9i. Luminescence

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9i-1. General Phenomena and Definitions. *Luminescence* is the phenomenon of light emission in excess of thermal radiation. This definition must be qualified, however, in order to exclude the Raman effect, Compton and Rayleigh scattering, and Cherenkov emission; and this is achieved by limiting luminescence to phenomena involving a time delay of emission after excitation which is long compared with the period of the emitted radiation, λ/c or approximately 10^{-14} sec. Luminescent emission involves optical transitions between electronic states characteristic of the radiating material. For ordinary luminescence the emission occurs by the Einstein spontaneous transition probability and is therefore incoherent; at high-excitation intensities the emission for *laser* materials occurs predominately by the Einstein induced transition probability and is therefore coherent. Although most investigations of luminescence have been concerned with visible emission and the term implies luminous or visible radiation, the same basic processes may yield infrared or ultraviolet radiation. Therefore, luminescence is also applied to such emission as is in excess of thermal radiation. Solid materials which luminesce when suitably excited are called *phosphors*. In many crystalline phosphors the luminescent emission originates in impurity systems called *activators*.

The general phenomenon of luminescence has been subdivided on the basis of the duration of the emission following excitation. Most investigators (refs. 1, 2, and 3) have made this subdivision by considering the mechanisms responsible for the afterglow. When the excitation is removed, there is invariably an exponential afterglow which depends on the lifetime of the emitting state of the activator. This spontaneous afterglow is called *fluorescence*. The time constant for the fluorescent emission may be as short as 10^{-8} or as long as 10^{-1} sec, depending on the phosphor, particularly on the identity of the activator. Frequently, there is an additional component to the afterglow which decays more slowly and with more complex kinetics. This component is called *phosphorescence*. In some phosphors, phosphorescence is attributed to metastable states of the activator; in others, to electron or hole traps spatially removed from the activator. Because thermal activation of the metastable activator or trap is prerequisite to emission, phosphorescence is strongly dependent on temperature. Phosphorescence may persist for times as short as milliseconds or as long as days or longer. During continuous excitation both the fluorescent and phosphorescent mechanisms contribute to the luminescent emission in proportions depending on the steady-state kinetics of these processes. Some authors (ref. 4) have chosen to define fluorescence

as luminescent emission during excitation, and phosphorescence as emission after the excitation has been removed.

Luminescence has also been subdivided according to type of excitation. This subdivision is indicated by a prefix. For example, *photoluminescence* refers to luminescence excited by photons, electromagnetic radiation in the visible, ultraviolet, or infrared. *Cathodoluminescence* involves excitation by cathode rays, energetic electrons impinging on the phosphor. *Electroluminescence* involves the excitation of luminescence as a result of the existence of an applied electrical potential difference in the phosphor. This phenomenon may occur by several different mechanisms: excitation involving the injection of minority electronic charge carriers in semiconducting phosphors is designated *injection* electroluminescence; excitation involving the impact excitation of activators by electrons which have been accelerated to high kinetic energies in high applied fields is designated *collision-excitation* electroluminescence. Mechanical excitation such as grinding is termed *triboluminescence*. The conversion of the energy of a chemical reaction into luminescent emission is *chemiluminescence*, whereas the excitation of luminescence by biological processes is *bioluminescence*.

Thermoluminescence, however, does not refer to thermal excitation but rather to the thermal stimulation of luminescence. The phenomenon is essentially phosphorescence measured during conditions of increasing temperature. The stimulation of luminescence by the visible or infrared is described as *optical stimulation*.

Double prefixes are used to describe more complex luminescent phenomena. The first prefix refers to the control of the luminescence which has been excited in accordance with the mechanism described in the second prefix. For example, *electrophotoluminescence* refers to the modulation of photoluminescence by an applied electric field, whereas *photoelectroluminescence* refers to the control of electroluminescence by incident photons.

9i-2. The Representation of Absorption and Emission Spectra. Most luminescent solids exhibit broad, bell-shaped absorption bands near the fundamental absorption edge and emission bands corresponding to smaller transition energies. The emission bands of many luminescent solids are also broad and structureless; however, the emission of some, particularly of solid-state lasers, are narrow bands. The photoluminescent excitation spectrum usually coincides with the absorption bands. The excitation and emission spectra are determined by the characteristics of the activator systems. The energies of the discrete, localized states of the activator system are a function of the nuclear coordinates of the crystal. Since the atoms which are near the activator interact differently, depending on the electronic states of the activator, the transition energy between these discrete states depends on the internuclear coordinates of these atoms. This effect combined with the Franck-Condon principle accounts for the Stokes' shift of the emission to smaller transition energies compared with absorption in the activator system and for the breadth of the absorption and emission bands. This is of course for systems in which the transition for emission is the inverse of the transition for photoexcitation except for differences in interaction with the lattice for excited and unexcited activator. For systems in which there is a nonradiative transition between quite different excited electronic states of the activator following photoexcitation, the Stokes' shift originates mainly from the difference in energies of these excited states, and the emission may be narrow bands.

