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Quenching, Stimulation, and Exhaustion Studies on Some Infrared Stimulable Phosphors

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As a continuation of earlier work on the two phosphor systems SrS:Ce, Sm and SrS:Eu, Sm, studies of the quenchings and the enhancements of fluorescent emission by visible and infrared radiation have been made. Two stimulation bands have been measured and the relative efficiencies of exhaustion and of stimulation of visible emissions by the two bands have been studied. These data have been correlated with the simplified band-theory model that had been proposed earlier. The measurements indicate that the two stimulation bands are associated with the same center. This can be represented by the assignment, to that center, of two energy levels within the energy gap.

INTRODUCTION

IN a previous paper[1] we reported on an investigation of two infrared stimulable phosphors. One phosphor system consisted of SrS activated with Ce and Sm, which was designated as *S*-1, and the other system consisted of SrS activated with Eu and Sm, which was designated as *S*-2. We measured various optical properties such as spectra of transmission, excitation, fluorescence, phosphorescence, stimulation, and stimulated emission. Relative storage efficiency as a function of various exciting wavelengths was determined as well as the time characteristics of phosphorescence and of infrared exhaustion. The dc photocurrents as a function of the wavelength of incident light were studied. On the basis of these measurements we presented a simplified band-theory model which correlated the experimental results with the electronic structures of the activators.

An essential feature of the conclusions drawn previously was that one could treat the activator ions almost as free gaseous ions. The activators are rare-earth ions, and the electrons involved in excitations, stimulations, and trapping are thought to be the $4f$ electrons. In the case of the rare earths, the Russell-Saunders approximation holds and the $\mathbf{L}\cdot\mathbf{S}$ coupling is larger than any crystalline field interactions. Since the crystal field interactions are small[2] due to the shielding of the $4f$ electrons by the $5s^25p^6$ electrons, one can talk about the ions as if they were almost free. Hence we used language involving concepts such as term signatures, ionization potentials, valences, stability of empty or half-filled orbitals, etc., and our results were understandable on the basis of these concepts.

In the previous investigation certain quenchings and enhancements of fluorescence had been observed and were tentatively explained. In the present work we have extended the region of measurements and will explain more adequately the mechanisms involved in the various quenchings and enhancements of the fluorescent emissions. Further, in the previous work, we measured a stimulation band in each phosphor located around 1 μ. There also had been reported elsewhere[3] an exhaustion of stored energy by means of visible light. In addition, we had observed a decaying photocurrent when the sample was irradiated with 590-mμ light following previous uv excitation. This decaying photocurrent was similar to that observed when the excited sample was irradiated with 1-μ light. In the present work we have measured more accurately both bands and have found them to be stimulation bands, each with roughly equal efficiencies of exhaustion and roughly equal efficiencies at stimulating visible emissions. We will extend the model proposed previously and will explain the data reported here in terms of this extended model.

CHEMICAL PREPARATIONS

The preparations were described in detail earlier.[1] *S*-1 consists of SrS, 6% $SrSO_4$, 6% CaF_2, 0.02% Ce, and 0.02% Sm. *S*-2 consists of SrS, 6% $SrSO_4$, 6% CaF_2, 0.02% Eu, and 0.02% Sm. The percentages are expressed in terms of molar percent. The materials were intimately mixed, dried, and heated in H_2S for two hours at 1100°C in quartz boats. The fired materials were then ground, sieved, and sprinkled on a surface that had been wetted with a 0.1% solution of Duco cement in amyl acetate. In reference 1 we mentioned that we found no changes in the wavelength location of various emissions when different fluxes were used. Generally, different fluxes affect the intensities of emissions, but not the wavelength locations. In the present investigation we are not concerned with such effects.

INSTRUMENTATION

The apparatus used was that which was described earlier.[1] Two monochromators were used in series. Radiation from a dc Xe arc lamp was focused into a Perkin-Elmer 112U monochromator. The resultant monochromatic radiation was incident upon the sample which was in the form of a peripheral ring on a disk

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[1] Keller, Mapes, and Cheroff, Phys. Rev. **108**, 663 (1957).

[2] S. P. Keller, J. Chem. Phys. **29**, 180 (1958).

[3] "Report on phosphors," Institute of Optics, University of Rochester, 1945 (unpublished).

