Tb^{3+} as a Recombination Center in ZnS†

W. W. ANDERSON

Microwave Laboratory, Stanford University, Stanford, California

(Received 29 April 1964)

The fluorescence and infrared-stimulated emission of ZnS:Tb has been studied. Excitation of the $4f^8$ electronic system of the Tb^{3+} ion occurs during recombination of a hole-electron pair at the rare-earth site. This is the predominant radiative recombination center in the crystal. Simple rate equations describe the infrared-stimulated release of holes from a trap 1.02 eV above the valence band and their recombination with electrons at the Tb^{3+} site. An estimate of the rate of resonance transfer of energy compared to direct radiative recombination shows the former to be at least 40 times faster.

INTRODUCTION

THE rare-earth ions in II–VI semiconductor lattices form an interesting system to study because of the energy transport and transfer mechanisms which come into play. The infrared-stimulable phosphors of the rare-earth-doped SrS family have been investigated for many years. A concise summary and bibliography is given by Curie.[1] Rare earths in ZnS have been less thoroughly investigated. Ibuki and Langer have found very narrow emission lines in ZnS: Ho and ZnS: Tm powder samples.[2] Oranoskii and Trapeznikova have observed the electroluminescence as well as the photoluminescence of ZnS: Er and ZnS: Nd.[3] The narrow rare-earth emission lines appear under both types of excitation. Unfortunately, they are superposed on a strong background emission due to Cu and Mn, which were added to make the phosphors electroluminescent. These experiments were repeated by Goldsmith *et al.*, who found the rare-earth lines without the strong background.[4]

In all of the systems mentioned, the host lattice plays an important role in the excitation of the rare-earth luminescence. Since we are dealing with semiconductors, energy transport can take place via hole and electron motion. The lattice can give up large quanta of energy in hole-electron recombination. These phenomena determine the emission properties of the system we have studied, terbium-doped ZnS. The conclusions are general and should be applicable to any of the rare-earth-doped ZnS phosphors or any of the family of II–VI compounds. The only restriction is that the ground-state to metastable-level transition of the trivalent rare-earth ion be a few tenths of an electron volt less than the band gap of the host lattice.
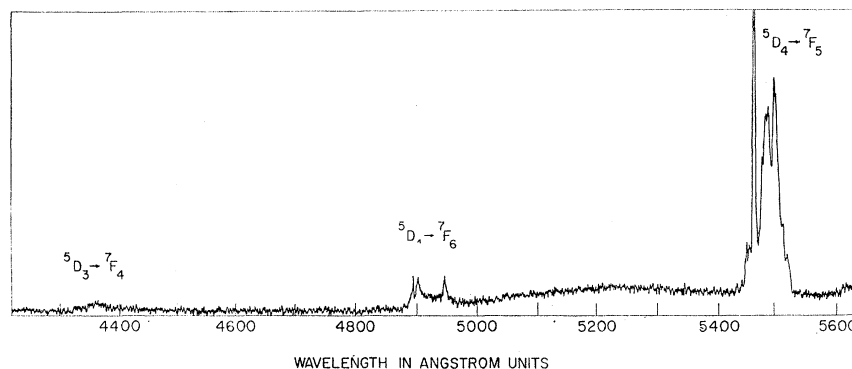
[1] D. Curie, *Luminescence in Crystals* (John Wiley & Sons, Inc., New York, 1963), pp. 195–198, 212–213.

[2] S. Ibuki and D. W. Langer, Appl. Phys. Letters 2, 95 (1963); S. Ibuki and D. W. Langer, J. Chem. Phys. 40, 796 (1964).

[3] V. E. Oranoskii and Z. A. Trapeznikova, Opt. i Spectroskopiya 5, 302 (1958).

[4] G. J. Goldsmith, S. Larach, R. E. Shroder, and P. N. Yocom, Solid State Commun. 1, 25 (1963).

MATERIAL PREPARATION AND INSTRUMENTATION

The crystals were prepared by first diffusing the terbium ion into a zinc sulfide powder at 1000°C and then slowly raising the temperature of the powder to 1250°C. Doped crystals of mm dimensions were deposited from the vapor phase in a slightly cooler ($\sim$1200°C) region of the furnace. The crystals were cooled to room temperature in 3 h. X-ray analysis indicated the wurtzite phase with stacking faults. The Tb concentration in the starting powder was 25% by weight, but less than 0.03% by weight was retained in the final crystals as determined by spectrographic analysis. The sublimation and recrystallization is a very effective distillation process. Other elements present as impurities were Si at 0.02% (probably from the quartz capsule in which the crystals were grown), and Ca, Mg, Ba, and Cu at 0.002%.

