Luminescent Solids (Phosphors)

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IT IS A CURIOUS FACT that man synthesized and used luminescent solids long before detecting luminescence from the natural luminescent solids which have existed on this earth since its genesis. About 350 years ago, the alchemist Casciarolo chanced to heat some native barium sulphate with charcoal and noticed that after exposure to daylight the cooled impure sulphide product glowed feebly in the dark. This mysterious solid, which was called a *phosphor* or phosphoros (Greek, "light bearer"), antedated the discovery of the chemical element phosphorus by about 70 years. Because the similarity of terms has caused some confusion, it should be noted that the luminescence of a phosphor is a solid-phase *physical* (electronic) action which occurs throughout the mass and which may continue indefinitely when the phosphor is in a vacuum; whereas the luminescence of the element misnamed phosphorus results from a gas-phase *chemical* action which occurs only at the surface and which ceases when the phosphorus is consumed or placed in a vacuum.

At the time phosphors were first prepared, daylight was the only known means for their excitation, and so luminescence was observable only when it was excitable by daylight and persisted long enough for the phosphor to be taken into a dark place. With the development of modern electronic and radioactive sources of invisible radiations, phosphors have been used not only for instantaneous detection of ultraviolet, X-rays, cathode-rays, alpha particles, etc., but also as a means of putting these invisible forms of energy to work in television, radar, electron microscopes, "fluorescent" lamps, infrared sniperscopes, X-ray fluoroscopes, and self-luminous dial markings. This article briefly outlines the present status of man-made phosphors, whose variety and capabilities greatly exceed those of the known natural luminescent solids. More detailed information may be obtained from the references at the end of this article.[1]

Before proceeding, it is worth emphasizing that the technology of phosphors, like that of other structure- and impurity-sensitive, electronically active solids (*e.g.*, photoconductors, semiconductors, ferroelectric and ferromagnetic materials), is in the process of growing from the status of an art to that of a science. Our imperfect understanding and control of electronically active solids is caused largely by the practical impossibility of completely segregating (purifying) and rectilinearly arranging (crystallizing) the enormous number of atoms ($10^{23}/\text{cm}^3$) in *real* crystals, so that real crystals are always impure and imperfect to some degree. It is known that the unavoidable imperfections (including impurities) in real crystals sometimes increase and sometimes decrease electronic activities such as excitation, internal ionization, radiative and nonradiative transitions, electron mobility, and trapping. Very often, certain crystal imperfections are incorporated deliberately to promote or suppress a given electronic activity. In the case of phosphors, the highly purified *host crystal* usually has a very small proportion of *activator* impurity which is either added initially or is induced to increase luminescence efficiency. The efficiency increase is generally accomplished by decreasing the proportion of excitation energy dissipated in the crystal as heat.

LUMINESCENCE

There is a maximum characteristic thermal radiation from any solid at a given temperature, T, and *luminescence* may be defined broadly as the production of photon emission in *excess* of this thermal radiation. In contrast with thermal radiation, luminescence emission generally decreases with increasing T and occurs as narrow spectral lines or bands (Fig. 1) whose locations and shapes are relatively insensitive to changes in T. Luminescence is generally a *nonequilibrium* process wherein extraneous photons or charged material particles (electrons, ions, etc.) bombard a material and excite a few of its atoms or groups of atoms (*centers*) to energy levels far higher than those attained by thermal excitation. The excited centers then return to lower energy levels and emit correspondingly high-energy photons.

Distinctive prefixes are used to denote luminescence produced by primary particles which differ in the manner in which they excite phosphors, *e.g.*, visible and near-visible photons excite *photoluminescence*, X-ray and gamma-ray photons excite *roentgenoluminescence*, electrons excite *cathodoluminescence*, and ions, such as alpha particles, excite *ionoluminescence*. The energies of these primary excitant particles generally exceed 2 electron volts (ev), where 1 ev =

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[1] Most of the information in this article is abstracted from the author's book, *Introduction to luminescence of solids*, New York: John Wiley, in press.

1.6×10^{-12} erg $= 3.8 \times 10^{-20}$ calorie $= 23$ kcal mole^{-1} (when each simple molecule has 1 ev), there being no known upper limit (at least to 10^8 ev) to the energy of a primary particle capable of exciting phosphors.

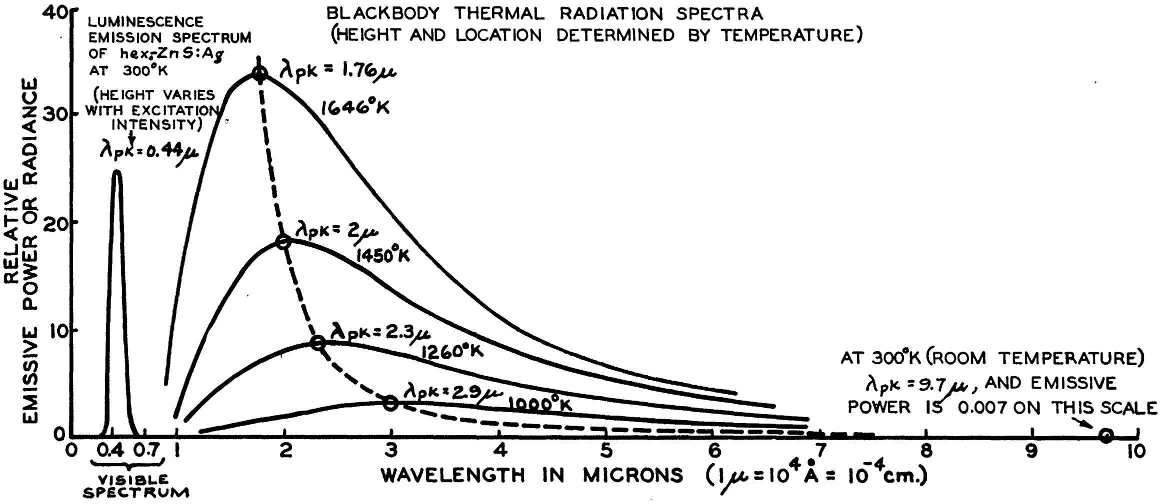


FIG. 1. Comparative spectral distributions of the emissions from a typical phosphor (narrow band at left) and a blackbody thermal emitter (broad bands at right).

The energies of the photons emitted during *conventional luminescence* range from about 1 ev ($1.24 = 10^{-4}$ cm $= 12{,}400$ Å) to 10 ev (0.124×10^{-4} cm $= 1{,}240$ Å), while the energies of emitted X-ray and gamma-ray luminescence photons extend well beyond this range up to about 10^7 ev. This article is concerned chiefly with the conventional visible and near-visible luminescence of solids, which generally involves transitions of the outer or valence electrons comprising the "skins" of atoms. These exposed electrons are sensitive to changes in the kind, number, spacing, and arrangement of neighboring atoms in a solid, and the luminescence of solids is thus a sensitive indicator of changes in composition, impurities or other imperfections, and crystal structure. Also, the valence electrons of an atom in a solid experience most strongly the jostling caused by thermal motion of atoms, so that increasing the temperature of the solid generally perturbs the luminescence process and increases the probability of conversion of high-energy excitation quanta into low-energy thermal quanta (phonons).

