

- <sup>94</sup> M. Cloupeau, *Phys. Fluids* **6**, 5, 679 (1963); also *Compt. Rend.* **254**, 213 (1962); **253**, 1160 (1961); and **251**, 918 (1960).
- <sup>95</sup> P. Jeanmaire, *Phys. Fluids* **6**, 1028 (1963).
- <sup>96</sup> R. G. Fowler, *Phys. Fluids* **6**, 548 (1963).
- <sup>97</sup> D. Bershader, *Rev. Mod. Phys.* **32**, 780 (1960).
- <sup>98</sup> Yu. V. Makarov and S. V. Nartov, *Soviet Phys.—Tech. Phys.* **8**, 541 (1963).
- <sup>99</sup> G. C. Vlases, *J. Fluid Mech.* **16**, 82 (1963).
- <sup>100</sup> G. C. Vlases, *Phys. Fluids* **7**, 1358 (1964).
- <sup>101</sup> O. K. Mawardi, *Phys. Fluids* **7**, Part 2, S9 (November 1964).
- <sup>102</sup> J. Keck, *Phys. Fluids* **7**, Part 2, S16 (November 1964).
- <sup>103</sup> J. M. Wilcox, E. Pugh, A. Dattner, and J. Eninger, *Phys. Fluids* **7**, Part 2, S51 (November 1964).
- <sup>104</sup> A. F. Haught, *Phys. Fluids* **5**, 1337 (1962).
- <sup>105</sup> J. M. Wilcox, F. I. Boley, and A. W. DeSilva, *Phys. Fluids* **3**, 15 (1960).
- <sup>106</sup> M. H. Brennan, I. G. Brown, P. P. Millar, and C. N. Watson-Munro, *J. Nucl. Energy, Part C, Plasma Phys.* **5**, 229 (1963).
- <sup>107</sup> M. H. Brennan, J. A. Lehane, D. D. Millar, and C. N. Watson-Munro, *Australian J. Phys.* **16**, 340 (1963).
- <sup>108</sup> L. Sharp and C. N. Watson-Munro, *Phys. Rev. Letters* **11**, 39 (1964).
- <sup>109</sup> W. H. Heiser, *Phys. Fluids* **7**, 143 (1964); also, "Axial Field Effects in a Magnetically Driven Shock Tube," MIT, R. L. E. Tech. Rept. 408 (29 March 1963).
- <sup>110</sup> R. B. Block, "The Onset of an Electromagnetic Shock Wave," Case Inst. Tech. Rept. No. A-23 (July 1963).
- <sup>111</sup> M. Naraghi, "A Study of Current Sheets in a Coaxial Plasma Gun," Case Inst. Tech. Rept. No. A-22 (June 1963).
- <sup>112</sup> M. Yasuhara, S. Tsuboi, and K. Ban, Tokyo, Univ. Aeron. Res. Lab. Rept. **3**, Special issue (September 1963).
- <sup>113</sup> D. W. Koopman, *Phys. Fluids* **7**, 1651 (1964).
- <sup>114</sup> J. C. Keck, *Phys. Fluids* **5**, 630 (1962).
- <sup>115</sup> F. J. Fishman and H. Petschek, *Phys. Fluids* **5**, 632 (1962).
- <sup>116</sup> H. Alfvén, *Rev. Mod. Phys.* **32**, 710 (1960).
- <sup>117</sup> G. A. Pearson and W. B. Kunkel, *Proceedings of the International Conference on Ionizing Phenomena in Gases, Paris, 1963*, edited by P. Hubert and E. Cremieu-Alcan (Minister of State in Charge Scientific Research pertaining to Atomic and Spacial Matter, Paris, 1963), Vol. I, p. 259; See also *Phys. Rev.* **130**, 864 (1963); Also UCRL Rept. 10366.
- <sup>118</sup> H. D. Weymann, *Phys. Fluids* **3**, 545 (1960).
- <sup>119</sup> P. Gloersen, *Phys. Fluids* **3**, 857 (1960).
- <sup>120</sup> D. L. Jones, *Phys. Fluids* **5**, 824 (1962).
- <sup>121</sup> L. Wetzel, *Phys. Fluids* **5**, 824 (1962); **6**, 750 (1963); **6**, 1660 (1963).
- <sup>122</sup> J. B. Gerardo, C. D. Henricks, and L. Goldstein, *Phys. Fluids* **6**, 1222 (1963).
- <sup>123</sup> H. Groening, *Phys. Fluids* **6**, 142 (1963).
- <sup>124</sup> A. C. Pipkin, *Phys. Fluids* **6**, 1382 (1963).
- <sup>125</sup> J. P. Barach and J. A. Sivinski, *Phys. Fluids* **7**, 1075 (1964).
- <sup>126</sup> R. J. Hill, *Phys. Fluids* **7**, 1865 (1964).
- <sup>127</sup> C. Ferrari and J. H. Clarke, *Brown Univ. Rept. Cm 1020* (1963).
- <sup>128</sup> R. A. Nelson, *Phys. Fluids* **8**, 23 (1965).
- <sup>129</sup> D. A. Tidman, *Phys. Fluids* **5**, 1104 (1962).
- <sup>130</sup> J. P. Wild, S. F. Smerd, and A. A. Weiss, *Ann. Rev. Astron. Astrophys.* **1**, 291 (1963).
- <sup>131</sup> S. A. Colgate, W. H. Grasberger, and R. H. White, *J. Phys. Soc. Japan* **17**, Supplement A, 111 (1962), Part III.
- <sup>132</sup> M. H. Johnson and S. A. Colgate, *Phys. Rev. Letters* **5**, (1960).
- <sup>133</sup> I. M. Cohen and J. H. Clarke, "The Influence of Viscosity on Shock Waves Structured by Radiation," Div. Engr. Brown Univ. Rept. Nonr. (562)35/5, October 1964.
- <sup>134</sup> Z. O. Bleviss, *The Structure of a Steady Magnetohydrodynamic Switch-on Shock Wave* (Stanford University Press, Stanford, California, 1959); also, Douglas Rept. No. SM 23720, Santa Monica Div. (October 1959).
- <sup>135</sup> H. E. Petcheck and S. Byron, *Ann. Phys. (N. Y.)* **1**, 270 (1957).
- <sup>136</sup> C. K. Chu and R. Taussig (private communication); see also *Proc. 1965 Appl. Math. Symp., Am. Math. Soc.* (to be published).

## Stimulation of Zinc Sulfide and Similar Inorganic Phosphors

D. E. MASON\*

*Electrical Engineering Department, University of Manchester, Manchester, England*

Further support is provided for a model of the stimulation process in inorganic phosphors recently proposed by Luchner, Kallmann, Kramer, and Wachter. A reasonable identification of the center responsible for the absorption of stimulating radiation (the main feature of this model) is made for zinc sulfide phosphors containing copper, but it is shown that no identification can be made as yet of the absorbing centers responsible for most of the peaks of stimulation spectra so far observed. Many of the apparently incompatible published observations can be reconciled with the aid of previously unpublished work.

### I. INTRODUCTION

In a recent paper by Luchner, Kallmann, Kramer, and Wachter,<sup>1</sup> a model for the stimulation process (in which the luminescence of a previously excited phosphor is temporarily enhanced by long-wavelength radiation incapable of exciting it) is proposed, which may, with profit, be enlarged upon. In this way, the

conflicting views of various authors may, to some extent, be resolved, using their own data as well as previously unpublished work of the author.<sup>2</sup>

The model of Luchner *et al.* (which we will call the LKKW model) is outlined below:

1. Trapped electrons exist mainly in the neighborhood of ionized activators and are coupled to them.
2. An infrared quantum is absorbed by the complex

\* A member of the staff of Ferranti Ltd., Manchester, England.  
<sup>1</sup> K. Luchner, H. Kallmann, B. Kramer, and P. Wachter, *Phys. Rev.* **129**, 593 (1963).

