PHYSICAL REVIEW VOLUME 113, NUMBER 3 FEBRUARY 1, 1959

# Phosphor with Fluorescence Larger Than the Energy Gap

SEYMOUR P. KELLER AND GEORGE D. PETTIT
*Research Laboratory, International Business Machines Corporation, Poughkeepsie, New York*

(Received October 10, 1958)

Under certain conditions of excitation a Pr$^{+3}$-activated SrS phosphor exhibits an emission which is energetically greater than the energy gap. This emission is observed at 77°K and not at room temperature. It is proposed that the excitation and short-wavelength emission take place between levels of the Pr$^{+3}$ center. At 77°K the reduction of lattice vibrations effects the isolation of the Pr$^{+3}$ site from the lattice and hence the probability of hole transfer from the activator to the lattice is diminished. The nature of the energy levels of the Pr ion is discussed.

IN previous investigations[1,2] of SrS phosphors activated with rare earth ions, the fluorescent emissions excited by 280 or 296 mμ radiation were examined both at room temperature and at 77°K. The exciting radiations were more energetic than the absorption edge which occurs at 354 mμ. The spectra were analyzed with respect to crystalline field interactions with the rare earth ions. In the case of the phosphor activated with Nd$^{+3}$, there resulted an emission band at a wavelength just shorter than an emission attributed to possible edge emission caused by band-to-band recombinations. This short-wavelength emission is observable at 77°K and not at room temperature. The present note describes a more striking example of fluorescence bands lying at wavelengths shorter than the energy gap, observable at 77°K and not at room temperature.

The sample in question is one containing Pr$^{+3}$ present in the SrS at a concentration of 0.04 mole percent. Its preparation, the apparatus, and the experimental procedure have been described in references 1 and 2. Radiation at 280 or 296 mμ is shorter than the absorption edge of SrS, and so excitation by either wavelength results in the generation of electrons and holes. Fluorescent emission occurs when electrons and holes recombine at Pr centers. When the sample is excited by 280- or 296-mμ light at room temperature there is broad emission between 450 and 650 mμ with peaks located near 496 mμ (2.50 ev) and near 540 mμ (2.30 ev), as reported in reference 1. With 296-mμ exciting light, there is also a shoulder located near 420 mμ (2.95 ev). When the sample is excited by 280-mμ light at 77°K the fluorescence is changed, as reported in reference 2, in the following manner: (1) the band near 496 mμ (2.50 ev) is greatly resolved and is the same as that shown near 496 mμ in Fig. 1, (2) there emerges a peak near 420 mμ (2.95 ev) which is seen as a shoulder in Fig. 1, and (3) the room-temperature peak near 540 mμ (2.30 ev) disappears. However, when the sample is excited with 296-mμ light at 77°K there is a marked change in the spectrum as seen in Fig. 1. In addition to the 420- and 496-mμ bands that occur at room temperature with either 280- or 296-mμ excitation and at 77°K with 280-mu excitation, there has emerged three new bands peaked at 334 mμ (3.71 ev), 357 mμ (3.48 ev), and 398 mμ (3.11 ev). Previously[3] we had determined the energy gap of SrS to be 3.50 ev at room temperature, but reflection measurements made at 77°K indicate that the gap shifts to about 3.60 ev. Hence we see from Fig. 1 that some emitted light is more energetic than the gap width. The observed emission is characteristic of Pr-activated phosphors only, and so we can rule out such explanations as exciton emission. The spectrum can be pictorially represented in the energy level diagram shown in Fig. 2. The arrows represent the observed optical transitions and the numbers represent the energy, in electron volts, of the transitions. The distances between levels are not to scale. The level labelled "excited state" was arbitrarily chosen as the initial state for the three most energetic transitions. The $^3P$ levels were not chosen as the initial states because of the lack of observable structure on these short-wavelength emissions. The lower levels drawn within the valence band represent levels occupied by inner-configuration electrons of the Pr ion. One normally does not expect discrete levels in the valence band, least of all deep-lying levels, to retain holes. However, the Pr$^{+3}$ ion is not in a simple substi-

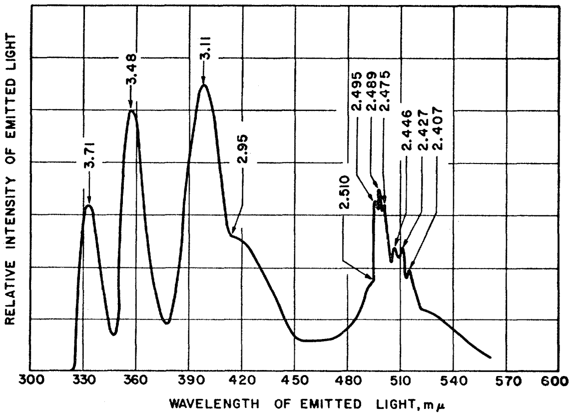

FIG. 1. Fluorescent emission of SrS:Pr$^{+3}$ at 77°K, excited by 296-mμ radiation.