All emission spectra were recorded on a Perkin-Elmer 12-G grating spectrometer with a 600-line/mm grating. On the most detailed runs, a spectral slit-width of 1.25 Å was used. The samples were immersed in a liquid-nitrogen bath. Excitation was by a 100-W point-source Hg lamp and filter to select the 3131- and 3025-Å groups of lines. The filter was a solution of 10-g NiCl$_2$·6H$_2$O and 8-g CuSO$_4$·7H$_2$O in 65-ml H$_2$O. This had a passband from 3350–2500 Å and weak transmission in the 5600–6200-Å and 9200–8600-Å regions. When it was desired to remove the Hg yellow lines, the liquid filter was followed by a Corning glass CS-7-54 filter.

Infrared stimulation was by a 500-W projection lamp and Corning glass CS-7-57 infrared pass filter. The infrared-stimulation spectrum was obtained with Bausch & Lomb 33-86-04 and 33-66-03 grating monochrometers and filters. The relative spectral intensity of the output of these monochrometers was determined by a Reedeer RSL-6C thermopile. There was insufficient source intensity to take the stimulation spectrum to wavelengths longer than 2.1 μ. Ultraviolet and infrared excitation were incident on the sample from opposite directions. Emission was observed at 90° from the excitation directions.
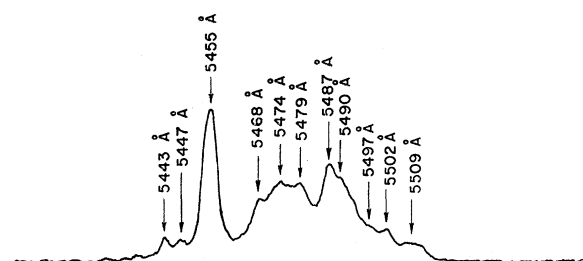
FIG. 1. Emission spectra of ZnS:Tb at 77°.

SPECTRA

The fluorescence spectrum at liquid-nitrogen temperature is shown in Fig. 1. The green lines of the $^5D_4 \rightarrow {}^7F_5$ transition within the $4f^8$ configuration of the Tb^{3+} ion predominate.[5,6] Groups of lines associated with the $^5D_4 \rightarrow {}^7F_6$ and $^5D_3 \rightarrow {}^7F_4$ transition are also seen. There is a broad but weak background emission associated with the ZnS lattice, possibly a Cu impurity or Zn interstitial. Details of the $^5D_4 \rightarrow {}^7F_5$ transition are shown in Fig. 2. The strongest line is only 5 Å wide. We have seen similar narrow lines in ZnS: Nd and Ibuki and Langer report narrow lines for ZnS: Tm and ZnS: Ho.[2] Eleven lines are resolved in this transition. The site symmetry of a Tb^{3+} ion substitutionally replacing a Zn^{++} ion is C_{3v}. The 9-fold degenerate $^5D_4$ level is split into three nondegenerate and three doubly-degenerate levels, while $^7F_5$ splits into three nondegenerate and four doubly-degenerate levels. Thirty-eight transitions should be allowed by crystal-field selection rules. Fewer than 38 transitions will be seen if only the lower levels of the Stark split-metastable $^5D_4$ level are populated at 77°K. More lines may be seen if charge compensating centers are located near the Tb^{3+} ion so that there are several "different" Tb^{3+} ion sites in the crystals.

The crystals were irradiated with ultraviolet light beyond the absorption edge of ZnS ($\lambda < 3400$ Å) to excite the fluorescence of the Tb^{3+} ion. Energy was absorbed by the host lattice in hole-electron pair production, not by the luminescent center. To further illustrate the role of the lattice, infrared-stimulation experiments were performed. The crystals were energized by ultraviolet and the emission spectra observed after the pump light was turned off and the infrared source turned on. The sequence of events is shown in Fig. 3 and the results in Fig. 4. From this it is clear that the host lattice is a source of energy for the Tb^{3+} ion. Although the spectrometer trace shows the stimulated emission about one-fourth as strong as the straight fluorescence emission, the *peak* intensities of the two emissions are about the same. The time development of the stimulated emission is determined by the kinetics of the recombination mechanisms.

