*Sensitization by Bismuth of the Luminescence of Manganese and Samarium in Calcium Sulfide Phosphors**

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Abstract

Calcium sulfide phosphors doubly activated with bismuth as sensitizer and with manganese or/and samarium as activator were studied, in order to throw light on the sensitization mechanism of photoconductive phosphors. Their optical properties, reflection, excitation and emission spectra, were observed. A few estimations were done about the emission efficiency and the range of sensitization using these results. The facts directly found were that manganese is sensitized more efficiently than samarium, but the quenching takes place significantly in manganese itself, so that manganese is said to act, to some extent, as a killer. As the sensitization mechanism, the resonance transfer is considered to be more predominant than the photoelectron transfer. The contribution of the energy transport among the sensitizers is suggested. In the case of the coexistence of manganese and samarium, there will be no significant interactions between them.

Introduction

It has been proved that the mechanism of the sensitized luminescence in the nonphotoconductive phosphors is explained by the resonance transfer of absorbed energy from sensitizer to activator[1,2]. In the photoconductive phosphors, however, the sensitization by a different mechanism has been considered to take place, such that electron and positive hole, released from the sensitizer by the photoabsorption, recombine at the activator, emitting its luminescence[3-5]. Hereafter this is called "photoelectron transfer". Then, the study of the real mechanism of the sensitization in the photoconductive phosphors is very interesting. In a study on the sensitized luminescence in zinc sulfide phosphors by one of the present writers[6,7], it has been concluded tentatively that the sensitization mechanism is the resonance transfer rather than the photoelectron transfer. The present study was undertaken to throw light on the sensitization mechanism in calcium sulfide phosphors, and here will be mentioned some results obtained until now.

Experimental

1. Preparation of Samples.—Bismuth as sensitizer and manganese or/and samarium as activator were selected. It has been known since earlier days that the sensitization takes place in these combinations[8,9]. The samples were prepared by mixing calcium oxide, excess sulfur, sodium sulfate as flux and the salts of activating impurities, and by firing the mixture for twenty min. at 950°C. The concentration of the sensitizer was constantly 10^{-4} (mole fraction relative to calcium, hereafter follow this), but that of the activator was varied from zero to 10^{-3}.

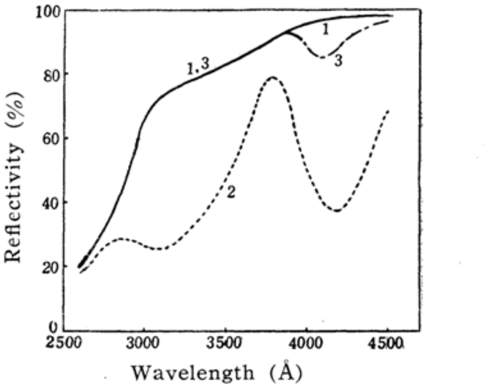

Fig. 1. Reflection spectra
(1) CaS (fired without any activating impurities)
(2) CaS:Bi(10^{-4})
(3) CaS:Mn(10^{-4})

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* This work was read at the Symposium on Photochemistry held by The Chemical Society of Japan on September 29, 1956.

1) Th. P. J. Botden, *Philips Res. Rep.*, **7**, 197 (1952).

2) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

3) N. F. Mott and R. W. Gurney, "Electronic Processes in Ionic Crystals" (1940) p. 207.

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5) H. A. Klasens, W. Ramsden and C. Quantie, *J. Opt. Soc. Am.*, **38**, 60 (1948).

6) S. Shionoya and K. Amano, *J. Chem. Phys.*, **25**, 380 (1956).

7) S. Shionoya, This Bulletin, **29**, 935 (1956).

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9) S. Makishima, Doctoral Thesis, University of Tokyo (1945).

2. Reflection Spectra.—As the samples were obtained only in the powder form, the reflection spectra were measured to learn the absorption characteristics. The measurement was done by means of "Shimazu's photoelectric spectrophotometer QB50". To eliminate the fluorescence (relatively weak in fact), a color filter, "Corning No. 9863", was inserted between the integral sphere and photomultiplier.

A part of the results is shown in Fig. 1. The long wavelength threshold of the fundamental absorption of the host crystal is located at 2500–2600Å. When bismuth is incorporated, a strong absorption appears in the long wavelength region beyond the above, the maxima of which are located at about 3100 Å and 4200 Å. The reflection spectrum due to bismuth corresponds to the spectrum of photoconduction[10]. The spectrum of the phosphor containing only manganese is very similar to that of the host crystal, but a weak absorption due to manganese appears at about 4100 Å. In the case of the phosphor containing only samarium, the spectrum is also very similar to that of the host crystal.

