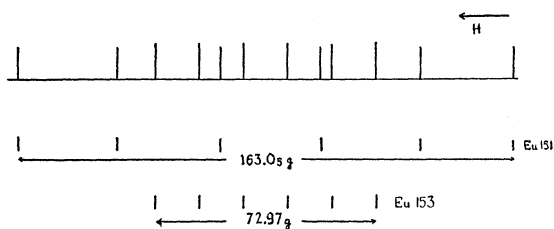


FIG. 2. The paramagnetic resonance spectrum of SrS:Eu,Sm. The hyperfine spectrum consists of two groups of 6 lines due to the two europium isotopes with nuclear spins of  $5/2$ . It confirms the presence of divalent europium in this phosphor.

grain sizes were investigated. The same spectrum was obtained at all times and at all temperatures. The observed spectrum is shown schematically in Fig. 2. These twelve lines were superimposed on a very broad line of roughly 100 gauss total width. The spectrum was centered around  $g=2.00$ . The signal increased with the amount of sample in the cavity without any noticeable broadening. The lines were very narrow, the half-width at half-intensity being slightly less than 2 gauss. As will be discussed later, the spectrum can be resolved into two groups of six lines each of nearly equal intensity, corresponding to the relative abundance of the two europium isotopes (47.8 percent and 52.2 percent).<sup>16</sup>

*B 1.*—This phosphor, containing Eu and Sm in a solid solution of SrS and SrSe, shows a broad line of roughly 100 gauss centered around  $g=2.00$ . There seemed to be some components superimposed on this line but of such small intensity that no quantitative measurements were made. Only one sample was tested.

*B 1 with additional manganese.*—The spectrum is shown in Fig. 3, as seen at room temperature. At liquid hydrogen temperature the spectrum saturates and broadens so that only 6 lines are seen. The spectrum is centered around  $g=2.00$ . The half-width at half-intensity was about 4-5 gauss. The two center lines were broader and could not be resolved into two components. The spectrum can be reconstructed as two groups of 6 lines, with the center of gravity of these lines nearly coinciding. The separation of the outermost components is 475 gauss, corresponding to a hyperfine structure constant  $A=95$  gauss; and of the next inner components 460 gauss, corresponding to  $A=92$  gauss.

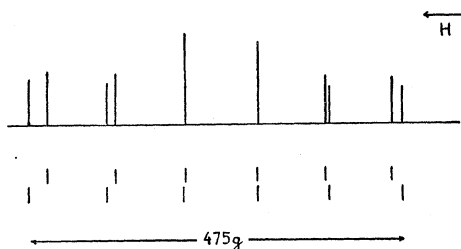


FIG. 3. The paramagnetic resonance spectrum of  $Mn^{2+}$  in a SrS:SrSe phosphor. The spectrum is centered around  $g=2.00$ .

<sup>16</sup> O. C. Hess, Phys. Rev. 74, 773 (1948).

*Std. VII.*—This line shows a fairly strong line close to  $g=2.00$  at room temperature (see Fig. 4). At liquid oxygen and liquid hydrogen temperatures, one can resolve two additional lines of smaller intensity asymmetrically placed with respect to the center line. Besides, at least two weaker components could be seen on the oscilloscope. In addition, there is at liquid hydrogen temperature a very intense, bell-shaped line of about 100 gauss total width at  $g=1.33$ . This line disappears at liquid oxygen temperature. Various phosphors were investigated, and in all phosphors essentially the same spectrum was obtained. Those phosphors which were made with LiF flux showed slightly greater absorption.