With respect to the duration of luminescence, *fluorescence* indicates a normal, unconstrained, spontaneous radiative return from the excited state (as in isolated nonmetastable atoms or ions), whereas *phosphorescence* indicates an abnormally long delay between excitation and emission, using *isolated* atoms or ions as standards of normal behavior. Fluorescence, then, is a limiting case of phosphorescence and corresponds to a natural excited-state lifetime, τ_F, of about 10^{-8} or 10^{-9} second for the nonmetastable excited states of isolated atoms or ions undergoing the optical transitions which occur in conventional luminescence. The natural lifetimes of isolated atoms are determined chiefly by oscillator damping (classically, $\tau_F \propto \nu^{-3} p_d^{-2}$ for radiation of photons of frequency ν from a dipole with moment p_d), and the width of a fluorescence emission *line* is determined by the indeterminacy of the excited-state energy level, ΔE^*, such that $\Delta E^* \geqq h/\pi\tau_F$, where $h = 6.62 \times 10^{-27}$ erg sec. This line width is only about 10^{-7} ev for conventional fluorescence with $\tau_F \approx 10^{-8}$ second, whereas many phosphors have emission bands nearly 1-ev wide and their emissions persist for seconds or days (*i.e.*, the band widths and persistences of phosphors are often unrelated). Most phosphors exhibit predominantly an abnormally delayed emission, which is called phosphorescence. Here, the abnormal delay may be caused by (1) the strong perturbing (constraining) influence of neighboring atoms on excited centers in solids, and/or (2) internal ionization and trapping. *Internal ionization* is the ejection of an electron from an excited atom or center, without the electron's leaving the solid. The vagrant excited electron may become trapped, particularly near imperfections in the crystal, and remain trapped for an indefinite time before being released by heat or other energy so that it can again wander to make a radiative recombination with an ionized center.

In general, phosphors begin to emit luminescence photons within 10^{-8} second after onset of excitation, but very often much of the excitation energy is stored in the form of prolonged (constrained) excited states or trapped excited electrons so that photon emission is extended for intervals ranging from a few seconds to a few years after cessation of excitation, the duration of phosphorescence depending on the nature of the phosphor and its conditions of excitation and operation. When a large proportion of the excitation energy is stored, the curve of luminescence output *vs.* time exhibits a detectable *growth* (Fig. 2) until equilibrium is established, *i.e.,* until the rate of filling and emptying of excited states and traps has stabilized in the excited volume of the solid. After cessation of excitation, there is a *decay* of luminescence output *vs.* time as the stored excitation energy is released. When there is simple excitation, without internal ionization and trapping, the rate of emission of luminescence photons, L, decreases exponentially with time, t, according to $L = L_0\epsilon^{-\alpha t}$, where L_0 is the luminescence output at cessation of excitation and the decay constant α $(=\tau^{-1})$ ranges from about 10^7 to 1 sec^{-1}, depending on the composition and structure of the phosphor. It is to be expected that τ will be larger and, hence, α will be smaller the more constraint an excited emitting atom or center experiences from its neighbors in the crystal, but the emitter itself is a primary factor in determining τ. In this case, the spontaneous *exponential decay* is little affected by changes in the temperature of the phosphor or the conditions of excitation.

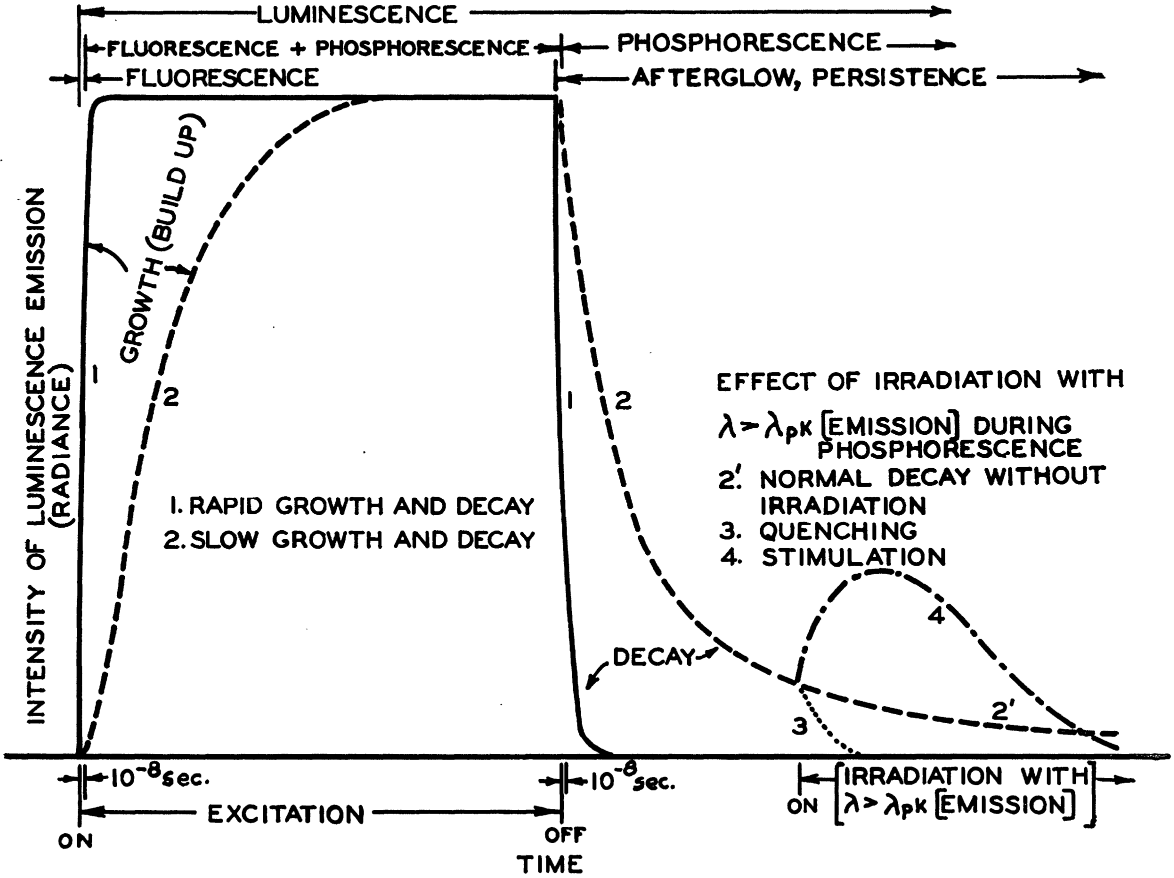


FIG. 2. Diagrammatic representation of the dynamics (growth and decay) and terminology of luminescence emission.

The emitting center loses control over τ when the energy storage in phosphors consists of trapped excited electrons or metastable states, for then additional *activation energy* must be supplied to release the trapped electrons. This activation energy may be supplied by heat, especially when the trap depth is equal to or less than about 30 kT (where $k = 1.38 \times 10^{-16}$ erg deg^{-1} $= 8.7 \times 10^{-5}$ ev deg^{-1}), or it may be supplied by additional photons or charged material particles. During ordinary phosphorescence at room temperature the activation energy is supplied by heat, so this process is thermostimulated phosphorescence. Under these conditions, so-called *power-law decays* are observed such that $L \propto L_0 t^{-n}$, where the exponent n is strongly dependent on the phosphor temperature and on the kind, intensity, and duration of excitation; also, n varies during the decay interval. In general, n has values lying between about 0.1 and 2, being near unity for most of the useful phosphorescence times of efficient long-persistent phosphors. The variability of *n* bespeaks the variable degree of filling and rate of emptying of traps of different densities and depths, and the variable occurrence of retrapping, since the density of excitation decreases in a roughly exponential manner as the beam of primary excitant particles penetrates into a phosphor crystal.

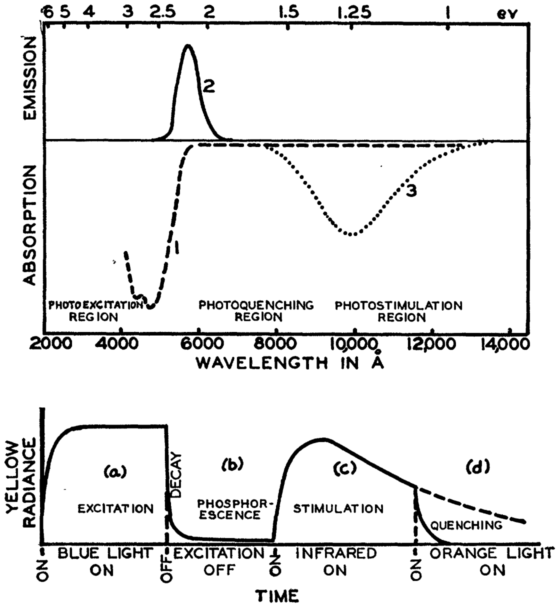


FIG. 3. *Above*: Spectral distributions of excitation, quenching, and stimulation for a cub.-Sr(S : Se) : $SrSO_4$: CaF_2 : Sm : Eu phosphor. *Below*: Dynamics of growth and decay of the above phosphor during and after (a) excitation, (b) decay, (c) stimulation, and (d) quenching.