Reflection characteristics of doubly activated samples are very similar to that of the sample containing only bismuth; in other words their characteristics are determined only by bismuth. Small fluctuations were found in the result of each sample, but it seems to be dependent on the difference of the preparation condition, and not on the variation of the activator concentration. Then the absorption intensity in the series of samples containing a known amount of bismuth is almost constant irrespective of the activator concentrations. Therefore the emission efficiency should be in proportion to the number of emitted photons only. Then we will use the relative number of emitted photons instead of the emission efficiency, so as to compare the character of the samples with each other.

3. Excitation Spectra.—Since the intensity of emission excited by the light which passed through a monochromator was very weak, and further since it took a very long time to build up the emission to a saturated value, only the following method could be used. Phosphor powder was coated uniformly on a glass plate, and a photographic film was stuck on the other side of the plate sandwiching between the glass plate and film a gelatin filter which passes only the luminescence band to be measured. They were set at the focal plane of a usual quartz spectrophotometer. Then, the phosphor was irradiated for a long time (2-3 hr.) by the exciting light from a hydrogen discharge lamp. Therefore the results were not so precise and only qualitative.

A schematic figure obtained for bismuth emission of CaS:Bi is shown in Fig. 2. The excitation band for the activator, manganese or samarium, in the doubly activated phosphor is similar to that for bismuth in the singly activated phosphor. It has three peaks located at about 4200 Å (this is called B_1 band), 3100 Å (B_2 band) and 2500 Å (*H* band), but the last one was not very clear.

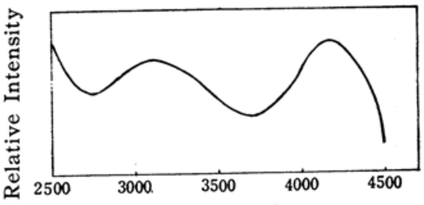

Fig. 2. Excitation spectra of CaS:Bi.

Comparing these results with reflection spectra, it is concluded that B_1 and B_2 bands are due to the absorption of bismuth, while *H* band is due to that of the host crystal. Then it is concluded from the above facts that the luminescence of manganese or samarium is sensitized by bismuth in the spectral region from 3000 to 4500 Å. In the present study only the luminescence sensitized by bismuth will come into question.

4. Emission Spectra.—The measurement was done with a glass monochromator coupled with a photomultiplier. As the excitation source the 3650Å line of a high pressure mercury discharge lamp was employed for bismuth excitation, and the 2537Å line of a low pressure mercury discharge lamp for the host excitation. Some examples of the results are shown in Figs. 3 and 4. Although it is known that samarium emission spectrum consists of six groups of line spectra[9], only two groups located in the shorter wavelength region were measured here and each group was incapable of being resolved into lines because of the limitation of the abilty of the apparatus.

As shown in Fig. 3, the emission intensity of bismuth is weakened in proportion to the increase in the activator concentration, and further the degree of the decrease of bismuth emission in

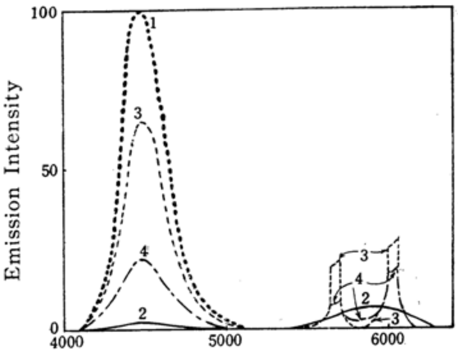

Fig. 3. Emission spectra under 3650 Å excitation. The ordinate is normalized by letting the bismuth emission peak of CaS:Bi be 100.

(1) CaS:Bi(10^{-4})
(2) CaS:[Bi(10^{-4})+Mn(10^{-3})]
(3) CaS:[Bi(10^{-4})+Sm(10^{-3})]
(4) CaS:[Bi(10^{-4})+Mn(3×10^{-3})+Sm(10^{-4})]

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[10] B. Gudden and R. W. Pohl, *Z. Phys.*, **3**, 98 (1920).