The infrared-stimulation spectrum is shown in Fig. 5. We interpret the sharp peak at 1.02 eV to be a deep-hole trap, possibly copper.[7,8] The trivalent Tb^{3+} ion is a donor in ZnS when substitutionally replacing Zn. We propose the model of the recombination process shown in Fig. 6. This is different from the model of
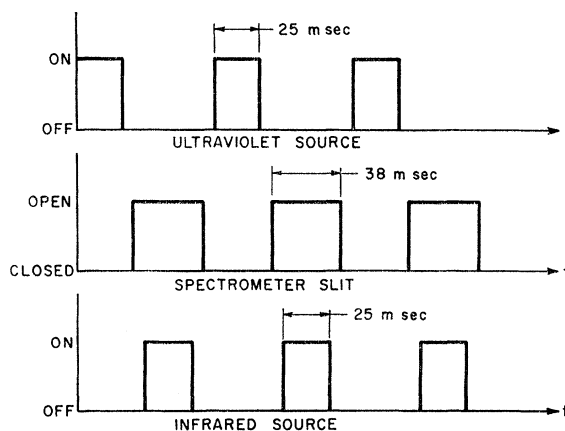

FIG. 2. Detail of $^5D_4 \rightarrow {}^7F_5$ transition in ZnS:Tb at 77°K.

FIG. 3. Sequence of events to observe infrared-stimulated emission.

[5] G. H. Dicke and H. M. Crosswhite, Appl. Opt. **2**, 675 (1963).
[6] L. G. Van Uitert and R. R. Soden, J. Chem. Phys. **32**, 1161 (1960).

[7] H. Kallmann and K. Luchner, Phys. Rev. **123**, 2013 (1961).
[8] K. M. Luchner, H. P. Kallmann, B. Kramer, and P. Wachter, Phys. Rev. **129**, 593 (1963).

(a) EMISSION DURING ULTRAVIOLET EXCITATION

(b) EMISSION AFTER ULTRAVIOLET EXCITATION
WITHOUT INFRARED STIMULATION

(c) EMISSION AFTER ULTRAVIOLET EXCITATION
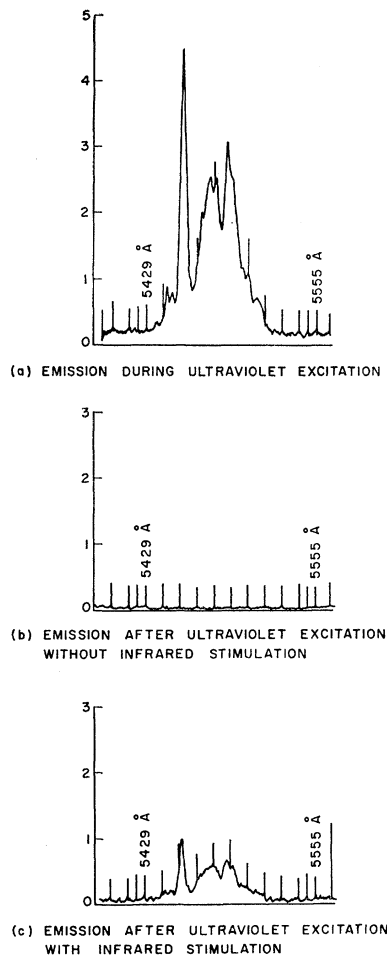WITH INFRARED STIMULATION

FIG. 4. Comparison of fluorescent spectrum and infra-red-stimulated emission spectrum.

Keller[9] for rare-earth-doped SrS since we show the inner shell levels of the rare earth somewhere below the valence band. The donor level associated with Tb^{3+} is due to the valence electrons, $6s^2 5d^1$, not the inner shell $4f^8$ electrons which are shielded from the lattice by the $5s^2 5p^6$ electrons. Our model corresponds to that of Williams for ZnS: Mn[10] in this respect.

RECOMBINATION KINETICS

After intense ultraviolet excitation, the hole traps will be saturated and electrons will be loosely attached to the donors (donor ionization energy about 0.4 eV on a simple hydrogenic model). At 77°K, the donors should not be ionized thermally. If C_t and C_r are the hole-capture constants for the traps and recombination centers, we can write the following equations for valence band, trap, and recombination-center hole populations after the ultraviolet excitation has been

turned off[11]:

$$dp/dt = gN_t f_t - pC_t N_t(1-f_t) - pC_r N_r(1-f_r), \quad (1)$$

$$df_t/dt = -gf_t + pC_t(1-f_t), \quad (2)$$

$$df_r/dt = pC_r(1-f_r), \quad (3)$$

$$p = N_t(1-f_t) - N_r f_r, \quad (4)$$

where p is the number of holes in valence band, N_t is the number of hole traps, f_t is the fraction of traps occupied by holes, N_r is the number of recombination centers, $(1-f_r)$ is the fraction of recombination centers occupied by electrons, and g is the infrared-stimulation rate. Thermally stimulated emission processes are negligible in the system under consideration. The initial conditions are:

$$f_{t0} = 1,$$

$$f_{r0} = 0.$$

The radiated intensity will be proportional to the metastable-level ($^5D_4$) population, N. This is given by the equation:

$$dN/dt = N_t(df_r/dt) - N/\tau, \quad (5)$$

where τ is the lifetime of the $^5D_4$ level. This equation assumes essentially instantaneous trickling down of the energy from the higher excited $4f^8$ levels to the $^5D_4$ level which seems to be the case in rare-earth salts where there are a number of closely spaced levels above the metastable level.[12,13] When τ is short compared to the time variation of other quantities, this equation may be approximated by

$$N/\tau \approx N_t(df_r/dt) \quad (6)$$

so that the observed intensity is proportional to df_r/dt.

The time development of the infrared-stimulated emission is shown in Fig. 7 for a 30 to 1 intensity range of the stimulating signal. The initial intensity is found to
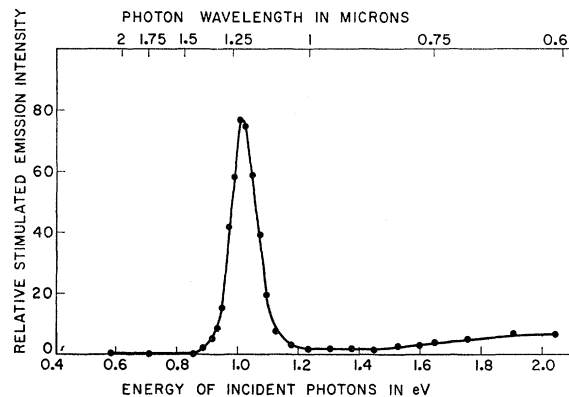

FIG. 5. Infrared-stimulation spectrum for ZnS:Tb at 77°K.

[9] S. P. Keller, Phys. Rev. 113, 1415 (1959). References to other work on rare-earth-doped SrS can be found in this paper.

[10] W. W. Piper and F. E. Williams, Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 6, p. 129.

[11] W. Shockley, Proc. I.R.E. 46, 973 (1958).

[12] G. H. Dieke and L. A. Hall, J. Chem. Phys. 27, 465 (1957).

[13] S. Yatsiv, Physica 25, 521 (1962).

be proportional to the square root of the intensity of the infrared signal. If $1/C_t N_t$, the hole lifetime in n-type ZnS, is short compared to times of interest here, Eq. (2) reduces to a quasisteady state:

$$gf_t = C_t N_t (1-f_t)^2 - C_t N_r f_r (1-f_t), \quad (7)$$

so that the initial intensity is found from Eq. (3) to be:

$$I \sim \frac{df_r}{dt}\Big|_{t=0+} = (C_r N_r)\frac{N_t}{N_r}$$

$$\times \left\{ \left[\frac{g}{C_t N_t} + \left(\frac{g}{2C_t N_t} \right)^2 \right]^{1/2} - \frac{g}{2C_t N_t} \right\}. \quad (8)$$