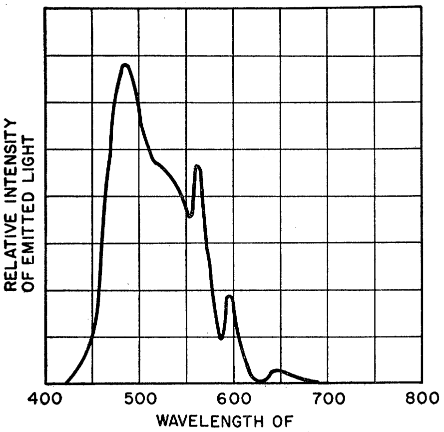

FIG. 1. Fluorescence spectrum resulting from 280-mμ excitation of S-1.

that could be rotated. The light emitted from the phosphor was then focused into the second monochromator, a Perkin-Elmer (P.E.) 98, detected and automatically recorded. Either monochromator could be scanned over the spectral region of interest. In fluorescent spectra measurements exciting radiation from the P.E. 112U was incident on the sample and the emitted light was analyzed by the P.E. 98. The measurements of the wavelength dependence of quenching or enhancement of fluorescence were effected by irradiating the sample with uv light from an externally mounted Hg lamp while the same area was irradiated with monochromatic light from the P.E. 112U. The resultant fluorescent spectra were determined for different wavelengths of quenching or enhancing light from the P.E. 112U. For the stimulation and stimulated-emission spectra, the phosphor was maintained at a constant level of excitation during the measurement by rotating the disk while an additional source of exciting radiation was incident at a point away from the viewing point. For the stimulation spectra, the P.E. 98 was fixed while the P.E. 112U was scanned over the range of stimulation. For the stimulated emission, the P.E. 112U was fixed at some stimulating wavelength while the P.E. 98 was scanned to analyze the emission. Measurements of efficiencies of exhaustion and efficiencies of stimulation of radiant energy are referred to the exhaustion and the stimulation of radiant energy effected by infrared light. The exact methods used in effecting the measurements will be described in greater detail in the appropriate sections.

The probable errors in wavelength due to reproducibility, calibration, slit widths, etc., amounted to ±1 to ±2 mμ over the spectrum covered. Reproducibility of certain spectral measurements was much less because of problems of reflected light. These problems were encountered when we had to subtract reflected light from emitted light, especially when they were close to each other in wavelength.

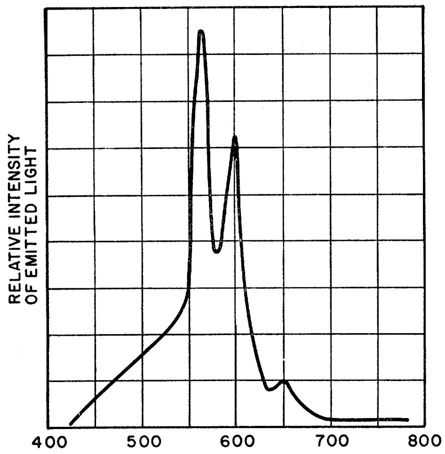

FIG. 2. Fluorescence spectrum resulting from 280-mμ excitation of S-2.

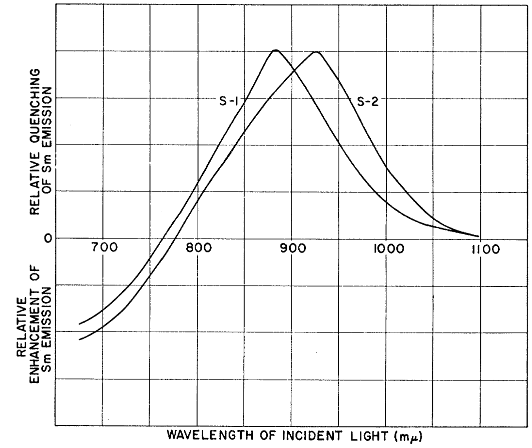

FIG. 3. Quenching and enhancement of Sm fluorescence corrected for constant number of photons of quenching and enhancing light.