#### INTERPRETATION OF RESULTS

There are two kinds of spectra to be considered, those which contain only rare earth activators and those which have manganese in addition. In the former the magnetic carriers are the  $4f$  electrons, and in the latter those in the  $3d$  shell. In the ion group the  $3d$

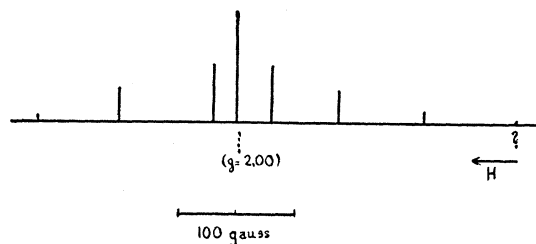


FIG. 4. The paramagnetic resonance spectrum of SrS:Ce,Sm. The spectrum is centered around  $g=2.00$ . The question mark indicates that the line was about of noise level intensity and could not be determined with any certainty.

shell is the outermost shell and is, therefore, exposed to very strong crystalline electric fields. The orbital component contributes only slightly to the spectroscopic splitting factor through spin-orbit coupling. The  $g$  factors of the iron group are, in general, close to two and show little anisotropy.

In the rare earth group the crystal field is much smaller than in the iron group and even less than the spin-orbit interaction. This is due to the fact that the  $4f$  electrons are partially shielded by the  $5s^25p^6$  electron shells and, therefore, do not feel the total neighboring charge, and is also due to the larger distance from the diamagnetic neighbors. The  $g$  factors in the rare earth group show considerable anisotropy and vary considerably from the value two. The relaxation time is, in general, much shorter than in the iron group and, therefore, in many cases can only be detected at very low temperatures.

*Std VI (SrS:Eu,Sm).*—As previously outlined, we may expect that the activators will have the following valencies:  $Eu^{2+}$ ,  $Eu^{3+}$ ,  $Sm^{2+}$ ,  $Sm^{3+}$ . The ground state of  $Eu^{3+}$  and  $Sm^{2+}$  is  ${}^7F_0$  and would not show any

resonance spectrum. The spectrum of  $\text{Sm}^{3+}$  has been found in an ethyl sulfate crystal.<sup>17</sup> It can only be detected at very high magnetic fields ( $g_{\parallel}=0.596$ ,  $g_{\perp}=0.604$ ) and at temperatures lower than liquid hydrogen. We would, therefore, not expect to detect this spectrum with the magnetic field and temperatures employed. The ground state of divalent europium is  $^3S_{7/2}$ . Its eightfold degeneracy is partially removed by means of the spin-orbit coupling in the cubic field. DeBoer and van Lieshout<sup>6</sup> calculated theoretically the energy levels in an external magnetic field. They find that the spectrum is strongly dependent on the orientation of the magnetic field with respect to the crystal-line electric field axes. In the powder only the  $\frac{1}{2} \rightarrow -\frac{1}{2}$  transition is observed. The energy levels in a strong field are given by

$$E_{\pm\frac{3}{2}} = \pm\beta H + [(5/4) + (45/4)\phi] \delta \pm \alpha_1 \delta^2 / \beta H + \dots, \\ \alpha_1 = 35/128 - (1135/64)\phi \\ + (10875/128)\phi^2 - (3675/32)\psi, \quad (2)$$

where  $\phi$  and  $\psi$  are the direction cosines of the magnetic field with respect to the cubic axes  $x$ ,  $y$ ,  $z$ . That is,

$$\phi = a_x^2 a_y^2 + a_y^2 a_z^2 + a_z^2 a_x^2, \\ \psi = a_x^2 a_y^2 a_z^2,$$

and  $8\delta$  is the over-all splitting at zero magnetic field due to spin-orbit interaction in a cubic field. The central transition then is given by

$$h\nu = E_{+\frac{3}{2}} - E_{-\frac{3}{2}} = g\beta H + 2\alpha_1 \delta^2 / \beta H, \quad (3)$$

where  $g = 2.0023$ .