Infrared is another useful source of activation energy which may (1) be unabsorbed (*i.e.*, be entirely reflected or transmitted) and hence cause no change in the normal decay curve shown as 2′ in Fig. 2, or (2) be absorbed and *quench* the phosphorescence emission, as shown in curve 3 of Fig. 2, or (3) be absorbed and *stimulate* the phosphorescence emission, as shown in curve 4 of Fig. 2. Because the quenching and stimulating effects for a given phosphor vary with wavelength, a broad-band source of red and infrared may act as both a quenching and stimulating agent simultaneously. The top portion of Fig. 3 shows the spectral relationships of excitation, emission, quenching, and stimulation for a complex infrared-stimulable phosphor of the type used in metascopes for infrared detection and signalling. The bottom portion of Fig. 3 shows how the yellow emission band may be produced by excitation with blue light ($\approx$ 4,500 Å), allowed to decay, stimulated by infrared ($\approx$ 10,000 Å), and quenched by orange light ($\approx$ 6,000 Å).

The complex chemical formula (which is really an oversimplification!) for the infrared-stimulable phosphor of Fig. 3 serves as an extreme example of the system of notation used in symbolizing luminescent solids. The chief ingredients of a good phosphor are the host crystal, one or more fluxes (fusible salts, which are not always used), and one or more activators (promoters of luminescence) which may be added deliberately or be induced by decomposition during crystallization at high temperatures. Examples of other useful phosphors and their notations are given in Table 1. According to the indicated simplified notation, a phosphor is symbolized by (1) the crystal system of the host crystal, followed by (2) the chemical formula of the host crystal, then by (3) any fluxes which are *incorporated* in the host crystal (this is not the case in examples 1–3 of Table 1), and finally by (4) the chemical identity of the activator *cation* [placed in square brackets when there is uncertainty as to its identity or presence] with the weight percent of activator cation relative to the weight of the host crystal given in parentheses.

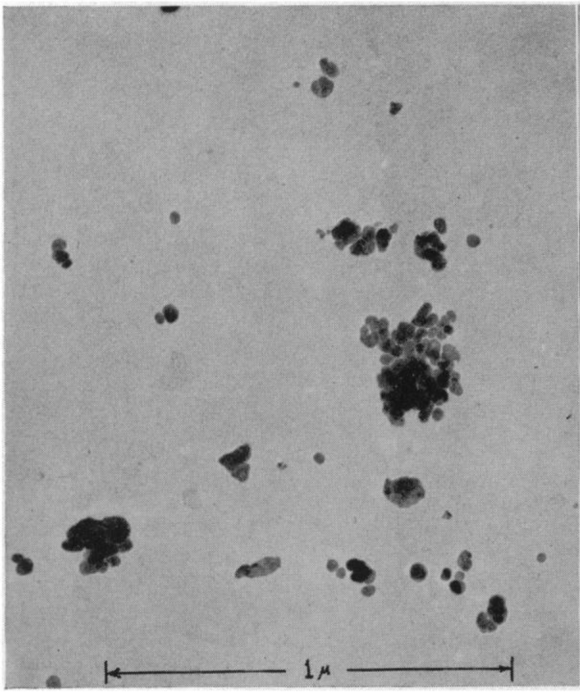
TABLE 1

COMPOSITIONS, PREPARATIONS, AND DESIGNATIONS OF SOME TYPICAL PHOSPHORS

No.	Ingredients			Cryst. temp.	Post-cryst. treatment	Phosphor notation	Decay type
	Host crystal	Flux	Added activator				
1.	1 ZnS (*i.e.*, 97.44 g ZnS)	2 g NaCl	......	1250° C	wash	hex.-ZnS : [Zn]	t^{-n}
2.	1 ZnS	2 g NaCl	0.017 g $AgNO_3$	"	"	hex.-ZnS : Ag (0.01)	"
3.	1 ZnS	2 g NaCl	0.013 g $CuCl_2$	"	"	hex.-ZnS : Cu (0.01)	"
4.	2 ZnO + 1 SiO_2 (162.76 g + 60.06 g)	....	......	"	...	rbhdl.-Zn_2SiO_4 : [Si]	$\varepsilon^{-at} \longrightarrow t^{-n}$
5.	2 ZnO + 1.02 SiO_2 (162.76 g + 61.26 g)	....	0.02 TiO_2 (1.6 g)	"	...	rbhdl.-Zn_2SiO_4 : Ti (0.4)	"
6.	2 ZnO + 1.012 SiO_2 (162.76 g + 60.78 g)	....	0.012 MnO (1.1 g)	"	...	rbhdl.-Zn_2SiO_4 : Mn (0.3)	"

EXEMPLARY SYNTHESES OF PHOSPHORS

The phosphor compositions given in Table 1 are sufficient to prepare efficient phosphors *if* exceptionally *pure ingredients* are used (especially when the optimum activator proportion is low), the ingredients are *thoroughly mixed,* and the mixtures, in acid-cleaned, covered, fused-silica crucibles, are *heated* in air to the indicated temperatures for ten to a hundred minutes. These examples are typical of the formation of most phosphors by reactions in the solid state, *i.e.,* reactions between solids at temperatures below their melting points and the melting points of their products. (Growth of phosphor crystals from melts is seldom successful because the melting points of the host crystals are usually so high that the melts react vigorously with their containers and the mixtures tend to decompose and volatilize selectively.) Under these conditions of solid-state reaction, the presence of a flux, such as sodium chloride, sometimes promotes crystallization by providing a fluid phase to facilitate material transport. Fig. 4a shows an electron micrograph of a pure, practically nonluminescent, precipitated-and-dried zinc sulphide, which was used as the initial ingredient in preparing phosphors 1–3 of Table 1. Fig. 4b shows a photomicrograph of the much larger phosphor crystals produced by heating this fine zinc sulphide (with flux) to 1,250° C. These hex.-ZnS: Ag(0.015) phosphor crystals are about 10^8 times larger (in volume and weight) than the initial 250-Å ingredient particles. In the case of the zinc-silicate phosphors, no flux is used, and the average particle size of the resultant phosphor is determined largely by the particle size of the initial silica, because the reaction proceeds by diffusion of the zinc and manganese oxides into the silica particles. This is illustrated in Fig. 5, which shows electron micrographs of two different lots of rbhdl.-Zn_2SiO_4: Mn(0.3) prepared from (a) exceptionally fine colloidal silica, and (b) an ordinary c.p. silica. (The electron micrographs in Figs. 4 and 5 were made by Dr. J. Hillier.)



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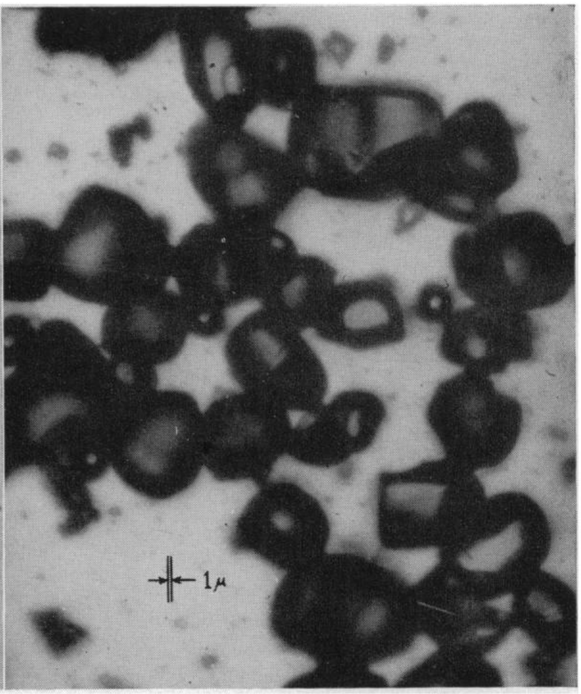

b

FIG. 4a. Electron micrograph of precipitated-and-dried luminescence-pure zinc sulphide.