EXPERIMENTAL RESULTS

1. Quenching and Enhancement Studies

The normal fluorescence spectra excited by 280-mμ radiation of S-1 and S-2 are presented in Fig. 1 and Fig. 2, respectively. In each phosphor the three sharp structures at 568, 600, and 650 mμ have been associated with the Sm center. In the case of S-1 the peak and shoulder located at 490 and 533 mμ, respectively, have been associated with the Ce center. Each center represents the +3 ion in an excited state. In the case of S-2 the Eu center, present as the +2 ion, has an emission at 590 mμ [as seen in Fig. 2 (d) of reference 1], which is however masked by the Sm emission.

As was mentioned earlier, the amount of quenching or enhancing of the various parts of the fluorescence was determined by measuring the fluorescence with the simultaneous irradiation of the sample with uv exciting light and visible or infrared quenching light. Zero quenching represents the unchanged fluorescence level. Figure 3 shows the results for the Sm emissions in both *S*-1 and *S*-2. The difference in the wavelength locations of the quenching peaks is probably within the experimental reproducibility. It can be seen that the three peaks at 568, 600, and 650 mμ are quenched in the infrared region but enhanced in the 650–750 mμ region. We were unable to extend the readings to shorter wavelengths because of the problems of reflected light. Figure 4 presents the results for the Ce emission in the case of *S*-1. It should be noted that a reciprocity exists between the Ce and the Sm emissions, namely, where the Ce emission is enhanced the Sm emission is quenched and where the Ce emission is quenched the Sm emission is enhanced. Once again we were limited in going to shorter wavelengths because of difficulty with reflected light. Since there was essentially no observable Eu emission in the case of *S*-2, no quenchings or enhancements could be determined.

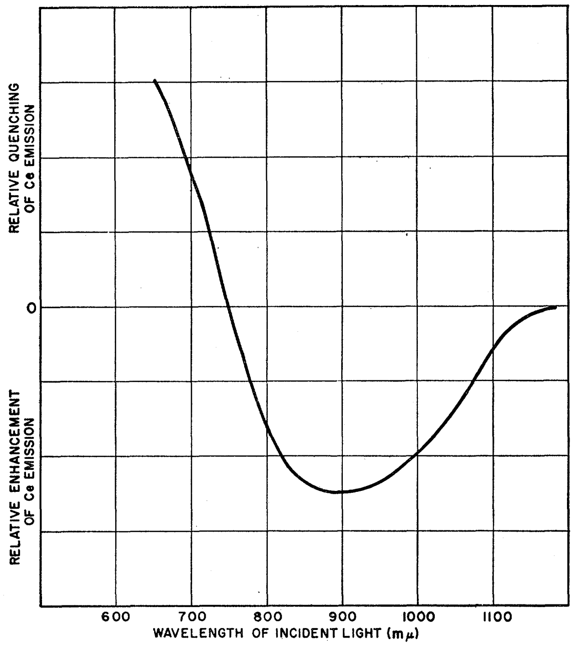

FIG. 4. Quenching and enhancement of Ce fluorescence corrected for constant number of photons of quenching and enhancing light.

2. Stimulation Spectra

In the earlier work[1] there was a slight unexplainable difference in the infrared stimulation peaks for *S*-1 and *S*-2. Upon remeasuring the stimulation spectra this discrepancy was removed. It had been determined elsewhere[3] that 590-mμ radiation caused an exhaustion of stored energy after the sample had been excited by uv radiation. Upon investigation, it developed that this visible exhaustion band was effective in producing optical emission. As a result the stimulation spectrum covering the visible region was determined. The measurements were carried out by setting the P.E. 98 at a fixed wavelength, located in the stimulated emission, and scanning the P.E. 112U, thus determining those wavelengths effective at causing stimulated emission. In the case of *S*-1, the P.E. 98 was fixed at approximately 490 mμ, the peak of the Ce emission. In the case of *S*-2, the P.E. 98 was fixed between 560 and 590 mμ, within the emission band of Eu. The results are shown in Fig. 5. We could go no further towards shorter wavelengths due to problems of reflected light.

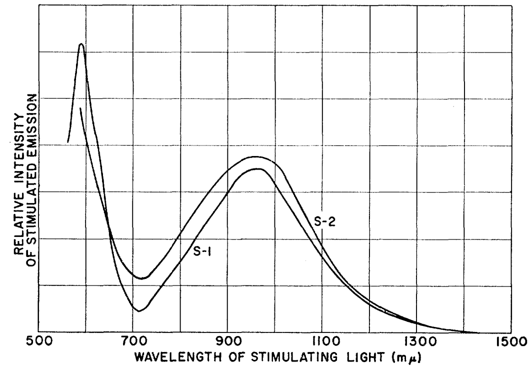

FIG. 5. Stimulation spectra effected by measuring the relative intensity of stimulated light as a function of the wavelength of stimulating light, corrected for constant number of photons of incident light.