We shall first consider the origin and representation of the spectra of phosphors with broad and structureless absorption and emission bands. For simple activator systems, describable in terms of a single internuclear coordinate q, *the probability of the transition* involving a photon of wave number $\bar{\nu}$ per wave-number interval $P_{\bar{\nu}}$ has been shown to be (ref. 5):

$$P_{\bar{\nu}} = M^2 \left(\frac{K}{2\pi kT}\right)^{\frac{1}{2}} \exp\left[\frac{-Kq^2}{2k\theta \coth(\theta/T)}\right] \frac{dq}{d\bar{\nu}} \qquad (9i\text{-}1)$$

TABLE 9i-1. ACTIVATOR ABSORPTION AND EMISSION BANDS OF ALKALI HALIDE PHOSPHORS*

Phosphor	Absorption maxima, $\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}			Emission maxima, $\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}			
NaCl:Tl	5.02	4.7	3.94	.....	3.35	.....	2.80[b]
KCl:Tl	5.10	4.8[e]	4.05	4 04[a,b]	3.27	2.62[b,c]	2.08[b]
RbCl:Tl	5.13	4.8	4.08	.....	3.16	2.89[b]	
CsCl:Tl	5.10	4.8	4.03				
NaBr:Tl	4.63	....	3.74	.....	3.38[d]		
KBr:Tl	4.76	....	3.83	.....	3.13[b]	2.80[b]	
RbBr:Tl	4.72	....	3.86				
CsBr:Tl	4.67	....	3.80				
NaI:Tl	4.27	....	3.41	.....	2.42		
KI:Tl	4.24	....	3.48	3.22[a]	2.39		
RbI:Tl	4.17	....	3.50	.....	2.30		
CsI:Tl	4.15	3.7	3.34	.....	1.68		
NaCl:Pb	5.18	....	3.65	.....	3.13	2.67	2.17
KCl:Pb	5.10	....	3.66	.....	2.89		
RbCl:Pb	5.05	....	3.68				
NaBr:Pb	4.54	....	3.29				
KBr:Pb	4.44	....	3.30				
NaCl:Sn	4.25[d]	....	3.51	.....	2.25		
KCl:Sn	4.31	....	3.56[d]	.....	2.01		
RbCl:Sn	.....	....	.....	.....	1.93		
NaBr:Sn	.....	....	.....	.....	2.15		
KBr:Sn	3.86[d]	....	3.28[d]	.....	1.93		
RbBr:Sn	.....	....	.....	.....	1.84		
LiI:Sn	.....	....	.....	.....	1.89		
NaI:Sn	.....	....	.....	.....	1.85		
KI:Sn	3.47[d]	....	2.85[d]	.....	1.78		
RbI:Sn	.....	....	.....	.....	1.73		
NaCl:Ga	4.60	....	3.75	.....	2.44	.....	1.99
KCl:Ga	4.61	....	.....	.....	.....	.....	1.99
KBr:Ga	4.42	....	3.64[e]	.....	.....	.....	1.78
NaCl:In	4.18	....	3.40	.....	2.41		
KCl:In	4.35[d]	....	3.51[d]	.....	2.30		
NaBr:In	4.00						
KBr:In	4.10	....	3.39[d]	.....	2.28		
KI:In	3.82						
NaCl:Ge	4.30[d]	....	3.74	.....	2.12[e]		
KCl:Ge	4.54[d]	....	.....	.....	1.85		
KBr:Ge	3.98[d]	....	.....	.....	1.75		
NaCl:Cu	3.94	....	.....	.....	2.81		
KCl:Cu	3.88[e]	....	.....	.....	2.53		
NaBr:Cu	3.86						
KBr:Cu	3.77	....	.....	.....	2.52		
KI:Cu	3.75	....	.....	.....	2.48	.....	1.91
NaCl:Ag	4.76						
KCl:Ag	4.55[e]						
NaBr:Ag	4.56						
KI:Ag	3.70[d]						
NaBr:Eu	.....	....	.....	.....	2.30		
KBr:Eu	4.00[d]	....	3.03[d]	.....	2.36		
KI:Eu	.....	....	.....	.....	2.28		

* The data of this table were assembled by P. D. Johnson, General Electric Research Laboratory.
[a] Excitation in large $\tilde{\nu}$ absorption band.
[b] Observed at low temperature.
[c] Observed with high activator concentration.
[d] Multiple band.
[e] Disagreement in literature.

where M is the electronic part of the matrix element for the transition, K is the force constant for the displacement q from equilibrium in the initial state, and $k\theta$ is the zero-point energy for the vibration associated with displacement q. If we make the harmonic approximation, that is, that M is independent of q, and also if we assume that the force constants for the initial and final states are equal, then $P_{\tilde{\nu}}$ is found to be gaussian in $\tilde{\nu}$.

TABLE 9i-2. PHOTOLUMINESCENT SPECTRA OF ZINC SULFIDE PHOSPHORS*

Phosphor	Band	$\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}	$h \times 10^{-4}$ cm^{-1}	Comments
Hex. ZnS:Ag,Cl.	Silver blue	2.29	0.12	
Hex. ZnS:Cu,Cl.	Copper blue	2.22	0.15	Band skewed to small $\tilde{\nu}$ because of copper green
Hex. ZnS:I.....	Self-activated blue	2.19	0.19	
Hex. ZnS:Cu,I..	Copper blue	2.19	0.16	Copper blue and self-activated blue resolvable at low temperature
Hex. ZnS.....	Self-activated blue	2.19	0.12	
Cub. ZnS:Ag,Cl.	Silver blue	2.21	0.14	
Cub. ZnS:Cu,Cl.	Copper blue	2.18	0.14	Band skewed to small $\tilde{\nu}$ because of copper green
Cub. ZnS.....	Self-activated blue	2.13	0.18	
Cub. ZnS:Al....	Self-activated blue	2.09	0.19	
Hex. ZnS:Cu,Cl.	Copper green	1.92	0.12	
Cub. ZnS:Cu,Cl.	Copper green	1.88	0.12	
Hex. ZnS:Ag,In.	Silver red	1.56	0.23	Spectrum at 77 K
Cub. ZnS:Cu....	Copper red	1.49	0.24	
Cub. ZnS:Cu....	Copper red	1.39	0.20	Spectrum at 77 K
Hex. ZnS:Au,Ib.	Gold infrared	1.20	0.22	Spectrum at 77 K

* Spectra at 298 K unless otherwise indicated. The author is indebted to J. S. Prener, General Electric Research Laboratory, for evaluating these data.