<sup>2</sup> D. E. Mason, Ph.D. thesis, University of Birmingham, England, 1950 (unpublished).

of ionized activator and trapped electron. This energy may be dissipated in the ways listed below.

- (a) It may be transferred to the crystal by lattice vibrations, with the complex returning to its original state.
- (b) Part of the absorbed energy may be used to raise the trapped electron to an intermediate level, from which it can radiatively recombine with the ionized activator without passing through the conduction band. This produces a stimulation of the afterglow without any stimulation of the conductivity.
- (c) The energy may be partially used to release an electron to the conduction band. A stimulation of the conductivity will result as well as a possible stimulation of the afterglow.
- (d) The energy may be used to free electrons and holes. Some thermal energy may be necessary for this process.

It is evident that the absorbing complex may be capable of fluorescence, so that the energy of the absorbed infrared quantum may be dissipated in the emission of another infrared quantum of lower energy. Thus we should add:

- (a') The energy may be dissipated as a quantum of infrared radiation.

The example of this phenomena we shall consider later (that occurring in the copper center in zinc sulfide) indicates that although the ionized activator and trapped electron form a complex, the influence of the trapped electron on the ionized activator may be very small, while the influence of the ionized activator on the trapped electron, by the transfer of energy, may be considerable.

The idea of the center complex was put forward in the very early days of luminescence theory by Lenard.<sup>3</sup> The center complex is an association of centers, such as ionized activators (or luminescence centers) and electron traps, whose interaction with one another does not essentially affect the properties of the centers. However, the interaction between centers within the complex is large compared with the interaction or "coupling" to the lattice. The concept of the center complex also contains the idea that the transfer of electrons between centers of the complex can occur without movement through the conduction or valence bands. A useful analogy to the center complex may be provided by a branched organic molecule set in a host lattice.

It is seen that the LKKW model disagrees with the model still held by Curie<sup>4</sup> and others which assumes that the infrared quantum is absorbed by the trapped electron. This view is untenable, as has been shown by

Garlick and Mason<sup>5</sup> from a study of the relation of stimulation spectrum to the prevailing distribution of trapped electrons and to the ejection of electrons from traps by infrared radiation. Mason,<sup>2</sup> in 1950, summarized the position in the following words: "Experimental evidence supports the assumption that an absorbing centre exists in the phosphor closely associated with an electron trap or traps but that this centre is not the electron trap itself. The absorption characteristics of such a centre (and hence the stimulability for various wavelengths) would not be directly related to the depths of the electron traps which must be filled for absorption to occur." Luchner *et al.* have added to this a definite postulate as to the nature of the absorbing center and have shown that their postulate is plausible. However, there is no reason to believe that only one type of absorbing center will be present in any phosphor. In this paper, we provide more evidence for the LKKW model, covering the bare bones of our extended version of the model.

## II. THE FORM OF THE STIMULATION SPECTRUM

The stimulation spectrum may be defined as the variation with quantum energy (or wavelength) of the increase in the luminescence per quantum of incident infrared or long-wavelength visible radiation. Since this definition includes both the probability of absorption and the probability of stimulation as a consequence of an absorbed quantum, it would be valuable to separate these factors. Thus, a spectrum could be similarly defined in terms of quanta of *absorbed* radiation. Although such a spectrum has not yet been used, advances in the growth and polishing of single crystals permitting the accurate measurement of absorption make its use in the future certain. We are, unless otherwise stated, concerned with the stimulation of the afterglow after excitation.

The last stage of the stimulation may involve a retrapping in shallow traps (as shown by the considerable afterglow after the stimulating radiation is cut off), but this does not affect the terminology used, which is merely intended to describe an observed phenomenon, not to imply a theoretical description of the mechanism involved. (Fluorescence is used, in the same way, to describe the luminescence while the phosphor is being excited,<sup>6</sup> not, as used by Curie,<sup>4</sup> to include afterglow due to forbidden transitions.)

The stimulation spectrum of inorganic phosphors contains a band, rising from zero at some long wavelength (which we shall call the long-wavelength limit) and increasing in intensity towards shorter wavelengths. This band is referred to as the S.W. (short wavelength) band. In addition, for certain phosphors, various sharp peaks are found near the long-wavelength limit. It is not possible to investigate the S.W. band at

<sup>3</sup> P. Lenard, *Ausleuchtung und Tilgung* (Verlag Winter, Heidelberg, 1918).

<sup>4</sup> D. Curie, *Luminescence in Crystals* (Methuen and Company Ltd., London, and John Wiley & Sons, Inc., New York, 1963).

<sup>5</sup> G. F. J. Garlick and D. E. Mason, *Trans. Electrochem. Soc.* **96**, 90 (1949).

<sup>6</sup> G. F. J. Garlick, *Luminescent Materials* (Oxford University Press, London, England, 1949).

wavelengths within the emission spectrum of the phosphor if this is a powder. However, using single crystals with accurately polished faces, it should be possible to discriminate between the incident beam and the resulting stimulated emission. Investigations with powder phosphors do, however, indicate that radiation of a wavelength in the emission band and (for the alkaline-earth sulfide phosphors) even in the ultraviolet beyond the emission band produces a

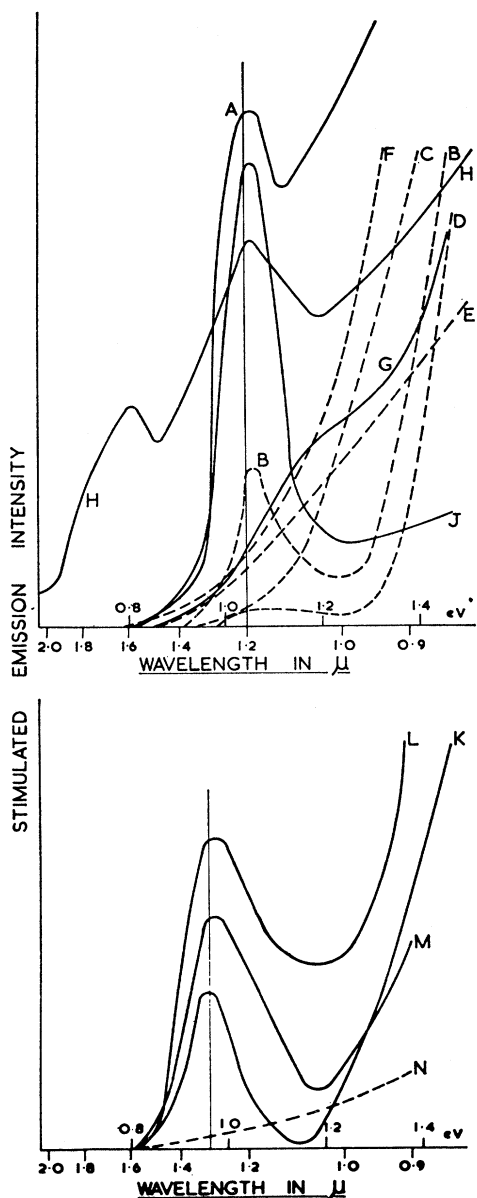


FIG. 1. Stimulation spectra of zinc sulfide phosphors. At 77°K: A, ZnS-Cu-Pb (specimen 3); B, ZnS-Cu-Pb (specimen 4); C, ZnS, self-activated (specimen 1); D, ZnS-Cu (specimen 4); E, ZnS-Ag (specimen 1); F, ZnS-Mn (specimen 1); G, ZnS-Mn-Pb; H, ZnS-Pb (specimen 1); J, ZnS-Pb (specimen 2). At 290°K: K, ZnS-Cu-Pb (specimen 4); L, ZnS-Pb (specimen 2); M, ZnS-Pb (specimen 1). At 160°K after excitation at 345°K: N, ZnS-Pb (specimen 1).