3. Stimulated Emission

The measurement was made by fixing the P.E. 112U at some fixed stimulating wavelength and scanning the P.E. 98 to determine the stimulated-emission spectrum. The measurements were made at different stimulating wavelengths. Problems due to reflected light were minimized with the use of interference filters in the incident beam. Figure 6 presents the results for *S*-1 and Fig. 7 presents the results for *S*-2. Comparisons of intensities for different spectra are not meaningful. Some of the data are incomplete as shown by dotted lines or incomplete curves. This arises from the inability to complete the measurements due to problems of reflected light. The spectra obtained by stimulating *S*-1 with 590-mμ light and *S*-2 with 620-mμ light were not obtained by continuously scanning the P.E. 98. Instead, at discrete but closely spaced wavelengths, we measured the reflected light from an exhausted sample and then measured the sum of the reflected plus the stimulated light from the excited sample. The difference of these two measurements was taken to be the stimulated emissions for each phosphor. In this fashion we were able to determine the stimulated emission closer in wavelength to the reflected light and were able to determine the complete spectra as shown in Figs. 6 and 7. The different wavelengths of stimulating light

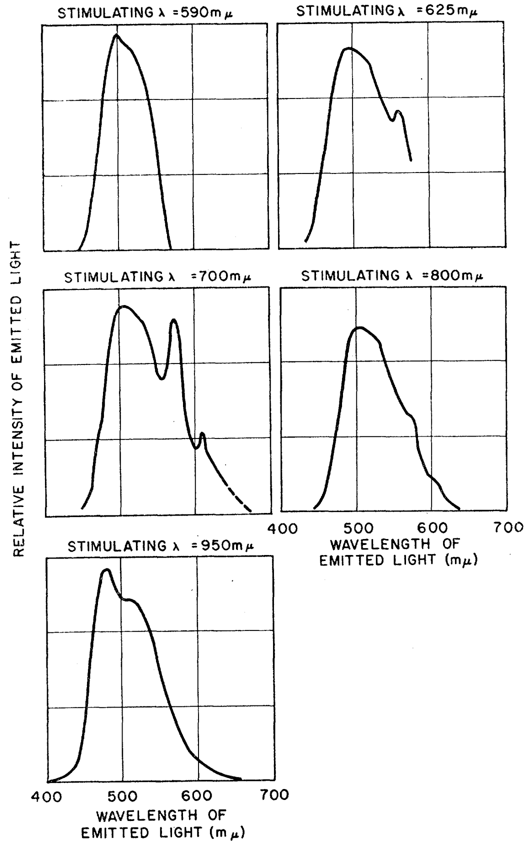

FIG. 6. Stimulated emission spectra for different wavelengths of stimulating radiation in the case of S-1.

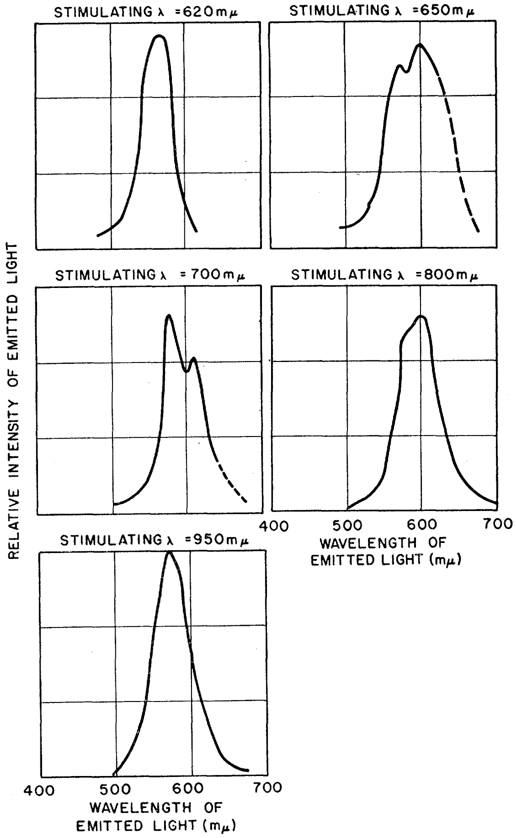

FIG. 7. Stimulated emission spectra for different wavelengths of stimulating radiation in the case of S-2.

