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"Survey of Methods used To Determine the Optical Properties of Phosphors"  
by W. B. Nottingham, 1949

SURVEY OF METHODS USED TO DETERMINE  
THE OPTICAL PROPERTIES OF PHOSPHORS

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RESEARCH LABORATORY OF ELECTRONICS  
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SURVEY OF METHODS USED TO DETERMINE THE OPTICAL PROPERTIES  
OF PHOSPHORS\*

W. B. Nottingham

Abstract

A brief review of the theory of phosphors is given in terms of the electron-band picture of impurity semiconductors in order to show the reasons for researches designed to obtain the optical properties of phosphors. The automatic spectroradiometer is described, since it is an instrument which yields so much information of value in phosphor research, development and quality control. Some problems of spectroradiometer standardization are discussed in detail, since the data obtained cannot be correctly explained by the I.C.I. system of color specification and interpretation unless satisfactory standards are maintained and used. A brief discussion is given of the application of the I.C.I. system to aid in the choice of phosphors required to produce a suitable "white" for television cathode-ray tubes. Other researches discussed include the determination of phosphor excitation curves, the emission of light as a function of temperature and of time, and the correlation of spectral excitation and absorption data.

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\* This paper is an abridged presentation of the invited paper given at the Meeting of the Optical Society of America, New York, March 10, 1949.

SOME OF THE METHODS USED IN DETERMINING THE PHYSICAL PROPERTIES  
OF THIN FILMS OF POLYMER

1. Introduction

The determination of certain physical properties of polymers in solution is of great importance in the study of their physical and chemical behavior. The methods used for this purpose are of two general types, those which are based on the measurement of the optical properties of the solution and those which are based on the measurement of the electrical properties of the solution. The optical methods are of two types, those which are based on the measurement of the refractive index of the solution and those which are based on the measurement of the optical density of the solution. The electrical methods are of two types, those which are based on the measurement of the conductivity of the solution and those which are based on the measurement of the dielectric constant of the solution.

The refractive index of a solution is a measure of the optical density of the solution and is a function of the concentration of the solution. The refractive index of a solution is a measure of the optical density of the solution and is a function of the concentration of the solution. The refractive index of a solution is a measure of the optical density of the solution and is a function of the concentration of the solution. The refractive index of a solution is a measure of the optical density of the solution and is a function of the concentration of the solution. The refractive index of a solution is a measure of the optical density of the solution and is a function of the concentration of the solution.

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# SURVEY OF METHODS USED TO DETERMINE THE OPTICAL PROPERTIES OF PHOSPHORS

## I. Introduction

The determination of certain optical properties of phosphors is motivated by three broad objectives: (1) research, (2) development, and (3) quality control. Despite the progress made during the past decade in the application of the electron-energy-band theory of solids to semiconductors and insulators, the systematic research needed to fill in the gaps in our knowledge of the experimental facts remains to be done. The development of new phosphors to fill specific practical needs, including such factors as efficiency, life under operating conditions, and specified spectral emission characteristics, will be aided by the satisfactory theoretical interpretation of new experimental research, while at the same time reliance will be given to the practical approach involving the systematic variation of impurities and processing techniques, with results evaluated largely by empirical methods. Even here, the theoretical explanations serve as a most useful guide to further empirical exploration. The need for the determination of certain optical properties of phosphors does not cease when a particular structure has been synthesized and a specific formula for production worked out. Constant vigilance is absolutely necessary as a means of quality control, because many of the most useful phosphor properties can be materially affected by the accidental introduction of undesired impurities in concentrations as small as a very few parts in a million.

Some pieces of optical equipment, particularly the spectroradiometer, are useful and, in fact, indispensable for research, development and control in the major industries which produce the unbelievably large quantities of phosphors now used in cathode-ray tubes and fluorescent lamps. The monochromator is also an important optical instrument used in both research on and development of phosphors, since a quantitative determination of excitation efficiency as a function of the wavelength of the radiation used to excite the phosphor is an important optical property.

The electron-multiplier type of phototube, now almost universally used as a means of quantitatively determining the radiant output of phosphors, has proven to be an indispensable accessory for a very large proportion of all measurements made in the past seven or eight years.

Optical observations made in studies of atomic and molecular excitation and radiant-energy emission involve the time history and the temperature conditions very indirectly as compared to the general case for phosphors. In the latter case, the time history of excitation, the time of observation and the temperature history during both excitation and observation are of

utmost importance and, in fact, serve as controllable variables through which the basic facts concerning the electron-band structure of the solid are exhibited.

## II. A Brief Review of the Theory of Phosphors

Nearly all practical phosphors are crystalline in structure and are very dependent on the presence and suitable disposition of selected impurities known generally as "activators". In certain types of phosphors, of which the silicates are typical, the activator fits into the lattice in a substitutional position for one of the atoms normally found in the basic crystal structure. Other phosphors, of which zinc sulphide is typical, require concentrations of activator which constitute a very small fraction of 1 per cent, since the necessary impurities take positions interstitially between the atoms of the crystalline substance. The outermost, or valence, electrons of a perfect crystal move from atom to atom throughout the crystal, even at extremely low temperatures. In spite of this freedom of motion, the application of small differences in potential to the crystal does not result in conductivity, because the electrons are so crowded into their only available quantum states that at low temperatures and with moderate electric fields the electrons cannot cross the energy gap, in which there are no available electronic energy levels, to find the greater freedom of motion associated with the higher "conduction" levels of the system. Support for this view of the electronic structure of insulators may be derived from experiments on the optical absorption of these crystals. If the energy ( $h\nu$ ) of the light quantum is insufficient to cause an electronic transition from an occupied to an unoccupied state, then the optical absorption of the crystal is small. Thus the measurement of the optical absorption of single crystals or even of polycrystalline material, when samples of uniform particle size and variable thickness may be used, serves to give direct information concerning the energy-level system of the phosphor.

The introduction of impurities into the crystal generally modifies, in a measurable way, the absorption characteristic of the material. This fact indicates the importance of the close coordination needed to relate the chemistry and production of phosphors to the optical-absorption characteristics of the substance.

By far the most common means of phosphor excitation depend either on the absorption of energy by the electrons from electromagnetic radiations in the visible or in the ultraviolet range of the spectrum or else on the absorption of energy which results from electron bombardment. Although many secondary effects are associated with phosphor excitation, the primary process involves the transfer of electrons from the stable valence-electron

band or from bound electrons located at impurity centers into normally unoccupied electronic levels of the conduction band. As a result of this transfer of the electron into a conduction band, a negative charge carrier becomes mobilized; in addition, the absence of an electron in the normally filled valence band is the equivalent of mobilizing a positive charge carrier or an "electron hole". The reverse process is the recombination of an electron with an electron hole and the simultaneous conversion of the potential energy thus temporarily stored into the radiant energy of a light quantum or into the vibrational energy of the neighboring atoms.

In many respects, the situation may be compared to the ionization of a gas in the plasma of a gas discharge. In the latter case, both the positive ions and the electrons are mobile and can maintain nearly equal volume concentrations, and yet free-space recombination is a relatively uncommon occurrence. If the ion becomes attached to an insulating wall, or if the electron becomes attached to an otherwise neutral atom or molecule, then recombination takes place very readily. A similar situation occurs in phosphors, and in other insulators and semiconductors. If the electron hole becomes trapped at an impurity atom, while the electron itself remains free, recombination is likely to occur. In a similar manner, electron holes which migrate to the surface of the crystal attract electrons and recombine with them there. Electrons may become trapped in other types of impurity centers but, nevertheless, recombination can take place because of the mobility of the holes. The last of the simple cases involves the trapping of both the holes and the electrons. A "metastable" situation is thus created, in which recombination is inhibited and becomes extremely temperature-sensitive, since it is by means of the absorption of temperature energy by the trapped electrons or holes that they are restored to mobility.

An investigation of spectral-emission data, interpreted in a manner thus briefly described, permits the observer to evaluate quantitatively the energy jump which the electron takes upon recombination. Since the energy jumps for a given transition in a particular phosphor are not exactly the same throughout the volume of the crystal, the radiant energy emitted is not confined to a narrow band of wavelengths, but spreads on each side of a most probable energy transition to create a relatively broad continuous set of emitted wavelengths. Thus the determination of the spectral-emission characteristic of a phosphor stands very high in the interests of all investigations, including research, development and quality control.

The lines of investigation which yield detailed information in support of the theoretical picture so far described include the determination of excitation efficiency as a function of the wavelength of the exciting radiation and as a function of the electron energy and current density used for



excitation. A quantitative determination of the influence of temperature on the light output and the time changes of light output can be interpreted to give quantitative data on the number and energy distribution of the trapping states. Simultaneous determination of the electrical conductivity of crystals during excitation yields valuable detailed material for analysis.

### III. Spectroradiometers

Basically, a spectroradiometer is a low-resolution spectrometer designed to give quantitative information concerning the radiant power at the exit slit found in a relatively wide band of wavelengths. Thus, accuracy in wavelength specification is seldom as good as 1 per cent and is often allowed to spread as much as  $\pm 5$  per cent from the nominal wavelength value. This sacrifice in wavelength resolution is necessary in order to have sufficient power delivered to the detector to make quantitative measurements relatively easy. The fact that most practical spectroradiometers have such poor wavelength resolution becomes an objection only under the relatively rare circumstance that the spectral-emission characteristic of the phosphor is one having important structural details which would be completely lost to the observer who places his entire reliance upon a low-resolution instrument.

The invention of the multiplier phototube as an electronic detecting element made it possible to increase the speed with which spectroradiometric measurements can be made and, in fact, permitted the development of automatic recording instruments which give valuable quantitative information ready for use and analysis in a matter of minutes. The first such instrument was that developed by Dr. Zworykin<sup>1</sup> and his group at RCA.

The Zworykin instrument has been further developed by Leverenz and Shrader, and has served to yield a vast quantity of recorded spectroradiometric data. Although this instrument was designed to have approximate corrections included automatically to yield a permanent record of the radiant-power output from an excited phosphor per unit range in wavelength as a function of the wavelength, it has not been found necessary for them to have high accuracy in this respect. The instrument has been used primarily as a means of discovering changes in the spectral output which follow from systematic changes in composition or in processing. These changes may be exhibited with all the accuracy required for practical purposes, without the development of a system which makes perfect compensation for such factors as slit-width variation, light absorption in the optical parts of the instrument, and variations in photomultiplier response.

Instruments of this type may be made very versatile, so that an analysis

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<sup>1</sup> V. K. Zworykin, J. Opt. Soc. Am. 29, 84 (1939).

can be given for phosphors excited in a demountable cathode-ray-tube arrangement (in which some 6 or 8 samples may be prepared for study at a given time), by the light derived from a phosphor used in a completed cathode-ray tube, or from phosphors excited by the absorption of ultra-violet radiation. Instruments used in connection with the development of phosphors for fluorescent lighting may also be adapted to receive and analyze the light produced in this manner.

A unique instrument has been developed under the direction of Dr. L. Headrick of the RCA Victor Division,<sup>2</sup> Lancaster, Pa. A twelve-inch cathode-ray tube, manufactured with a long-persistence P-7 cascade phosphor type of screen, is used to record radiant output as a function of wavelength. The approximate time for the production of a complete record is 13 seconds and the pattern remains visible for at least 1 or 2 minutes. Since it is possible to shift very rapidly the samples being investigated, advantage is taken of the fact that two or three records can be run on in rapid sequence, thus permitting a direct comparison between samples. It is evident that a recorder of this type is very suitable for quality control, in that one of the samples may be the "standard" and the other a phosphor or phosphor blend which must come within certain, rather narrowly specified, limits of the standard pattern in order to be acceptable. Whenever a permanent record of the observations is desired, a camera mounted directly on the instrument is used to photograph the pattern.

Considerable care has been taken in the construction of this instrument and in its calibration, in order to warrant its use as a means of color identification by the I.C.I. color system. The need for instrumental accuracy, when the data are to be used for color specification, has also been recognized by Bowie and Martin.<sup>3</sup> Figure 1 shows diagrammatically the main features of the Sylvania automatic spectroradiometer. A typical record of the blended phosphor identified as P-4 and described as being "television white" is shown in Figure 2. This figure also serves to indicate the reproducibility of the recording instrument, in that the line has been widened slightly, so that three separate runs on the same material are covered completely by the line shown.

Attention should be directed to a recent development of Dr. F. J. Studer,<sup>4</sup> as a result of which an automatic spectroradiometer has been designed for service in the Research Laboratory of the General Electric Company. This equipment has the advantage of noteworthy simplicity and, at the same

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<sup>2</sup> A. E. Hardy, *Tran. Electrochem. Soc.* 91, 221 (1947).

<sup>3</sup> R. N. Bowie and A. E. Martin, *Proc. I.R.E.* 36, 1023 (1948).

<sup>4</sup> F. J. Studer, *J. Opt. Soc. Am.* 38, 467 (1948).