The spectrum observed confirms the presence of  $\text{Eu}^{++}$ . The narrow lines indicate that the spectrum must indeed be isotropic. The measured  $g$  factor is  $1.9912 \pm 0.001$ , very close to 2.0023. Assuming that the deviation from the free spin value is entirely due to spin-orbit coupling (and not to spin-spin interaction arising in a distorted electron distribution), we can calculate the zero-field splitting. Using  $\bar{\phi} = \frac{1}{2}$ ,  $\langle \phi^2 \rangle_{\text{av}} = 1/21$ ,  $\bar{\psi} = 1/1.5$ , one finds  $\delta = 0.023 \text{ cm}^{-1}$  and the over-all splitting  $8\delta = 0.18 \text{ cm}^{-1}$ . There are no experimental data from susceptibility measurements which might give the zero-field splitting for divalent europium. In trivalent gadolinium, which has the same ground state as divalent europium, in the salt  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ , Benzie and Cooke<sup>18</sup> find a splitting of  $0.94 \text{ cm}^{-1}$ . In the paramagnetic spectrum of gadolinium ethyl-sulfate, Bleaney *et al.*<sup>19</sup> find that the main splitting is due to spin-spin interactions in the noncubic field of these crystals. Nevertheless, they find that the  $g$  factor is also 1.991, indicating that the deviations of the  $g$  factor in both substances is probably due to

spin-orbit coupling. This splitting should be compared with the cubic contribution of  $0.0134 \text{ cm}^{-1}$  in the ferric alums<sup>20</sup> and the even smaller splitting of  $0.001 \text{ cm}^{-1}$  in the manganese salts.<sup>2</sup> This seems to support the contention that the splitting observed here is mainly due to spin-orbit coupling which is much weaker in the iron group.

The nuclear information obtained from the hyperfine structure has been discussed elsewhere.<sup>7</sup> The spectrum can be described by the formula:

$$h\nu = g\beta H + Am + \frac{1}{2}(A^2/h\nu)\{I(I+1) - m^2\}, \quad (4)$$

with  $g = 1.9912 \pm 0.001$ ,  $A_{151} = 30.82 \pm 0.2$ ,  $A_{153} = 13.79 \pm 0.2$  ( $A$  in units of  $10^{-4} \text{ cm}^{-1}$ ). It confirms<sup>21</sup> the nuclear spin of  $5/2$  for the two isotopes and gives the anomalous large ratio of the nuclear magnetic moments as  $\mu_{151}/\mu_{153} = 2.235 \pm 0.03$ . The hyperfine structure probably has its origin in the configurational coupling of  $4s^2 4f^7 5s^2$  and  $4s^2 4f^7 5s 6s$ . This will not appreciably influence the theory of Elliott and Stevens.<sup>22</sup> Rough calculations on erbium and other rare earth ethyl-sulfates, taking into account a configurational interaction of this magnitude, show a slightly better agreement between the theory and the experimental data.

The narrow lines observed with SrS might make it possible to observe the spectrum of trivalent gadolinium and see whether any hyperfine structure can be resolved. It is planned to try to make such a phosphor.

The quantum efficiency of some of these phosphors has been studied. Urbach<sup>23</sup> reports that in some of Std. VI phosphors there is one photon emitted per three samarium activators. Ellickson,<sup>24</sup> studying Std. VII, comes to the conclusion that only 1 photon is emitted per 8 samarium ions, and in his phosphor this corresponds to 1 photon per 60 cerium activators. In all these phosphors the dominant activator was present in larger quantities than the auxiliary activator. Their measurements involve the assumptions that (a) in the preparation of the phosphors the mole ratio of the components has not changed, i.e., that all the activators have been incorporated in the strontium sulfide lattice; and (b) that all the activators have the proper valencies before excitation so that they can contribute to the phosphorescence. If either of these assumptions should not be correct, the efficiency would be higher.

The failure to observe any change in the signal-to-noise ratio in our measurements seems to indicate that the efficiency is less than one photon per 10 europium ions. Unlike Urbach's and Ellickson's phosphors, these phosphors have a larger amount of samarium than europium as activators.

<sup>17</sup> G. S. Bogle and H. E. M. Scovil, Proc. Phys. Soc. (London) **A65**, 368 (1952).