FIG. 4b. Photomicrograph of hex.-ZnS: Ag(0.015), prepared by heating the fine-particle ZnS shown in Fig. 4a (with activator and about 6-percent halide flux) at 1,250° C.

As may be seen from Figs. 4 and 5, the average particle sizes of useful phosphors are generally a few microns or less, because finely divided ingredients must be used to obtain complete solid-state reaction in a reasonably short time. The small particle size of phosphors is desirable to increase the absorption of primary ultraviolet in "fluorescent" lamps, and to improve the image definition and optical efficiency of television cathode-ray-tube screens, but it makes difficult the determination of certain fundamental physical characteristics such as absorption spectra, absorption coefficients, and conductivities. It is in only a few cases, such as cub.-KCl: Tl, rbhdl.-Al_2O_3: Cr (artificial ruby), and tetr.-$CaWO_4$: [W] (artificial scheelite), that efficient luminescent crystals of centimeter size have been prepared from their melts. Insofar as the effect of crystal size on luminescence is concerned, the luminescence of phosphors is a *volume* effect, as evidenced by the fact that (1) cathodoluminescence efficiency increases as the penetration of the primary electrons increases, and (2) the two different lots of rbhdl.-Zn_2SiO_4 : Mn(0.3) phosphor shown in Fig. 5 have practically the same efficiency of cathodoluminescence and photoluminescence despite the great difference in their particle sizes.

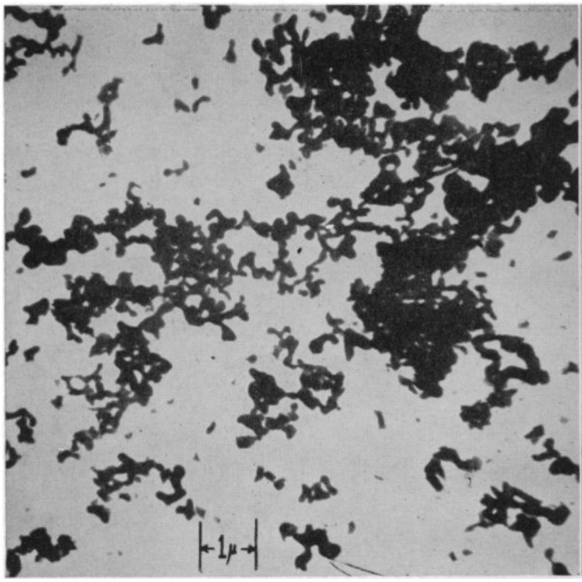

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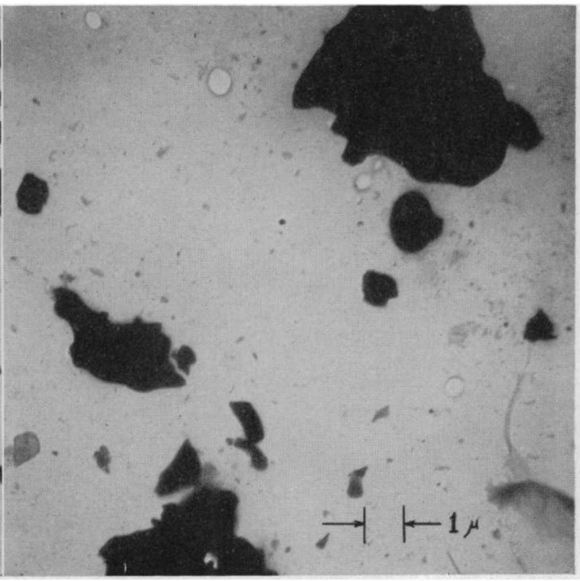
FIG. 5a. Electron micrograph of very-fine-particle rbhdl.-Zn_2SiO_4 : Mn which was prepared by reaction of zinc hydroxide and manganese hydroxide with colloidal silica.



b

FIG. 5b. Electron micrograph of commercial rbhdl.-Zn_2SiO_4 : Mn prepared by reaction of the oxides, using conventional pure silica with an average particle size of about one micron.

EFFECTS PRODUCED BY IMPURITIES

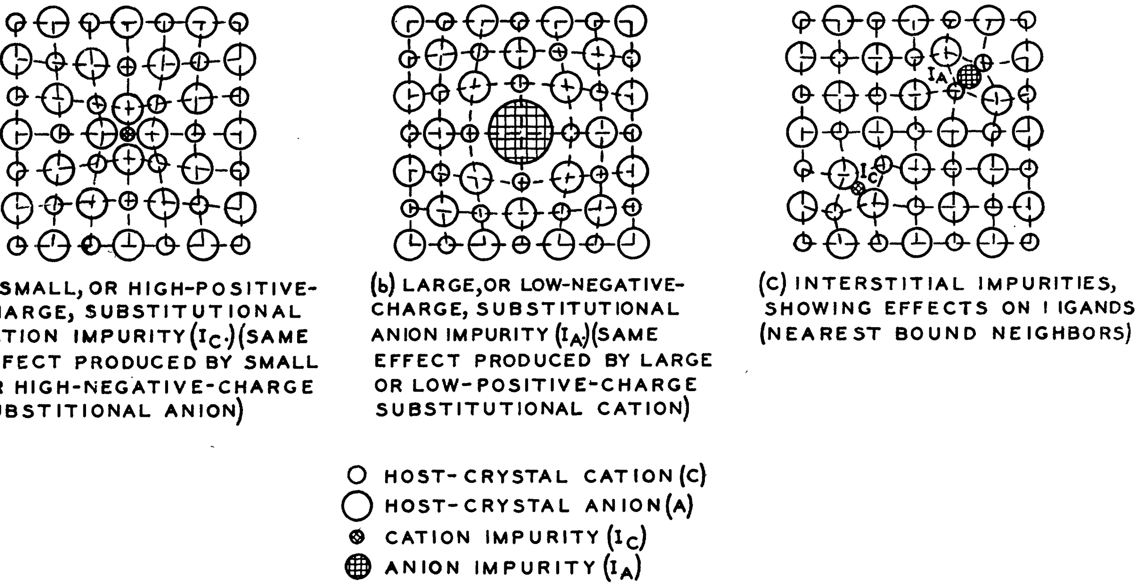
In general, phosphors consist of relatively nonluminescent host crystals containing a small proportion of added or induced impurities. Impurities can form many different local distorted regions (*e.g.*, centers), as depicted in Fig. 6, and a given impurity may: (1) act as an *intensifier activator* by intensifying a weak or latent host-crystal emission spectrum, (2) act as an *originative activator* by producing a new emission spectrum, (3) act as a *sensitizer* by producing a new excitation spectrum without altering the emission spectrum, (4) act as a *trap* by altering the duration and intensity of power-law-type phosphorescence, and (5) act as a *"poison"* (or "killer") by decreasing luminescence efficiency.

These examples illustrate these effects and show how a given impurity may function in several of the following roles.

(1) When very pure zinc silicate is crystallized at 1,250° C, the product is found to have an inefficient cathodoluminescence emission shown as curve 4 in Fig. 7. This emission comes from some of the excited tetrahedral SiO_4 groups which are presumably perturbed by a slight excess of silicon [Si] (or [Zn]?) produced by selective volatilization of oxygen. Here the [Si] acts as an *intensifier activator,* probably by upsetting the selection rules which govern electronic transitions in ideal crystals. When about a percent of titania is incorporated in this phosphor, the same emission band is obtained with about a tenfold increase in efficiency (cf. curve 5, Fig. 7). Here, the titanium (in the combined form!) is an additional intensifier activator. In the same way, silver appears to act as an intensifier activator for zinc-sulphide phosphors, operating to increase the efficiency with only a slight shift and narrowing of the emission band (curves 1 and 2, Fig. 7).