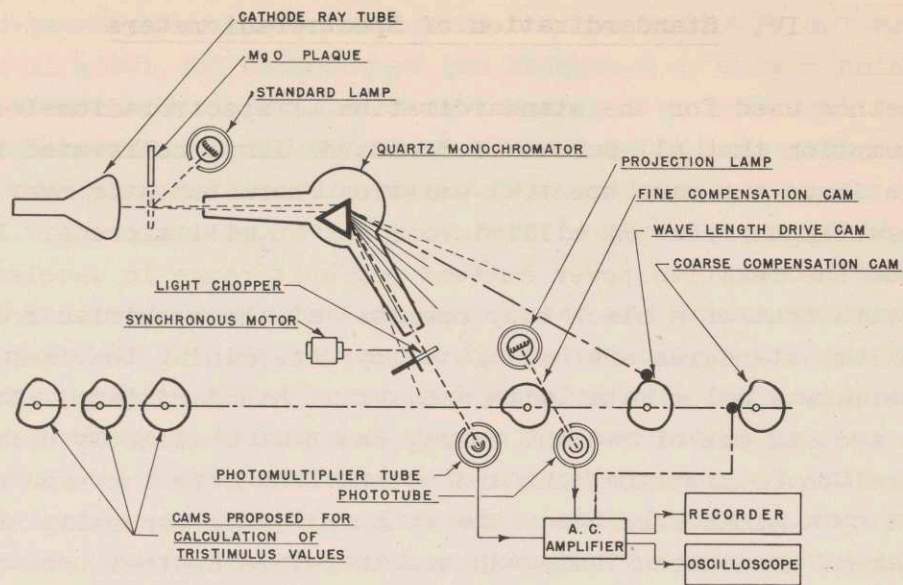


Fig. 1 Diagram of C.R.T. spectroradiometer  
(Physics Laboratories, Sylvania Electric Products Inc.).

time, comparison tests showed excellent agreement between the automatically recorded spectral-power distribution and the point-by-point study made by Dr. B. T. Barnes in which a double monochromator was used. Since the wavelength band transmitted through the Studer instrument may be of the order of 5 to 10 millimicrons, some care must be taken with such low-resolution equipment when it is used with phosphors which change intensity rapidly with wavelength.

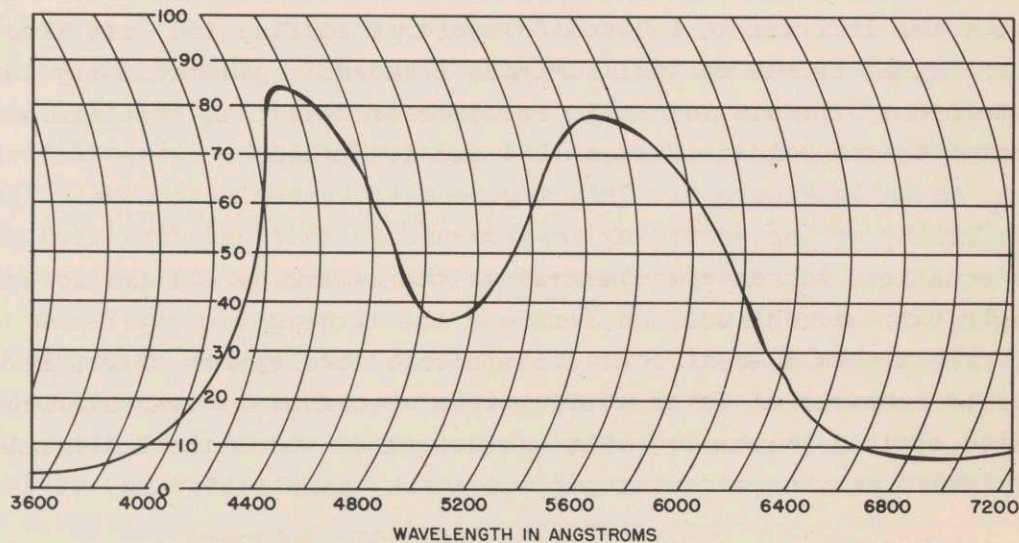


Fig. 2 Superposition of test runs 1, 2 and 3;  
P-4 phosphor in 10BP4 tube taken on spectroradiometer of Sylvania Electric Products Inc.

#### IV. Standardization of Spectroradiometers

The method used for the standardization of spectroradiometers depends on the assumption that all Bureau of Standards lamps calibrated for "color temperature" have the same spectral-emission characteristic over the entire range in wavelength from 380 millimicrons to 720 millimicrons. It is also assumed that the relative power emitted per unit range in wavelength is identical with that of a black body operated at the specified color temperature. The lamp standards are calibrated by determining the lamp current required to make a color match with a B. of S. standard lamp. It is well known that two sources of radiant energy can have distinctly different relative spectral-power distributions and yet have exactly the same color as interpreted by a human observer. The standard lamps generally used are coiled-filament projection lamps and are therefore neither true black-body sources nor tungsten-emission sources. It follows, therefore, that if two lamps which differ in mechanical structure in terms of the spacing between coils and the effect of cooling at the filament supports have the same color, they will, nevertheless, differ appreciably in their true relative spectral-power emission properties. It is impractical to consider the use of a high-temperature black-body source for standardization. It might even be considered impractical to use a large-area ribbon filament as a working standard in a particular laboratory. A practical solution for the standardization of the spectroradiometers could, however, be worked out along the following lines. First, the spectral emissivity of tungsten viewed in a direction normal to the surface must be known for the entire range of wavelength and temperature of importance. The data published by Forsythe and Worthing<sup>5</sup> are in excellent agreement with recently determined but still-unpublished data obtained by the writer.<sup>6</sup> The Forsythe and Worthing data are well represented by the empirical formula which follows:

$$e_{\lambda T} = 0.5364 + 5.24 \times 10^{-6}T - (9,187 + 3.822T) \times 10^{-8} \times \lambda \quad .$$

In this equation,  $e_{\lambda T}$  is the spectral emittance and is a function of the wavelength expressed in millimicrons and the temperature expressed in degrees Kelvin. The true temperature of a tungsten ribbon can be determined from an accurate measurement of the "brightness" temperature evaluated by a well-calibrated optical pyrometer. The wavelength at which the brightness match

<sup>5</sup> W. E. Forsythe and A. G. Worthing, *Astrophysics J.* 61, 146 (1925).

<sup>6</sup>  $e_{\lambda T} = 0.5308 + 5.24 \times 10^{-6}T - (9,187 + 3.90T) \times 10^{-8} \times \lambda \quad ;$

W. B. Nottingham and W. E. Mutter, *Phys. Rev.* 47, 1261 (1948).

is made must be known and the emittance can be obtained from the above equation as a result of successive approximations. An optical system can be so arranged that the only light entering the spectroradiometer comes from the uniformly hot part of the ribbon filament. If consideration is given to the absorption of the glass envelope surrounding the ribbon filament and if geometrical factors are also taken into account, then the absolute spectral irradiance can be computed. In general, it is only the relative spectral irradiance which is needed and the method by which this information is used involves the introduction of gain-correcting adjustment, as indicated in the schematic of Figure 1, so that the recorded output curve coincides with the calculated relative-irradiance curve.

The second step in standardization would involve the substitution of a particular standard "color-temperature" lamp of the coiled-filament type and the running of a spectral-emission curve for this lamp. Having once made a determination of the true relative spectral emission of this practical secondary standard, one can then use it to maintain the instrument in calibration without recourse to the primary ribbon-filament standard.

#### V. I.C.I. Interpretation of the Spectroradiometric Data

Through the cooperative activity of the International Commission on Illumination (I.C.I.), a system of color specification has been developed by which the determination of two numbers is sufficient to identify a color appearance to the so-called "standard" observer. These two numbers are known as the "trichromatic coefficients". In the application of this system, use is made of three sets of numerical data represented by the symbols  $\bar{x}_\lambda$ ,  $\bar{y}_\lambda$  and  $\bar{z}_\lambda$ . The numerical values of these functions are available<sup>7</sup> and the arithmetical calculation in which they are used is represented by the following three equations:

$$U = \int_0^{\infty} \bar{x}_\lambda h_\lambda d\lambda \quad ,$$

$$V = \int_0^{\infty} \bar{y}_\lambda h_\lambda d\lambda \quad ,$$

$$W = \int_0^{\infty} \bar{z}_\lambda h_\lambda d\lambda \quad .$$

<sup>7</sup> D. B. Judd, J. Opt. Soc. Am. 23, 359 (1933); A. C. Hardy, Handbook of Colorimetry, The Technology Press, (Cambridge, 1936).

For discussion of the system, see W. B. Nottingham, Radiation Lab. Report 804 (December 1945) NDRC, Div. 14, OEMsr-262 "Notes on Photometry, Colorimetry and in Explanation of the Centibel Scale".

In these equations,  $h_\lambda$  represents the relative spectral-power distribution of the source being evaluated. The trichromatic coefficients are defined finally by the following expressions:

$$x = \frac{U}{U + V + W} ,$$

$$y = \frac{V}{U + V + W} .$$

The numerical evaluation of the three quantities U, V and W may be carried out in either of two ways as soon as the spectral-power distribution, similar to that shown in Figure 2, has been determined. One method involves the direct graphical integration of the product curve obtained by the direct multiplication of the particular tristimulus distribution function  $\bar{x}_\lambda$ ,  $\bar{y}_\lambda$  or  $\bar{z}_\lambda$  by the  $h_\lambda$  function. The second method of computation involves the "selected ordinate" summation. For each of the tristimulus distribution functions, tables of wavelength values at which the ordinate of the spectral power distribution curve should be evaluated have been prepared.<sup>8</sup> Bowie and Martin have prepared transparent sheets of plastic on which the 30 selected abscissa lines are drawn for each of the tristimulus distribution functions. They superimpose these engraved lines over the record similar to Figure 2 and tabulate the ordinate values at each intersection between the engraving and the relative power-distribution curve of the phosphor under examination. The simple sum of the 30 numbers thus obtained is directly proportional to the value of U, V or W, depending on which engraving is used. In general, the use of the selected-ordinate method is superior in terms of convenience and accuracy to the straight integration scheme.

The use to which the trichromatic coefficients x and y may be put is well illustrated by Figures 3 and 4, in which data published by Hardy<sup>9</sup> are shown by way of illustration. The reader may be reminded that in the diagram of Figure 3, the solid line marked "pure spectrum locus" closed at the lower end by a straight line joining the extreme blue region with the extreme red region encloses the entire domain of realizable colors. The pure spectrum colors lie on the locus line and any combination whatsoever of spectrum colors used to make up a particular spectral-power distribution must lie inside the domain of realizable colors, because a mixture of any two of them results in a representative point in the diagram which lies on the straight line joining the components of the mixture. This rule of color mixture also applies, as is illustrated in Figure 4, to the mixing of broadband sources

<sup>8</sup> Committee on Colorimetry, J. Opt. Soc. Am. 34, 633 (1944).

<sup>9</sup> A. E. Hardy, RCA Review 8, 554 (1947).

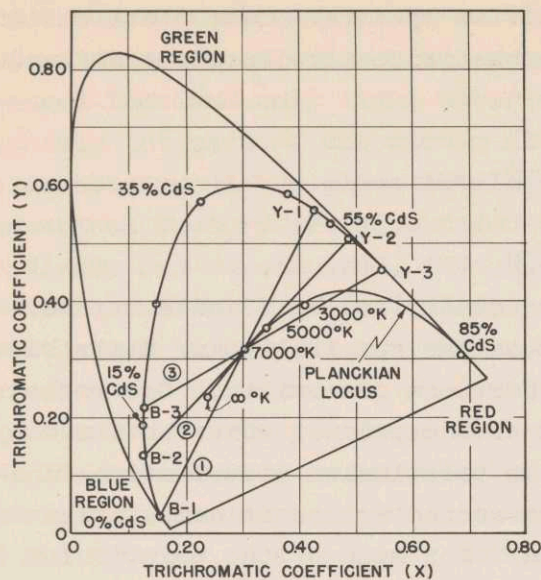


Fig. 3 Mixture diagram showing ZnCdS:Ag phosphor color locus as a function of per cent CdS (A. E. Hardy, RCA Review).

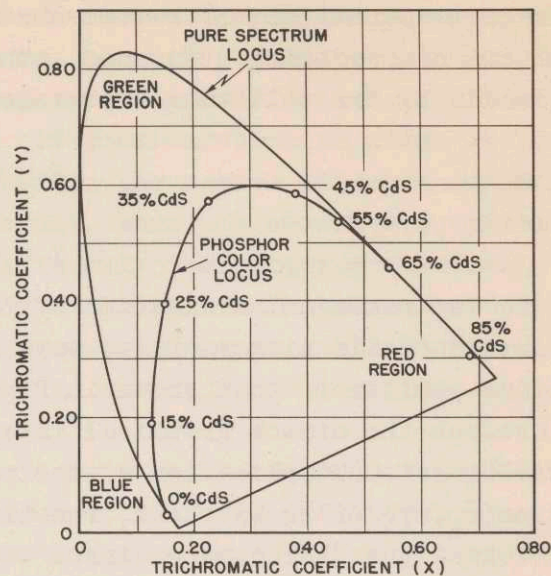


Fig. 4 Mixture diagram showing three phosphor pairs (A. E. Hardy, RCA Review).

such as we have for excited phosphors just as well as for the narrow-band sources associated with individual spectrum colors.

Although qualitative inspection of the light emitted by phosphors of systematically variable composition may be recognized easily, the quantitative representation shown in Figure 3 for the various solid-solution proportions of ZnCdS:Ag (for the range 0 - 85 per cent in CdS proportion) is of great practical value.