produce different stimulated-emission spectra. The 590- and the 950-mμ stimulation bands produce the same emission, and in the case of S-1 the emission spectrum is that of Ce while in the case of S-2 the emission spectrum is that of Eu. The 950-mμ stimulation band coincides with the quenching band of the Sm emission as shown in Fig. 3 and with the enhancement band of the Ce emission as shown in Fig. 4. It is seen that stimulation with light in the Sm enhancement band (equivalent to the Ce quenching band) around 700 mμ produces the 568-, 600-, and 650-mμ Sm peaks[4] in addition to the Ce emission in S-1 and Eu emission in S-2.

4. Exhaustion Efficiency and Efficiency in Stimulating Optical Emission

We make a distinction between exhaustion efficiency and efficiency in stimulating visible light output. The stored energy can be exhausted by means of radiationless, or thermal, recombinations. We wanted to determine whether the processes involved in each stimulation band were the same. If the ratio of the rate of exhaustion effected by a particular wavelength of light to the rate effected by 950-mμ light is the same as the ratio of the amount of emitted light caused by that wavelength to the amount of emitted light caused by 950 mμ, then the same degree of stored energy is released in the form of emitted light for both wavelengths. Using the emitted light resulting from 950-mμ stimulation and using the amount of exhaustion caused by given amounts of 950-mμ stimulation as standards, we have measured relative efficiencies in causing visible emissions and relative exhaustion efficiencies for different wavelengths of light.

The method of measuring the exhaustion efficiency of a given wavelength is described below.

(1) With a given excitation of a completely exhausted sample, we measured the decaying visible emission resulting from 950-mμ stimulation. This emission starting from time $t=0$ is defined as primary emission.

(2) With the same excitation of a completely exhausted sample, we irradiated the sample with a given wavelength of light, λ_i (e.g., 590 mμ), for a time t_i.

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[4] Actually, the two observed spikes are displaced by about 10 mμ to longer wavelength and the energy corresponding to this emission is thus decreased by about 0.03 ev. This energy shift may be explained by assuming a narrow band of allowed energies for the excited state of the centers as was done in reference 2. The band results from crystalline-field splittings of excited states. By making appropriate assumptions as to thermal relaxation times in this band, we could explain this shift. It is not important to the results of this paper to concern ourselves with this shift; however, we are investigating it further.

(3) Following this irradiation we exposed the sample to 950-mμ light and measured the decaying light output which we define as secondary emission.

(4) We superimposed this element of secondary emission on the primary emission by means of a translation along the time axis. We call this time where the waves become coincident, $t_{i'}$. The area under the primary emission curve between $t=0$ and $t_{i'}$ is due to the exhaustion caused by λ_i.

(5) We measured off on the decaying primary emission curve the time t_i from $t=0$.

(6) The ratio of the area under the primary emission curve between $t=0$ and $t_{i'}$ to the area between $t=0$ and t_i we define as the ratio of the exhaustion efficiencies of λ_i and 950 mμ.

By varying λ_i we have determined the wavelength dependence of the exhaustion efficiency. The data are presented in Fig. 8 for *S*-1 and *S*-2. The exhaustion curve is analogous to the stimulation curve in Fig. 5, and the exhaustion whether caused by either 590-mμ or 950-mμ stimulation goes by the same process.