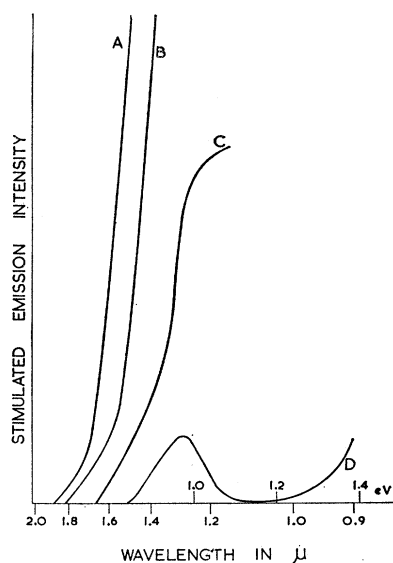


FIG. 2. Stimulation spectra for a ZnS-Ag-Cu-Pb phosphor.

Curve	$T_D$	Decay time (min)	$T_S$
A	90	1	90
B	90	20	90
C	150	$\ll 1$	90
D	290	1	290.

similar ejection of electrons from traps to that observed with infrared radiation.

Several authors (including Morehead<sup>7</sup>) believe that the stimulation spectrum of zinc sulfide phosphors varies little with activator or from specimen to specimen. However, we have not found this to be true, considerable variations occurring in the long-wavelength limit of the S.W. band (Figs. 1 and 2). These long-wavelength limits range from 1.0 to 1.9  $\mu$  (1.24 to 0.65 eV) at 77°–90°K, depending on activator, if excited at the temperature at which they are stimulated. If excited at a higher temperature ( $\sim 290^\circ\text{K}$ ) the long-wavelength limit at 77°–90°K may move to shorter wavelengths (say from 1.0 to 0.7  $\mu$ ). Since few ZnS phosphors are stimulative at 290°K (except for those containing lead), less information about variations in long-wavelength limit with excitation temperature is available for stimulation at 290°K. However, ZnS-Cu-Pb has a long-wavelength limit of 1.05  $\mu$  while ZnS-Pb (both blue-green-emitting and orange-emitting specimens) and ZnS-Mn-Cu have a limit at approximately 1.5  $\mu$ . Consider now the sharp peaks observed in the stimulation spectrum. In ZnS phosphors, the peaks so far reported are<sup>8</sup> 2.5 and<sup>5,9</sup> 1.2  $\mu$  at 77°–90°K and 1.3  $\mu$  at temperatures from 180°K to at least 350°K. To these we<sup>2</sup> can add a 1.6- $\mu$  peak in ZnS-Pb and a 1.0- $\mu$  peak in ZnS-Mn-Pb at 90°K (Fig. 1, curves H and G). The curves of Browne<sup>8</sup> would indicate

<sup>7</sup> F. F. Morehead, *J. Phys. Chem. Solids* **24**, 37 (1963).

<sup>8</sup> P. F. Browne, *J. Electron. Ser.* **1**, 2, 1 (1956-7).

<sup>9</sup> I. Broser and R. Broser-Warminsky, *J. Phys. Radium* **17**, 791 (1956).

the presence of further stimulation bands (including perhaps the 1.6- $\mu$  band). However, these curves are unsatisfactory in several respects. Firstly, the form of the peaks is improbable for any spectrum, indicating distortion of the spectrum as a result of experimental inadequacies. Secondly, the method of traversing the spectrum used by Browne (following a technique used by Garlick and Mason<sup>5</sup>) introduces interaction between the conditions produced by different wavelengths of stimulating radiation. The use of this method becomes justifiable only if the stimulation spectrum consists of the same spectral peaks (at different relative intensities) for varying distributions of trapped electrons. This precaution, which is most important with complex spectra, has not been taken by Browne. However, it is clear from Browne's curves that bands not present in the earlier Birmingham specimens are present in his specimens, which were prepared under rather different conditions.

It is normally assumed that the sharp peaks represent some transition associated with the absorption of the infrared quantum. However, Morehead<sup>7</sup> believes that the 1.2- $\mu$  stimulation peak in ZnS is not attributable to a definite narrow-band transition, but to the overlap of the stimulation and "quenching" edges at that point. He thus infers that the stimulation is of the form we have indicated for a S.W. band, but that a similar (but totally nonradiative, hence "quenching") process intervenes which has a spectrum similar to a S.W. band. This band has a long-wavelength limit at a shorter wavelength than that of the stimulation spectrum. We do not accept his explanation for the following reasons:

1. There are two sharp peaks on curve H of Fig. 1, the stimulation spectrum, at 90°K, of ZnS-Pb (specimen 1). To account for this, Morehead's idea requires elaboration which would result in the loss of its main merit, simplicity.

2. If the rise of the 1.2- $\mu$  band is assumed to be the long-wavelength limit of a S.W. band, the short-wavelength side of the peak must be formed by the intervention of a nonradiative process (the "quenching" referred to by Morehead). However, this mechanism would result in an efficiency of producing stimulated emission from the energy stored by trapped electrons which is much smaller for short-wavelength irradiation than for long. This efficiency (the *stimulation efficiency* or SE) is usually not known, since the number of electrons trapped can usually be determined from the thermal glow curve only, which may give a completely erroneous result. Thus, we will define an *apparent stimulation efficiency* as the ratio of the number of quanta emitted as stimulation to the decrease in the number of quanta emitted as thermoluminescence attributable to the irradiation producing the stimulation. The apparent stimulation efficiencies (ASE) ob-

tained for ZnS-Pb (specimen 1) are, for the 1.6-, 1.2- $\mu$ , and S.W. bands, 1.5, 1.0, and 0.5, respectively. The reduction of the ASE by a factor of 3 from 1.6 to 0.9  $\mu$  would not account for the form of the stimulation spectrum and it is unlikely that the ratio of the SE for these wavelengths will exceed that of the ASE.

The opinion of Kallmann and Luchner<sup>10</sup> that the wavelength dependence of the stimulation of ZnS-Cu phosphors is very similar, consisting of a band at 1.3  $\mu$  and a S.W. band (giving a minimum at 1.0  $\mu$ ) independent of temperature is not well-supported. In our investigations,<sup>2</sup> for all ZnS phosphors containing copper (usually also lead) the 1.3- $\mu$  peak varies in magnitude with temperature, but not in position. It disappears below 160°-180°K. At 77°-90°K, a new peak may be present which appears to be different in origin from the 1.3- $\mu$  peak. Broser and Broser-Warminsky<sup>9</sup> agree with our results. The results of Browne<sup>8</sup> might be taken to indicate that certain ZnS phosphors may exhibit a 1.3- $\mu$  band at 77°-90°K. The 1.2- $\mu$  peak appears only at low temperatures (usually below 100°K) and the closeness of the 1.2- and 1.3- $\mu$  peaks appears fortuitous. This is supported by the absence of a 1.2- $\mu$  peak in a ZnS-Cu-Pb phosphor (specimen 2) in which the 1.3- $\mu$  peak is very strong. The existence of further isolated peaks at 1.6 and 1.0  $\mu$  renders valueless the simplicity attained by assuming that the 1.2- and 1.3- $\mu$  peaks are attributable to the same transition.