Although none of the phosphors found on the "phosphor color locus" line would be acceptable as "white" for a television cathode-ray tube, an infinite number of combinations could be chosen which would be indistinguishable in their whiteness by the "standard" observer. In Figure 4, three of these combinations are illustrated by the straight lines 1, 2 and 3, all of which intersect at a common point close to the 7000°K "Planckian locus". The coordinates  $x = 0.333$  and  $y = 0.333$  locate the representative point which would be obtained if the source observed were an "equal-energy" white; that is, the source radiates an equal amount of power per unit range in wavelength over the entire visible spectrum. We note, therefore, that phosphor combinations which analyze by the I.C.I. system to give a representative point at 7000°K are very close in appearance, although definitely different in spectral-power distribution, to the equal-energy white.

## VI. Optical Excitation Function

In the cathode-ray-tube applications of phosphors, excitation following

the absorption of electromagnetic radiation is generally considered to be of secondary importance, whereas the reverse is true for phosphors used in fluorescent lamps. A method which is useful for the determination of the optical excitation function has been described by Fonda and Studer<sup>10</sup>: the light from the continuous spectral distribution of power from a hydrogen arc is passed through a monochromator and allowed to fall directly on the thin deposit of phosphor under investigation. A sufficient fraction of the light emitted by the phosphor passes through it and also through the glass plate upon which the phosphor is deposited to give rise to sufficient photoelectric current in the detecting multiplier phototube to serve as an accurate measure of the luminescence of the phosphor. This information, combined with the knowledge of the relative power impinging on the phosphor as a function of wavelength, allows for the quantitative determination of the relative efficiency of the different wavelengths in the spectrum for the excitation of luminescence. Results so obtained are significant from both the theoretical and the practical points of view. Systematic changes in the excitation curve, depending on the nature and the quantity of activating agent, have been observed.

Fonda and Studer have also shown the value of a determination of the spectral-absorption characteristic of a phosphor by studying its diffuse reflectance. They have found useful correlations between the absorption spectrum, the excitation spectrum and the phosphor composition and treatment. These and similar data are needed on a wide variety of phosphors in order to fill in quantitative information needed for the formulation of an adequate theory to account for the optical properties of phosphors.

#### VII. Phosphorescence and Other Studies Involving Time and Temperature

One of the most interesting developments of the past decade has been the study of phosphor "glow curves". The experiment involves the excitation of a phosphor by ultraviolet light while it is maintained at a very low temperature. In general, luminescence will be observed during the excitation period, but immediately thereafter the phosphorescence will fall rapidly to a negligible value. However, if the phosphor is permitted to warm up gradually, measurable phosphorescence will very likely develop in the temperature range 100° to 200°K and a reproducible curve will be obtained for the power radiated as a function of the temperature. Obviously, such curves depend on the constant time rate of change of temperature used in the experiment and on the composition and structure of the phosphor. A summary of some of the work and a discussion of the theory may be found in the report by

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<sup>10</sup> G. R. Fonda and F. J. Studer, J. Opt. Soc. Am. 38, 1007 (1948).



Garlick<sup>11</sup> and the paper by Williams and Eyring.<sup>12</sup>

Equipment designed with all the refinements necessary to get good quantitative data, at very slow rates of increase in temperature with time, could also be used to determine the time change in phosphorescence at fixed points in temperature. Aside from the studies made at room temperature, relatively little has been done on the decay of phosphorescence at low temperature. Another closely related line of experimentation would involve the maintenance of the excited phosphor at a very low temperature and the observation of the nature of the phosphorescence decay under the stimulation of monochromatic infrared radiation. It is evident that all these studies, if applied to a given sample of phosphor, would yield most valuable information from which the number and energy depth of the electronic trapping states could be determined.

Extensive studies were made during the past few years on the natural and stimulated decay properties of phosphorescent substances, with the major attention given to the development of phosphors useful for particular military applications. These studies demonstrated that, broadly speaking, there are two types of decay most commonly found: (1) "Exponential", and (2) "Inverse Time". These decay types are easily identified by the fact that the exponential yields a fairly good straight line when the logarithm of the phosphorescent output is plotted against a linear time scale. The slope of the line thus obtained is very nearly independent of the degree of excitation and the length of time of excitation over quite wide ranges of these variables. As a class, the silicates, the fluorides and the tungstates generally exhibit exponential decay curves. The sulphides fall in the "inverse time" grouping, and here an approximately linear plot is obtained if the logarithm of the phosphorescent power is plotted as a function of the logarithm of the time of observation. The slopes of the observed lines vary from approximately 0.8 to 2.0. Since the characteristic slope for a simple bimolecular process would have been 2.0, it is evident that phosphorescence cannot be explained in such a simple manner. Considerable experimental data have been made available<sup>13</sup> recently, and it is probable that additional information will be accumulated slowly, since there exists in the various

<sup>11</sup> G. R. Fonda and F. Seitz, "Solid Luminescent Materials", Wiley and Sons, Inc., (New York, 1948) ch. 5 (G. F. J. Garlick) p. 87.

<sup>12</sup> F. Williams and H. Eyring, J. Chem. Phys. 15, 289 (1947).

<sup>13</sup> G. R. Fonda and F. Seitz, *op. cit.* Also J. T. Soller, T. M. A. Starr and G. E. Valley, "Cathode Ray Tube Displays", Radiation Lab. Series, Vol. 22, McGraw-Hill Book Co. (New York, 1948), (see Chapter 18 "Screens for Cathode Ray Tubes", by W. B. Nottingham). See also F. A. Kroger, W. Hoogenstraaten, M. Bottema and T. P. J. Botden, *Physica* 14, 81 (1948); and F. A. Kroger and W. Hoogenstraaten, *Physica* 14, 425 (1948).

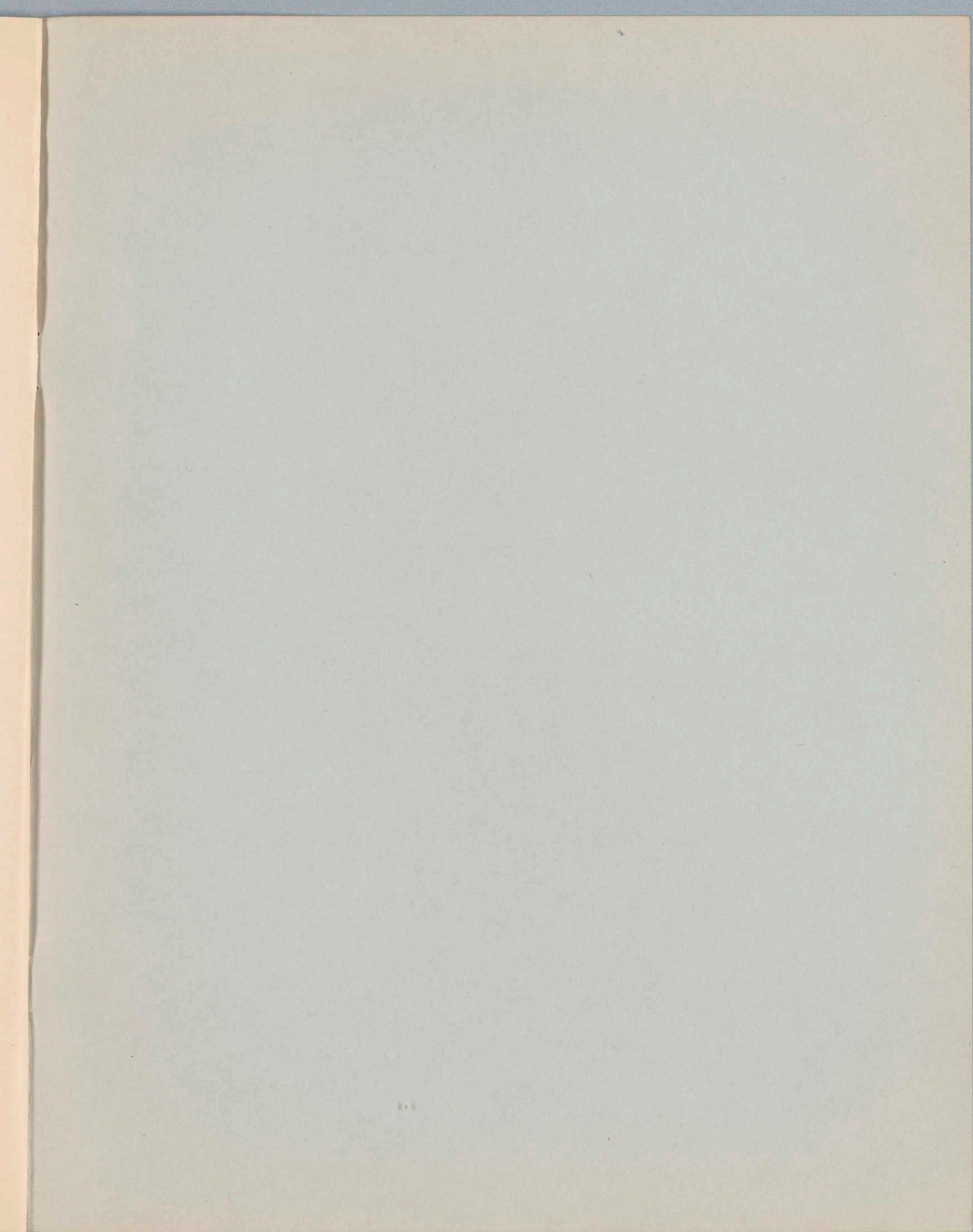
research laboratories the equipment for making such studies. Relatively little attention is being given to this matter at present.

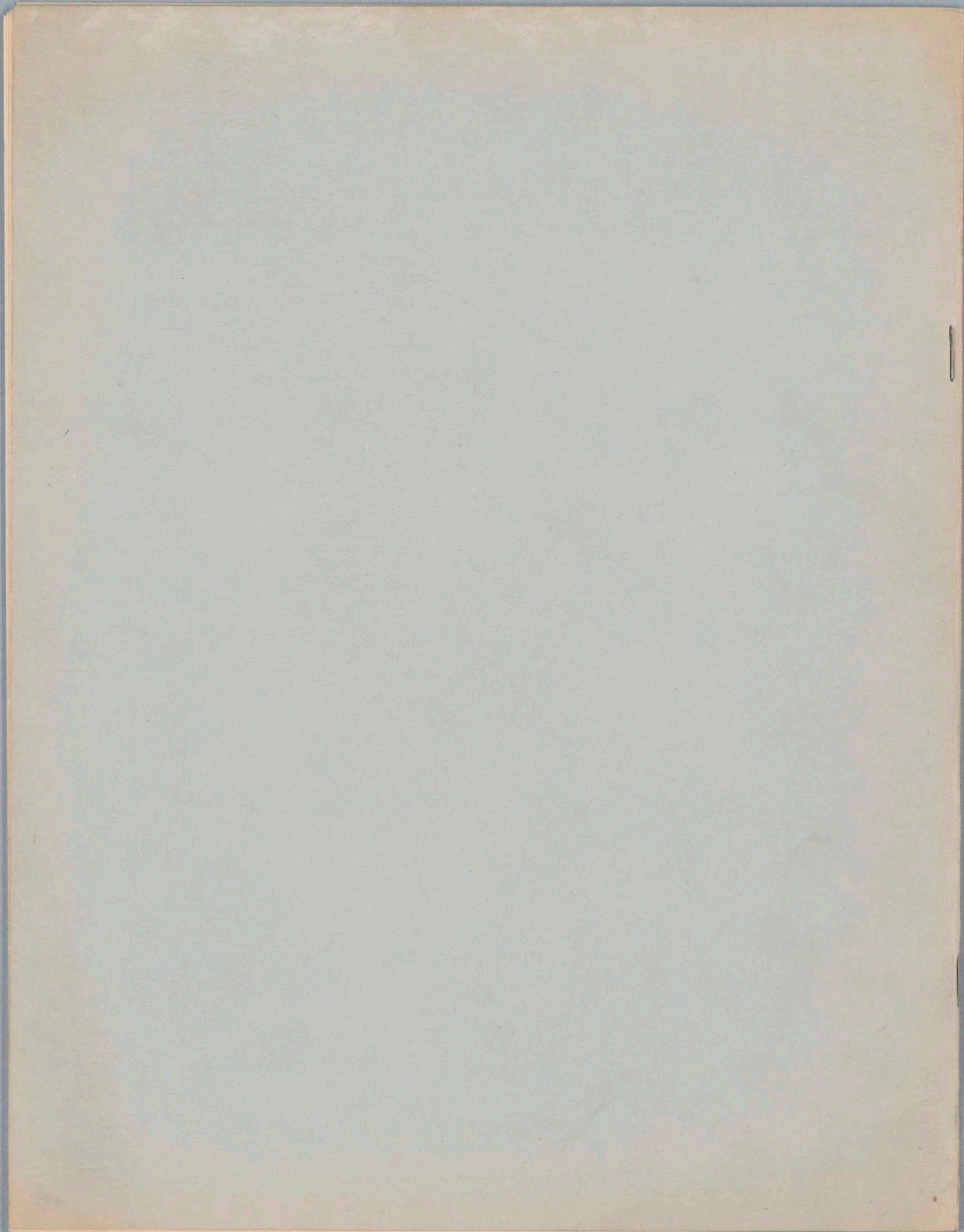
#### VIII. Conclusion

The means for the determination of many of the optical properties of phosphors have been developed and enough information has been obtained to show that researches in this field have, in reality, just begun. In spite of the complications, various approaches yield interlocking parts to this scientific jigsaw puzzle. More attention is being given at present to the quantitative determination of the spectral-power distribution emitted by phosphors and determined by means of automatic spectroradiometers. It is understandable that so much emphasis is placed on this particular line of research, because it is so important from all of the motivating points of view, including research, development and product control.