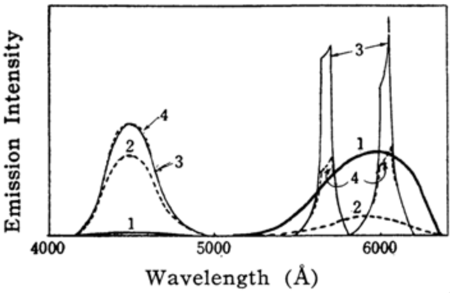

Fig. 4. Emission spectra under 2537Å excitation. The ordinate chosen arbitrarily.
(1) $CaS:[Bi(10^{-4})+Mn(10^{-3})]$
(2) $CaS:[Bi(10^{-4})+Mn(10^{-5})]$
(3) $CaS:[Bi(10^{-4})+Sm(10^{-3})]$
(4) $CaS:[Bi(10^{-4})+Sm(10^{-5})]$

Bi-Mn series is larger than in Bi-Sm series. These facts are due to the transfer of excitation energy absorbed in sensitizer to activator. In Bi-Sm series, samarium emission increases in proportion to its concentration, but in Bi-Mn series manganese emission does not become so strong in proportion to its concentration. This fact indicates that in Bi-Mn series the quenching of luminescence takes place in the manganese center after the energy transfer from bismuth to manganese.

These facts are made clearer by the estimation of the number of the emitted photons. The results of the estimation are shown in Figs. 5 and 6. The difference (N_d) of the numbers of photons emitted by bismuth between the case containing no activator and that containing it should be equal to the number of photons emitted by the activator. The ratio of the observed number of photons emitted by manganese to N_d in Bi-Mn series, which gives the efficiency of manganese emission, is shown in Table I. The efficiency is about 10–20%, indicating that the enormous quenching takes place in manganese activator itself. This is also understood by the fact that the curve (3) in Fig. 5 showing the sum of numbers of photons emitted by bismuth and manganese decreases with the increase in the manganese concentration. Then manganese may be considered, as a matter of fact, to act, to some extent, as a killer. Moreover, in the case of the higher concentration of manganese, the concentration quenching also takes place. In Bi-Sm series the value of the ratio N_d to the number of photons emitted by two groups of line spectra measured is always about 3.3, and as shown by the curve (3) in Fig. 6 the sum of the numbers of photons emitted by

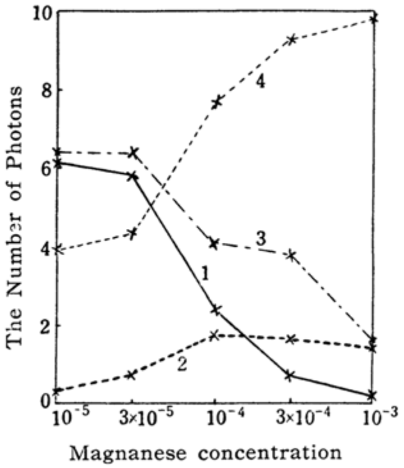

Fig. 5. The number of emitted photons for $CaS:(Bi+Mn)$ series. The number for bimuth emission of CaS:Bi is put to be 10.
(1) Bismuth emission
(2) Manganese emission
(3) Sum of (1) and (2)
(4) The number of photons regarded to be transferred from bismuth to manganese, i.e. 10 minus (1)

TABLE I

EMISSION EFFICIENCY OF MANGANESE IN $CaS: [Bi(10^{-4})+Mn]$

manganese	1×10^{-5}	3×10^{-5}	1×10^{-4}	3×10^{-3}	1×10^{-3}
efficiency (%)	8.3	17	23	17	14

TABLE II

VALUES OF z

A. $CaS: [Bi(10^{-4})+Mn]$

manganese	1×10^{-5}	3×10^{-5}	1×10^{-4}	3×10^{-4}	1×10^{-3}
z	5.1×10^{4}	1.8×10^{4}	1.4×10^{4}	8.8×10^{3}	3.9×10^{3}

B. $CaS: [Bi(10^{-4})+Sm]$

samarium	1×10^{-5}	3×10^{-5}	1×10^{-4}	3×10^{-4}	1×10^{-3}
z	2.8×10^{4}	9.1×10^{3}	4.4×10^{3}	1.5×10^{3}	5.0×10^{2}

C. $CaS: [Bi(10^{-4})+Mn+Sm]$

manganese	1×10^{-4}	3×10^{-5}	1×10^{-4}	1×10^{-3}	1×10^{-4}
samarium	3×10^{-5}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-3}
sum of manganese and samarium	1.3×10^{-4}	1.3×10^{-4}	2×10^{-4}	1.1×10^{-3}	1.1×10^{-3}
z	1.2×10^{4}	6.1×10^{3}	7.6×10^{3}	3.8×10^{3}	9.5×10^{2}