It appears that the long-wavelength peaks are attributable to a transition between two well-defined states. The S.W. bands are probably of a different nature, consisting of a superposition of bands with different long-wavelength limits. Thus the effect of quanta of different energies within the S.W. band may vary considerably. Evidence for the existence of separate bands is provided by the different stimulation spectra found at 77°-90°K for various temperatures of decay ( $T_D$ ) above 77°-90°K after excitation at a lower temperature. In general, the long-wavelength limit moves to shorter wavelengths as  $T_D$  increases. Figure 2 illustrates this for a ZnS-Ag-Cu-Pb phosphor.

It should be noted that the stimulability (stimulated emission intensity per incident stimulating quantum) of ZnS phosphors is small at room temperature compared to that at 77°-90°K, even for the phosphors specially developed for their infrared stimulability at room temperature. Rarely does the stimulability at the 1.3- $\mu$  peak at room temperature exceed one-tenth of that at the 1.2- $\mu$  peak at 90°K in phosphors showing both stimulation bands. Also the stimulability (at 77°-90°K) of the ZnS phosphors developed for stimulation at room temperature does not differ from that for conventional phosphors.

<sup>10</sup> H. Kallmann and K. Luchner, Phys. Rev. **123**, 2013 (1961).

### III. THE MODEL OF THE COPPER LUMINESCENCE CENTER PRESENTED BY BROSER AND SCHULZ AND ITS RELATION TO THE STIMULATION OF ZnS PHOSPHORS SHOWING A 1.3- $\mu$ BAND

#### A. The 1.3- $\mu$ Stimulation Band and the Excitation Spectrum for the Infrared Fluorescence of ZnS-Cu Phosphors

The nature of the centers responsible for the sharp peaks in the stimulation spectra of zinc and alkaline-earth sulfide phosphors is obscure. However, Broser, and Schulz<sup>11</sup> have shown that the excitation spectrum of the infrared luminescence of ZnS-Cu is very similar to the stimulation spectra of ZnS-Cu-Pb phosphors (Fig. 3, curve D, and curves F and G, respectively). Furthermore, when the crystal of ZnS-Cu is irradiated with blue light at 77°K, an increase in excitability (intensity of excitation spectrum) and, thus, in infrared fluorescence intensity is observed (Fig. 3, curve E) because of the transference of electrons to traps from copper centers containing two electrons, thus forming copper centers containing one electron. The irradiation with blue light also produces a change in the absorption spectrum, this change having the same form as the excitation spectrum for the infrared fluorescence (Fig. 3, curves C and E, respectively.) Further, it is found (Fig. 9 of Ref. 11) that 1.3- $\mu$  irradiation excites this additional infrared fluorescence at 77°K without destroying the state set up by the blue light. Irradiation of shorter wavelengths does, however, destroy this state at this temperature.

These results may now be compared with the phenomena observed in ZnS-Cu-Pb phosphors. In these, 1.3- $\mu$  radiation does not stimulate until a temperature of 160° to 180°K is reached. By contrast, short-wavelength radiation stimulates at temperatures above 80° to 130°K depending on the specimen. As the state set up by the blue light (as indicated by additional infrared luminescence) was found by Broser and Schulz to decay in about 20 min while the stimulation we<sup>2</sup> observed, decays in about 20 sec at the intensities used, the rise temperatures measured by Broser and Schulz would be expected to be a little lower than those we observed. Thus, it would be expected that 1.3- $\mu$  radiation would be absorbed by the excited phosphor at 77°K, but that this energy would be dissipated as infrared fluorescence at this temperature. It is tempting to postulate that, at higher temperatures, this energy is used to eject electrons from traps thus giving rise to stimulated emission. The work of Browne<sup>3</sup> (on the variation of the efficiency of the infrared fluorescence with temperature) does not ap-

<sup>11</sup> I. Broser and H.-J. Schulz, *J. Electrochem. Soc.* **108**, 545 (1961).

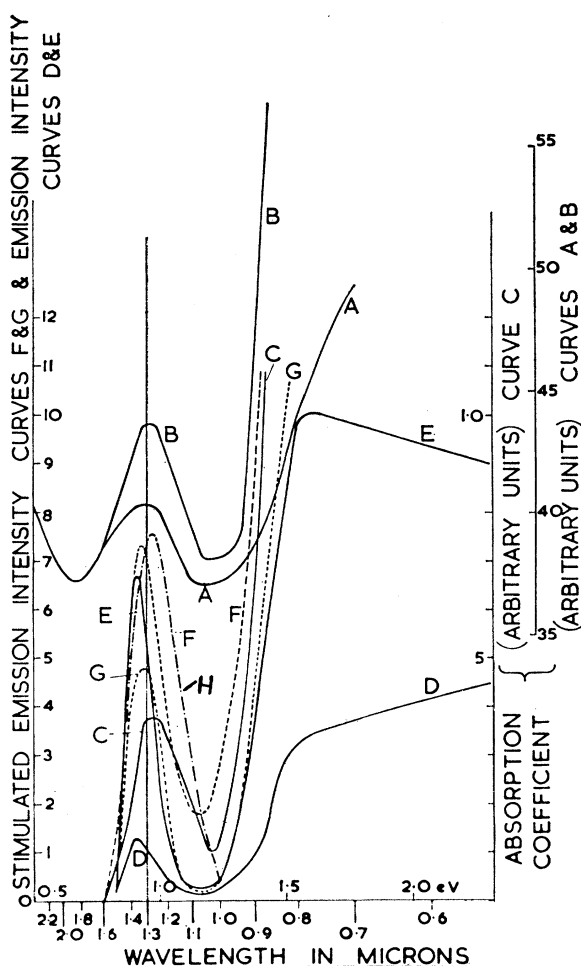


FIG. 3. Effects in ZnS-Cu and ZnS-Cu-Pb associated with the absorption of infrared radiation. Absorption spectra at 78°K of ZnS-Cu (from the data of Broser and Schulz): A, without additional blue exciting radiation of wavelengths between 0.33  $\mu$  and 0.49  $\mu$ ; B, with such blue radiation; C, additional absorption produced by blue exciting radiation. Excitation spectra for the infrared luminescence of ZnS-Cu at 77°K (from the data of Broser and Schulz): D, without additional blue irradiation (0.436  $\mu$ ); E, with such irradiation. Stimulation spectra of ZnS-Cu-Pb phosphors at 290°K: F, specimen 3; G, specimen 4; H, additional absorption produced by blue exciting radiation. The curve has been corrected to eliminate the component due to the S.W. band. The scale has been adjusted to permit easy comparison with curves F and G.

pear to assist us greatly on this point. It does, however, indicate that this transfer process is not limiting the infrared luminescence efficiency at high temperatures in his phosphors and also that, in suitable phosphors, the infrared fluorescence may persist above 350°K without being limited by any other dissipative process.

It is now necessary to consider, in greater detail, the model of Broser and Schulz, before we can discuss the nature of the process whereby the absorbed energy is transferred to the trapped electron.

### B. The Energy-Level Diagram of ZnS-Cu According to Broser and Schulz

Broser and Schulz assume that the copper center in ZnS has two energy levels (both of which may be occupied by electrons) in the lower part of the forbidden band. The interaction of electrons in these levels with the lattice is assumed to be considerable, so that the position of these levels in the energy diagram will depend on the number of electrons occupying them. Also, for the one-electron situation, it will depend on which level is occupied. The Franck-Condon principle implies, however, that these levels do not change their energy during an optical transition.

By attributing the observed emissions and absorptions to suitable transitions within the various types of center, Broser and Schulz have evolved a self-consistent system of levels. This system is shown in Fig. 4, where filled levels are shown by unbroken lines and empty levels by broken lines. The center (in its various states of equilibrium with the lattice when containing an electron or electrons in the appropriate level or levels) will be referred to in the following way. The number of electrons in the center will be enclosed in square brackets and, in the one-electron case, a superscript  $U$  or  $L$  will be added to show whether the electron is in the upper or lower level.