(2) When rbhdl.-Zn_2SiO_4 : [Si] is reheated at 1,250° C with increasing proportions of manganese oxide, the [Si] emission band decreases and a new emission band rises in the green until, at about one percent Mn, only the strong green emission is evident (curve 6, Fig. 7). Here, the Mn (which substitutes for Zn) acts as a *poison* in preventing the [Si] emission, and simultaneously acts as an *originative activator* in producing the new centers which emit luminescence photons with high efficiency. Similarly,

copper activator poisons the blue [Zn] emission band of hex.-ZnS: [Zn] while producing a new green emission band (curve 3, Fig. 7). Present evidence indicates that the best originative activators are added ions, which exhibit more than one formal valence (*e.g.,* Mn^{++}, Mn^{++++} and Cu^{+}, Cu^{++}), whereas intensifier activators may be either added or induced, and need not be multivalent (*e.g.,* [Zn^{++}], [Si^{++++}]; Ti^{+++}, Ti^{++++}; and Ag^{+}, Ag^{++}).


(a) SMALL, OR HIGH-POSITIVE-CHARGE, SUBSTITUTIONAL CATION IMPURITY (I_C) (SAME EFFECT PRODUCED BY SMALL OR HIGH-NEGATIVE-CHARGE SUBSTITIONAL ANION)

(b) LARGE, OR LOW-NEGATIVE-CHARGE, SUBSTITUTIONAL ANION IMPURITY (I_A) (SAME EFFECT PRODUCED BY LARGE OR LOW-POSITIVE-CHARGE SUBSTITUTIONAL CATION)

(c) INTERSTITIAL IMPURITIES, SHOWING EFFECTS ON LIGANDS (NEAREST BOUND NEIGHBORS)

FIG. 6. Examples of typical distortions produced by impurities in host crystals.

(3) When calcium carbonate or calcium silicate is crystallized with about one percent of manganese activator, the phosphors are found to have efficient red-orange cathodoluminescence, but no appreciable photoluminescence under 2,537-Å ultraviolet. If, however, these phosphors are recrystallized with a small proportion of lead oxide in addition to the added manganese oxide, then the same red-orange emission is obtained as before and the phosphors are now readily excited by 2,537-Å ultraviolet. Here the (combined) lead acts as a *sensitizer* which introduces a new absorption band in the spectral region around 2,537 Å.

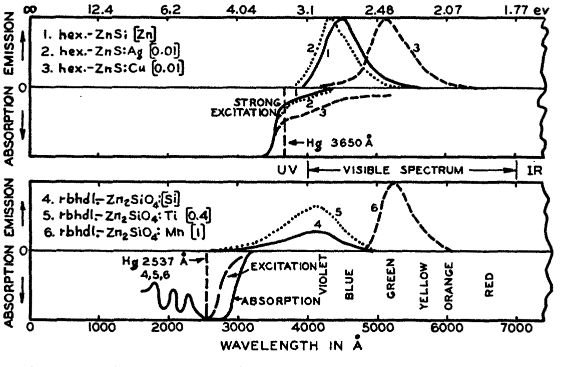


FIG. 7. Spectral distribution of absorption, excitation, and luminescence emission of some typical zinc-sulphide-type and zinc-silicate-type phosphors.

(4) In the previous example of hex.-ZnS: Cu, the multivalent Cu acts not only as a poison and an activator but also as a *trapping agent.* This is evidenced by intense and prolonged phosphorescence at room temperature and by pronounced glow curves (curves of light output *vs.* temperature and time as a phosphor previously excited at very low temperatures is warmed). By incorporating a lead compound in this phosphor, it is found that the lead provides very deep traps, such that the phosphor performs in the same manner as the infrared-stimulable material in Fig. 3. In the case of rbhdl.-Zn_2SiO_4: Mn, it has been found that tin and arsenic compounds are effective in providing traps without altering the emission spectrum of the phosphor.

(5) In addition to the previous examples of poisons, it may be mentioned that manganese in trace amounts is a strong *poison* to the emission of calcium-tungstate phosphors. Also, certain other transition elements, particularly iron and cobalt, are strong poisons in almost all phosphors.

EFFECTS PRODUCED BY CHANGES IN STRUCTURE

The pronounced influence of structural changes on the luminescence of solids is shown in the following examples:

(1) When rbhdl.-Zn_2SiO_4: Mn (denoted as the α-form) is melted at 1,600° C and then quenched, it

crystallizes in a new (β-form; undetermined) structure having a different diffraction pattern. On comparing the α and β products, it is found that: (1) the emission band of the α-form peaks at 5,250 Å, whereas the emission band of the β-form peaks at 5,630 Å; (2) the β-form has about 75 percent of the cathodoluminescence and photoluminescence efficiency of the α-form; and (3) the α- and β-forms have practically identical exponential decay characteristics. On heating the yellow-emitting β-form to about 950° C, it reverts to the green-emitting α-form, demonstrating that the observed effects are caused by changes in structure rather than composition.

(2) When ZnS: [NaCl(2)]: Ag(0.01) is heated at 780° C it crystallizes in the cubic system, whereas on heating at 1,200° C it crystallizes in the hexagonal system. On comparing these two products, it is found that: (1) the emission band of the cubic material peaks at 4,480 Å, whereas the emission band of the hexagonal material peaks at 4,330 Å; (2) the hexagonal material has about four times the peak output of both cathodo- and photoluminescence relative to the cubic material; and (3) although both materials have power-law decays, the intensity and duration of phosphorescence emission of the hexagonal material is much greater than that of the cubic material at room temperature. On grinding, the hexagonal crystals are transformed into the cubic structure.

Luminescence Excitation

When a beam of primary excitant particles impinges upon a phosphor crystal, some particles are reflected, whereas others are transmitted into the interior of the crystal. The energy of a transmitted primary *photon* is absorbed all at once or not at all (neglecting Compton scattering) in one absorption act wherein the photon is annihilated. The energy of a fast primary *electron or ion*, on the other hand, is usually absorbed bit-wise, where the average energy bit is about 25 ev. Differences in excitation processes are evident, also, with respect to *where* the energy is absorbed in a phosphor crystal. Low-energy primary ultraviolet photons often excite phosphor centers directly, because the centers generally have lower characteristic frequencies than the atoms of the host crystal. High-energy primary particles (*e.g.*, X-ray and gamma-ray photons, and fast electrons and ions), however, give up their energies indiscriminately, so that most of their energy is absorbed by the preponderant host-crystal atoms. In this case, the absorbed energy must be transported to the centers and the efficiency of such energy transport depends strongly on the degree of perfection of the crystal. Hence, there are many photoluminescent glasses and crystals with high efficiency, but only highly crystalline phosphors give high efficiency of roentgenoluminescence, cathodoluminescence, and ionoluminescence. The high rate of degradation (into heat) of energy transported in vitreous matter accounts, also, for the fact that only crystalline phosphors give efficient, long-persistent, power-law-decay phosphorescence involving wandering and remote trapping of excited electrons.

It is probable that most of the energy transport in phosphors is by excited "free" electrons, although other means are: positive holes, excitons, photons, and exchange-type energy transfers which occur when the wave functions of atoms and centers overlaps in a suitable manner. Positive holes are residual regions of excess positive charge produced by internal ionization, and excitons are mobile pairs of positive holes and nearly-"free" excited electrons. The problems of energy transport in solids are complicated by the interplay of ionic (electrostatic) and covalent (shared-electron) bonding between the atoms, and by the pronounced influences of imperfections and different structural arrangements in crystals.