For $g/C_t N_t \ll 1$, the initial intensity will be proportional to the square root of the infrared intensity as found experimentally. In Fig. 7 we also show solutions of Eq. (3) for $C_r N_r = 125$ sec⁻¹, $N_t/N_r = 30$, and the appropriate range of $g/C_t N_r$ values. These parameter values were chosen to give a best fit of all of the decay curves when plotted on log-log paper. The large trap to
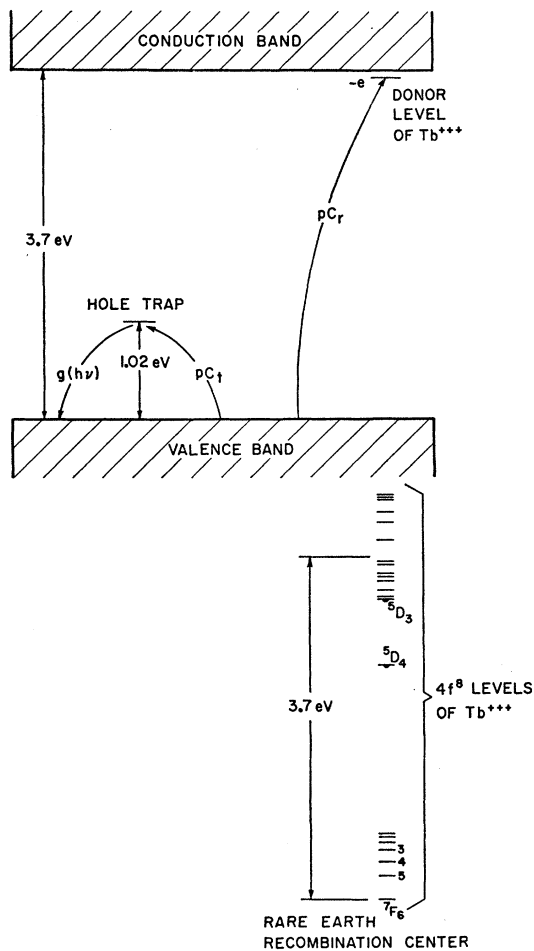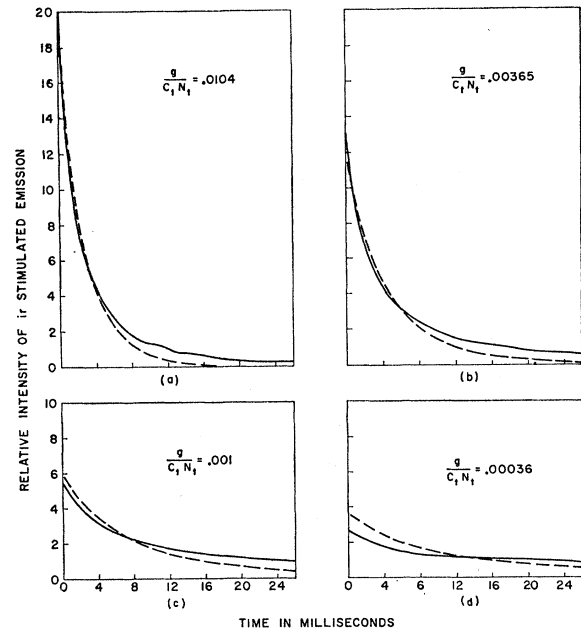

FIG. 7. Decay curves of infrared-stimulated emission. Solid curves are experimental. Dashed curves calculated with parameter values $N_t/N_r = 30$ and $C_r N_r = 125$ sec⁻¹.

recombination-center density casts some doubt on assigning the trap to a Cu impurity in view of the known Tb and Cu concentrations.

The most significant departure of the experimental decay curves from the calculated curves is a rather abrupt change of slope near 12 msec which shows up in many of the traces. This is probably due to regions of different active ion concentrations in the crystals. Visual examination of the crystals showed some regions glowing stronger than others. The theoretical curves are consistently lower than the experimental curves in the tail of the decay. This may be due to experimental errors in reading the oscilloscope trace at low intensities, but is more likely another manifestation of the non-uniform doping.

RESONANCE TRANSFER

Based on the model of Fig. 6, the observed effectiveness of Tb³⁺ as a recombination center, and some of the known properties of ZnS, we can estimate the relative probability of a direct radiative recombination compared to a resonant energy transfer process at the recombination center. Again, using a hydrogenic model of the rare-earth donor, we find the electron Bohr orbit about the Tb³⁺ ion to be about 2.5 Å, i.e., the electron is moving over the four nearest-neighbor S²⁻ ions. In an ionic model of the bonding in ZnS, the donor electron can recombine when a hole moves onto one of these four nearest-neighbor sulfurs. Let us assign this process a spontaneous transition probability (Einstein "A" coefficient) A_1. The rate at which energy

FIG. 6. Model of recombination process.

is transferred nonradiatively to another electronic system may be estimated from the following formula[14]:

$$W_{12} = \left(\frac{\lambda}{2\pi r_0}\right)^6 \frac{3}{4} \frac{A_1 A_2}{n^4} \pi \int_{-\infty}^{\infty} \rho_1(\omega)\rho_2(\omega)d\omega, \quad (9)$$

where A_2 is the spontaneous transition probability for the second system and r_0 is the distance between systems. Here $\rho_1(\omega)$ and $\rho_2(\omega)$ are normalized line-shape functions for the two transitions, λ is the resonant wavelength and n is the refractive index of the medium. Assuming Lorentzian line shapes, the spectral overlap integral can be evaluated to give:

$$\int_{-\infty}^{\infty} \rho_1\rho_2 d\omega = \frac{1}{\pi} \frac{\Delta\omega_1 + \Delta\omega_2}{(\omega_1-\omega_2)^2 + (\Delta\omega_1 + \Delta\omega_2)^2}, \quad (10)$$

where $\Delta\omega_1$, $\Delta\omega_2$ are the half-widths at half-maximum intensity and ω_1, ω_2 are the line centers of the transitions. Since the second system involves transitions within the $4f^8$ configuration of Tb^{3+},

$$\Delta\omega_2 \ll \Delta\omega_1.$$

Furthermore, there are a large number of energy levels of the Tb^{3+} ion within the range of 3.7–3.3 eV, so the integral can be simplified to

$$\int_{-\infty}^{\infty} \rho_1\rho_2 d\omega \approx \frac{1}{\pi\Delta\omega_1}, \quad (11)$$

because $(\omega_1-\omega_2)^2 \ll (\Delta\omega_1)^2$ for some Tb^{3+} transitions.

The transfer probability will now be estimated using the following numbers: $\lambda = 3750$ Å, the bandgap energy less the estimated donor ionization energy of 0.4 eV; $r_0 = 2.33$ Å, the Zn—S distance in wurtzite[15]; $A_2 = 10^3 \sec^{-1}$ which corresponds to an oscillator strength of 1.5×10^{-5}, typical for transitions within the $4f^n$ configuration of the rare-earth ions[16,17]; $n = 2.27$,which may be low due to the neglect of the ionic contribution to the effective dielectric constant[18]: $\Delta\omega_1 = 2 \times 10^{14}$ rad/sec, half-width of ZnS: Cu and ZnS:Ag blue lines at 77°K.[19]

From these values we find

$$W_{12} \approx 40A_1. \quad (12)$$

This indicates that the nonradiative transfer occurs much faster than spontaneous emission. We have underestimated W_{12} since there are many more than one $4f^8$ energy levels nearly resonant with the recombination transition, and the assumed oscillator strength is low by an order of magnitude as will be discussed below. Also, at this small separation, energy transfer by electric-quadrupole–electric-dipole overlap which goes as $(\lambda/r_0)^8$ or electric-quadrupole–electric-quadrupole overlap which goes as $(\lambda/r_0)^{10}$ can be appreciable.[14] The excited $4f^8$ state can relax to a lower energy rapidly by cascading through a number of closely spaced levels to the metastable level from which it will then radiate.

FLUORESCENT LIFETIME

We attempted to measure τ by the fluorescent decay after exciting the Tb^{3+} ion directly and after hole-electron pair production in the ZnS. Under both types of excitation, the decay time was shorter than 100 μsec. Therefore, the approximations of Eqs. (6) and (7) are good. The short relaxation time compared to Tb^{3+} in other lattices[12,20] can be attributed to the fact that the rare-earth site does not have inversion symmetry. The lowest order term in the crystal field is $(r/r_0)^3(Y_3^2 - Y_3^{-2})$ which is very effective in mixing $5d$ wave functions into the $4f$ functions.[17] This will then give strong transitions among the perturbed $4f^n$ levels. For this reason alone our estimate of $A_2 \approx 10^3 \sec^{-1}$ in Eq. (9) was conservative by an order of magnitude or two.

CONCLUSION

In terbium-doped ZnS, the Tb^{3+} ion is the predominant radiative recombination center. We have proposed a simple model for the recombination mechanism which is consistent with the experimental observations. This system is of special interest since the emission center and lattice absorption are well known. We can thus focus our attention on the energy transport and transfer mechanisms within the crystal.

[14] D. L. Dexter, J. Chem. Phys. **21**, 836 (1953); N. Bloembergen, S. Shapiro, P. S. Pershan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

[15] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers Inc., New York, 1960), Vol. 1, Chap. III, table, p. 31.

[16] L. J. F. Broer, C. J. Gorter, and J. Hoogschagen, Physica **11**, 231 (1945).

[17] B. R. Judd, Phys. Rev. **127**, 750 (1962).

[18] T. S. Moss, *Optical Properties of Semiconductors* (Butterworths, Scientific Publications, London, 1961), pp. 209–210.

[19] H. W. Leverenz, *Luminescence of Solids* (John Wiley & Sons, Inc., New York, 1950), pp. 189–190.

[20] Unpublished work in this laboratory has determined the fluorescent lifetime of Tb^{3+} in various glasses to be 2000 μsec, and $CaWO_4$:Tb to be 670 μsec.