This is not found to be precisely the situation experimentally, and actually *the radiant energy* of wave number $\tilde{\nu}$ per unit wave-number interval $E_{\tilde{\nu}}$ was empirically found to be the more accurately gaussian in $\tilde{\nu}$ (refs. 6 to 9)

$$E_{\tilde{\nu}} = b \exp\left[- \frac{(\tilde{\nu} - \tilde{\nu}_0)^2}{1.44h^2} \right] \qquad (9i\text{-}2)$$

where $2h$ is the half width of the band with maximum at $\tilde{\nu}_0$. $P_{\tilde{\nu}}$ and $E_{\tilde{\nu}}$ are, of course, related as follows: $E_{\tilde{\nu}} = hc\tilde{\nu}P_{\tilde{\nu}}$.

The parameters $\tilde{\nu}_0$ and h of Eq. (9i-2) are used to characterize the emission spectra in Tables 9i-1 to 9i-6. This permits the most precise representation of the spectra with two parameters and also permits the straightforward transformation to and from

the wavelength scale. The latter is of some importance, because many of the spectral data on phosphors are given as radiant energy of wavelength λ per unit wavelength interval E_λ. The relation between $E_\tilde{\nu}$ and E_λ is as follows: $E_\tilde{\nu} = -\lambda^2 E_\lambda$. The maximum at λ_0 in the plot of E_λ vs. λ does not coincide with the maximum $\tilde{\nu}_0$ in the

TABLE 9i-3. EMISSION SPECTRA AND QUANTUM EFFICIENCIES OF FLUORESCENT-LAMP PHOSPHORS*

Phosphor	$\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}	$h \times 10^{-4}$ cm^{-1}	η†	Comments
$(Ca,Zn)_3(PO_4)_2$:Tl	3.18	0.17	0.9	
$BaSi_2O_5$:Pb	2.88	0.18		
$Ca_3(PO_4)_2$:Ce	2.74	0.17	0.7	
$CaWO_4$	2.21	0.29	0.7	
$Ca_3(PO_4)_2$:Cu,Sn	2.07	0.18		
$Ca_3(PO_4)_2$:Cu	2.05	0.18		
$3Ca_3(PO_4)_2 \cdot Ca(F,Cl)_2$:Sb,Mn	2.04 1.69	0.28 0.11	0.8–0.95	Evidence of additional Mn emission at small $\tilde{\nu}$; relative intensities depend on Sb and Mn concentrations; $\tilde{\nu}_0$ depends slightly on F/Cl composition
$MgWO_4$	2.01	0.29	0.9	
$3Sr_3(PO_4)_2 \cdot Ca(F,Cl)_2$:Sn,Mn	1.93 1.76	0.28 0.10	.....	Relative intensities of Sb and Mn bands depend on Sb and Mn concentration
Zn_2SiO_4:Mn (willemite)	1.89	0.09	0.8	Slightly skewed to small $\tilde{\nu}$
$CaSiO_3$:Pb,Mn	2.80 1.74 1.60	0.33 0.10 0.10	.....	R = 0.42 for overlapping Mn bands; R depends on Mn concentrations
$(Sr,Mg)_3(PO_4)_2$:Sn	1.58	0.13		
$Cd_2B_2O_5$:Mn	1.58	0.11	0.7	

* Excitation predominantly by 2,537-A radiation. The spectra, from which the $\tilde{\nu}_0$ and h were derived, were provided by H. C. Froehlich and F. J. Studer of Large Lamp Engineering of General Electric.
† J. Tregellas-Williams, *J. Electrochem. Soc.* 105, 173 (1958).

plot $E_\tilde{\nu}$ vs. $\tilde{\nu}$, but rather the latter occurs at slightly smaller wave number

$$\tilde{\nu}_0 = 1/(\lambda_0 + \Delta\lambda)$$

where $\Delta\lambda = 1.44h^2\lambda^3$. The parameters $\tilde{\nu}_0$ and h for each band were determined, in accordance with Eq. (9i-2), by minimizing the sum of squared deviations in fitting the logarithm of $E_\tilde{\nu}$ to a quadratic function of $\tilde{\nu}$. For multiple-band emission arising from a single activator, a third parameter R is also given in Tables 9i-3 and 9i-4.