Luminescence Mechanism

For lack of specific information about the energy levels in phosphors, two complementary types of simplified energy-level diagrams have been devised to give a generalized picture of the mechanism of luminescence. One such diagram, shown in Fig. 8, depicts the allowed potential energies of a *luminescence center* as a function of averaged interatomic spacing, $\bar{x}$, where $\bar{x}_0$ is the averaged spacing between the atoms

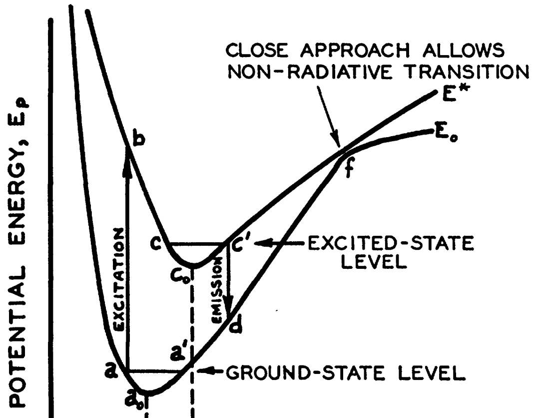


FIG. 8. Configuration-coordinate energy-level diagram of a phosphor impurity center, where the potential energy of the center is plotted as a function of the *average* distance between the atoms in the center.

of the unexcited center at equilibrium. At 0°K, the ground-state energy level would be very near a_0, corresponding to minimum potential energy and minimum atomic vibration. At room temperature, however, the system (center) has considerable vibrational energy, so the ground-state level lies higher, such as at a, where the amplitude of atomic vibration is proportional to a'-a (imagine the system passing through a_0 as it rolls from a to a' and back, in the potential well). When a bit of excitation energy of adequate magnitude, usually greater than 2 ev, is transmitted to the center, the energy of the center may be raised from a on the ground-state curve, E_0, to b on the excited-state curve, E^*. Within about 10^{-12} second after excitation, the atoms of the excited center readjust to a new equilibrium spacing, $\bar{x}^*$, and the energy difference b-c is given up as heat to the surrounding host crystal. With the center in the excited-state level c, the probability of a radiative transition from c' to d is determined by the natures of the impurity and host crystal, being practically independent of temperature, but the probability of a nonradiative transition to the ground state via $c' \rightarrow f \rightarrow a$ increases exponentially with temperature. Here, then, the observed phosphorescence for this luminescence without internal ionization is practically independent of the temperature when $kT << \Delta E$, or of the kind, duration, and intensity of excitation; and the decay proceeds according to

$$L = L_0 \epsilon^{-(\alpha + \nu_a \epsilon^{-\Delta E/kT})t}$$

where the atomic vibration frequency, ν_a, is about 10^{12} sec^{-1}, and the thermal activation energy, ΔE, is the energy difference $f - c_0$. The observed decrease of luminescence efficiency with increasing temperature may be visualized as a raising of level c so that an increasing proportion of excited states "spill over" via f without producing radiation. If, at any given temperature, the levels c and f practically coincide, then the center is a *poison* in that it is a means for rapidly degrading excitation energy into heat. This picture, then, illustrates how a center which produces luminescence at low temperatures may be a poison center at higher temperatures. The number of available efficient phosphors decreases rapidly with increasing operating temperature, with hardly any phosphors having useful efficiencies above 400° C. In general, phosphors should be operated at as low temperatures as possible, although some power-law-decay phosphors exhibit an intermediate optimum operating temperature where traps are efficiently emptied by thermal energy.

Another type of energy-level diagram, shown in Fig. 9, depicts the energy levels of a luminescence center as a function of distance along a row of atoms in the crystal. This type of diagram emphasizes the fact that the discrete energy levels of isolated atoms are spread out into bands in solids, the broadening being caused by interaction of the electrons of all the atoms in the crystal, because the Pauli exclusion principle allows only two electrons (of opposite spin) to occupy the same energy level in a given system. The diagram is drawn for a specific $\bar{x}$, so one must imagine that the spacings and potential barriers between the atoms change with every energy change of the center. According to the diagram, the impurity atom, I_C: (1) lowers the normal potential barriers between the host-crystal atoms in its vicinity, (2) introduces an additional occupied level, E_I, into the forbidden zone of host-crystal energies, and (3) introduces additional discrete unoccupied excited-state levels, $E^*_{I_n}$, whose extensions into the surrounding crystal increase as $E^*_{I_n}$ increases until, in the conduction band, E^*_C, an excited electron is free to move through the host crystal. The excitation transition $E_I \rightarrow E^{**}_{I_1}$ in Fig. 9 corresponds to $a \rightarrow b$ in Fig. 8, and the radiative return $E^*_{I_1} \rightarrow E^*_I$ corresponds to $c' \rightarrow d$. As drawn, this process is highly localized, and the spontaneous decay is exponential. When the low-lying, highly localized excited state, $E^*_{I_1}$, is absent, and the center is excited to higher levels wherein the excited electron may wander some distance away from its parent atom, then the electron may become trapped at a distant point, where it must be released by an additional activation energy before it can return to make a radiative transition from a low-lying $E^*_{I_n}$ level. When the excited electron travels through the conduction band, E_C, it may be trapped by a remote unexcited center, forming a new filled level (*e.g.*, E_{I^-}). This type of trapping is most probable when the impurity is a multivalent ion; for example, a Sm^{+++} impurity can trap an extra electron to become Sm^{++}. Regardless of whether the excited electron is trapped in a metastable state in its center of origin or in a remote center, the phosphorescence is strongly dependent on temperature and on the kind, duration, and intensity of excitation. The complex decay then proceeds by thermally activated release of trapped electrons according to

$$L = L_{0_1} \epsilon^{-\nu_{a_1} t \epsilon^{-\Delta E_1/kT}} + L_{0_2} \epsilon^{-\nu_{a_2} t \epsilon^{-\Delta E_2/kT}} \cdots + L_{0_N} \epsilon^{-\nu_{a_N} t \epsilon^{-\Delta E_N/kT}}$$

where the subscripts *1, 2, 3* $\cdots$ N denote traps of different densities and depths ΔE_1, ΔE_2, ΔE_3, $\ldots$ ΔE_N which make different contributions L_{0_1}, L_{0_2}, L_{0_3}, $\ldots$, L_{0_N} to the luminescence output at time $t = 0$. This lengthy expression is usually shorthanded by the power-law-decay *approximation* $L = L_0 t^{-n}$, since, as previously noted, *n* varies not only with the type of phosphor, but with the temperature, decay time, and conditions of operation. Both exponential and power-law decays can occur, without change in spectral distribution, by exciting a center such as the one generalized in Fig. 9 to $E_{I_1}^{**}$ and higher levels, as long as the final radiative transitions take place from $E_{I_1}^{*}$ to E_I^*. Almost all phosphors which exhibit initial exponential decays eventually trail off into power-law "tails" which bespeak the delayed returns of distant trapped electrons that make the same final radiative transition as do the highly localized untrapped excited electrons responsible for the predominant exponential decay. As is to be expected from Fig. 9, electronic conduction parallels the growth and decay of many power-law-decay phosphors, whereas little or no conduction is observed when the decay is predominantly exponential.