The efficiency in stimulating optical emissions was measured by storing energy with a constant amount of exciting uv light and then by stimulating the phosphor with a given wavelength of stimulating light. The optical emission is one varying in time and the total light output was detected by a phototube. The maximum height of the signal was taken as a measure of the energy released by means of optical transitions.[5] It was determined that this measure was directly proportional to the intensity of stimulating light, whether the light was located at 590 mμ or 950 mμ. As a result we made our measurements by irradiating the samples with a constant number of photons of stimulating light, the peaks of which bands occur at 590 and 950 mμ. The efficiencies of exhaustion and of stimulation of optical emission of the 590-mμ light relative to those of the 950-mμ light are presented in Table I. The ratio of the exhaustion efficiencies equals the ratio of the stimulation efficiencies, within experimental accuracy, for *S*-1 and *S*-2. This indicates that the exhaustion of the phosphor by 590-mμ light results in optical emissions and not in thermal emissions if one assumes that exhaustion of the phosphors by 950-mμ light goes only by optical emission. From this one concludes that the 590- and the 950-mμ stimulations go by means of at least very similar mechanisms. The difference of the efficiencies for the two phosphors is surprising in view of the fact that, as will be discussed later, both the 590- and the 950-mμ stimulations are associated with th Sm centers in each phosphor. If, as we shall assume, the two stimulations are associated with the same center, then it is difficult to understand why the ratios of the various efficiencies are not unity without assuming inequalities of transition probabilities. However, it is of course unlikely that transitions involving different levels would have the same probabilities.

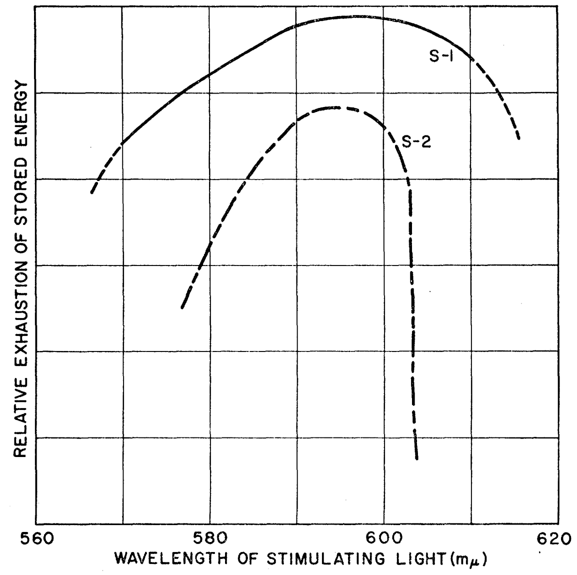

FIG. 8. Exhaustion efficiency as a function of the wavelength of stimulating light with a constant number of photons of stimulating light incident on the sample.

TABLE I. Exhaustion efficiencies and efficiencies at stimulating optical emission caused by 590-mμ light compared to the corresponding efficiencies of 950-mμ light.

	S-1	*S*-2
$\left(\frac{\text{Exhaustion eff. of 590 m}\mu}{\text{Exhaustion eff. of 950 m}\mu}\right)$	1.77	1.31
$\left(\frac{\text{Stimulation eff. of 590 m}\mu}{\text{Stimulation eff. of 950 m}\mu}\right)$	1.71	1.26

CONCLUSION

In the previous work[1] we proposed an energy band model that was consistent with all of the facts. We drew a simplified energy level diagram in which the distance between any one level and the conduction band was the ionization potential of the center responsible for that level in the SrS matrix. Before we present these diagrams we propose to make a modification concerning the 590- and 950-mμ stimulation bands. From Figs. 6 and 7 we see that the 590- and 950-mμ bands produce the same emission. From Table I we see that each band is essentially equal at releasing the stored energy (which energy is due to trapped electrons) and each band is essentially equal at producing optical emission. From these facts we conclude that both bands are associated with the same center in the phosphor. This center has been proposed to be an electron trapped at a Sm^{+3} site which, of course, produces a Sm^{+2} site. We

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[5] G. Cheroff and S. P. Keller, J. Opt. Soc. Am. **47**, 440 (1957), showed that the rise times of the stimulated emissions from each phosphor were essentially the same.

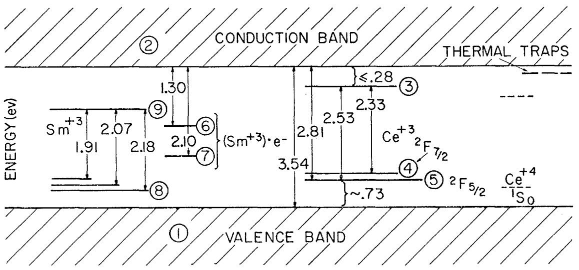

FIG. 9. Energy level diagram for *S*-1.

now propose that the electron is trapped in an outer orbital of Sm^{+3}, a situation we represent by $(\mathrm{Sm}^{+3})\cdot e^-$ which at a point far from the site appears to be Sm^{+2}.