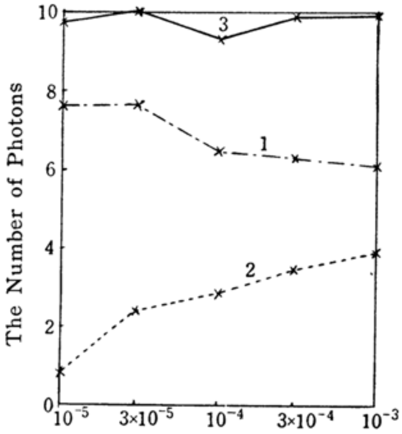

Fig. 6. The number of emitted photons for CaS:(Bi+Sm) series. The number for bismuth emission of CaS:Bi is put to be 10.
(1) Bismuth emission
(2) Samarium emission multiplied by 3.3
(3) Sum of (1) and (2)

bismuth and samarium is almost constant irrespective of the variation in the samarium concentration. Then it is considered that the quenching in the samarium activator does not take place, and that the above values of the ratio, 3.3, are really significant because only one third of the groups of the total ones of line spectra were measured. Comparing the decrease of bismuth emission in Bi-Mn series with that in Bi-Sm series, it is suggested that the ability of manganese to capture the excitation energy from bismuth is almost a hundred times that of samarium.

The emission spectra of the samples containing both manganese and samarium as activator are shown in Fig. 3. The emission intensity of bismuth is decreased with the incorporation of activators and the emissions of both activators appear.

TABLE III

THE NUMBER OF THE EMITTED PHOTONS UNDER 2537Å EXCITATION (ARBITRARY UNIT)

CaS: Bi(10^{-4})	4.7×10^{2}
CaS: Mn(10^{-3})	4.1×10^{3}
CaS: Sm(10^{-3})	3.0×10^{3}

The ratio of the number of photons which is regarded to be transferred from bismuth to activator to that of photons emitted as bismuth luminescence, B, was calculated. Using B and the concentration of activator, z defined below which represents the range of sensitization can be calculated. z is defined as the number of lattice sites surrounding a given sensitizer, and it is assumed that if any one of these z sites is occupied by an activator, the sensitization can occur always with an efficiency of 100%, but that if none of them is occupied by an activator, the emission of the sensitizer itself is caused. Moreover it should be assumed that all activators are distributed at random over all the lattice sites and the transfer of energy between sensitizers never occurs. By means of the probability calculation⁷⁾,

$$z=-\frac{\log(1+B)}{\log(1-C_a)}$$

is obtained, where C_a is the mole fraction of activator. Although it is open to question whether the above assumptions are satisfied in this cases, at any rate z was calculated. The results are shown in Table II.

The emitted photons of each emission band under 2537Å excitation were calculated by means of Fig. 4. The results are shown in Table III. The unit was selected arbitrarily. Those of samarium are 3.3 times the value observed.

5. Emission under the Bismuth Excitation. —The measurement of perfect emission spectra under the excitation by each of the two peaks of the bismuth excitation band was impossible, because the suitable excitation source which is strong enough could not be obtained. Then, only the ratio of emission intensity of activator to that of sensitizer was possibly measured by means of separating each emission band with color filters. As an excitation source a $CaWO_4$-coated fluorescent lamp was employed with filter, Matsuda UV-D2, for B_1 excitation, and $Ca_3(PO_4)_2$:Tl-coated fluorescent lamp with nickel sulfate solution filter for B_2 excitation. For the selection of bismuth emission or activator's one, filter, Schott GG3 plus Matsuda VC-1, or Matsuda VO-2 were employed, respectvely.

The calculated ratios of the emission peak intensity of an activator to that of a sensitizer are shown in Fig. 7 for the three kinds of excitation. In Bi-Sm series, the ratios under two

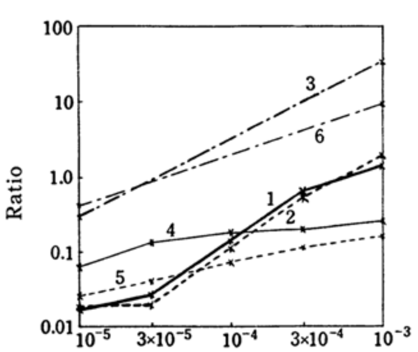

Fig. 7. The ratio of the emission peak intensity of activator to that of sensitizer under each excitation.
CaS:(Bi+Mn) series: (1) B_1 excitation (2) B_2 excitation (3) Host excitation
CaS:(Bi+Sm) series: (4) B_1 excitation (5) B_2 excitation (6) Host excitation

kinds of bismuth excitation are different from each other, and the sensitization efficiency under B_1 excitation is higher than under B_2, while in Bi-Mn series such a tendency is not found. In the case of the host excitation,the ratios in both sesies are so different from the case of bismuth excitation that it is suggested that there is a difference of luminescent mechanism between two cases.