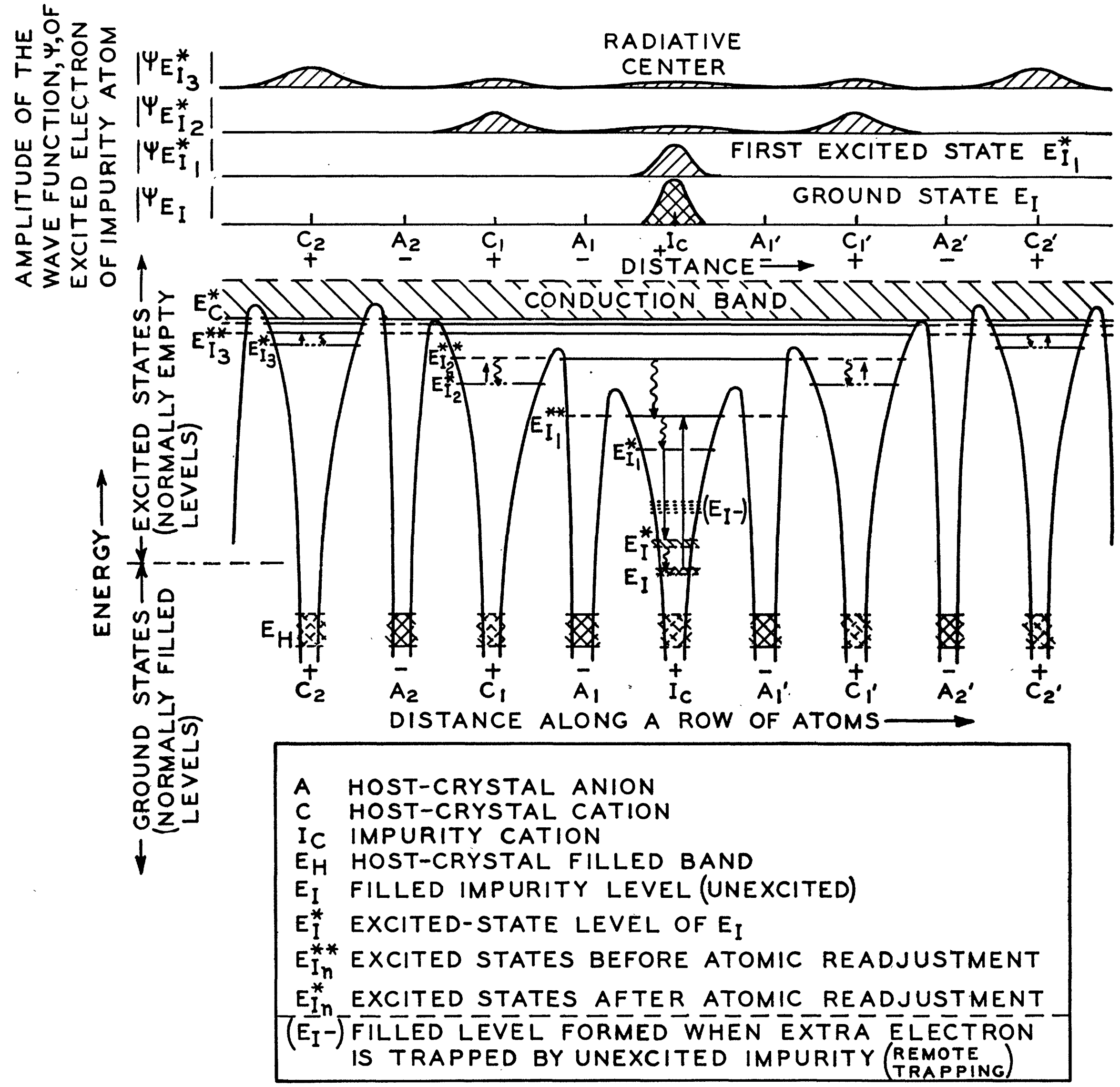


FIG. 9. Energy-level diagram of a row of atoms in a phosphor impurity center. The lower part of the figure shows the lowering of the potential barriers in the neighborhood of the impurity, and the relatively discrete occupied and excited-state energy levels introduced by the impurity. The upper part of the figure shows a plot of the absolute value of the wave function, ψ, of the optical electron responsible for luminescence (ψ^2 is a measure of the probability of finding the electron in a given location). The breadths of the excited-state levels increase with height and so the upper levels may overlap each other and the conduction band.

Stimulation of phosphorescence by low-energy (long-wavelength) photons, as in Fig. 3, is readily understood by picturing the weak photons as having just enough energy to raise trapped electrons out of their traps so they can make radiative recombinations with the parent ionized centers. Quenching of phosphorescence by higher-energy photons, however, apparently involves exciting the system to a high-energy level near or above f in Fig. 8, *i.e.,* the trapped excited electron is raised so high in energy that the surrounding atoms are set in violent agitation and the excitation energy is dissipated as heat.

LUMINESCENCE EMISSION SPECTRA

Both line and band emission spectra may be produced separately or simultaneously by phosphors. Line spectra are obtained when radiative transitions take place between discrete highly localized energy levels. Such discrete levels often occur when well-oxidized impurity ions with incomplete inner shells (*e.g.,* Eu^{+++} and Cr^{+++}) form luminescence centers. For example, $ThSiO_4:Eu(1)$, crystallized at 1,250° C in oxygen, gives a line emission spectrum attributable to electrons with unpaired spins in the *inner,* well-shielded, incomplete 4f shell of Eu^{+++} making transitions between discrete subatomic levels having different resultant spin quantum numbers. When this phosphor is heated in a reducing atmosphere, however, the unpaired 4f-shell spins are apparently paired and a band emission is obtained in place of the previous line emission. The band emission is attributed to the *outer* valence electrons of Eu^{++} making transitions between levels having different principal and angular-momentum quantum numbers (where at least one of the levels is a band).

The chemical and structural constitutions of phosphors determine, of course, the locations and breadths of their emission lines and bands. Of about 10^5 different samples of artificial inorganic phosphors that have been synthesized here and abroad, the most useful phosphors have band widths of the order of 0.7 ev, although lines narrower than 10^{-3} ev and bands broader than 2ev have been obtained in some cases. Empirical methods for controlling the locations of emission bands in almost any part of the visible and near-visible spectrum have been developed for several efficient phosphor families where variations in host-crystal composition, in particular, afford excellent control over the properties of the resultant phosphors. For example, increasing partial substitution of cadmium for zinc (or selenium for sulphur) in any of the three zinc-sulphide phosphors shown in Fig. 7 gradually shifts the emission spectrum toward the infrared. At present, the white-emitting luminescent screens of direct-viewing television cathode-ray tubes are made of a mixture of blue-emitting hex.-$ZnS:Ag(0.01)$ and complementary yellow-emitting hex.-$1.3ZnS \cdot CdS:Ag(0.01)$. (The latter phosphor is also useful for X-ray fluoroscope screens.) Similarly, luminescent screens for direct-viewing color television may be obtained by selecting appropriate blue-, green-, and red-emitting members of this phosphor family. In the case of the outstandingly useful phosphor family based on rbhdl.-$Zn_2SiO_4:Mn(1)$, increasing substitution of germanium for silicon produces a gradual shift of the emission band toward the red, but when beryllium is substituted in increasing proportions for the zinc, the original green emission band peaked at 5,250 Å decreases and a new orange-red emission band rises at 6,300 Å. The high activator proportions of silicate phosphors make them particularly useful for operation under conditions of intense excitation. For example, the three different luminescent screens for the three (trinoscope) cathode-ray tubes used in laboratory demonstrations of color television on a theatre scale may be made of blue-emitting rbhdl.-$Zn_2SiO_4:Ti(1)$, green-emitting rbhdl.-$Zn_2SiO_4:Mn(1)$, and red-emitting rbhdl.-$Zn_8BeSi_5O_{19}:Mn(2)$. White-emitting luminescent screens for "fluorescent" lamps are made either by mixing blue-emitting monocl.-$Mg_2WO_5:[W]$ with yellow-emitting rbhdl.-$(Zn:Be)_2SiO_4:Mn$, or by using a cadmium (or calcium)-fluoro (chloro)-phosphate: Mn: Sb phosphor whose two different activators produce two complementary emission bands. It may be noted that the influence of new host-crystal atoms should depend not only on the nature of the new atom, but also on whether the new atom becomes an immediate neighbor or just a near neighbor of the emitting atom or center, and whether the luminescent center is founded on a substitutional or interstitial impurity.

LUMINESCENCE EFFICIENCY

When phosphors are excited by low-energy photons (*photoluminescence*), quantum efficiencies exceeding 90 percent have sometimes been obtained. For example, the phosphor coating of a green-emitting "fluorescent" lamp converts over 90 percent of the input 2,537-Å (4.9-ev) primary photons into emitted luminescence photons having an average energy of about 2.4 ev (5,250 Å). On an energy basis, this luminescence process is $(2.4/4.9)90 \approx 45$ percent efficient. In some cases, the energies of the primary and emitted photons lie even closer together, so that the energy efficiency may be higher. It is rare, however, that the energy efficiency of photoluminescence of phosphors exceeds about 80 percent, because there is always some gap between the peaks of their excitation and emission bands (*cf.* Fig. 7). For a given average energy of the emitted photons $h\bar{\nu}_{em}$, the energy efficiency, $\mathcal{E}$, decreases with increasing energy of the excitant photons, $h\bar{\nu}_{ex}$; i.e., $\mathcal{E} \propto \bar{\nu}_{em}/\bar{\nu}_{ex}$. This is true until $\bar{v}_{ex}$ becomes large enough to produce internal photoelectrons with sufficient energy to produce in turn more than one luminescence photon. When this happens, as it does for excitation by X-rays and gamma-rays (*roentgenoluminescence*), the luminescence process is essentially cathodoluminescence.