Stimulation by 950-mμ light can release this outer trapped electron. We propose that stimulation by 590-mμ light excites an inner electron from the $(\mathrm{Sm}^{+3})\cdot e^-$ site which is immediately followed by the outer electron dropping into the vacated inner orbital. We have looked for an emission corresponding to this latter process but have not found it. Possibly, the outer electron dissipates its energy thermally in making the transition to the inner orbital. The hypothesis of two sets of levels for the $(\mathrm{Sm}^{+3})\cdot e^-$ center supplies an answer to a problem that was pointed out in reference 2. In that work the fluorescence spectra of SrS phosphors activated by single rare-earth ions were measured and energy level diagrams for each rare-earth ion were presented. It was pointed out that there appeared to be an anomaly since in *S*-1 and *S*-2 the Sm^{+2} center has an ionization potential of approximately 1.2 ev whereas the Eu^{+2} center has an ionization potential of 2.6 ev.[1] In view of the fact that the ionization potentials of all the rare-earth ions of like charge are roughly equal whether they are free ions or in a SrS matrix, it seemed difficult to resolve the discrepancy in the ionization potentials of the two +2 ions. In the light of the above discussion concerning the 590-mμ exhaustion band we see that the actual ionization potential of Sm^{+2} is closer to 2.10 ev (590 mμ) than to 1.3 ev (950 mμ). (In reference 1 the value was listed as 1.2 ev in *S*-1 and 1.13 ev in *S*-2. Remeasurement indicates the value is 1.3 ev for both phosphors.) There is still the discrepancy in ionization potentials between the 2.6 ev for Eu^{+2} and the 2.10 ev of Sm^{+2}, but this is not large and it can be understood if one assumes the Eu^{+2} is in a substitutional site and the Sm^{+2} is in an interstitial site. An interstitial ion would be expected to have a lower ionization potential than a similar substitutional ion due to the greater interaction with neighboring charge distributions of the former site. The phosphors are made by the inclusion of Eu^{+2} and Sm^{+3} (it is because of electron trapping that the Sm achieves a +2 state), and hence the Eu^{+2} might well be incorporated into the divalent-divalent SrS lattice in a substitutional site whereas the Sm^{+3} might not be.

We present in Figs. 9 and 10 the corrected energy band models of *S*-1 and *S*-2, respectively. In our discussion that follows we will apply our remarks to *S*-1 and Fig. 9 for the sake of brevity. What we say could also apply to *S*-2 and Fig. 10, but to avoid redundancy we will not present a detailed discussion of *S*-2.

The uv excitation corresponds to the SrS base absorption and it results in electrons being excited from 1 to 2 (as indicated in Fig. 9) with holes remaining in the valence band. Holes can be trapped by levels 4 and 5 of Ce^{+3} which becomes Ce^{+4} whose levels are shown dotted in Fig. 9. The Ce^{+4} can then trap an electron from the conduction band and become Ce^{+3} with a proper rearrangement of levels, the electron occupying level 3. In this process we start out with Ce^{+3} in its ground state and end up with the Ce^{+3} in an excited state. The system returns to the ground state by transitions from 3→5, 4 resulting in the 494-mμ peak and 533-mμ shoulder of the Ce emission shown in Fig. 1.

In addition, an electron may be trapped at a Sm^{+3} site which becomes a $(\mathrm{Sm}^{+3})\cdot e^-$ site indicated by levels 6 and 7. This site may trap a hole and the levels would undergo a rearrangement to become those represented by levels 9 and 8. The electron would occupy level 9 and the process results in a Sm^{+3} center in the ground state becoming a Sm^{+3} center in an excited state. The system returns to the ground state by transitions from level 9 to level 8 resulting in the 568-, 600-, and 650-mμ spikes of the Sm^{+3} emission.

If there are no holes available for trapping by the $(\mathrm{Sm}^{+3})\cdot e^-$ site (a not unreasonable situation since Ce^{+3} is more effective at trapping holes), then the electron remains trapped at this site. The net result of the uv excitation in this case is that a hole has become trapped by Ce^{+3} and an electron has become trapped by Sm^{+3}. In addition to this storage of energy the uv excitation produces the fluorescence described.