TABLE 9i-4. EMISSION SPECTRA AND AFTERGLOW OF CATHODOLUMINESCENT SCREENS*

Screen	Phosphor	$\bar{\nu}_0 \times 10^{-4}$ cm^{-1}	$\lambda \times 10^{-4}$ cm^{-1}	Afterglow τ, sec	Comments
P1.....	Zn_2SiO_4:Mn(rhbhd.)†	1.89	0.09	1.1×10^{-2}	
P2.....	ZnS:Cu,Ag (hex.)†	1.85	0.14	Medium, intensity-dependent hyperbolic	Ag blue only about 1/3 of Cu green band
		2.22	0.15	6×10^{-2}	
P3.....	$(Zn,Be)_2SiO_4$:Mn	1.84	0.09		Slightly concave upward exponential afterglow; $R = 0.30$
		1.64	0.11		
P4.....	ZnS:Ag (hex.)†	2.22	0.15	Medium short, hyperbolic	White screen composed of two phosphors
	(Zn,Cd)S:Ag (hex.)†	1.76	0.16		
P5.....	$CaWO_4$	2.21	0.29	1.1×10^{-4}	
P6.....	ZnS:Ag (hex.)	2.22	0.15	Short hyperbolic	Same as P4, except more (ZnCd)S/ZnS for less blue white
	(Zn,Cd)S:Ag (hex.)	1.76	0.16		
P7.....	ZnS:Ag (hex.)	2.26	0.17	Blue flash followed by slow yellow hyperbolic afterglow	Two-layer screen: electrons excite ZnS:Ag, whose emission excites (ZnCd)S:Cu
	(Zn,Cd)S:Cu	1.78	0.15		
P11‡....	ZnS:Ag,Ni (cub.)	2.11	0.19	Short hyperbolic, current dependent	
P12.....	$(Zn,Mg)F_2$:Mn	1.68	0.11	8.5×10^{-2}	Tends to burn at high currents
P13.....	$MgSiO_3$:Mn	1.54	0.10	1.7×10^{-2}	
P14.....	ZnS:Ag (hex.)	2.26	0.17	Blue flash followed by yellow-orange afterglow	Same as P7, except that higher Cd content in (Zn,Cd)S:Cu yields orange afterglow
	(Zn,Cd)S:Cu (hex.)†	1.65	0.16		
P15.....	ZnO	3.15	0.12	Ultraviolet 2×10^{-6}	
		2.42	0.24	Visible 4×10^{-7}	
P16.....	$(Ca,Mg)SiO_3$:Ce	2.60	0.20	4×10^{-8}	
P17.....	ZnO	2.21	0.15	10^{-6}	Similar to P7, except ZnO substituted for ZnS:Ag
	(Zn,Cd)S:Cu	1.78	0.15	Medium hyperbolic	
P18.....	$(Ca,Mg)SiO_3$:Ti	2.34	0.40	2×10^{-5}	
	$(Zn,Be)SiO_4$:Mn	1.84	0.09		
		1.64	0.11	6×10^{-2}	$R = 0.71$
P19.....	$KMgF_3$:Mn	1.68	0.09	7.5×10^{-2}	Tends to burn at higher currents
P20.....	(Zn,Cd)S:Ag	1.76	0.16	Medium short, hyperbolic	
P21.....	MgF_2:Mn	1.66	0.08	8×10^{-2}	Also weak blue band present; tends to burn at high currents
P22§....	ZnS:Ag	2.22	0.15	Short hyperbolic	Three-color screen
	Zn_2SiO_4:Mn	1.80	0.09	1.1×10^{-2}	
	$Zn_3(PO_4)_2$:Mn	1.56	0.09	1.2×10^{-2}	
P23.....	ZnS:Ag	2.22	0.15	Medium short, hyperbolic afterglow	Similar to P4
	(Zn,Cd)S:Ag	1.73	0.16		
P24.....	ZnO	1.93	0.21	1.4×10^{-7}	No ultraviolet emission as in P15
P25.....	$CaSiO_3$:Pb,Mn	2.80	0.33		
		1.74	0.10		
		1.60	0.10	1.6×10^{-2}	$R = 0.42$ for Mn bands
P26.....	ZnF_2:Mn	1.67	0.09	8.3×10^{-2}	Tends to burn at high currents
P27.....	$Zn_3(PO_4)_2$:Mn	1.56	0.09	1.2×10^{-2}	
P28.....	(Zn,Cd)S:Cu,Ag	....	....	Long hyperbolic	Multiple emission bands in yellow green, two-phosphor screen

TABLE 9i-4. EMISSION SPECTRA AND AFTERGLOW OF CATHODOLUMINESCENT SCREENS* (*Continued*)

Screen	Phosphor	$\bar{\nu}_0 \times 10^{-4}$ cm^{-1}	$h \times 10^{-4}$ cm^{-1}	Afterglow τ, sec	Comments
P29.....	ZnS:Cu,Ag $CaWO_4$	....	....	Medium persistence	Two-component screen composed of P2 and P5

* Based on "Optical Characteristics of Cathode Ray Tube Screens," compiled by the Joint Electron Tube Engineering Council, Oct. 1, 1959.

† Available as standard phosphors from the National Bureau of Standards.

‡ P8 and P9 are obsolete; P10 is the dark trace KCl screen which is not a luminescent material. P11 is also available as a transparent screen.

§ The blue and red components are currently for most P22 screens (Zn,Cd)S:Ag and Eu-doped vanadate, respectively.

This parameter R is the ratio of the parameter b of Eq. (9i-2) for the band with the large $\bar{\nu}$ to b with the smaller $\bar{\nu}_0$.

The parameters describing the absorption spectra as a function of wave number and wavelength are simply related. Because the absorption coefficient α is the probability of absorption of a photon of wave number $\bar{\nu}$ or of wavelength λ per centimeter of absorbing medium, the maximum at λ_0 in the plot of $\alpha(\lambda)$ vs. λ coincides with the maximum $\bar{\nu}_0$ in the plot of $\alpha(\bar{\nu})$ vs. $\bar{\nu}$; that is, $\bar{\nu}_0 = 1/\lambda_0$.