<sup>18</sup> R. J. Benzie and A. H. Cooke, Proc. Phys. Soc. (London) **A63**, 213 (1950).

<sup>19</sup> Bleaney, Scovil, and Trenam, Proc. Roy. Soc. (London) **A223**, 15 (1954).

<sup>20</sup> B. Bleaney and R. S. Trenam, Proc. Roy. Soc. (London) **A223**, 1 (1954).

<sup>21</sup> H. Schuler and T. Schmidt, Z. Physik **94**, 547 (1935).

<sup>22</sup> R. J. Elliott and K. W. H. Stevens, Proc. Roy. Soc. (London) **A218**, 553 (1953).

<sup>23</sup> See reference 9, pp. 119.

<sup>24</sup> R. T. Ellickson, J. Opt. Soc. Am. **36**, 501 (1946).

*B 1.* (SrS: SrSe, Eu, Sm).—No information can be obtained. The spectrum is probably similar to Std. VI.

*B 1 with manganese* (SrS: SrSe, Eu, Sm, Mn).—The spectrum of  $Mn^{2+}$  has been discussed in detail by Bleaney and Ingram.<sup>2</sup> Abragam and Pryce<sup>3</sup> showed that the spectrum in a pure cubic field could be represented by

$$\mathcal{H} = g\beta\mathbf{H} \cdot \mathbf{S} + (a/6)(S_1^4 + S_2^4 + S_3^4) + A(S_x I_x) + B(S_x I_x + S_y I_y), \quad (5)$$

where  $g$  is the spectroscopic splitting factor,  $\beta$  the Bohr magneton,  $H$  the external field,  $S$  the electron spin operator,  $I$  the nuclear spin operator,  $a$  the measure of zero-field splitting resulting from the cubic field interaction which has terms proportional to  $S_1^4$ ,  $S_2^4$ ,  $S_3^4$ , where the  $S_i$  are the components referred to the cubic axes.  $A$  and  $B$  are hyperfine structure constants of nearly equal magnitude. In case there is a noncubic portion of the symmetry, the energy levels will be split much more as the operator in this case would be quadratic in  $S$ .

The hyperfine structure of  $Mn^{55}$  has nearly a constant value in various salts investigated and is isotropic within a few percent.

With a powder of cubic structure only the  $\frac{1}{2} \rightarrow -\frac{1}{2}$  transition is observed,<sup>5,25</sup> with its characteristic 6 hyperfine lines.

The spectrum observed, as shown in Fig. 3, shows in the main the spectrum of  $Mn^{2+}$  incorporated in a cubic lattice of SrS. The splitting of the 6 lines into narrow doublets, with the center of gravity nearly constant, is somewhat puzzling. According to Abragam,<sup>26</sup> the hyperfine structure is due to configurational interaction and should, therefore, be the property of the free ion. Possibly these two groups of 6 lines are due to the two nonequivalent manganese ions, one surrounded by sulfur, the other by selenide neighbors. This would indicate that the amount of configurational interaction might be dependent to a small degree on the crystalline surrounding. If a distortion in the cubic field be present, this would also produce a hyperfine structure but probably less than  $10^{-4} \text{ cm}^{-1}$ , or less than 1 gauss.

The sulfide to selenide ratio in these phosphors was of the order of 1:5. The signals of the two groups of lines was, however, of nearly equal intensity. If the above interpretation is correct, this would indicate that  $Mn^{2+}$  is more easily substituted in the strontium sulfide than in the strontium selenide. Further experiments with widely different ratios of selenide to sulfide might clarify this point.