The centers are, therefore, described as  $[0]$ ,  $[1]^L$ ,  $[1]^U$ ,  $[2]$ . Thus, the change with increased temperature from the blue emission (characteristic of center  $[0]$ ) to green emission (characteristic of center  $[1]^L$ ) is to be expected, because of either the thermal activation (from the valence band) of an electron into the center, or the restoration to the center of an electron held in a trap at low temperatures. Thus the transition made by an electron in the conduction band will be  $E_2$  (green) instead of  $E_1$  (blue). Considering Fig. 4, it would appear that the restoration of the electron held in a trap would be to a center  $[1]^L$  with the emission of a quantum of green light, while the thermal activation would be to a center  $[1]^U$  preventing the emission of a quantum of infrared radiation. Thus, the probability of the change from blue to green emission should be enhanced, at a given temperature, by irradiation with infrared radiation capable of exciting the infrared fluorescence. However, one fact in particular does not appear to be in accord with their theory. If the blue emission is attributable to the transition  $E_1$  (Fig. 4) in the center  $[0]$ , it would appear that there is a parallel process consisting of the transition  $E_3$  (red emission) in the center  $[0]$ , followed by  $E_4$ ,  $E_5$ , or  $E_6$  (infrared emissions) in the center  $[1]^U$  when this center has reached equilibrium with the lattice. However, the emission spectrum of Fig. 2 of Ref. 11 indicates that the number of quanta of red light emitted under ultraviolet excitation is much less than the number of quanta of infrared radiation. The number of quanta of infrared radiation is much more nearly equal to the

number of quanta of blue light. It appears improbable that the transition  $E_3$  becomes nonradiative while the transitions  $E_4$ ,  $E_5$ , and  $E_6$  remain radiative. A difficulty therefore remains. The absence of infrared emission at 295°K would be expected in a ZnS-Cu phosphor which became green-fluorescent at this temperature, since the ground state of the center would always be occupied.

The occurrence of the infrared fluorescence because of the S.W. absorption, ascribed to the transition  $A_4$ , also presents difficulties. After the absorption  $A_4$  has taken place, the center contains two electrons, whilst now a hole exists in the valency band. Before infrared

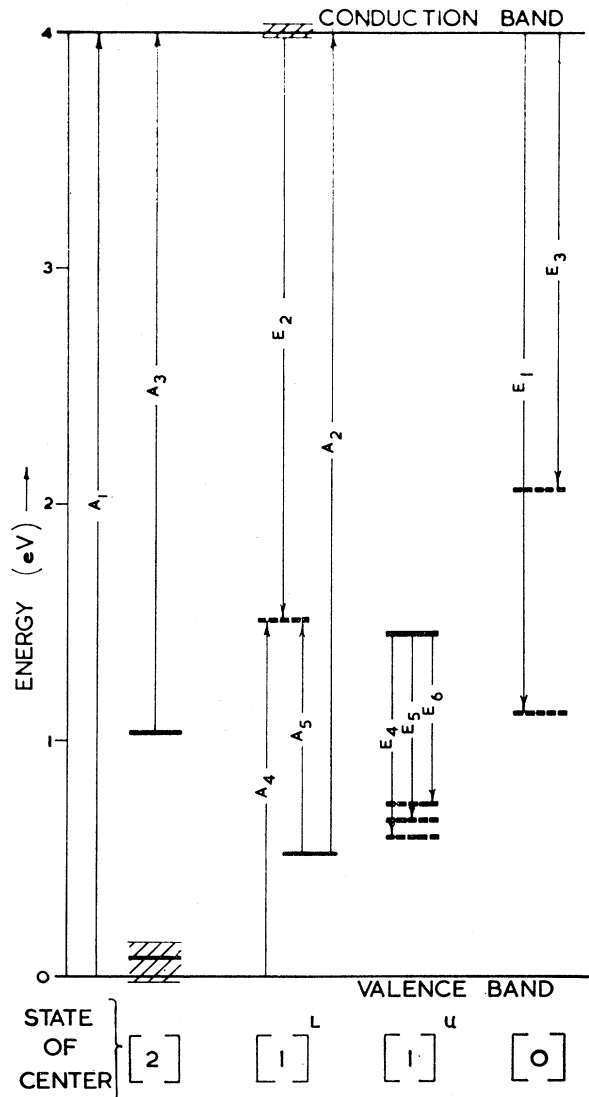


FIG. 4. The energy level diagram of Broser and Schulz for ZnS-Cu, showing the two-level centers in various states—the number of electrons in the center is indicated in the brackets. Full lines represent filled levels of the center, while broken lines represent empty levels. The hatched region represents the uncertainty in the position of the level it surrounds, as deduced from the absorption and emission data. The absorption processes are labeled  $A_{1-6}$  and the emission processes are  $E_{1-6}$ .

fluorescence can occur, the electron in the ground state of the center must be transferred elsewhere. Since the center contains two electrons, its energy levels when in equilibrium with the lattice will be as shown in Fig. 4 for the  $[2]$  center, so that the energy to be dissipated in the recombination of hole and electron is negligible (less than 0.15 eV). Thus, a high rate of recombination is probable, provided that the hole has not diffused away while the center was attaining equilibrium. The attraction of the additional electronic charge may assist in retaining the hole.

If the hole does move away, both ground states of the center remain filled and no luminescence transition can occur within the center. If the energy of relaxation of the  $[1]^L$  center to the  $[2]$  configuration (according to Fig. 4, approximately 0.5 eV for each electron, making a total of 1 eV) can be transferred to an associated trapped electron to eject it, this electron will be released under conditions in which no simple radiative loss of energy is possible, so that a nonradiative loss is probable. The hole is, also, likely to assist nonradiative processes elsewhere.

If we consider the absorption spectra of Fig. 3 in conjunction with the excitation spectra, we can deduce the relative quantum efficiencies of the 1.3- $\mu$  and S.W. excitation of infrared fluorescence. Since the absorption spectrum, in the absence of additional blue exciting radiation, probably includes background absorption, it is better to use the changes in both absorption and excitation spectra produced by blue light when determining the relative efficiency (curves C and E, respectively). Thus it appears that 1.3- $\mu$  radiation is six times more efficient than 0.8- $\mu$  radiation in exciting the infrared fluorescence. (The apparent efficacy of S.W. radiation is a result of the higher relative absorption.)

Thus, in considering the effects of infrared radiation on copper centers in phosphors with stimulation spectra of the type shown in Fig. 3, curve F (1.3- $\mu$  band and S.W. band), the situation has been reached in which both 1.3- $\mu$  and S.W. radiation can produce an excited center of the  $[1]^V$  type. The attraction of the picture presented in Sec. I (of the trapped electrons existing in the neighborhood of the ionized activators) is that it is then easy to visualize the transfer of the energy of the  $[1]^V$  center to the trapped electron by a resonance transfer<sup>11a</sup> (see, for instance, Curie<sup>6</sup>). The difference to be expected, on this model, between the effects of 1.3- $\mu$  and S.W. radiation would be due to the

large (local) concentration of positive holes produced by S.W. radiation.

Thus the behavior of the 1.3- $\mu$  stimulation band of ZnS-Cu-Pb and similar phosphors is probably due to the center responsible for the infrared fluorescence of ZnS-Cu, since the excitation spectrum for this fluorescence is the same as for the stimulation. Thus the  $[1]^L$  center of ZnS-Cu (using our terminology for the features of the model of Broser and Schulz) is probably the only center responsible for stimulation so far identified.