TABLE 9i-5. EMISSION, PULSE HEIGHT, AND DECAY TIME OF SCINTILLATION PHOSPHORS

Phosphor	$\bar{\nu}_0 \times 10^{-4}$ cm^{-1}	Approximate energy conversion efficiency η_E, % for β-rays	Decay time τ, sec	Comments
Anthracene.....	2.4, 2.3, 2.2	5	3×10^{-8}	Several overlapping bands
Naphthalene...	3.16, 3.12, 3.07, 3.02, 2.97, 2.92	1	8×10^{-8}	Series of narrow overlapping bands; sublimes
Stilbene.....	2.5, 2.4	3	8×10^{-9}	Several overlapping bands
Terphenyl.....	2.6, 2.5, 2.3	2	1.2×10^{-8}	Several overlapping bands
NaI:Tl.....	2.42	15	2.5×10^{-7}	Very hygroscopic
KI:Tl.....	2.39	2	10^{-6}	
CsI:Tl.....	1.68	9	$\sim 10^{-6}$	Hygroscopic
ZnS:Ag.....	2.29	25	$\sim 10^{-5}$	$h = 1.2 \times 10^3$ cm^{-1}, also efficient for α-particles
$CaWO_4$.....	2.21	5	1.1×10^{-5}	$h = 2.9 \times 10^3$ cm^{-1}, stable

TABLE 9i-6. EMISSION SPECTRA OF ELECTROLUMINESCENT PHOSPHORS

Phosphor*	Emission maximum, $\bar{\nu}_0 \times 10^{-4}$ cm^{-1}	Width, $h \times 10^{-4}$ cm^{-1}	Temperature, K
ZnS:Cu, Br	2.16	0.14	300
ZnS:Cu, Cl	1.91	0.15	300
ZnS:Cu, Cl, Mn	1.69	0.09	300
GaP:Zn, S	1.79	0.02	20
	1.73	0.04	300
GaP:Cd, O	1.49	0.07	20
	1.43	0.09	300
SiC:B, N†	1.73	0.19	300

* Electroluminescence of ZnS phosphors occurs by collision-excitation mechanism; for GaP and SiC, by minority-carrier injection.
† 6*H* polymorph.

For materials with narrow-band emission such as some of those in Table 9i-6 and all of those in Tables 9i-7 to 9i-9 we shall be concerned with somewhat different characteristics. Some of these materials are becoming important as sources of ordinary luminescent emission, however, their most striking characteristics become evident under the conditions for the generation of coherent emission. Under these conditions the narrow emission is important because in order to satisfy the requirement that the induced probability be large compared to the spontaneous probability, $\rho B > A$, where ρ is the radiation density per unit frequency or wave number, the same flux of radiant energy in a narrow frequency or wave-number interval yields a lower threshold power for laser action. The conditions for the generation of coherent optical radiation were first predicted (ref. 10) and then first observed (ref. 11) for ruby, $Al_2O_3:Cr^{3+}$. Since then, many solid-state lasers have been reported and reviewed (refs. 12 and 13). Some characteristics are tabulated in Tables 9i-7 to 9i-9.

Consistent with the accuracies of both the original data and the analyses, the values of the parameters given in Tables 9i-1 to 9i-9 are for most materials reliable to plus or minus 1 in the last digit given.

9i-3. Tabulated Spectra, Efficiencies, and Afterglow Characteristics. In Table 9i-1, which describes the absorption and emission bands of *alkali halide phosphors*, only the maxima $\bar{\nu}_0$ in the plots of α and $E_{\bar{\nu}}$ vs. $\bar{\nu}$ are given. Except for a few materials such as KCl:Tl, the data for these materials are not sufficiently complete to resolve the overlapping bands and attribute accurate half widths to each band. The value of the parameter h for these phosphors is a monotonic function of $\bar{\nu}_0$, so that the correction $\Delta\lambda$ involved in the transformation E_λ to $E_{\bar{\nu}}$ can be made within the accuracy of the data. The bands described in Table 9i-1, unless otherwise indicated, describe the spectra with quite low activator concentrations, e.g., 10^{-4} atomic fraction or less. At higher concentrations, additional bands at lower $\bar{\nu}$ frequently appear.

In Table 9i-2 the parameters $\bar{\nu}_0$ and h for the photoluminescent emission of *zinc sulfide phosphors* are given. For the same activator, e.g., copper, silver, or gold, a number of different emission bands are observed whose relative intensities depend on coactivator concentration and on the atmosphere during crystallization. The coactivator is an additional impurity which is necessary for luminescence in sulfide phosphors but which does not have the pronounced effect on the emission spectrum that the activator has. In this class of phosphors the coactivators have been identified, according to semiconductivity terminology, as donors; the activators, as acceptors (refs. 14 and 15). In semiconducting phosphors in general, radiative deexcitation has frequently been found to occur via donor-acceptor pairs (ref. 16). The substitution of