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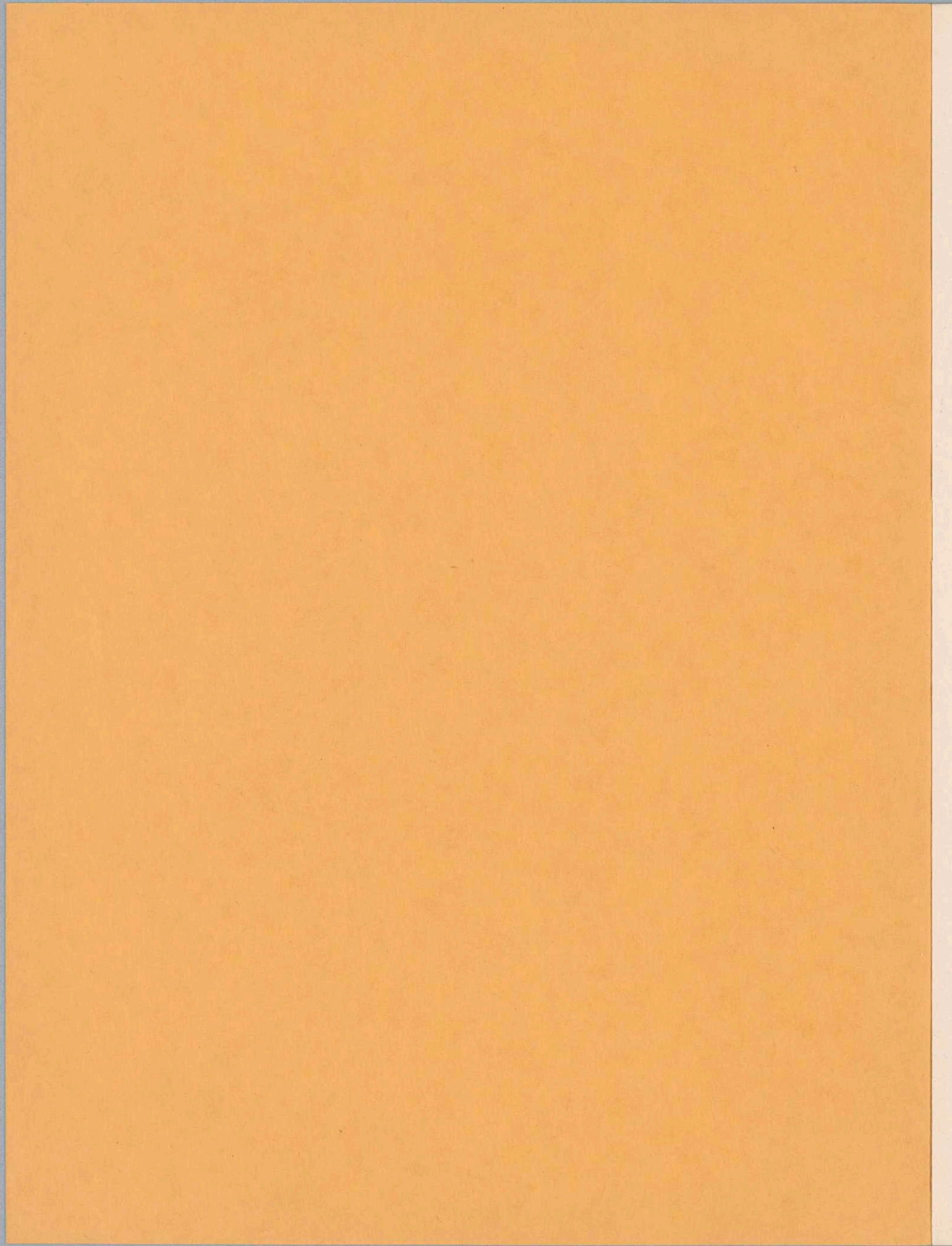




A Survey of Present Methods Used to Determine the Optical Properties  
of Phosphors

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## A Survey of Present Methods Used to Determine the Optical Properties of Phosphors<sup>\*,\*\*</sup>

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(Received May 6, 1949)

A brief review of the theory of phosphors is given in terms of the electron-band picture of impurity semiconductors in order to show the reasons for researches designed to obtain the optical properties of phosphors. The automatic spectroradiometer is described since it is an instrument which yields so much information of value in phosphor research, development, and quality control. Some problems of spectroradiometer standardization are discussed in some detail, since the data obtained cannot be correctly interpreted by the I.C.I. system of color specification and interpretation unless satisfactory standards are maintained and used. A brief discussion is given of the application of the I.C.I. system to help in the choice of phosphors required to produce a suitable "white" for television cathode-ray tubes. Other researches discussed include the determination of phosphor excitation curves, the emission of light as a function of temperature and of time, and the correlation of spectral excitation and absorption data.

### INTRODUCTION

THE determination of certain optical properties of phosphors is motivated by three broad objectives, which are (1) research, (2) development, and (3) quality control. In spite of the progress made during the past decade in the application of the electron energy band theory of solids to semiconductors and insulators, the systematic research needed to fill in the gaps in our knowledge of the experimental facts remains to be done. The development of new phosphors to fill specific practical needs, including such factors as efficiency, life under operating conditions, and specified spectral emission characteristics will be aided by the satisfactory theoretical interpretation of new experimental research, while at the same time reliance is given to the practical approach involving the systematic variation of impurities and processing techniques with results evaluated

largely by empirical methods. Even here the theoretical explanations serve as a most useful guide to further empirical exploration. The need for the determination of certain optical properties of phosphors does not stop when a particular structure has been synthesized and a specific formula for production worked out. Constant vigilance is absolutely necessary as a means of quality control because many of the most useful phosphor properties can be materially interfered with by the accidental introduction of undesired impurities in concentrations as small as a very few parts in a million.

Some pieces of optical equipment, and in particular I refer to the spectroradiometer, are useful and in fact indispensable for research, development, and control in the major industries that produce such unbelievably large quantities of phosphors now used in cathode-ray tubes and fluorescent lamps. The monochromator is an important optical instrument used both in research and development of phosphors, in that a quantitative determination of excitation efficiency as a function of the wave-length of the radiation used to excite the phosphor is an important optical property.

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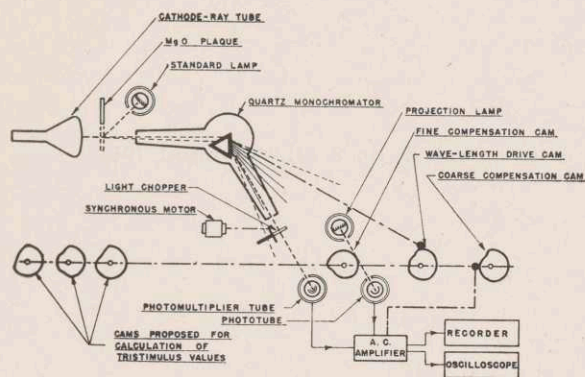


Fig. 1. Diagram—C.R.T. spectroradiometer. (Sylvania Electric Products, Inc., Physics Laboratories.)

The electron multiplier type of photo-tube, now almost universally used as a means of quantitatively determining the radiant output of phosphors, has proven to be an indispensable accessory for a very large proportion of all measurements made in the past seven or eight years.

Optical observations made in the study of atomic and molecular excitation and radiant energy emission involve the time history and the temperature conditions very indirectly as compared to the general case for phosphors. In the latter case, the time history of excitation, the time of observation, and the temperature history during both excitation and observation are of utmost importance and, in fact, serve as controllable variables through which the basic facts concerning the electronic band structure of the solid are exhibited.

#### A BRIEF REVIEW OF THE THEORY OF PHOSPHORS

Nearly all practical phosphors are crystalline in structure and are very dependent on the presence and suitable disposition of selected impurities known generally as "activators." In certain types of phosphors, of which the silicates are typical, the activator fits into the lattice in a substitutional position for one of the atoms normally found in the basic crystal structure. Phosphors of which zinc sulfide is typical, require concentrations of activator that constitute a very small fraction of 1 percent, since the necessary impurities take positions interstitially between the atoms of the crystalline substance. The outermost or valence electrons of a perfect crystal move from atom to atom throughout the crystal even at extremely low temperature. In spite of this freedom of motion, the application of small differences in potential to the crystal does not result in conductivity, because the electrons are so crowded into their only available quantum states that at low temperatures and with moderate electric fields the electrons cannot cross the energy gap, in which there are no available electronic energy levels, to find the greater freedom of motion associated with the higher "conduction" levels of the system. Support for this view of the

electronic structure of insulators may be derived from experiments on the optical absorption of these crystals. If the energy ( $h\nu$ ) of the light quantum is insufficient to cause an electronic transition from an occupied to an unoccupied state, then the optical absorption of the crystal is small. Thus, the measurement of the optical absorption of single crystals, or even of polycrystalline material when samples of uniform particle size and variable thickness may be used; serve to give direct information concerning the energy level system of the phosphor.

The introduction of impurities into the crystal generally modifies in a measurable way the absorption characteristic of the material. This fact indicates the importance of the close coordination needed to relate the chemistry and production of phosphors to the optical absorption characteristics of the substance.

By far the most common means of phosphor excitation depend either on the absorption of energy by the electrons from electromagnetic radiations in the visible or in the ultraviolet range of the spectrum, or else by the absorption of energy that results from electron bombardment. Although many secondary effects are associated with phosphor excitation, the primary process involves the transfer of electrons from the stable valence electron band or from bound electrons located at impurity centers into normally unoccupied electronic levels of the conduction band. As a result of this transfer of the electron into a conduction band, a negative charge carrier becomes mobilized, and, in addition, the absence of an electron in the normally filled valence band is the equivalent of mobilizing a positive charge carrier or an "electron hole." The reverse process is the recombination of an electron with an electron hole and the simultaneous conversion of the potential energy thus temporarily stored into the radiant energy of a light quantum or into the vibrational energy of the atoms nearby.

In many respects, the situation may be compared to the ionization of a gas in the plasma of a gas discharge. In that case, both the positive ions and the electrons are mobile and can maintain nearly equal volume concentrations, and yet free space recombination is a relatively uncommon occurrence. If the ion becomes attached to an insulating wall, or if the electron becomes attached to an otherwise neutral atom or molecule, then recombination takes place very readily. A similar situation occurs in phosphors, and other insulators and semiconductors. If the electron hole becomes trapped at an impurity atom, while the electron itself remains free, recombination is likely to occur. In a similar manner, electron holes that migrate to the surface of the crystal attract electrons and recombine with them there. Electrons may become trapped in other types of impurity centers, but, nevertheless, recombination can take place because of the mobility of the holes. The last of the simple cases involves the trapping of both the holes and

the electrons. A "meta-stable" situation is thus created in which recombination is inhibited and becomes extremely temperature sensitive, since it is by means of the absorption of temperature energy by the trapped electrons or holes that they are restored to mobility.

An investigation of spectral emission data, interpreted in a manner thus briefly described, permits the observer to evaluate quantitatively the energy jump that the electron takes upon recombination. Since the energy jumps for a given transition in a particular phosphor are not exactly the same throughout the volume of the crystal, the radiant energy emitted is not confined to a narrow band of wave-lengths, but spreads on each side of a most probable energy transition to create a relatively broad continuous set of emitted wave-lengths. Thus, the determination of the spectral emission characteristic of a phosphor stands very high in the interests of all investigations, including research, development, and quality control.

The lines of investigation that yield detailed information in support of the theoretical picture thus described, include the determination of excitation efficiency as a function of the wave-length of the exciting radiation and as a function of the electron energy and current density used for excitation. A quantitative determination of the influence of temperature on the light output and of the time changes of light output can be interpreted to give quantitative data on the number and energy distribution of the trapping states. Simultaneous determination of the electrical conductivity of crystals during excitation yields valuable detailed material for analysis.

#### SPECTRORADIOMETERS

Basically, a spectroradiometer is a low resolution spectrometer designed to give quantitative information concerning the radiant power at the exit slit found in a relatively wide band of wave-lengths. Thus, accuracy in wave-length specification is seldom as good as 1 percent and is often allowed to spread as much as  $\pm 5$  percent from the nominal wave-length value. This sacrifice in wave-length resolution is necessary in order to have sufficient power delivered to the detector to make quantitative measurements relatively easy. The fact that most practical spectroradiometers have such poor wave-length resolution becomes an objection only under the relatively rare circumstance that the spectral emission characteristic of the phosphor is one that has important structural details which would be completely lost to the observer who places his entire reliance upon a low resolution instrument.