#### IV. THE DISTRIBUTION, IN TRAPS OF VARIOUS DEPTHS, OF THE ELECTRONS WHOSE ENERGY IS RELEASED IN STIMULATED EMISSION

It is now necessary to consider the source of the energy released in stimulation, namely the energy stored as the potential energy of electrons in traps. The methods of determining which of the trapped electrons are responsible for the stimulation (under given conditions) may be divided into two main categories. The first (A) is to vary the distribution of electrons in traps and observe the effect of this variation on the stimulation spectrum. The second (B) is to compare the distribution of electrons in traps of various depths, with and without irradiation of wavelengths producing stimulation. The distribution of filled electron traps of various depths may be determined by any suitable means, for example, from the thermal glow curve. These means will now be considered in detail.

##### A. The Effect of Varying the Distribution of Trapped Electrons on the Stimulation Observed

###### 1. The Use of Different Decay Times

If the phosphorescence is allowed to decay for various times before the phosphor is stimulated, any changes in the stimulated-emission intensity could be attributed to the decrease in the number of filled traps in which electrons have life times less than the decay time (usually a few minutes) at the temperature of the experiment. However, an alternative explanation is possible. If the absorption of stimulating radiation can only occur when the ground state of a luminescence center is empty, the return of electrons from traps to luminescence centers during phosphorescence will reduce the absorption and hence the stimulation. If an electron excited from a particular luminescence center only could enter one specific trap, this distinction between processes would be real, but would not affect the observed phenomena, since the absorbing transition would be inoperative only when no trapped electron was available to stimulate. If no close association between luminescence centers and traps exists, this alternative explanation is not important, since the reduction in the number of luminescence centers available (because of the decay of phosphorescence) is relatively small, unless only very shallow traps exist.

<sup>11a</sup> Such resonance transfer between a luminescence center and a trapped electron has been observed in recent work of this laboratory. The intensity of the yellow emission band of ZnS-In is reduced (*suppressed*) due to the resonance transfer of the energy of the excited yellow-emitting center to a trapped electron. These trapped electrons give rise to green luminescence when thermally ejected. The investigation of this system is much easier than the investigation of the Cu system since the luminescence suppressed is visible radiation for which detectors of much greater sensitivity are available.

If only very shallow traps receive electrons from a particular type of luminescence center, the effect of this decay on the total stimulation observed may be considerable.

It is often observed that the height of the stimulation spectrum may be halved by increasing the decay time from one minute to several minutes, the form remaining comparatively unchanged. At 77°–90°K, this effect is usually most marked for the sharp (long-wavelength) peaks, if these are present. Even more interesting effects are observed for ZnS–Cu–Pb phosphors showing the 1.3- $\mu$  stimulation peak. In the specimens we have examined, the 1.3- $\mu$  peak is not observed at temperatures below 160°–180°K (depending on the specimen). However, at any temperature between 180° and 290°K, the stimulation spectrum often decreases rapidly with increased decay time showing that shallow traps are important at temperatures in this interval. Thus a wide distribution of trap depths may contribute to the stimulability for 1.3- $\mu$  radiation. The position is further complicated when it is observed that the intensity of the 1.3- $\mu$  peak first increases, then decreases as the temperature ( $T_S$ ) at which the phosphor is stimulated is lowered, after excitation at 290°K. The stimulability reaches a maximum at a temperature of about 250°K and then decreases to zero at a temperature of 160°–180°K. Thus, although the filling of shallow traps increases the intensity of the stimulated emission, it does not alter the temperature range over which the 1.3- $\mu$  peak is observed. It would appear that the temperature variation is not a property of the trap, since so similar a variation with temperature is unlikely for traps of widely dissimilar depths. The S.W. band shows a similar type of variation with temperature, disappearing at 80°–130°K after excitation at 290°K. However, while the 1.3- $\mu$  band forms a sharp peak which is easily recognized even in the presence of other bands (especially the 1.2- $\mu$  band), the S.W. band is not distinctive in form and is probably a superposition of bands. Thus, it is difficult to determine precisely which traps contribute to its strength.

## 2. *The Use of a Distribution of Filled Traps Stable at a Temperature Higher than that at which Stimulation Takes Place*

A useful distribution of filled traps may be set up by exciting a phosphor at a temperature  $T_X$ , and then raising it, without irradiation, to a higher temperature  $T_D$ , when traps in which electrons have short lifetimes at  $T_D$  become empty. Thus only electron traps with glow temperatures above approximately  $T_D$  remain filled. This distribution of filled traps may be determined using the thermal-glow experiment.

The properties of this distribution of filled traps may now be examined at any desired lower temperature. If this examination is by stimulation, the temperature will be known as  $T_S$ . Care must be taken, however, in interpreting the results of changes in the

filled-trap distribution brought about in this way. Firstly, the electrons which would fill the traps in which they would be stable between  $T_S$  and  $T_D$  (if the decay at  $T_D$  had been omitted) may now be occupying levels in which they interfere with the absorption process. Secondly, these empty traps can capture electrons, ejected from other traps, which might otherwise give rise to stimulated emission. For example, ZnS–Pb (specimen 2) when excited at 290°K may be stimulated with 0.8- $\mu$  irradiation at 90°K. The *optical light sum* (that is, the number of quanta of stimulated emission) emitted during irradiation for a suitable short time (in this instance, 38 sec) at 90°K was only one-sixth of the *thermal light sum* (number of quanta emitted as thermoluminescence) subsequently obtained because of the retrapping in shallow traps of electrons ejected from deeper traps by this irradiation. Since electrons in shallow traps are much more sensitive to this irradiation than those in deeper traps,<sup>5</sup> retrapping must be much more probable under these conditions than capture in a luminescence center. It has been found that half the ejected peak may be retrapped in shallower traps. Thus, re-ejection of electrons may be an important process.

It should be mentioned that no effect of excitation temperature  $T_X$  on the trap distribution obtained after decay at a higher temperature  $T_D$  has been detected for zinc sulfide *powder* phosphors. This is not, however, true of many other groups of phosphors, including some of the alkaline-earth sulfide powder phosphors discussed later.

The technique of varying the decay temperature may be used to obtain some estimate of the trap distribution in phosphors which do not show any thermoluminescence after being allowed to decay at a given temperature  $T_D$ , but do show stimulation (at a suitable temperature  $T_S$ ) after such a decay procedure. The trap distribution is then given by the rate of change of the optical-light sum with  $T_D$ . The results obtained by this method (which has been described previously<sup>12</sup>) must be treated with the greatest care for the following reasons:

(1) Only some of the filled traps present may be stimuable under any conditions, the others retaining their electrons under irradiation.

(2) At low temperatures, some traps may cease to be stimuable due to the non-ejection of electrons contained in them, while at high temperatures (at which ejection from traps can occur) the ejected electrons may lose their energy nonradiatively. It is possible that the temperature at which ejection from traps becomes possible is above that at which nonradiative loss intervenes. Thus, although the traps are emptied, no stimulated emission is observed at any temperature.

Such trapped electrons may be responsible for the increases in conductivity resulting from infrared irradiation.

<sup>12</sup> C. Bull and D. E. Mason, J. Opt. Soc. Am. **41**, 718 (1951).



ation observed by Kallmann, Kramer, and Perlmuter,<sup>13</sup> even when no stimulation was observed.

### B. The Effect of Stimulating Radiation on the Thermal-Glow Curve Observed

One seemingly direct method of determining the distribution of filled traps, which provide the energy released as stimulated radiation, is to compare the glow curves after identical conditions of excitation and times of decay, first irradiating with stimulating radiation and then, as a control, leaving the specimen in the dark. The difference between these curves may be attributed to the effect of the radiation. In general, it is found that short-wavelength radiation is more effective in removing electrons from deep traps than long-wavelength radiation and that for both the long-wavelength peaks and the S.W. band, electrons are preferentially removed from shallow traps. A good example of this is provided by the curves for ZnS-Pb (specimen 2) given in Fig. 5. Radiation of 1.2- $\mu$  wavelength ejects electrons mainly from shallow traps while having a very small effect on traps with glow temperatures above 300°K. Short-wavelength radiation (0.9  $\mu$ ) has a much more general effect on traps of all depths. The use of heterochromatic radiation enables greater intensities to be obtained and shows clearly the resistance of the deep traps to emptying by infrared radiation. However, at least 90% of the traps of any depth are emptied by 5-min heterochromatic irradiation.