Discussion

1. Sensitization Mechanism.—If the previous two assumptions on the calculation of z were realized truly, z should be constant irrespective of the variation of the activator concentration. In the present case, however, z decreases with the increase in the activator concentration, showing that the assumption will not be justified. Indeed, in the first place, it is considered that the assumption expressing no energy transfer between sensitizers is not realized, since the absorption spectrum of bismuth overlaps remarkably with its emission spectrum. The overlapping of an emission band with an absorption one is a necessary condition for the occurrence of resonance transfer, the probability of which is proportional to the degree of this overlapping. Then, it is considered that the sensitization in this case is caused by an energy transport, from sensitizer to activator, by which is meant a series of successive energy transfers such as sensitizer → sensitizer ···→ sensitizer → activator, and that the value of z indicates the mean path of this transport. The higher the concentration of the activator becomes, the more frequent the chance of energy transfer from sensitizer to activator is, so that the mean path of transport becomes shorter. From this fact, the decrease of z with the increase in the activator concentration previously mentioned will be explained.

Comparing z of Bi-Mn series with that of Bi-Sm series, it is shown that the values of both series tend to approach each other in the lower activator concentrations, but that in the higher concentrations the values of Bi-Mn series become larger than those of Bi-Sm by about one order of magnitude. As will be mentioned below, the range of interaction between sensitizers themselves is known to be larger than that between sensitizer and activator. In the lower activator concentration, therefore, it is considered that the path of energy transport determines mainly the range of sensitization. On the other hand, in the higher concentration the direct transfer between sensitizer and activator becomes predominant. The degrees of the sensitizer-activator interaction in both series might be different from each other by one order of magnitude—this will not be improbable. If so, the above facts will be reasonable.

It may be considered that the emission of the activator under the host excitation is caused by the recombination of photoelectron with hole both created by the photoabsorption. If so, it would be deduced reasonably, at first consideration, that the emission of the activator under the bismuth excitation band, in which photoconduction is known to occur, is also caused by the same mechanism. But there are some different points to be taken into consideration between the former the and latter case as mentioned below.

Referring to the knowledge about zinc sulfide crystal[11], it is considered that calcium sulfide crystal is an n-type semiconductor, i.e. the majority carrier is an electron. In the case of the host excitation, hole is created at the sulfur ion, one of the constituents of the host lattice. Therefore the probability of the creation of hole in the vicinity of any activator may be high enough in order that the activator can catch hole to emit luminescence, although the mobility of hole is rather low. But in the case of bismuth excitation, hole is formed at the ground state of bismuth, which is scattered throughout the whole crystal. This hole must be released thermally into the filled band in order that the sensitization can occur. Even if the probability of this release is large, the probability of the existence of an activator in the vicinity of any bismuth is so low, and the hole mobility is considered to be so low that the hole released from bismuth will scarcely be able to reach an activator to cause its luminescence. Then, although the electron migrates the sensitization by bismuth by means of the recombination of electron and hole will seldom take place.

On account of the above consideration, in the case of the crystal in which the mobility of one of the two charge carriers, electron and hole, is much higher than that of the other, it is expected that the sensitization by an incorporated impurity by means of the recombination hardly ever

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11) G F J. Garlick and A. F. Gibson, *J Opt. Soc. Am.*, **39**, 935 (1949).

takes place, although under the host excitation this can be done. As already mentioned, it has been concluded that the impurity sensitization in the non-photoconductive phosphors is caused by the resonance transfer. Also in the photoconductive phosphors the sensitization by this mechanism will be able to occur. In this case the occurrence of the photoconductivity itself is not the essential condition. In the present case, for the reason which will be mentioned below, it is considered that the resonance transfer rather than the photoelectron transfer is the predominant mechnism.