The invention of the multiplier photo-tube as an electronic detecting element made it possible to increase the speed with which spectroradiometric measurements can be made and, in fact, permitted the development of automatic recording instruments that give valuable quantitative information ready for use and analysis in a

matter of minutes. The first such instrument was that developed by Dr. Zworykin<sup>1</sup> and his group at RCA.

The Zworykin instrument has been further developed by Leverenz and Shrader and has served to yield a vast quantity of recorded spectroradiometric data. Although this instrument was designed to have approximate corrections included automatically to yield a record of the radiant power output from an excited phosphor per unit range in wave-length as a function of the wave-length, it has not been found necessary for them to have high accuracy in this respect. The instrument has been used primarily as a means of discovering *changes* in the spectral output that follow systematic changes in composition or in processing. These changes may be exhibited with all the accuracy required for practical purposes, without the development of a system which makes perfect compensation for such factors as slit-width variation, light absorption in the optical parts of the instrument, and variations in photo-multiplier response.

Instruments of this type may be made very versatile, so that an analysis can be given for phosphors excited either in a demountable cathode-ray tube arrangement in which some 6 or 8 samples may be prepared for study at a given time, or the light may be derived from a phosphor used in a completed cathode-ray tube or from phosphors excited by the absorption of ultraviolet radiation. Instruments used in connection with the development of phosphors for fluorescent lighting may also be adapted to receive and analyze the light produced in this manner.

A unique instrument has been developed for use under the direction of Dr. L. Headrick of the RCA Victor Division,<sup>2</sup> Lancaster, Pennsylvania. A twelve-inch cathode-ray tube, manufactured with a long persistence P-7 cascade phosphor type of screen, is used to record the radiant output as a function of the wave-length. The approximate time for the production of a complete record is 13 sec. and the pattern remains visible for at least 1 or 2 min. Since it is possible to shift the samples being investigated very rapidly, advantage is taken of

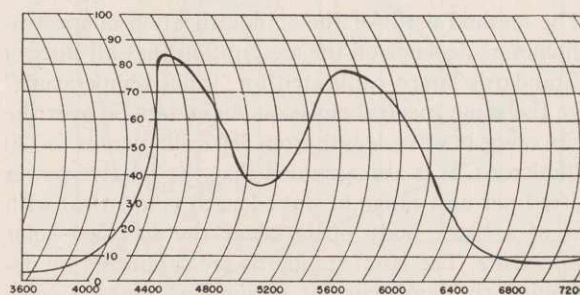


FIG. 2. Superposition of test runs 1, 2, and 3 P-4 phosphor in 10BP4 tube taken on spectroradiometer of Sylvania Electric Products, Inc.

<sup>1</sup> V. K. Zworykin, J. Opt. Soc. Am. 29, 84 (1939).

<sup>2</sup> A. E. Hardy, Trans. Am. Electrochem. Soc. 91, 221 (1947).

the fact that two or three records can be run on in rapid sequence and thus permit a direct comparison between samples. It is evident that a recorder of this type is very suitable for quality control, in that one of the samples may be the "standard" and the other sample a phosphor or phosphor blend which must come within certain, rather narrowly specified, limits of the standard pattern in order to be acceptable. Whenever a permanent record of the observations is desired, a camera mounted directly on the instrument is used to photograph the pattern.

Considerable care has been taken in the construction of this instrument and in its calibration, in order to warrant its use as a means of color identification by the I.C.I. color system. The need for instrumental accuracy, when the data are to be used for color specification, has also been recognized by Bowie and Martin.<sup>3</sup> Figure 1 shows by diagram the main features of the Sylvania automatic spectroradiometer. A typical record of the blended phosphor identified as P-4 and described as being television white is shown in Fig. 2. This figure also serves to indicate the reproducibility of the recording instrument in that the line has been widened slightly, so that three separate runs on the same material are covered completely by the line shown.

Attention should be directed to a recent development of Dr. F. J. Studer,<sup>4</sup> as a result of which an automatic spectroradiometer has been designed for service in the Research Laboratory of the General Electric Company. This equipment has the advantage of noteworthy simplicity and at the same time comparison tests showed excellent agreement between the automatically recorded spectral power distribution and the point by point study made by Dr. B. T. Barnes in which a double monochromator was used. Since the wave-length band transmitted through the Studer instrument may be of the order of 5 to 10 millimicrons, some care must be taken with such low resolution equipment when it is used with phosphors that change intensity rapidly with wave-length.

#### STANDARDIZATION OF SPECTRORADIOMETERS

The method used for the standardization of spectroradiometers depends on the assumption that all Bureau of Standards lamps calibrated for "color temperature" have the same spectral emission characteristic over the entire range in wave-length from 380 millimicrons to 720 millimicrons. It is also assumed that the relative power emitted per unit range in wave-length is identical with that of a black body operated at the specified color temperature. The lamp standards are calibrated by determining the lamp current required to make a color match with a B. of S. standard lamp. It is well known that two sources of radiant energy can have distinctly

different relative spectral power distributions and yet have exactly the same color as interpreted by a human observer. The standard lamps generally used are coiled filament projection lamps and are therefore neither true black body sources nor tungsten emission sources. It follows, therefore, that if two lamps that differ in mechanical structure in terms of the spacing between coils and the effect of cooling at the filament supports have the same color, they will nevertheless differ appreciably in their true relative spectral power emission properties. It is impractical to consider the use of a high temperature black body source for standardization. It might even be considered impractical to use a large area ribbon filament as a working standard in a particular laboratory. A practical solution for the standardization of the spectroradiometers could, however, be worked out along the following lines. First, the spectral emissivity of tungsten viewed in a direction normal to the surface must be known for the entire range of wave-length and temperature of importance. The data published by Forsythe and Worthing<sup>5</sup> are in excellent agreement with recently determined, but still unpublished, data obtained by the writer.<sup>6</sup> The Forsythe and Worthing data are well represented by the empirical formula:

$$e_{\lambda T} = 0.5364 + 5.24 \times 10^{-6} T - (9187 + 3.822T) \times 10^{-8} \times \lambda.$$

In this equation,  $e_{\lambda T}$  is the spectral emittance and is a function of the wave-length expressed in millimicrons and the temperature expressed in degrees Kelvin. The true temperature of a tungsten ribbon can be determined from an accurate measurement of the "brightness" temperature evaluated by a well-calibrated optical pyrometer. The wave-length at which the brightness match is made must be known, and the emittance can be obtained from the above equation as a result of successive approximations. An optical system can be arranged so that the only light that enters the spectroradiometer comes from the uniformly hot part of the ribbon filament. If consideration is given to the absorption of the glass envelope surrounding the ribbon filament, and if geometrical factors are also taken into account, then the absolute spectral irradiance can be computed. In general, it is only the *relative* spectral irradiance that is needed and the method by which this information is used involves the introduction of gain-correcting adjustment, as indicated in the schematic of Fig. 1, so that the recorded output curve coincides with the calculated relative irradiance curve.

The second step in standardization would involve the substitution of a particular standard "color-temperature" lamp of the coiled filament type and the running of a spectral emission curve for this lamp. After having once made a determination of the true relative spectral emission of this practical secondary standard, one can

<sup>3</sup> R. N. Bowie and Alfred E. Martin, Proc. I.R.E. 36, 1023 (1948).

<sup>4</sup> Frank J. Studer, J. Opt. Soc. Am. 38, 467 (1948).

<sup>5</sup> W. E. Forsythe and A. G. Worthing, Astrophys. J. 61, 146 (1925).

<sup>6</sup> W. B. Nottingham and W. E. Mutter, Phys. Rev. 47, 1261 (1948);  $e_{\lambda T} = 0.5308 + 5.24 \times 10^{-6} T - (9187 + 3.907T) \times 10^{-8} \times \lambda.$

then use it to maintain the instrument in calibration without recourse to the primary ribbon filament standard.

### I.C.I. INTERPRETATION OF THE SPECTRORADIOMETRIC DATA

Through the cooperative activity of the International Commission on Illumination (I.C.I.), a system of color specification has been developed by which the determination of two numbers is sufficient to identify a color appearance to the so-called "standard" observer. These two numbers are known as the "trichromatic coefficients." In the application of this system, use is made of three sets of numerical data represented by the symbols  $\bar{x}_\lambda$ ,  $\bar{y}_\lambda$ , and  $\bar{z}_\lambda$ . The numerical values of these functions are available,<sup>7</sup> and the arithmetical calculation in which they are used is represented by the three equations:

$$U = \int_0^\infty \bar{x}_\lambda h_\lambda d\lambda,$$

$$V = \int_0^\infty \bar{y}_\lambda h_\lambda d\lambda,$$

$$W = \int_0^\infty \bar{z}_\lambda h_\lambda d\lambda.$$

In these equations  $h_\lambda$  represents the relative spectral power distribution of the source being evaluated. The trichromatic coefficients are defined finally by the expressions:

$$x = U/(U+V+W), \quad y = V/(U+V+W).$$

The numerical evaluation of the three quantities  $U$ ,  $V$ , and  $W$  may be carried out in either one of two ways as soon as the spectral power distribution similar to that shown in Fig. 2 has been determined. The one method involves the direct graphical integration of the product curve obtained by the direct multiplication of the particular tristimulus distribution function  $\bar{x}_\lambda$ ,  $\bar{y}_\lambda$ , or  $\bar{z}_\lambda$  by the  $h_\lambda$  function. The second method of computation involves the "selected ordinate" summation. For each of the tristimulus distribution functions, tables of wavelength values at which the ordinate of the spectral power distribution curve should be evaluated have been prepared.<sup>8</sup> Bowie and Martin have prepared transparent sheets of plastic on which the 30 selected abscissa lines are drawn for each of the tristimulus distribution functions. They superimpose these engraved lines over the record similar to Fig. 2 and tabulate the ordinate values at each intersection between the engraving and the

relative power distribution curve of the phosphor under examination. The simple sum of the 30 numbers thus obtained is directly proportional to the value of  $U$ ,  $V$ , or  $W$  depending on which engraving is used. In general, the use of the selected ordinate method is superior in terms of convenience and accuracy to the straight integration scheme.

The use to which the trichromatic coefficients  $x$ ,  $y$  may be put is well illustrated by Figs. 3 and 4, in which data published by Hardy<sup>9</sup> are shown by way of illustration. The reader may be reminded that in the diagram of Fig. 3, the solid line marked "pure spectrum locus" closed at the lower end by a straight line joining the extreme blue region with the extreme red region, encloses the entire domain of realizable colors. The pure spectrum colors lie on the locus line and any combination whatsoever of spectrum colors used to make up a particular spectral power distribution must lie inside of the domain of realizable colors, because a mixture of any two of them results in a representative point in the diagram that lies on the straight line joining the components of the mixture. This rule of color mixture also applies, as is illustrated in Fig. 4, to the mixing of broad band sources such as we have for excited phosphors just as well as for the narrow band sources associated with individual spectrum colors.

Although qualitative inspection of the light emitted by phosphors of systematically variable composition may be recognized easily, the quantitative representation shown in Fig. 3 for the various solid solution proportions of ZnCdS:Ag for the range in CdS propor-

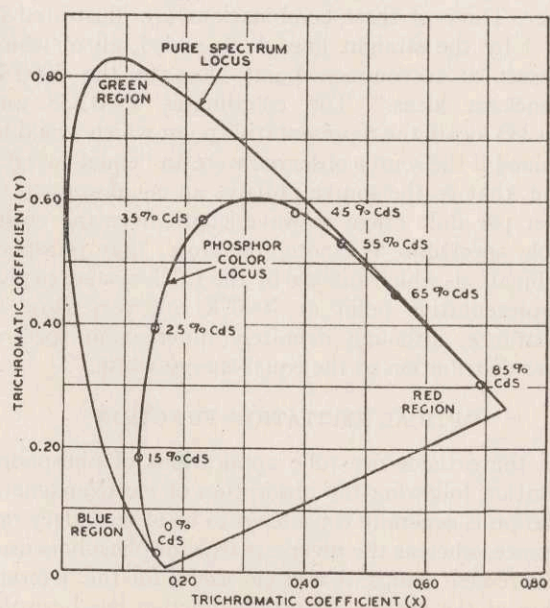


FIG. 3. I.C.I. color system. Mixture diagram showing ZnCdS:Ag phosphor color locus as a function of percent CdS. (A. E. Hardy, RCA Review.)

<sup>7</sup> D. B. Judd, *J. Opt. Soc. Am.* **23**, 359 (1933). A. C. Hardy, *Handbook of Colorimetry* (The Technology Press, M.I.T., Cambridge, 1936). For discussion of system, W. B. Nottingham, Radiation Lab. Rep. 804 (December, 1945) NDRC, Div. 14, OEMsr-262 "Notes on photometry, colorimetry and in explanation of the centibel scale."

<sup>8</sup> Committee on Colorimetry, *J. Opt. Soc. Am.* **34**, 633 (1944).

<sup>9</sup> Austin E. Hardy, *RCA Review* **8**, 554 (1947).