TABLE 9i-7. LASER MATERIALS AND TRANSITIONS*

Material	Transition	Emission, $\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}	Terminal state, cm^{-1}	Excitation, $\nu \times 10^{-4}$ cm^{-1}
Al_2O_3: 0.05% Cr^{3+}	$^2E(\bar{E}) \rightarrow {}^4A_2$	1.4422	0	2.38–3.12
	$^2E(\bar{A}) \rightarrow {}^4A_2$	1.4432	0	1.66–2.00
Al_2O_3: 0.5% Cr^{3+}	$^2E(\bar{A}) \rightarrow {}^4A_2$	1.4432	0	
	pair lines	1.4267	100	
	pair lines	1.4202	100	
	pair lines	1.3037	100	
MgF_2: 1% Co^{2+}	$^4T_2 \rightarrow {}^4T_1$	0.5714	1,087	1.81–2.27
		0.5546	1,256	1.33–1.66
ZnF_2: 1% Co^{2+}	.....	0.3829		
MgF_2: 1% Ni^{2+}	$^3T_2 \rightarrow {}^3A_2$	0.6165	340	2.08–2.63
				1.01–1.47
				0.64–0.91
$CaWO_4$: 0.5% Pr^{3+}	$^1G_4 \rightarrow {}^3H_4$	0.9552	377	2.04–2.33
LaF_3: 1% Pr^{3+}	$^3P_0 \rightarrow {}^3H_6$	1.6708	~4,200	2.08–2.33
CaF_2: 1% Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.9560	~2,000	
$CaMoO_4$: 1.8% Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.9425	~2,000	
$CaWO_4$: 1% Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{9}{2}}$	1.0934	471	1.67–1.75
	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.9389	2,016	1.32–1.35
	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{13}{2}}$	0.7467	4.004	
Glass: Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.94	1,950	
LaF_3: 1% Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.9404	2,187	
$Y_3Al_5O_{12}$: Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.9423	2,001	
		0.9391	2,111	
CaF_2: 0.01% Sm^{2+}	$^5D_0 \rightarrow {}^7F_1$	1.4118	263	2.22–2.50
SrF_2: 0.01% Sm^{2+}	$^5D_0 \rightarrow {}^7F_1$	1.4353	263	1.47–1.72
Y_2O_3: 5% Eu^{3+}	$^5D_0 \rightarrow {}^7F_2$	1.6358	859	3.57–5.00
				2.13–2.17
				1.85–1.92
CaF_2: 0.01% Dy^{2+}	$^5I_7 \rightarrow {}^5I_8$	0.4239	30	
CaF_2: Ho^{3+}	$^5S_2 \rightarrow {}^5I_8$	1.8142	~370	
$CaWO_4$: 0.5% Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	0.4887	250	2.17–2.27
$Y_3Al_5O_{12}$: Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	0.4769	462	2.17–2.27
		0.4781	.....	0.85–0.88
		0.4711	518	0.51–0.53
Glass: Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	0.5128		
$Ca(NbO_3)_2$: Er^{3+}	$^4I_{\frac{13}{2}} \rightarrow {}^4I_{\frac{15}{2}}$	0.6211		
$CaWO_4$: 1% Er^{3+}	$^4I_{\frac{13}{2}} \rightarrow {}^4I_{\frac{15}{2}}$	0.6203	375	3.57–5.00
$Y_3Al_5O_{12}$: Er^{3+}	$^4I_{\frac{13}{2}} \rightarrow {}^4I_{\frac{15}{2}}$	0.6023	525	3.57–5.00
		0.6078	.....	2.12–2.17
				1.85–1.92
CaF_2: 0.01% Tm^{3+}	$^2F_{\frac{5}{2}} \rightarrow {}^2F_{\frac{7}{2}}$	0.8960	0	2.94–3.57
				2.17–2.56
				1.59–1.89
$CaWO_4$: Tm^{3+}	$^3H_4 \rightarrow {}^3H_6$	0.5232	325	2.08–2.17
				0.82–0.86
		0.5219	325	0.55–0.59
Er_2O_3: Tm^{3+}	$^3H_4 \rightarrow {}^3H_6$	0.5170		
$Y_3Al_5O_{12}$: Tm^{3+}	$^3H_4 \rightarrow {}^3H_6$	0.5309	240	2.08–2.17
				0.82–0.86
		0.4967	582	0.55–0.59
$Y_3Al_5O_{12}$: Yb^{3+}	$^2F_{\frac{5}{2}} \rightarrow {}^2F_{\frac{7}{2}}$	0.9712	623	1.00–1.11
Glass (1): Yb^{3+}	$^2F_{\frac{5}{2}} \rightarrow {}^2F_{\frac{7}{2}}$	0.9900	400	
Glass (2): Yb^{3+}	$^2F_{\frac{5}{2}} \rightarrow {}^2F_{\frac{7}{2}}$	0.9823		
CaF_2: 0.05% U^{3+}	$^4I_{\frac{11}{2}} \rightarrow {}^4I_{\frac{9}{2}}$	0.3982	505	0.77–0.83
		0.3827	609	
SrF_2: U^{3+}	$^4I_{\frac{11}{2}} \rightarrow {}^4I_{\frac{9}{2}}$	0.4154	334	

* Modified from Z. J. Kiss and R. J. Pressley, *Proc. IEEE*, **54**, 1238 (1966), and L. G. Van Uitert, "Luminescence of Inorganic Solids," Goldberg, ed., pp. 520–523, Academic Press, Inc., New York, 1966.