The first reason is the fact that the nature of the emission under B_1 and B_2 excitation band are different from each other in the Bi-Sm series, whereas they are not so different in the Bi-Mn series. If photoelectron transfer were predominant, the difference would be the same grade in both series since the condition for the photoelectron transfer may be the same for both series. But, if the resonance transfer is predominant, this difference may be probable, because the absorption bands of samarium and manganese may be different from each other—the absorption character is the factor of resonance probability.

The second reason is mentioned below. Comparing the number of the photons emitted by manganese with that by samarium under 2537 Å excitation shown in Table III, both in the singly activated samples, it is considered that the capture cross sections of manganese and samarium for the electron and the hole are almost the same. In all cases except the sample of Bi-10^{-3} Mn, bismuth emissons are almost equal irrespective of the activator concentration, but the intensities of the activator emissions are lower than those of singly activated samples. Then it is considered that free electron and hole are captured preferentially by bismuth, and that in the process of luminescence the interaction between activator and sensitizer is very weak. But in the case of Bi-10^{-3} Mn this interaction seems to become fairly strong. Since, as mentioned above, the capture cross sections of manganese and samarium are not so different, it is most reasonable to consider, as the reason for this fact, that electron and hole are trapped at bismuth as the first step and then the resonance transfer occurs from bismuth to manganese. If the sensitization under bismuth excitation is due to the resonance transfer, this consideration is reasonably concluded. In all cases except Bi-10^{-3}Mn, because of the low activator concentration and the lower transfer probability, such a tendency scarcely appeared.

The third reason is that the estimated values of the range of sensitization, especially the relationships among them, are understood reasonably assuming the predominance of the resonance transfer. But, assuming the predominance of photoelectron transfer, these values are considered to be fortuitous. According to the theoretical treatment by Dexter[2)], the sensitization range is the order of 10^4-10^3 lattice sites in the case of Bi-Bi type, and the order of 10^2 or 10 in the case of Bi-Mn or Bi-Sm. These are values for the typical cases, and considered to vary very much case by case. Now we are not speaking of the values themselves, but we are discussing relative tendencies. In the case of the lower activator concentration in which several successive steps of transfer may occur, the values lay in the order of 10^4. In the higher concentration region, even though the transfer between sensitizers may yet take place, the values were the order of 10^3-10^2. The difference of about one order between the Bi-Mn and Bi-Sm series will be probable on the premise that the resonance transfer is predominant and further the absorption band and the other factors are different between manganese and samarium.

So far, the distribution of activator and sensitizer has not been discussed, but implicitly assumed to be at random. The mode of distribution gives a serious influence on the sensitization efficiency. It is not fairly probable that the distribution is at random, but it is certainly considered that the activator and sensitizer form a kind of aggregate, and further that the aggregate states of Bi-Mn and Bi-Sm might be different from each other. If so, such a tendency will have the function to increase the sensitization efficiency, and true value of z will be smaller than those estimated here.

2. The Quenching in Manganese.—It is known that in manganese several excited states are involved, and that the states from which the luminescence is emitted is the lowest one[12)]. In zinc sul-

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[12)] C. C. Klick, *Brit. J. App. Phys.*, Sup. No. 4 ("Luminescence"), p. 74 (1955).

fide phosphors the absorption of manganese from the ground state to the lowest excited one occurs at about 5100Å[13]. Since the position of the emission peak of CaS: Mn is not so different from that of ZnS: Mn, the position of manganese absorption peak to the lowest excited state in the former is probably not so different from that in the latter. The maximum of bismuth emission in calcium sulfide phosphor is located at about 4500 Å, so that the resonance transfer to manganese will take place to its higher excited state rather than to the emitting one. It is considered that there are appreciable chances to cause the radiationless transition within manganese center during the stepping down from the higher excited state to the lowest one, and then this will be the cause of the quenching mentioned in Experimental 4. Moreover, in the case of the higher manganese concentration, the concentration quenching also seems to occur simultaneously.

3. Interaction between Manganese and Samarium.—The phosphors containing both somarium and manganese as activators were prepared to investigate whether the interaction between them exists. But conclusive facts were not obtained, because the separation of their emission bands was impossible. From the results of calculation of z shown in Table II, it is seen in the comparison between two samples in which the sum of the concentration of two kinds of activator is the same that samples containing more manganese show larger z's. This also suggests that manganese catches more energy than samarium. Since z's in this case lie in the same region as in the case of singly activated ones, it may be concluded that a large interaction between manganese and samarium will not functions.

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[13] R. H. Bube, *Phys. Rev.*, **90**, 70 (1953).