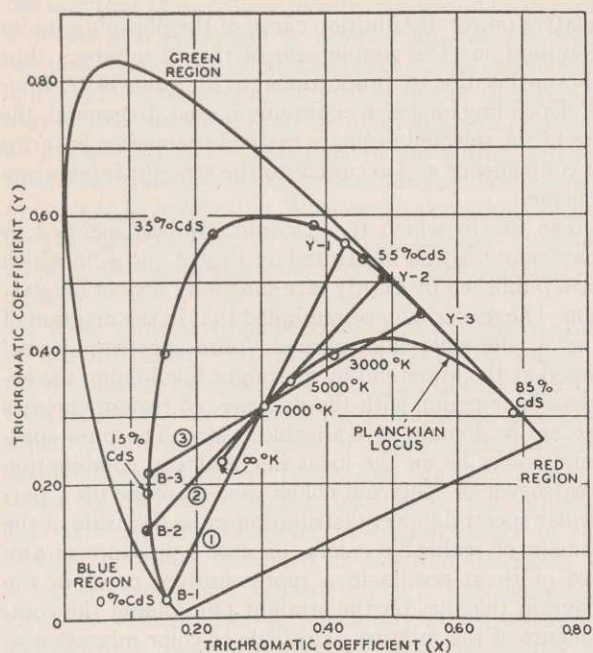


FIG. 4. Mixture diagram showing three phosphor pairs. (A. E. Hardy, RCA Review.)

tion from 85 percent down to 0 percent is of great practical value.

Although none of the phosphors found on the "phosphor color locus" line would be acceptable for a television cathode-ray tube as being "white," an infinite number of combinations could be chosen that would be indistinguishable in their whiteness by the "standard" observer. Three of these combinations are illustrated in Fig. 4 by the straight lines 1, 2, and 3, all of which intersect at a common point close to the 7000°K "Planckian locus." The coordinates  $x=0.333$  and  $y=0.333$  locate the representative point which would be obtained if the source observed were an "equal-energy" white, that is, the source radiates an equal amount of power per unit range in wave-length over the entire visible spectrum. We note, therefore, that phosphor combinations which analyze by the I.C.I. system to give a representative point at 7000°K are very close in appearance, although definitely different in spectral power distribution to the equal-energy white.

#### OPTICAL EXCITATION FUNCTION

In the cathode-ray tube applications of phosphors, excitation following the absorption of electromagnetic radiation is generally considered to be of secondary importance, whereas the reverse is true for phosphors used in fluorescent lamps. A method useful for the determination of the optical excitation function has been described by Fonda and Studer,<sup>10</sup> in which the light from the continuous spectral distribution of power from a

hydrogen arc is passed through a monochromator and allowed to fall directly on the thin deposit of phosphor under investigation. A sufficient fraction of the light emitted by the phosphor passes through it and also through the glass plate upon which the phosphor is deposited to give rise to sufficient photoelectric current in the detecting multiplier photo-tube to serve as an accurate measure of the luminescence of the phosphor. This information, combined with the knowledge of the relative power impinging on the phosphor as a function of wave-length, allows for the quantitative determination of the relative efficiency of the different wave-lengths in the spectrum for the excitation of luminescence. Results so obtained are significant both from the theoretical and the practical points of view. Systematic changes in the excitation curve depending on the nature and the quantity of activating agent have been observed.

Fonda and Studer also have shown the value of a determination of the spectral absorption characteristic of a phosphor by studying its diffuse reflectance. They have found useful correlations between the absorption spectrum, the excitation spectrum, and the phosphor composition and treatment. These and similar data are needed on a wide variety of phosphors in order to fill in quantitative information needed for the formulation of an adequate theory to account for the optical properties of phosphors.

#### PHOSPHORESCENCE AND OTHER STUDIES INVOLVING TIME AND TEMPERATURE

One of the most interesting developments of the past decade has been the study of phosphor "glow curves." The experiment involves the excitation of a phosphor by ultraviolet light while it is maintained at a very low temperature. In general, luminescence will be observed during the excitation period but immediately thereafter the phosphorescence will fall rapidly to a negligible value. However, if the phosphor is permitted to warm up gradually, measurable phosphorescence will very likely develop in the temperature range 100° to 200°K and a reproducible curve will be obtained for the power radiated as a function of the temperature. Obviously, such curves depend on the constant time rate of change of temperature used in the experiment and on the composition and structure of the phosphor. A summary of some of the work and a discussion of the theory may be found in the report by Garlick<sup>11</sup> and the paper by Williams and Eyring.<sup>12</sup>

Equipment designed with all of the refinements necessary to get good quantitative data at very slow rates of increase in temperature with time, could also be used to determine the time change in phosphorescence at fixed

<sup>11</sup> G. F. J. Garlick, Chapter 5, p. 87 of *Solid Luminescent Materials* by G. R. Fonda and F. Seitz (John Wiley and Sons, Inc., New York, 1948).

<sup>12</sup> Ferd Williams and Henry Eyring, *J. Chem. Phys.* **15**, 289 (1947).

<sup>10</sup> Gorton R. Fonda and Frank J. Studer, *J. Opt. Soc. Am.* **38**, 1007 (1948).

points in temperature. Outside of the studies made at room temperature, relatively little has been done on the decay of phosphorescence at low temperature. Another closely related line of experimentation would involve the maintenance of the excited phosphor at a very low temperature and the observation of the nature of the phosphorescence decay under the stimulation of monochromatic infra-red radiation. It is evident that all of these studies, if applied to a given sample of phosphor, would yield most valuable information from which the number and energy depth of the electronic trapping states could be determined.

Extensive studies were made during the past few years on the natural and stimulated decay properties of phosphorescent substances, with the major attention given to the development of phosphors useful for particular military applications. These studies demonstrated that broadly speaking, there are two types of decay most commonly found, which are: (1) "exponential" and (2) "inverse time." These decay types are easily identified by the fact that the exponential yields a fairly good straight line when the logarithm of the phosphorescent output is plotted against a linear time scale. The slope of the line thus obtained is very nearly independent of the degree of excitation and the length of time of excitation over quite wide ranges of these variables. As a class, the silicates, the fluorides, and the tungstates generally exhibit exponential decay curves. The sulfides fall in the "inverse time" grouping and here an approximately linear plot is obtained if the logarithm of the phosphorescent power is plotted as a function of the logarithm of the time of observation. The slopes of

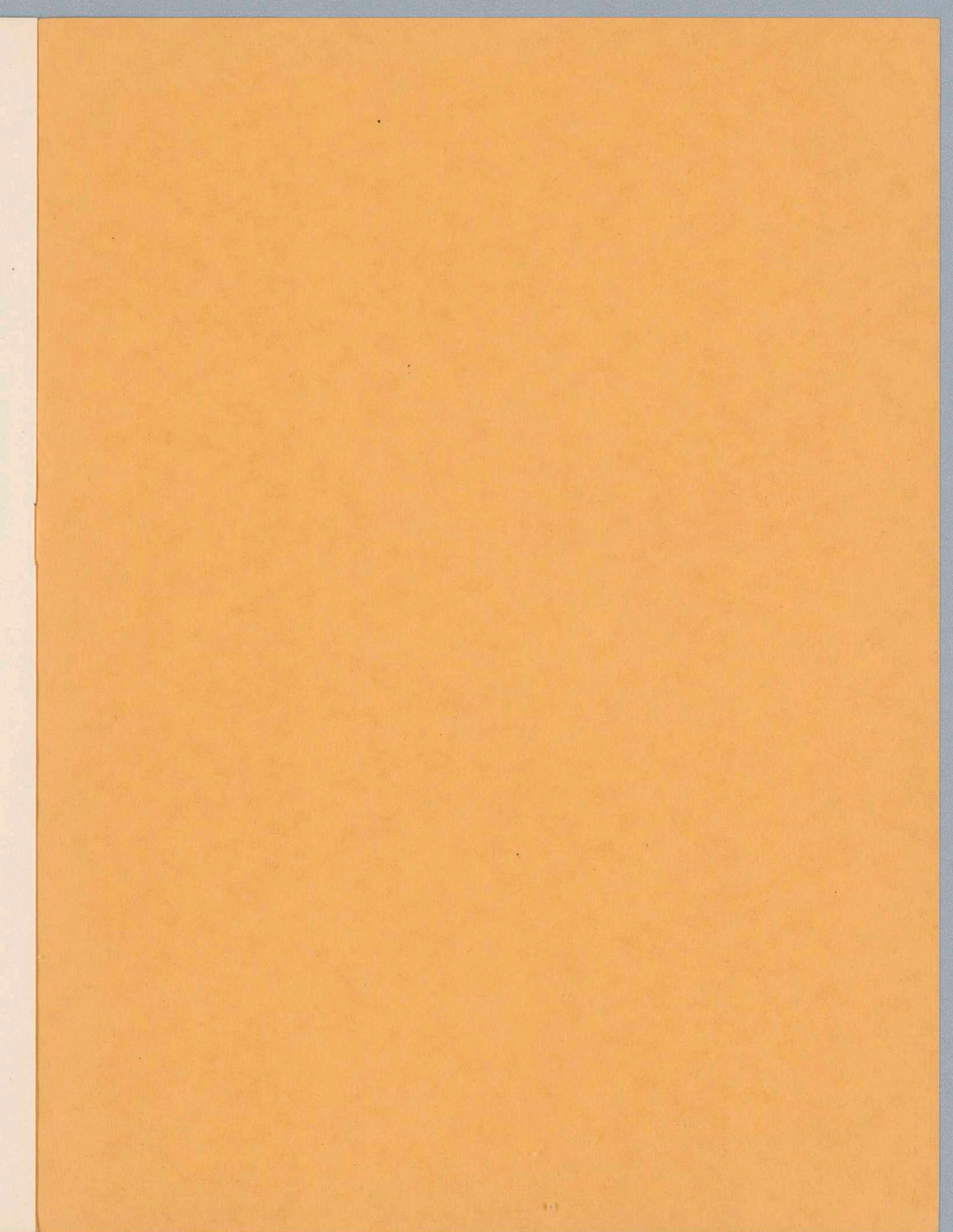
the observed lines vary from approximately 0.8 to 2.0. Since the characteristic slope for a simple bimolecular process would have been 2, it is evident that phosphorescence cannot be explained in such a simple manner. Considerable experimental data have been made available<sup>13</sup> recently and it is probable that additional information will be accumulated slowly, since there are in existence in the various research laboratories equipment for making such studies. Relatively little attention is being given to this matter at present.

#### CONCLUDING REMARKS

The means for the determination of many of the optical properties of phosphors have been developed and enough information obtained to show that researches in this field have in reality just begun. In spite of the complications, various approaches yield interlocking parts to this scientific jigsaw puzzle. More attention is being given at present to the quantitative determination of the spectral power distribution emitted by phosphors and determined by means of automatic spectroradiometers. It is understandable that so much emphasis is placed on this particular line of research, because it is so important from all of the motivating points of view that include research, development, and product control.

<sup>13</sup> G. R. Fonda and F. Seitz, *Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948). Also Soller, Starr, and Valley, *Cathode Ray Tube Displays* (McGraw-Hill Book Company, Inc., New York, 1948), Radiation Lab. Series, Vol. 22. (See Chapter 18, "Screens for cathode ray tubes" by W. B. Nottingham.) Kröger, Hoogenstraaten, Bottema, and Botden, *Physica* 14, 81 (1948) and F. A. Kröger and W. Hoogenstraaten, *Physica* 14, 425 (1948).







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### INTRODUCTION

THE determination of certain optical properties of phosphors is motivated by three broad objectives, which are (1) research, (2) development, and (3) quality control. In spite of the progress made during the past decade in the application of the electron energy band theory of solids to semiconductors and insulators, the systematic research needed to fill in the gaps in our knowledge of the experimental facts remains to be done. The development of new phosphors to fill specific practical needs, including such factors as efficiency, life under operating conditions, and specified spectral emission characteristics will be aided by the satisfactory theoretical interpretation of new experimental research, while at the same time reliance is given to the practical approach involving the systematic variation of impurities and processing techniques with results evaluated

largely by empirical methods. Even here the theoretical explanations serve as a most useful guide to further empirical exploration. The need for the determination of certain optical properties of phosphors does not stop when a particular structure has been synthesized and a specific formula for production worked out. Constant vigilance is absolutely necessary as a means of quality control because many of the most useful phosphor properties can be materially interfered with by the accidental introduction of undesired impurities in concentrations as small as a very few parts in a million.

Some pieces of optical equipment, and in particular I refer to the spectroradiometer, are useful and in fact indispensable for research, development, and control in the major industries that produce such unbelievably large quantities of phosphors now used in cathode-ray tubes and fluorescent lamps. The monochromator is an important optical instrument used both in research and development of phosphors, in that a quantitative determination of excitation efficiency as a function of the wave-length of the radiation used to excite the phosphor is an important optical property.

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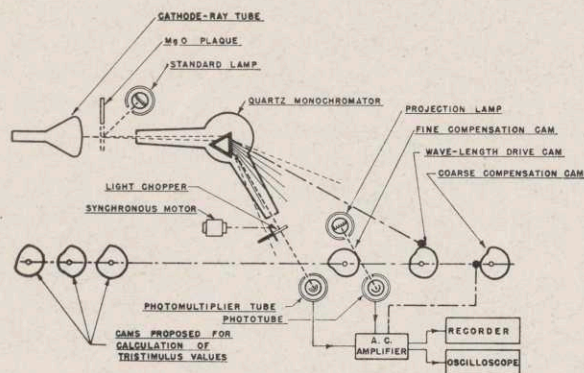


FIG. 1. Diagram—C.R.T. spectroradiometer. (Sylvania Electric Products, Inc., Physics Laboratories.)