*Std. VII* (SrS: Ce, Sm).—Cerium can be in the divalent, trivalent, and quadrivalent states. In the quadrivalent state it is diamagnetic. In the trivalent state the ground state is  $^2F_{5/2}$  and in the divalent state if it exists the ground state is  $^3H_4$  (as in trivalent

praseodymium). No measurements on a single crystal of cubic symmetry have been made so far. In trivalent cerium, in a single crystal of cerium ethylsulfate, Bogle *et al.*<sup>27</sup> find at liquid helium temperatures two resonance lines, one due to the  $\pm 5/2$  levels and the other to the  $\pm \frac{1}{2}$  level, the latter lying lower. Their values are  $g_{||}(\frac{1}{2}) = 0.955$ ,  $g_{\perp}(\frac{1}{2}) = 2.183$ ,  $g_{||}(5/2) = 3.72$ ,  $g_{\perp}(5/2) = 0.2$ . Lancaster and Gordy<sup>28</sup> find in powdered concentrated cerium oxalate a spectrum at  $g = 1.95$  at room temperature with the narrow line width of 170 gauss. Similarly, Kurenev and Salikhov<sup>29</sup> report a spectrum at room temperature in cerium sulfate. Cerium has no odd isotopes and, therefore, no hyperfine spectrum.

We cannot account for the spectrum shown in Fig. 4 with certainty. It is possible that the central strong line with  $g$  slightly less than 2 is due to the trivalent cerium level of  $\frac{1}{2}$ . This would be very similar to the line observed by Lancaster and Gordy. As the  $g$  factor seems to be very anisotropic, the  $g_{\perp}$  would be very strongly weighted corresponding to the fact that the majority of ions lie perpendicular to the field. This would peak the line near  $g = 2.00$ . But as rare earths are difficult to obtain with very high purity, one cannot be sure whether the central line may not be the results of gadolinium or possibly neodymium ( $g_{\perp} = 2.073$ ), which may be present as small impurities. The other weak lines are probably impurities as well.

We similarly cannot assign the very strong line at  $g = 1.33$  seen only at liquid hydrogen temperatures. It is possible that this line may be due to praseodymium, which has been shown to have a hyperfine structure of about 90 gauss.<sup>30,31</sup> This illustrates how difficult it is to get any definite information from powdered specimens.

## CONCLUSIONS

The work with strontium sulfide phosphors has indicated that quantitative information in powders can be obtained only with magnetic activators which have a very isotropic spectrum, like ions with an  $S$  ground state. With these ions one finds very narrow lines. In the case of europium-activated phosphors, we confirm the presence of divalent europium and could calculate the zero-field splitting. The quantum efficiency is less than 1 photon per ten europium activators. An apparatus is being set up which will make it possible to measure the changes on excitation (by x-rays) *in situ* and thus determine the efficiency with greater accuracy.

The narrow lines seen give hope that a hyperfine structure in gadolinium may be observed. We have

<sup>27</sup> Reported by B. Bleaney and K. W. H. Stevens, Repts. Progr. Phys. **16**, 149 (1952).

<sup>28</sup> F. W. Lancaster and W. Gordy, J. Chem. Phys. **19**, 1181 (1951).

<sup>29</sup> V. Y. Kurenev and S. G. Salikhov, Zhur. Exsptl. Teort. i Fiz. **21**, 864 (1951).

<sup>30</sup> B. Bleaney and H. E. D. Scovil, Phil Mag. **43**, 999 (1952).

<sup>31</sup> Davis, Kip, and Malvano, Atti acad. nazl. Lincei **11**, 77 (1951).

<sup>25</sup> J. S. Van Wieringen, Physica **19**, 397 (1953).

<sup>26</sup> A. Abragam, Phys. Rev. **79**, 534 (1950).

embarked on a systematic study of all rare earth activators in strontium sulfide. An attempt will be made to grow single crystals.

Part of this work was done while the author spent the summer at the Clarendon Laboratory, Oxford.

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## Temperature Dependence of the Width of the Band Gap in Several Photoconductors

RICHARD H. BUBE

*Radio Corporation of America, RCA Research Laboratories, Princeton, New Jersey*

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The temperature dependence of the width of the forbidden band gap has been determined, between 90° and 400°K, for cadmium sulfide, cadmium selenide, cadmium telluride, and zinc selenide, by measurement of photosensitivity as a function of wavelength. The location of the maximum photosensitivity, often very sharp, at the wavelength corresponding approximately to the width of the band gap, makes this method very convenient for the determination. Structure exists in the photosensitivity maxima of cadmium sulfide and cadmium selenide, suggesting the existence of double conduction or valence bands.