---

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

[2] S. P. Keller and G. D. Pettit, J. Chem. Phys. (to be published).

[3] Cheroff, Okrasinski, and Keller, J. Opt. Soc. Am. **27**, 330 (1957).

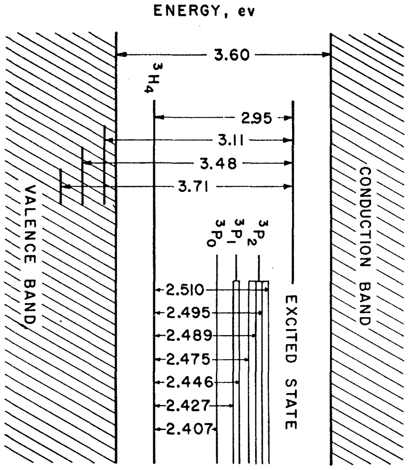

FIG. 2. Energy level diagram for $Pr^{+3}$ in SrS. The numbers represent energy in electron volts and the double-headed arrows represent observed optical transitions.

tutional site, as pointed out in reference 2, a conclusion based upon the amount of crystal field splitting observed for the $^3P$ levels. Since the $Pr^{+3}$ ion is not part of the periodic lattice, it seems reasonable that its levels, especially the deeper lying ones, can be distinct from those of the lattice. The isolation of the $Pr^{+3}$ from the lattice would be more complete at low temperatures where lattice vibrations are diminished. As a result, one would expect the discrete levels of the $Pr^{+3}$ to retain holes more readily at low temperature than at room temperature where the lattice vibrations supply a mechanism for and increase the probability of hole transfer. This is verified by the fact that the short-wavelength emissions are seen only at low temperature and not at room temperature.

The role of the exciting radiation is now examined. Excitation spectra for the various emissions were determined. These were obtained by measuring the effectiveness of various wavelengths of exciting light in causing the emission of different wavelengths of fluorescent light at 77°K. The results are presented in Fig. 3. The excitation peak at 290 mμ has been attributed in an earlier work[4] to absorption by the base material SrS. The excitation peaks at 301 and 316 mμ are attributed to absorptions by the $Pr^{+3}$ and excitations in these regions result in emissions peaked at 334, 357, and 398 mμ. Excitations at 290 mμ or lower result in the emissions peaked near 420 and 496 mμ. An emission at about 412 mμ shows excitation peaks in both the SrS and the $Pr^{+3}$ excitation regions since it is located between the emission bands characteristic of each. An emission near 494 mμ has its major excitation in the SrS excitation region but there is also excitation in the $Pr^{+3}$ region which indicates that the excitations at 316 mμ possibly involves an excitation to the state labelled "excited state" of Fig. 2 with a subsequent transition to the $^3P$ levels and hence to the $^3H_4$ level. It is possible that the 316-mμ excitation peak involves excitations to the "excited state" level whereas the 301-mμ excitation peak involves excitations to the conduction band.

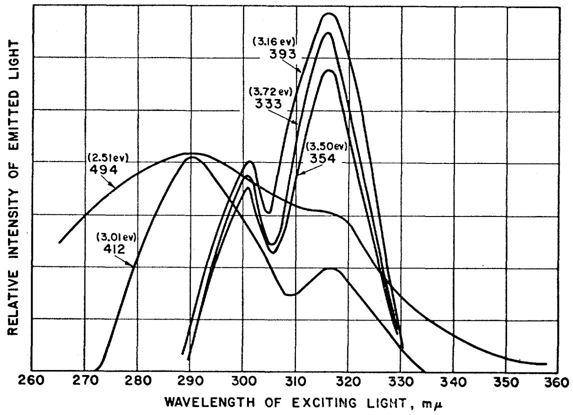

FIG. 3. Excitation spectra for various wavelengths of emitted light, determined at 77°K. The open numbers indicate the wavelength, in mμ, and the numbers in parentheses indicate the energy, in ev, of the emitted light. Comparisons of relative intensities of different curves are not meaningful.

Our data do not allow us to identify unambiguously the lower levels drawn within the valence band which we attribute to Pr inner configurations. Nor can we state clearly what exact transitions occur during the 301- and 316-mμ excitations. However, the data do enable us to talk about $Pr^{+3}$ ions being largely isolated from neighboring lattice sites and giving rise to fluorescent emission larger than the energy gap of the host material SrS due to excitations and emissions occurring within the Pr ion.

---

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