The electron trapped at the $(\mathrm{Sm}^{+3})\cdot e^-$ can be released in either of two ways. Stimulation with 950-mμ light causes the electron in the outer orbital to make a transition from level 6 to 2. The free electron will then recombine with the trapped hole at the Ce^{+4} site resulting in the emission characteristic of the excited Ce^{+3} center. Stimulation with 590-mμ light causes an electron in an inner orbital to make a transition from level 7 to level 2. Again, the free electron will combine with the

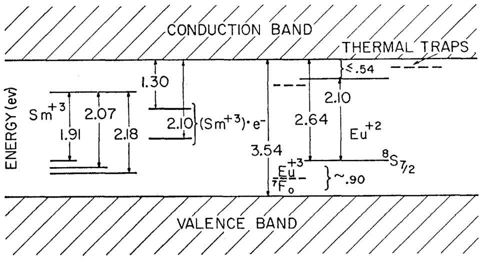

FIG. 10. Energy level diagram for *S*-2.

trapped hole at the Ce^{+4} site resulting as before in the emission characteristic of the excited Ce^{+3} center. In this process it is expected that a transition from 6⟶7 would follow. As mentioned before, we have looked for an optical emission corresponding to this transition but have not observed it. These two mechanisms explain the first and last spectra of Fig. 6. In the middle spectra two of the three spikes at 568, 600, and 650 mμ, corresponding to Sm^{+3} emission, begin to appear as the stimulating wavelength is decreased from 950 mμ. The heights of spikes go through maxima around 700 mμ and then they get weaker again as the stimulating wavelength approaches the 590-mμ stimulation band. We ascribe this to the fact that free holes are being created in the valence band by excitation of electrons from the valence band to the levels corresponding to Ce^{+4} sites. (As the electron approaches the Ce^{+4} site there is a rearrangement of levels to a configuration which will approximate that ascribed to the Ce^{+3} site. The energy for this electron transition would then be expected to be close to that required for 1⟶5 and 4, namely, 0.73 ev. From Fig. 13 of reference 1 we saw that the peak of the uv excitation was 0.85 ev more than the energy gap. This presumably is due to the distributions of states in the valence and conduction bands. If we assume that most of this 0.85 ev is taken up by the distribution in the valence band, the required energy for the promotion of an electron from the valence band to a Ce^{+4} site is within experimental uncertainty of the 700 mμ reported in the stimulated emission spectrum of Fig. 6 and the quenching and enhancement effects in Figs. 3 and 4.) The free holes thus generated can then be trapped by a $(Sm^{+3})\cdot e^-$ site resulting in an excited Sm^{+3} center. This in turn leads to transitions from 9⟶8 with the emission of the three spikes at 568, 600, and 650 mμ. Hence, the appearance of spikes (only two are observed, the third being relatively weak normally) in the middle spectra of Fig. 6 are explained. In the quenching and enhancement experiments there is further evidence for the process in which holes are generated in the valence band followed by their recombination with the $(Sm^{+3})\cdot e^-$ sites.

The quenching and enhancing data shown in Figs. 3 and 4 are consistent with the above model. If the sample is irradiated by uv and 950-mμ light simultaneously, the latter empties level 6 of some of the $(Sm^{+3})\cdot e^-$ centers and hence there are fewer electron-hole recombinations via a Sm^{+3} center, and so the Sm fluorescent emission is quenched. At the same time the rate of electron-hole recombination at the Ce^{+3} center is increased and so there is an enhancement of the Ce emission.

If the sample is irradiated by uv and by light in the region of 700–750 mμ, according to our assumptions above the latter radiation raises electrons into Ce^{+4} centers that had been formed by hole trapping. In this way the number of Ce^{+4} centers active in trapping electrons is decreased and the Ce emission during fluorescence is quenched. However, the hole screated in this process are free to recombine with electrons at $(Sm^{+3})\cdot e^-$ centers and hence the Sm emission is enhanced.

Presumably, if we irradiated the sample with uv and 590-mμ light, the effects would be the same as those described with the uv and 950-mμ excitation. This was experimentally too difficult for us to do because of problems of reflected light masking the emitted light.

The above model with its interpretation of the experimental results ties together the data of this paper and the data of reference 1. In the various processes certain emissions should be detectable if the transitions are optical ones. We plan to search for these emissions and by doing so we hope to establish such things as the unknown positions of the Sm^{+3} levels (8 and 9 in Fig. 9) within the energy gap.