An interesting exception to the rule that shallow traps are emptied most easily is provided by Fig. 5a of Ref. 4, where although 1.2- $\mu$  radiation empties mainly shallow traps, 0.8- $\mu$  radiation empties none of the shallowest traps although deeper traps are emptied.

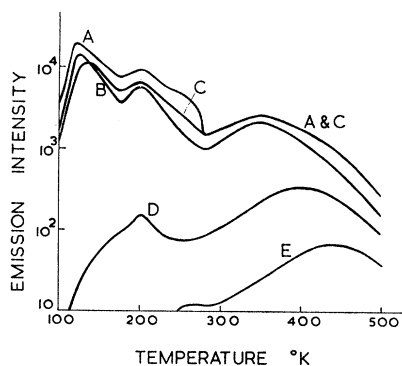


FIG. 5. Thermal glow curves for a ZnS-Pb phosphor (specimen 2) excited at 90°K, after the following irradiations:

Curve	Wavelength (microns)	Duration (sec)
A	...	0
B	0.9	60
C	1.2	60
D	heterochromatic	50
E	heterochromatic	300.

<sup>13</sup> H. Kallmann, B. Kramer, and A. Perlmuter, *Phys. Rev.* **99**, 391 (1955).

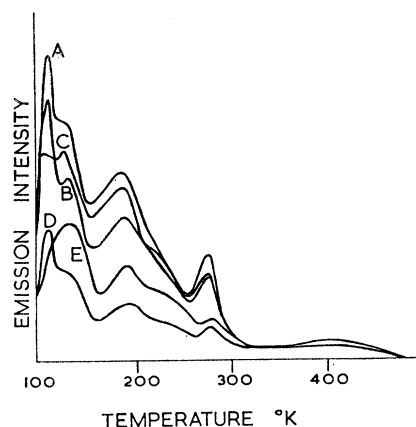


FIG. 6. Thermal glow curves for a ZnS-Pb phosphor (specimen 1) excited at 90°K, after the following irradiations:

Curve	Wavelength ( $\mu$ )	Duration (sec)
A	...	0
B	0.55	180
C	1.60	150
D	0.90	170
E	1.20	120.

So remarkable was this observation that a check was made by irradiating only the middle of the phosphor patch with 0.8- $\mu$  infrared radiation, when it was observed that the middle irradiated patch was indistinguishable from the unirradiated patch, until temperatures above 100°K were reached.

In view of the exhibition of two sharp (long-wavelength) peaks by ZnS-Pb (specimen 1) at 1.6  $\mu$  and 1.2  $\mu$ , the ejection curves for this specimen are of interest (Fig. 6). It should be noted that although stimulation in the 1.6- $\mu$  band cannot be obtained for temperatures of excitation above 90°K, ejection of electrons occurs not only from the traps with glow temperatures of 120° and 140°K, but to a lesser extent, from deeper traps with glow temperatures up to 300°K. Similarly, the 1.2- $\mu$  stimulation band does not appear for excitation above 160°K, but 1.2- $\mu$  irradiation also ejects electrons from traps with glow temperatures up to 300°K. Only 0.9- $\mu$  radiation has any considerable effect on the glow peak at 400°K. The selective effects on the peaks at 120° and 140°K are noticeable. Radiation of 1.2- $\mu$  wavelength removes the peak at 120°K in preference to that at 140°K, 0.9  $\mu$  and 0.55  $\mu$  removed the 140°K peak in preference to the 120°K peak, while 1.6- $\mu$  radiation has no very distinct preferential effect. However, once a preferential effect exists it may be exaggerated by retrapping provided that electrons are also ejected from deeper traps. Consider Fig. 7, where the effect of retrapping due to 1.0- $\mu$  irradiation at 90°K is shown. It would appear that approximately half of the electrons ejected from the peak at 290°K are retrapped in shallow traps and are not subsequently ejected. (Other retrapped electrons will have been ejected.) Thus, a group of traps which is less affected by radiation of a given wavelength than another group

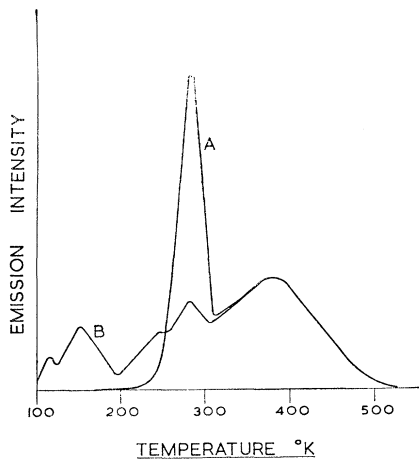


FIG. 7. Thermal glow curves for a ZnS-Pb phosphor (specimen 1), after excitation at 245°K, showing the effect of retrapping of electrons: A, after cooling to 90°K; B, after 1.0- $\mu$  irradiation at 90°K.

of traps will tend to fill some of its empty traps by re-trapping electrons ejected from the other traps.

The effect of heterochromatic irradiation for varying times on the glow curve of this phosphor (Fig. 8) illustrates the greatly varying properties of some of these traps. After 180-sec irradiation, the glow peak at 300°K has only been reduced by  $10^2$ , while the peak at 400°K has been reduced by  $10^4$ , and the 140°K peak by an even greater factor.

If the maximum temperature of decay  $T_D$  for which stimulation at any temperature is possible is  $(T_D)_{max}^s$ , it is found that electrons which are thermally stable in traps at  $(T_D)_{max}^s$  and have glow temperatures considerably above  $(T_D)_{max}^s$  are ejected by the stimulating radiation. Thus, this ejection does not appear to assist the stimulation process. Also, considerable ejection occurs after the stimulated-emission intensity has decayed to a negligible value. Thus, stimulation

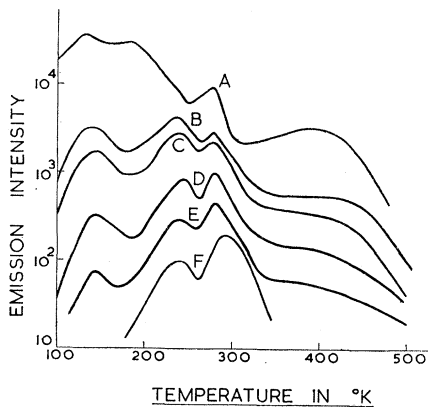


FIG. 8. Thermal glow curves for a ZnS-Pb phosphor (specimen 1) showing the ejection of trapped electrons at 90°K by heterochromatic irradiation of the following durations (in sec):

A	B	C	D	E	F
0	0.5	2	10	40	180

processes of greatly varying efficiency (S.E.) appear to occur in the phosphor at the same time. The ejection of electrons in deeper traps (160° to 300°K) by 1.6- and 1.2- $\mu$  irradiation of the ZnS-Pb(1) phosphor we have been considering is a good example of such inefficient use of the energy of ejected electrons.