### INTRODUCTION

THE temperature dependence of the width of the forbidden gap of a semiconductor is commonly determined by measuring the dependence of the absorption on wavelength, at a number of different temperatures. Such measurements have been made by Kroeger,<sup>1</sup> Seiwert,<sup>2</sup> and Hoehler<sup>3</sup> for cadmium sulfide. Their results indicate that the absorption-edge shifts to longer wavelengths at the rate of about 1 Å/°K for increasing temperature.

Because of the broadness of the absorption edge in most semiconductors, it is somewhat difficult to determine a width for the forbidden gap accurately, and hence to determine accurately the temperature dependence of the gap width. In many cases, such striving for greater accuracy may be pointless, because of an inherent lack of definition in the band edges themselves. But, at least experimentally, it is much simpler to determine a quantity which is very nearly equal to the width of the forbidden gap for photoconducting crystals, by measuring the photosensitivity as a function of wavelength. Most photoconducting crystals show a rather sharp maximum of photosensitivity at a wavelength corresponding closely to the width of the forbidden gap, as determined from measurements of absorption. Niekisch<sup>4</sup> and Caspary and Mueser,<sup>5</sup> have determined the temperature dependence of the forbidden gap for cadmium sulfide from measurements of photosensitivity as a function of wavelength. Their results also indicate approximately a 1 Å/°K shift in absorption edge.

The purpose of this paper is to present data on the variation of the width of the forbidden gap with temperature between 90° and 400°K, for crystals of cadmium sulfide, cadmium selenide, cadmium telluride, and zinc selenide.

### EXPERIMENTAL

#### Materials

The preparation of single crystals of "pure" cadmium sulfide, cadmium selenide, and zinc selenide by S. M. Thomsen, by reaction between the elements in the vapor phase, has been described in a previous publication.<sup>6</sup> The growth of crystals of cadmium telluride by D. A. Jenny and E. B. Lawton, by slow cooling from the melt, has also been previously reported.<sup>7</sup>

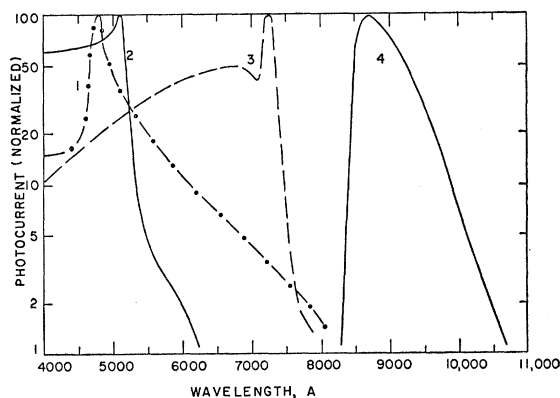


FIG. 1. Spectral curves of photosensitivity for (1) zinc selenide, (2) cadmium sulfide, (3) cadmium selenide, and (4) cadmium telluride, at room temperature.

<sup>1</sup> F. A. Kroeger, *Physica* **7**, 1 (1940).

<sup>2</sup> R. Seiwert, *Ann. Physik* **6**, 241 (1949).

<sup>3</sup> G. Hoehler, *Ann. Physik* **4**, 371 (1949).

<sup>4</sup> E. A. Niekisch, *Ann. Physik* **8**, 291 (1951).

<sup>5</sup> R. Caspary and H. Mueser, *Z. Physik* **134**, 101 (1952).

<sup>6</sup> R. H. Bube and S. M. Thomsen, *J. Chem. Phys.* **23**, 15 (1955).

<sup>7</sup> D. A. Jenny and R. H. Bube, *Phys. Rev.* **96**, 1190 (1954).