TABLE 9i-8. SENSITIZED LASER MATERIALS AND TRANSITIONS*

Material†	Transition	Emission, $\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}	Terminal state, cm^{-1}
$Y_3Al_5O_{12}$: Yb^{3+}, Er^{3+}, Tm^{3+}, Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	0.4697	530
		0.4710	520
		0.4765	460
$Er_3Y_3Al_{10}O_{24}$: $Er^{3+} \rightarrow Ho^{3+}$	$^5I_7 \rightarrow {}^5I_8$	0.4766	462
$Y_3Al_5O_{12}$: Cr^{3+}, Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	0.4767	462
		0.4711	510
Glass: Yb^{3+}, Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	0.481	~300
$CaMoO_4$: Er^{3+}, Ho^{3+}	$^5I_7 \rightarrow {}^5I_8$	0.4821	
		0.4829	~250
		0.4864	
$Er_3Y_3Al_{10}O_{24}$: $Er^{3+} \rightarrow Tm^{3+}$	$^3H_4 \rightarrow {}^3H_6$	0.4965	582
		0.5307	240
		0.5319	228
$Y_3Al_5O_{12}$: Yb^{3+}, Tm^{3+}	$^3H_4 \rightarrow {}^3H_6$	0.4966	580
		0.5308	
$Y_3Al_5O_{12}$: Cr^{3+}, Tm^{3+}	$^3H_4 \rightarrow {}^3H_6$	0.4967	582
		0.4952	~600
Er_2O_3: $Er^{3+} \rightarrow Tm^{3+}$	$^3H_4 \rightarrow {}^3H_6$	0.5170	
$CaMoO_4$: Er^{3+}, Tm^{3+}	$^3H_4 \rightarrow {}^4H_6$	0.5231	~325
		0.5246	
Glass: $Yb^{3+} \rightarrow Er^{3+}$	$^4I_{\frac{13}{2}} \rightarrow {}^4I_{\frac{15}{2}}$	0.6482	
Glass (silicate): UO_2^{2+}, Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.94	~2,000
Phosphate glass: Mn^{2+}, Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.94	~2,000
$Y_3Al_5O_{12}$: Cr^{3+}, Nd^{3+}	$^4F_{\frac{3}{2}} \rightarrow {}^4I_{\frac{11}{2}}$	0.9423	2,001
Glass: Nd^{3+}, Yb^{3+}	$^2F_{\frac{5}{2}} \rightarrow {}^2F_{\frac{7}{2}}$	0.982	
Silicate glass: UO_2^{2+}, Yb^{3+}	$^2F_{\frac{5}{2}} \rightarrow {}^2I_{\frac{7}{2}}$	0.985	~400

* Modified from L. G. Van Uitert, "Luminescence of Inorganic Solids," Goldberg, ed., pp. 520–523, Academic Press, Inc., New York, 1966. The excitation is in the characteristic bands of sensitizer or laser dopant.

† The last dopant in the formula is the activator with the lasing transition.

TABLE 9i-9. SEMICONDUCTOR LASERS*

Material	Emission, $\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}	Excitation†	Material	Emission, $\tilde{\nu}_0 \times 10^{-4}$ cm^{-1}	Excitation†
$Pb_{0.73}Sn_{0.27}Te$	0.036	PL	In(P,As)	1.13	EL
$Pb_{0.8}Sn_{0.2}Te$	0.038	PL	GaAs	1.18	EL, CR, PL
PbSe	0.118	EL, CR	$GaAs_xP_{1-x}$	1.14–1.69‡	EL
PbTe	0.154	EL, CR, PL	CdTe	1.25	CR
InSb	0.19	EL, CR, PL	CdSe	1.45	CR
PbS	0.233	EL, CR	GaSe	1.67	CR
$Cd_{0.3}Hg_{0.7}Te$	0.25	PL	CdS	2.02	CR, PL
Te	0.27	CR	ZnSe	2.17	CR
InAs	0.31	EL, CR, PL	ZnO	2.67	CR
GaSb	0.62	EL, CR	ZnS	3.06	CR
InP	1.11	EL			

* Modified from R. Rediker, *Proc.* 1966 *Intern. Conf. Luminescence*, edited by G. Szigeti (Hungarian Academy of Sciences, Budapest, 1968) p. 1756; M. R. Lorenz and M. H. Pilkuhn, *IEEE* Spectrum **4**, 87 (1967); D. C. Reynolds, *Trans. Met. Soc. AIME*, **239**, 300 (1967).

† CR = cathode ray, EL = electric injection, PL = photoexcitation.

‡ Depends on x in formula $GaAs_xP_{1-x}$.

cadmium sulfide for part of the zinc sulfide shifts the emission band to smaller $\bar{\nu}$ in accordance with the reduction in band gap of the material. The zinc sulfide phosphors activated with phosphorus, arsenic, and antimony are not included, since their emission spectra are not unambiguously described in the literature. The photoluminescence described in Table 9i-2 is efficiently excited by 3650-Å ultraviolet radiation.

The *fluorescent-lamp phosphors* described in Table 9i-3 have probably had their emission spectra most accurately measured. In some cases the parameters $\bar{\nu}$ and h are derived from data taken on experimental lamps; in other cases, on the phosphors directly. In either case, the excitation is predominantly by 2537-Å ultraviolet radiation. The calcium halophosphate phosphors merit additional comment. The emission spectrum consists of two broad and structureless bands. The intensity of the blue band depends on the antimony activator concentration; that of the orange band on the manganese activator concentration. In addition, $\bar{\nu}_0$ for the manganese emission shifts to smaller $\bar{\nu}$ with increasing chloro- to fluorophosphate content, with a maximum shift of approximately 2 percent of $\bar{\nu}_0$. The antimony emission shifts only 1 percent of $\bar{\nu}_0$ with complete chloride substitution. In contrast to most phosphors activated with divalent manganese, there is evidence for a second, less intense manganese band at smaller $\bar{\nu}$ (ref. 8). The quantum efficiencies shown in Table 9i-3 are based on the analysis by Tregellas-Williams (ref. 17).

Another class of photoluminescent phosphors are those activated by tetravalent manganese. Their emission is characterized by a fine structure consisting of bands approximately 100 cm^{-1} in width separated by approximately 200 cm^{-1}. This material and the magnesium arsenate maintain high photoluminescent (ref. 9) efficiencies to 650 K. The high-temperature stability combined with their red emission leads to their use for color correction in the medium-pressure mercury lamp. Rare-earth phosphors related to those in Tables 9i-7 and 9i-8 are becoming important in discharge lamps.

In principle, the *cathodoluminescent screens* described in Table 9i-4 are not confined to particular phosphors; however, the screen specifications are set up so that in practice only a particular phosphor or combination of phosphors meets the specifications. For screens composed of two or more phosphors, either as a mixture or as two distinct layers, the contribution of each phosphor to the emission spectrum may be slightly altered because of absorption by the other components. This accounts for some of the small discrepancies between the parameters given in Table 9i-4 which are based on the screen performance characteristics and the parameters based on data obtained on the separate phosphors. A single time constant does not describe the afterglow of the sulfide phosphors, because the afterglow is hyperbolic, rather than exponential, and is markedly dependent on current density. This arises from a broad distribution in energy of trapping states whose occupational probabilities depend on density of excitation.