The electron multiplier type of photo-tube, now almost universally used as a means of quantitatively determining the radiant output of phosphors, has proven to be an indispensable accessory for a very large proportion of all measurements made in the past seven or eight years.

Optical observations made in the study of atomic and molecular excitation and radiant energy emission involve the time history and the temperature conditions very indirectly as compared to the general case for phosphors. In the latter case, the time history of excitation, the time of observation, and the temperature history during both excitation and observation are of utmost importance and, in fact, serve as controllable variables through which the basic facts concerning the electronic band structure of the solid are exhibited.

#### A BRIEF REVIEW OF THE THEORY OF PHOSPHORS

Nearly all practical phosphors are crystalline in structure and are very dependent on the presence and suitable disposition of selected impurities known generally as "activators." In certain types of phosphors, of which the silicates are typical, the activator fits into the lattice in a substitutional position for one of the atoms normally found in the basic crystal structure. Phosphors of which zinc sulfide is typical, require concentrations of activator that constitute a very small fraction of 1 percent, since the necessary impurities take positions interstitially between the atoms of the crystalline substance. The outermost or valence electrons of a perfect crystal move from atom to atom throughout the crystal even at extremely low temperature. In spite of this freedom of motion, the application of small differences in potential to the crystal does not result in conductivity, because the electrons are so crowded into their only available quantum states that at low temperatures and with moderate electric fields the electrons cannot cross the energy gap, in which there are no available electronic energy levels, to find the greater freedom of motion associated with the higher "conduction" levels of the system. Support for this view of the

electronic structure of insulators may be derived from experiments on the optical absorption of these crystals. If the energy ( $h\nu$ ) of the light quantum is insufficient to cause an electronic transition from an occupied to an unoccupied state, then the optical absorption of the crystal is small. Thus, the measurement of the optical absorption of single crystals, or even of polycrystalline material when samples of uniform particle size and variable thickness may be used, serve to give direct information concerning the energy level system of the phosphor.

The introduction of impurities into the crystal generally modifies in a measurable way the absorption characteristic of the material. This fact indicates the importance of the close coordination needed to relate the chemistry and production of phosphors to the optical absorption characteristics of the substance.

By far the most common means of phosphor excitation depend either on the absorption of energy by the electrons from electromagnetic radiations in the visible or in the ultraviolet range of the spectrum, or else by the absorption of energy that results from electron bombardment. Although many secondary effects are associated with phosphor excitation, the primary process involves the transfer of electrons from the stable valence electron band or from bound electrons located at impurity centers into normally unoccupied electronic levels of the conduction band. As a result of this transfer of the electron into a conduction band, a negative charge carrier becomes mobilized, and, in addition, the absence of an electron in the normally filled valence band is the equivalent of mobilizing a positive charge carrier or an "electron hole." The reverse process is the recombination of an electron with an electron hole and the simultaneous conversion of the potential energy thus temporarily stored into the radiant energy of a light quantum or into the vibrational energy of the atoms nearby.

In many respects, the situation may be compared to the ionization of a gas in the plasma of a gas discharge. In that case, both the positive ions and the electrons are mobile and can maintain nearly equal volume concentrations, and yet free space recombination is a relatively uncommon occurrence. If the ion becomes attached to an insulating wall, or if the electron becomes attached to an otherwise neutral atom or molecule, then recombination takes place very readily. A similar situation occurs in phosphors, and other insulators and semiconductors. If the electron hole becomes trapped at an impurity atom, while the electron itself remains free, recombination is likely to occur. In a similar manner, electron holes that migrate to the surface of the crystal attract electrons and recombine with them there. Electrons may become trapped in other types of impurity centers, but, nevertheless, recombination can take place because of the mobility of the holes. The last of the simple cases involves the trapping of both the holes and

the electrons. A "meta-stable" situation is thus created in which recombination is inhibited and becomes extremely temperature sensitive, since it is by means of the absorption of temperature energy by the trapped electrons or holes that they are restored to mobility.

An investigation of spectral emission data, interpreted in a manner thus briefly described, permits the observer to evaluate quantitatively the energy jump that the electron takes upon recombination. Since the energy jumps for a given transition in a particular phosphor are not exactly the same throughout the volume of the crystal, the radiant energy emitted is not confined to a narrow band of wave-lengths, but spreads on each side of a most probable energy transition to create a relatively broad continuous set of emitted wave-lengths. Thus, the determination of the spectral emission characteristic of a phosphor stands very high in the interests of all investigations, including research, development, and quality control.

The lines of investigation that yield detailed information in support of the theoretical picture thus described, include the determination of excitation efficiency as a function of the wave-length of the exciting radiation and as a function of the electron energy and current density used for excitation. A quantitative determination of the influence of temperature on the light output and of the time changes of light output can be interpreted to give quantitative data on the number and energy distribution of the trapping states. Simultaneous determination of the electrical conductivity of crystals during excitation yields valuable detailed material for analysis.

#### SPECTRORADIOMETERS

Basically, a spectroradiometer is a low resolution spectrometer designed to give quantitative information concerning the radiant power at the exit slit found in a relatively wide band of wave-lengths. Thus, accuracy in wave-length specification is seldom as good as 1 percent and is often allowed to spread as much as  $\pm 5$  percent from the nominal wave-length value. This sacrifice in wave-length resolution is necessary in order to have sufficient power delivered to the detector to make quantitative measurements relatively easy. The fact that most practical spectroradiometers have such poor wave-length resolution becomes an objection only under the relatively rare circumstance that the spectral emission characteristic of the phosphor is one that has important structural details which would be completely lost to the observer who places his entire reliance upon a low resolution instrument.

The invention of the multiplier photo-tube as an electronic detecting element made it possible to increase the speed with which spectroradiometric measurements can be made and, in fact, permitted the development of automatic recording instruments that give valuable quantitative information ready for use and analysis in a

matter of minutes. The first such instrument was that developed by Dr. Zworykin<sup>1</sup> and his group at RCA.

The Zworykin instrument has been further developed by Leverenz and Shrader and has served to yield a vast quantity of recorded spectroradiometric data. Although this instrument was designed to have approximate corrections included automatically to yield a record of the radiant power output from an excited phosphor per unit range in wave-length as a function of the wave-length, it has not been found necessary for them to have high accuracy in this respect. The instrument has been used primarily as a means of discovering *changes* in the spectral output that follow systematic changes in composition or in processing. These changes may be exhibited with all the accuracy required for practical purposes, without the development of a system which makes perfect compensation for such factors as slit-width variation, light absorption in the optical parts of the instrument, and variations in photo-multiplier response.

Instruments of this type may be made very versatile, so that an analysis can be given for phosphors excited either in a demountable cathode-ray tube arrangement in which some 6 or 8 samples may be prepared for study at a given time, or the light may be derived from a phosphor used in a completed cathode-ray tube or from phosphors excited by the absorption of ultraviolet radiation. Instruments used in connection with the development of phosphors for fluorescent lighting may also be adapted to receive and analyze the light produced in this manner.

A unique instrument has been developed for use under the direction of Dr. L. Headrick of the RCA Victor Division,<sup>2</sup> Lancaster, Pennsylvania. A twelve-inch cathode-ray tube, manufactured with a long persistence P-7 cascade phosphor type of screen, is used to record the radiant output as a function of the wave-length. The approximate time for the production of a complete record is 13 sec. and the pattern remains visible for at least 1 or 2 min. Since it is possible to shift the samples being investigated very rapidly, advantage is taken of

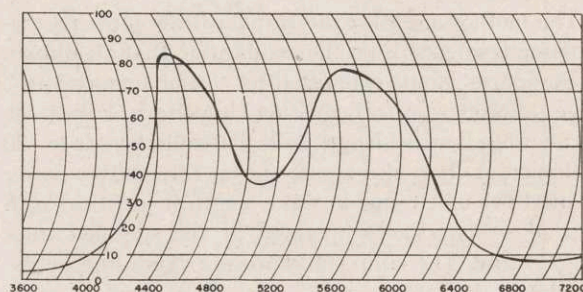


FIG. 2. Superposition of test runs 1, 2, and 3 P-4 phosphor in 10BP4 tube taken on spectroradiometer of Sylvania Electric Products, Inc.

<sup>1</sup> V. K. Zworykin, *J. Opt. Soc. Am.* **29**, 84 (1939).

<sup>2</sup> A. E. Hardy, *Trans. Am. Electrochem. Soc.* **91**, 221 (1947).

the fact that two or three records can be run on in rapid sequence and thus permit a direct comparison between samples. It is evident that a recorder of this type is very suitable for quality control, in that one of the samples may be the "standard" and the other sample a phosphor or phosphor blend which must come within certain, rather narrowly specified, limits of the standard pattern in order to be acceptable. Whenever a permanent record of the observations is desired, a camera mounted directly on the instrument is used to photograph the pattern.

Considerable care has been taken in the construction of this instrument and in its calibration, in order to warrant its use as a means of color identification by the I.C.I. color system. The need for instrumental accuracy, when the data are to be used for color specification, has also been recognized by Bowie and Martin.<sup>3</sup> Figure 1 shows by diagram the main features of the Sylvania automatic spectroradiometer. A typical record of the blended phosphor identified as P-4 and described as being television white is shown in Fig. 2. This figure also serves to indicate the reproducibility of the recording instrument in that the line has been widened slightly, so that three separate runs on the same material are covered completely by the line shown.

Attention should be directed to a recent development of Dr. F. J. Studer,<sup>4</sup> as a result of which an automatic spectroradiometer has been designed for service in the Research Laboratory of the General Electric Company. This equipment has the advantage of noteworthy simplicity and at the same time comparison tests showed excellent agreement between the automatically recorded spectral power distribution and the point by point study made by Dr. B. T. Barnes in which a double monochromator was used. Since the wave-length band transmitted through the Studer instrument may be of the order of 5 to 10 millimicrons, some care must be taken with such low resolution equipment when it is used with phosphors that change intensity rapidly with wave-length.

#### STANDARDIZATION OF SPECTRORADIOMETERS

The method used for the standardization of spectroradiometers depends on the assumption that all Bureau of Standards lamps calibrated for "color temperature" have the same spectral emission characteristic over the entire range in wave-length from 380 millimicrons to 720 millimicrons. It is also assumed that the relative power emitted per unit range in wave-length is identical with that of a black body operated at the specified color temperature. The lamp standards are calibrated by determining the lamp current required to make a color match with a B. of S. standard lamp. It is well known that two sources of radiant energy can have distinctly

different relative spectral power distributions and yet have exactly the same color as interpreted by a human observer. The standard lamps generally used are coiled filament projection lamps and are therefore neither true black body sources nor tungsten emission sources. It follows, therefore, that if two lamps that differ in mechanical structure in terms of the spacing between coils and the effect of cooling at the filament supports have the same color, they will nevertheless differ appreciably in their true relative spectral power emission properties. It is impractical to consider the use of a high temperature black body source for standardization. It might even be considered impractical to use a large area ribbon filament as a working standard in a particular laboratory. A practical solution for the standardization of the spectroradiometers could, however, be worked out along the following lines. First, the spectral emissivity of tungsten viewed in a direction normal to the surface must be known for the entire range of wave-length and temperature of importance. The data published by Forsythe and Worthing<sup>5</sup> are in excellent agreement with recently determined, but still unpublished, data obtained by the writer.<sup>6</sup> The Forsythe and Worthing data are well represented by the empirical formula:

$$e_{\lambda T} = 0.5364 + 5.24 \times 10^{-6} T - (9187 + 3.822 T) \times 10^{-8} \times \lambda.$$

In this equation,  $e_{\lambda T}$  is the spectral emittance and is a function of the wave-length expressed in millimicrons and the temperature expressed in degrees Kelvin. The true temperature of a tungsten ribbon can be determined from an accurate measurement of the "brightness" temperature evaluated by a well-calibrated optical pyrometer. The wave-length at which the brightness match is made must be known, and the emittance can be obtained from the above equation as a result of successive approximations. An optical system can be arranged so that the only light that enters the spectroradiometer comes from the uniformly hot part of the ribbon filament. If consideration is given to the absorption of the glass envelope surrounding the ribbon filament, and if geometrical factors are also taken into account, then the absolute spectral irradiance can be computed. In general, it is only the *relative* spectral irradiance that is needed and the method by which this information is used involves the introduction of gain-correcting adjustment, as indicated in the schematic of Fig. 1, so that the recorded output curve coincides with the calculated relative irradiance curve.

The second step in standardization would involve the substitution of a particular standard "color-temperature" lamp of the coiled filament type and the running of a spectral emission curve for this lamp. After having once made a determination of the true relative spectral emission of this practical secondary standard, one can

<sup>3</sup> R. N. Bowie and Alfred E. Martin, Proc. I.R.E. 36, 1023 (1948).

<sup>4</sup> Frank J. Studer, J. Opt. Soc. Am. 38, 467 (1948).

<sup>5</sup> W. E. Forsythe and A. G. Worthing, Astrophys. J. 61, 146 (1925).