When phosphors are excited by fast charged material particles (*cathodoluminescence* and *ionoluminescence*), the energy efficiency is vanishingly small for low primary-particle energies because slow particles dissipate their energies in the inefficient (distorted and chemically different) surface layers of the phosphor crystals. It is only in rare cases that detectable luminescence output can be obtained from phosphors excited by 5-ev primary electrons, and even at primary energies of thousands of volts the energy efficiency does not exceed about 10 percent. The low efficiency which obtains even when the primary particles penetrate well into the efficient volumes of phosphor crystals is attributed to the large difference between the absorbed energy bits (approximately 25-ev average) and the emitted photons (approximately 2.5-ev) and to the difficulties of energy transfer from the predominant host-crystal absorber atoms to the fewer activator centers.

LUMINESCENCE OUTPUT

The radiances of phosphors *during* excitation by photons are limited mostly by the low intensities of available photon sources. With available sources of ultraviolet, for example, the maximum luminances of visible-light-emitting phosphor screens are of the order of 5,000 millilamberts (mL), or about 2×10^{16} photons emitted per square centimeter per second. On the other hand, brief instantaneous luminances exceeding 10^7 mL (over 10^{20} photons cm^{-2} sec^{-1}) can be obtained from phosphor screens struck by a well-focused, high-voltage, scanning cathode-ray beam, although the sustained averaged luminance of such a scanned screen generally may not exceed about 10^5 mL (4×10^{17} photons cm^{-2} sec^{-1}) without heating the screen above the temperature range in which appreciable luminescence efficiency is obtained. (It may be recalled that fresh snow in full sunlight has a painful luminance of about 10^4 mL.) In a conventional direct-viewing television cathode-ray tube, producing 50 to 100 mL in the image highlights, a given screen element the size of the cathode-ray-beam area is excited for about 1.5×10^{-7} second, 30 times a second, for a summed duration of only 16 seconds of actual operation time per 1,000 hours of total operation time. On this basis alone, it seems odd that the efficiency of the screen should change somewhat during 1,000 hours elapsed (16 seconds actual) time of operation. During the actual operation time, however, the instantaneous power input into a screen element is about 10,000 volts $\times 2 \times 10^{-4}$ ampere/0.001 $cm^2 = 2000$ watts/cm^2. This power loading is almost ten times as high as the 250 watts/cm^2 absorbed power input (and radiated power output) of a tungsten filament in an ordinary incandescent lamp. In projection cathode-ray tubes, the power loadings may be several orders of magnitude higher than in direct-viewing cathode-ray tubes.

The radiances of phosphors *after* excitation are determined by their decay characteristics and light sums under the operating conditions. The *light sum* is the total radiance per unit area integrated over the entire afterglow interval. Integration of the decay curves of trap-type phosphors such as hex.-ZnS:Cu and cub.-Sr(S:Se):$SrSO_4$:CaF_2:Sm:Eu (taking into account the penetration of the primary particles) has shown that about 10^{18} potential photons/cm^3 may be stored in the excited volumes of some phosphor crystals under favorable conditions. This number is of the same order of magnitude as the number of Cu or Sm impurity centers in the cited phosphors, thus lending additional support to the idea that these impurities are the trapping agents. To a first approximation, the light sum is proportional to (1) the number of excitable centers and traps per unit volume, (2) the depth of penetration of the primary particles, and (3) the intensity and duration of the excitation (up to saturation).

The time interval in which the light sum is practically all released may be varied enormously by careful choice of phosphors and operating conditions. For example, (1) screens of hex.-ZnO:[Zn], cub.-MgS:Sb, and rhomb.-$BaSO_4$:Pb give up most of their stored luminescence energy in about 10^{-6} second in cathode-ray tubes used for flying-spot image pickup in television, (2) a cascade screen, wherein a cathodoluminescent blue-emitting hex.-ZnS:Ag phosphor excites a photoluminescent yellow-emitting hex.-9ZnS · CdS:Cu phosphor, emits about 0.03 mL 3 seconds after excitation in radar cathode-ray tubes, and has luminances which are detectable by the well-dark-adapted eye for many hours, and (3) screens of photoluminescent cub.-Sr(S:Se):$SrSO_4$:CaF_2:Sm:Eu retain most of their light sums for about six months at room temperature, thereby providing useful long-duration retentivity of information and infrared stimulability.

CONCLUDING REMARKS

Man-made phosphors, which were unimportant alchemical novelties during the 17th and 18th centuries, found their first important uses in the 19th century as visible indicators of certain invisible energetic particles, such as ultraviolet and x-ray photons, cathode rays, and alpha particles. In recent years of the 20th century, the *direct* conversion of the energies of these invisible particles into light, at operating temperatures near room temperature, has become a major commercial function of phosphors which are now produced at the rate of over 200,000 kilograms a year. Meanwhile, phosphors are finding increasing scientific use in detecting these invisible particles and others, including infrared and gamma-ray photons, fast-moving ions, and even neutrons, by converting their energies into radiations which the human eye may detect directly, or indirectly through other photosensitive devices, such as multiplier phototubes (usually coupled with oscilloscopes or meters), photographic films, or other phosphors used in cascade.

In addition to the practical progress already made by empirical phosphor research, some progress has been made toward developing a qualitative theory of luminescence of solids, although a useful quantitative theory is not yet available. Luminescence is such a convenient and sensitive indicator of changes of composition, structure, and atomic interactions in solids that it has contributed much to our improved understanding of the solid state of matter. In the future, the practical consequences of this broad aspect of luminescence research may well overshadow the tangible results already obtained.

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The Nature of the Organizer

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APPROXIMATELY TWENTY-FIVE YEARS AGO, Spemann and Hilde Mangold demonstrated that the dorsal lip of the blastopore acts as the primary organizer of the amphibian embryo after it is carried inside the gastrula to form a layer of chordamesoderm beneath the ectoderm. The contact thus established between these two layers results in an induction by the chordamesoderm (organizer) of nervous tissue in the overlying ectoderm. Since this discovery was made, an intensive search has been conducted for an explanation of both the stimulus and the response in this reaction. In terms of biochemistry and cellular physiology, however, the precise nature of embryonic induction still eludes us. It may be useful, nevertheless, to summarize the current ideas on the nature of the organizer.

First, let us consider the question of specificity of organizer action. Many studies have suggested that the inducing stimulus is nonspecific. It has been shown that amphibian ectoderm capable of response (competent) can be induced to form neural tissue by an array of inductors, some of which are: 1) living organizers from other vertebrate embryos; 2) extracts from whole embryos or parts of embryos; 3) tissues from the embryonic or adult bodies of many kinds of animals, providing the tissues are first killed by heat, drying, freezing, or treatment with organic solvents; 4) certain chemical compounds, such as cephalin, digitonin, and various polycyclic hydrocarbons; and 5) chemical or physical conditions that cytolyze some of the ectodermal cells with the release of toxic products evoking a neuralizing response in the surviving cells. Actually there may be no distinction between the last two categories.

Spemann (*11*) himself was finally inclined to the conclusion that the inducing stimulus is nonspecific and Holtfreter (*8*, p. 34) has recently taken this position, pointing out that neuralization of competent ectoderm "can be achieved by the application of various agents which have not more in common than the faculty of increasing the permeability of the cell membrane, and of causing cytolysis if applied in excess." If this interpretation is correct it follows that the factors for specificity of the reaction lie within the ectoderm.

On the other hand, there are studies which suggest that inductors are not qualitatively alike and that the specificity of induction does not reside entirely within the reacting system. Evidence supporting this interpretation includes the following points. 1) The results of experiments on regional determination indicate differences in the action of the organizer along the primary axis of the embryo. Thus, anteriormost mesoderm induces brain and sense organs, whereas more posterior levels induce spinal cord. 2) Dead