Both organic and inorganic phosphors are used in *scintillation counters*. The emission spectra of the organic phosphors consist of a series of narrow bands compared with the broad, structureless emission bands of the inorganic phosphors. The persistences of the organic phosphors are shorter, whereas the efficiencies of the inorganic phosphors are greater for particles which produce large ionization densities. The characteristics of the phosphors commonly used in scintillation counters are given in Table 9i-5.

Electroluminescent materials are of two classes: those which operate by the collision-excitation mechanism, and those which operate by minority-charge carrier injection. Zinc sulfide is the principal representative of the first class; silicon carbide and gallium phosphide are the most important members of the second class. The first are used as particles in a dielectric matrix with an applied a-c field; the second, as single crystals with either a-c or d-c fields. The parameters describing the emission of these materials are given in Table 9i-6.

9i-4. Formulas for Some Luminescent Characteristics. In addition to Eqs. (9i-1) and (9i-2), which are the theoretical and empirical formulas, respectively, for the optical spectra of activator systems, there are a number of other simple formulas for interpreting or describing luminescent phenomena.

There are, of course, the *formulas for the afterglow*. The simplest is the exponential decay of the emission intensity,

$$I = I_0 \exp(-At) \tag{9i-3}$$

where A is the spontaneous transition probability or the reciprocal of the *lifetime* τ shown in Tables 9i-4 and 9i-5. At high temperatures the lifetime of the emitting state decreases because of nonradiative deexcitation, and under these conditions the afterglow is of the form (ref. 18):

$$I = I_0 \exp\left\{-\left[A + s \exp\left(-\frac{\epsilon}{kT}\right)\right] t\right\} \tag{9i-4}$$

where s is the frequency factor, and ϵ is the activation energy for the nonradiative process. Concurrently, under these conditions the luminescent efficiency decreases with increasing temperature (ref. 19):

$$\eta = \frac{1}{1 + (s/A) \exp(-\epsilon/kT)} \tag{9i-5}$$

The luminescent efficiency is also dependent on activator concentration, and for activators distributed at random lattice sites and capable of efficient luminescence if no other activators occupy the z nearest-neighbor sites, the efficiency is of the form (ref. 20):

$$\eta = \frac{c(1-c)^z}{c + \kappa(1-c)} \tag{9i-6}$$

where c is the atomic fraction of activator impurity, and κ is the ratio of capture cross sections for nonradiative and radiative processes.

The afterglow observed for zinc sulfide phosphor is fundamentally quite complex, since a distribution of electron traps and retrappings are apparently involved. Empirically, the following hyperbolic form has been extensively used:

$$I = I_0(1 + \alpha t)^{-n} \tag{9i-7}$$

Simple bimolecular recombination leads to an equation of his form with $n = 2$; however, experimentally $n \approx 1$ is usually found.

The distribution of trapping states is more clearly evident from thermoluminescent measurements. For traps which empty by first-order kinetics without retrapping and in accord with the activation energy ϵ' and frequency factor s', the thermoluminescent intensity at temperature T is (refs. 21 and 22):

$$I = n_0 s' \exp\left(-\frac{\epsilon'}{kT}\right) \exp\left[-\frac{s'}{dT/dt}\int_{T_0}^{T} \exp\left(-\frac{\epsilon'}{kT}\right) dT\right] \tag{9i-8}$$

where n_0 is the initial concentration of occupied trapping states, T_0 is the initial temperature, and dT/dt is the rate of temperature increase. Equations which include retrapping have also been formulated.

As noted earlier, radiative recombination of electrons and positive holes at donor-acceptor pairs is an important luminescent process in semiconductors. The transition energy for this emission at the ith pair with interimpurity distance R_i is as follows, neglecting overlap of the effective mass functions for donor electron and acceptor hole (ref. 16):

$$hc\bar{\nu}_i = E_g - (E_A + E_D) + \frac{e^2}{KR_i} \tag{9i-9}$$

where E_g is the band gap; E_A and E_D are the absolute values of the ionization energies of separated acceptor and donor, respectively; and K is the dielectric constant.

Various formulas have been proposed to describe the voltage dependence of the brightness of phosphors which electroluminesce by the collision-excitation mechanism. The most successful for present electroluminescent cells are of the following form (refs. 23 and 24):

$$B = V^m \exp\left(-\frac{d}{V^{\frac{1}{2}}}\right) \tag{9i-10}$$

where $m = 0, 2$ have been used; V is the applied voltage; and d is a constant.

For injection electroluminescence involving a p-n junction the dependence of current J on applied voltage is

$$J = J_0 \exp\frac{eV}{\beta kT} \tag{9i-11}$$

where β is found to be of the order of 1 or 2.

The solid-state laser acts as a resonance cavity with an amplifying medium. The threshold power for oscillation is (ref. 12):

$$P = \frac{3h^2c^2(1 - R)\Delta\tilde{\nu}}{8\pi^2\tau Ml} \tag{9i-12}$$

where R is the product of reflectivities of the end mirrors, τ is the lifetime of the excited state, M is the dipole matrix element of the transition, and l is the length of the cavity. As noted earlier, the threshold power is less for emission bands of narrower width $\Delta\tilde{\nu}$. In Eq. 9i-12, h and c are respectively Planck's constant and the velocity of light.

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