<sup>6</sup> W. B. Nottingham and W. E. Mutter, Phys. Rev. 47, 1261 (1948);  $e_{\lambda T} = 0.5308 + 5.24 \times 10^{-6} T - (9187 + 3.907 T) \times 10^{-8} \times \lambda$ .

then use it to maintain the instrument in calibration without recourse to the primary ribbon filament standard.

### I.C.I. INTERPRETATION OF THE SPECTRORADIOMETRIC DATA

Through the cooperative activity of the International Commission on Illumination (I.C.I.), a system of color specification has been developed by which the determination of two numbers is sufficient to identify a color appearance to the so-called "standard" observer. These two numbers are known as the "trichromatic coefficients." In the application of this system, use is made of three sets of numerical data represented by the symbols  $\bar{x}_\lambda$ ,  $\bar{y}_\lambda$ , and  $\bar{z}_\lambda$ . The numerical values of these functions are available,<sup>7</sup> and the arithmetical calculation in which they are used is represented by the three equations:

$$U = \int_0^\infty \bar{x}_\lambda h_\lambda d\lambda,$$

$$V = \int_0^\infty \bar{y}_\lambda h_\lambda d\lambda,$$

$$W = \int_0^\infty \bar{z}_\lambda h_\lambda d\lambda.$$

In these equations  $h_\lambda$  represents the relative spectral power distribution of the source being evaluated. The trichromatic coefficients are defined finally by the expressions:

$$x = U/(U+V+W), \quad y = V/(U+V+W).$$

The numerical evaluation of the three quantities  $U$ ,  $V$ , and  $W$  may be carried out in either one of two ways as shown in Fig. 2 has been determined. The one method involves the direct graphical integration of the product curve obtained by the direct multiplication of the particular tristimulus distribution function  $\bar{x}_\lambda$ ,  $\bar{y}_\lambda$ , or  $\bar{z}_\lambda$  by the  $h_\lambda$  function. The second method of computation involves the "selected ordinate" summation. For each of the tristimulus distribution functions, tables of wavelength values at which the ordinate of the spectral power distribution curve should be evaluated have been prepared.<sup>8</sup> Bowie and Martin have prepared transparent sheets of plastic on which the 30 selected abscissa lines are drawn for each of the tristimulus distribution functions. They superimpose these engraved lines over the record similar to Fig. 2 and tabulate the ordinate values at each intersection between the engraving and the

relative power distribution curve of the phosphor under examination. The simple sum of the 30 numbers thus obtained is directly proportional to the value of  $U$ ,  $V$ , or  $W$  depending on which engraving is used. In general, the use of the selected ordinate method is superior in terms of convenience and accuracy to the straight integration scheme.

The use to which the trichromatic coefficients  $x$ ,  $y$  may be put is well illustrated by Figs. 3 and 4, in which data published by Hardy<sup>9</sup> are shown by way of illustration. The reader may be reminded that in the diagram of Fig. 3, the solid line marked "pure spectrum locus" closed at the lower end by a straight line joining the extreme blue region with the extreme red region, encloses the entire domain of realizable colors. The pure spectrum colors lie on the locus line and any combination whatsoever of spectrum colors used to make up a particular spectral power distribution must lie inside of the domain of realizable colors, because a mixture of any two of them results in a representative point in the diagram that lies on the straight line joining the components of the mixture. This rule of color mixture also applies, as is illustrated in Fig. 4, to the mixing of broad band sources such as we have for excited phosphors just as well as for the narrow band sources associated with individual spectrum colors.

Although qualitative inspection of the light emitted by phosphors of systematically variable composition may be recognized easily, the quantitative representation shown in Fig. 3 for the various solid solution proportions of ZnCdS:Ag for the range in CdS propor-

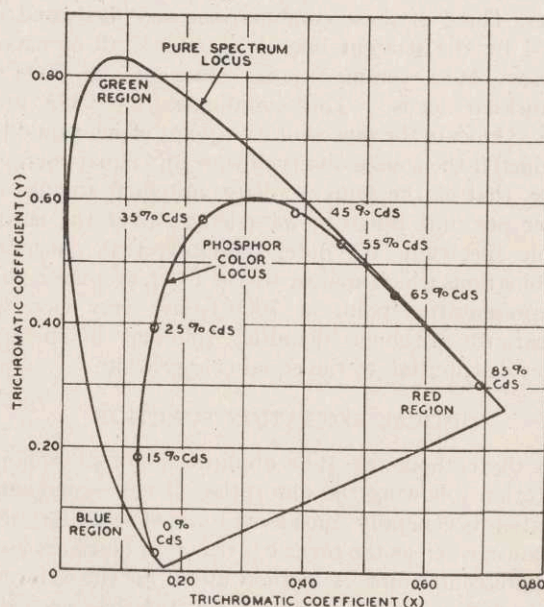


Fig. 3. I.C.I. color system. Mixture diagram showing ZnCdS:Ag phosphor color locus as a function of percent CdS. (A. E. Hardy, RCA Review.)

<sup>7</sup> D. B. Judd, *J. Opt. Soc. Am.* **23**, 359 (1933). A. C. Hardy, *Handbook of Colorimetry* (The Technology Press, M.I.T., Cambridge, 1936). For discussion of system, W. B. Nottingham, *Radiation Lab. Rep.* 804 (December, 1945) NDRC, Div. 14, OEMsr-262 "Notes on photometry, colorimetry and in explanation of the centibel scale."

<sup>8</sup> Committee on Colorimetry, *J. Opt. Soc. Am.* **34**, 633 (1944).

<sup>9</sup> Austin E. Hardy, *RCA Review* **8**, 554 (1947).

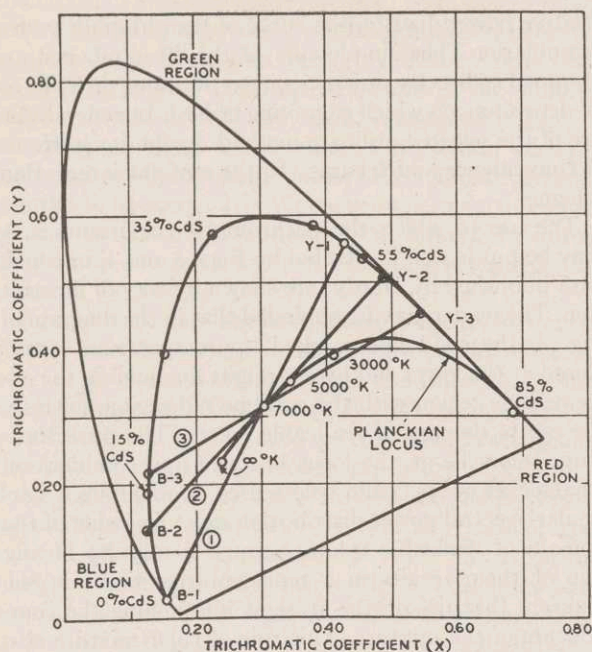


FIG. 4. Mixture diagram showing three phosphor pairs. (A. E. Hardy, RCA Review.)

tion from 85 percent down to 0 percent is of great practical value.

Although none of the phosphors found on the "phosphor color locus" line would be acceptable for a television cathode-ray tube as being "white," an infinite number of combinations could be chosen that would be indistinguishable in their whiteness by the "standard" observer. Three of these combinations are illustrated in Fig. 4 by the straight lines 1, 2, and 3, all of which intersect at a common point close to the 7000°K "Planckian locus." The coordinates  $x=0.333$  and  $y=0.333$  locate the representative point which would be obtained if the source observed were an "equal-energy" white, that is, the source radiates an equal amount of power per unit range in wave-length over the entire visible spectrum. We note, therefore, that phosphor combinations which analyze by the I.C.I. system to give a representative point at 7000°K are very close in appearance, although definitely different in spectral power distribution to the equal-energy white.

#### OPTICAL EXCITATION FUNCTION

In the cathode-ray tube applications of phosphors, excitation following the absorption of electromagnetic radiation is generally considered to be of secondary importance, whereas the reverse is true for phosphors used in fluorescent lamps. A method useful for the determination of the optical excitation function has been described by Fonda and Studer,<sup>10</sup> in which the light from the continuous spectral distribution of power from a

<sup>10</sup> Gorton R. Fonda and Frank J. Studer, *J. Opt. Soc. Am.* **38**, 1007 (1948).

hydrogen arc is passed through a monochromator and allowed to fall directly on the thin deposit of phosphor under investigation. A sufficient fraction of the light emitted by the phosphor passes through it and also through the glass plate upon which the phosphor is deposited to give rise to sufficient photoelectric current in the detecting multiplier photo-tube to serve as an accurate measure of the luminescence of the phosphor. This information, combined with the knowledge of the relative power impinging on the phosphor as a function of wave-length, allows for the quantitative determination of the relative efficiency of the different wave-lengths in the spectrum for the excitation of luminescence. Results so obtained are significant both from the theoretical and the practical points of view. Systematic changes in the excitation curve depending on the nature and the quantity of activating agent have been observed.

Fonda and Studer also have shown the value of a determination of the spectral absorption characteristic of a phosphor by studying its diffuse reflectance. They have found useful correlations between the absorption spectrum, the excitation spectrum, and the phosphor composition and treatment. These and similar data are needed on a wide variety of phosphors in order to fill in quantitative information needed for the formulation of an adequate theory to account for the optical properties of phosphors.

#### PHOSPHORESCENCE AND OTHER STUDIES INVOLVING TIME AND TEMPERATURE

One of the most interesting developments of the past decade has been the study of phosphor "glow curves." The experiment involves the excitation of a phosphor by ultraviolet light while it is maintained at a very low temperature. In general, luminescence will be observed during the excitation period but immediately thereafter the phosphorescence will fall rapidly to a negligible value. However, if the phosphor is permitted to warm up gradually, measurable phosphorescence will very likely develop in the temperature range 100° to 200°K and a reproducible curve will be obtained for the power radiated as a function of the temperature. Obviously, such curves depend on the constant time rate of change of temperature used in the experiment and on the composition and structure of the phosphor. A summary of some of the work and a discussion of the theory may be found in the report by Garlick<sup>11</sup> and the paper by Williams and Eyring.<sup>12</sup>

Equipment designed with all of the refinements necessary to get good quantitative data at very slow rates of increase in temperature with time, could also be used to determine the time change in phosphorescence at fixed

<sup>11</sup> G. F. J. Garlick, Chapter 5, p. 87 of *Solid Luminescent Materials* by G. R. Fonda and F. Seitz (John Wiley and Sons, Inc., New York, 1948).

<sup>12</sup> Ferd Williams and Henry Eyring, *J. Chem. Phys.* **15**, 289 (1947).

points in temperature. Outside of the studies made at room temperature, relatively little has been done on the decay of phosphorescence at low temperature. Another closely related line of experimentation would involve the maintenance of the excited phosphor at a very low temperature and the observation of the nature of the phosphorescence decay under the stimulation of monochromatic infra-red radiation. It is evident that all of these studies, if applied to a given sample of phosphor, would yield most valuable information from which the number and energy depth of the electronic trapping states could be determined.

Extensive studies were made during the past few years on the natural and stimulated decay properties of phosphorescent substances, with the major attention given to the development of phosphors useful for particular military applications. These studies demonstrated that broadly speaking, there are two types of decay most commonly found, which are: (1) "exponential" and (2) "inverse time." These decay types are easily identified by the fact that the exponential yields a fairly good straight line when the logarithm of the phosphorescent output is plotted against a linear time scale. The slope of the line thus obtained is very nearly independent of the degree of excitation and the length of time of excitation over quite wide ranges of these variables. As a class, the silicates, the fluorides, and the tungstates generally exhibit exponential decay curves. The sulfides fall in the "inverse time" grouping and here an approximately linear plot is obtained if the logarithm of the phosphorescent power is plotted as a function of the logarithm of the time of observation. The slopes of

the observed lines vary from approximately 0.8 to 2.0. Since the characteristic slope for a simple bimolecular process would have been 2, it is evident that phosphorescence cannot be explained in such a simple manner. Considerable experimental data have been made available<sup>13</sup> recently and it is probable that additional information will be accumulated slowly, since there are in existence in the various research laboratories equipment for making such studies. Relatively little attention is being given to this matter at present.

#### CONCLUDING REMARKS

The means for the determination of many of the optical properties of phosphors have been developed and enough information obtained to show that researches in this field have in reality just begun. In spite of the complications, various approaches yield interlocking parts to this scientific jigsaw puzzle. More attention is being given at present to the quantitative determination of the spectral power distribution emitted by phosphors and determined by means of automatic spectroradiometers. It is understandable that so much emphasis is placed on this particular line of research, because it is so important from all of the motivating points of view that include research, development, and product control.

<sup>13</sup> G. R. Fonda and F. Seitz, *Solid Luminescent Materials* (John Wiley and Sons, Inc., New York, 1948). Also Soller, Starr, and Valley, *Cathode Ray Tube Displays* (McGraw-Hill Book Company, Inc., New York, 1948), Radiation Lab. Series, Vol. 22. (See Chapter 18, "Screens for cathode ray tubes" by W. B. Nottingham.) Kröger, Hoogenstraaten, Bottema, and Botden, *Physica* **14**, 81 (1948) and F. A. Kröger and W. Hoogenstraaten, *Physica* **14**, 425 (1948).



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