### V. THE EFFECT OF NONRADIATIVE PROCESSES DURING STIMULATION AND THERMOLUMINESCENCE

Bril<sup>14</sup> has suggested that a reasonable assessment of nonradiative processes during fluorescence may be made from the excitation spectra. With efficient phosphors, the maximum quantum efficiency obtained in the bands characteristic of such impurities as copper ( $\sim 0.365\text{-}\mu$  excitation) is about 30%, while for absorption just within the absorption edge of the crystal ( $\sim 0.33\text{-}\mu$

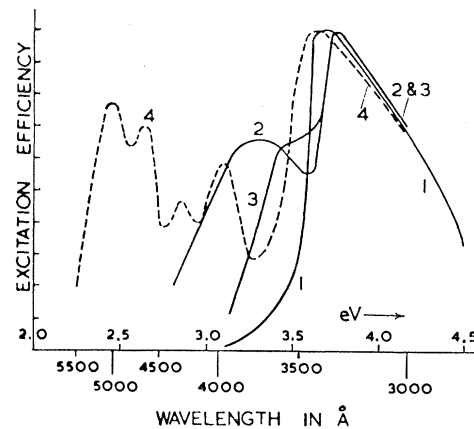


FIG. 9. Excitation spectra of ZnS phosphors (after Bube): (1) ZnS; (2) ZnS-Cu ( $3 \times 10^{-4}$ ); (3) ZnS-Ag ( $10^{-4}$ ); (4) ZnS-Mn ( $10^{-2}$ ).

excitation) it may reach 80%. It then decreases as the absorption coefficient increases, producing a greater density of excitation, mainly of the surface layers. Examples of such excitation spectra are given by Bube<sup>15</sup> (Fig. 9). According to Bril, such efficient phosphors are only obtained by large-scale manufacture. Most ZnS phosphors investigated show a rapid decrease in efficiency for wavelengths shorter than  $0.365\ \mu$  due to the greater probability of nonradiative processes when free electrons and holes are produced. Thus, except in the most efficient phosphors, nonradiative processes are important and often dominant. The importance of nonradiative processes in determinations of thermal-glow curves is even greater. The light sum emitted during stimulation may be  $10^5$  times that emitted from the same distribution of trapped electrons during thermoluminescence. In one ZnS-Mn-Pb phosphor, the thermal light sum of the electrons retrapped in shallow traps during irradiation, was 20 times the original thermal light sum, while the light emitted

<sup>14</sup> A. Bril (private communication).

<sup>15</sup> R. A. Bube, Phys. Rev. **90**, 70 (1953).

during irradiation was 100 times the original thermal light sum (Fig. 5 of Ref. 12).

It is important to remember that the trap distribution given by the thermal-glow curve may not only be incorrect in intensity, but may be completely misleading in form. Thus, Garlick and Gibson<sup>16</sup> studied in detail the thermoluminescence of a SrSiO<sub>3</sub>-Eu phosphor which appeared to possess the peculiarly simple property of an isolated, narrow glow peak at 370°K. However, they found that the half-width of this peak was less than the theoretical half-width. This state of affairs was obviously most unsatisfactory. However, using the variation of optical light sum with decay temperature  $T_D$ , we later found<sup>12</sup> that far greater numbers of traps exist than appear in the thermal-glow curve, and that the temperatures at which these would be released during thermoluminescence ("glow temperature" being an unsuitable description) extended over a wide range of temperatures around 370°K. As the energy of all these trapped electrons is lost non-radiatively during thermoluminescence, it is not surprising that the 370°K glow peak is narrowed because of a similar process.

Many of the phosphors investigated at Birmingham<sup>2,5,12</sup> show very considerable numbers of traps at higher temperatures whose existence would not have been suspected from the thermal glow curve. Such ZnS phosphors are those activated by Cu and Pb, Mn and Pb, and Mn and Cu. However, specimens of ZnS-Pb provided by Kröger showed distinct glow peaks up to 600°K, the corresponding traps appearing to be the sources of the electrons for stimulation. It is thus possible that either the combinations of activators we used tended to produce nonradiative effects during thermoluminescence, or that our specimens contained undesirable impurities which had this effect. We have previously found<sup>5</sup> that the addition of nickel to ZnS-Cu-Pb phosphors produced the following effects as the concentration was increased: First, the afterglow at room temperature disappears, corresponding to the disappearance of thermal glow just above room temperature; then the 1.3- $\mu$  stimulation band is no longer observable; next the S.W. band also cannot be observed; and lastly, a substantial decrease in fluorescence efficiency occurs. Thus, impurities similar to nickel might have the effect observed.

Although Urbach *et al.*<sup>17</sup> found linearity between stimulated emission intensity and (heterochromatic) infrared intensity over four orders of magnitude for some alkaline-earth sulfide phosphors and one ZnS-Cu-Pb specimen, we have found<sup>2</sup> considerable departures from linearity with zinc sulfide phosphors, the stimulability being greater at high infrared intensities. This type of behavior is observed during the "thermal quenching" of the fluorescence of phosphors, non-

radiative processes becoming less important at higher excitation intensities at any given temperature. Measurements on ZnS-Pb (specimen 1) would thus be interpreted as indicating that nonradiative processes are important in the stimulation of this phosphor, even though the deep traps still give rise to thermoluminescence. For example, a threefold decrease in the intensity of 1.3- $\mu$  stimulating radiation at 290°K results in approximately a sixfold decrease in stimulated emission. A ZnS-Mn-Cu phosphor (specimen 2) showed only a small change in stimulability with a 27:1 change in infrared intensity. In this case heterochromatic radiation was used, all effective wavelengths being within the S.W. band as no other band is present. The heterochromatic radiation is more intense than the monochromatic radiation available, and is therefore likely to favor radiative processes. However, the optical light sum of the stimulated emission was proportional to the logarithm of the stimulating radiation intensity, an increase of 27-fold in stimulating-radiation intensity producing a fourfold increase in optical light sum.

It is thus clear that considerable care must be taken in allowing for the effects of nonradiative transitions when investigating the nature of the processes involved in the stimulation of phosphors.

## VI. THE TEMPERATURE DEPENDENCE OF THE STIMULATION PROCESS

The variation with temperature of the 1.3- $\mu$  and S.W. bands of ZnS-Cu-Pb and similar phosphors has already been described [Sec. IVA(1)]. Because of the very large probability of retrapping when a phosphor is stimulated at a temperature below the temperature at which the filled traps were allowed to decay ( $T_S < T_D$ ), we had not considered it profitable to attempt to deduce thermal activation energies for the stimulation process from our data. However Levshin and Orlov<sup>18</sup> have given activation energies for ZnS-Cu-Pb phosphors for trap distributions stable at 77° and 290°K. It is not clear how temperature dependencies were measured for distributions of filled traps which were not stable over the temperature range used. However, they deduced that the activation energy for traps with glow temperatures between 90° and 270°K is 0.04 eV and is independent of wavelength (between 0.7 and 1.4  $\mu$ ), and that the activation energy for the filled traps stable at room temperature is 0.19 eV for wavelengths between 1.1 and 1.4  $\mu$ . In neither case was the form of the stimulation spectrum given.

For certain of our specimens it has been possible to estimate activation energies, although the presence of retrapping throws considerable doubt upon their accuracy. For ZnS-Cu-Pb (specimen 4), which shows a 1.3- $\mu$  band well separated from the S.W. band, the activation energy for traps stable at 290°K is 0.16 eV agreeing with the value given by Levshin and Orlov. For ZnS-Pb (specimen 1), excited at 345°K to fill

<sup>16</sup> G. F. J. Garlick and A. F. Gibson, Proc. Phys. Soc. (London) **60**, 574 (1948).

<sup>17</sup> F. Urbach, H. Hemmendinger, and D. Pearlman, in *Solid Luminescent Materials* (John Wiley & Sons, Inc., New York, 1948), Paper 16, p. 279.

<sup>18</sup> V. L. Levshin and B. M. Orlov, Opt. Spectry. (USSR) **7**, 330 (1959).

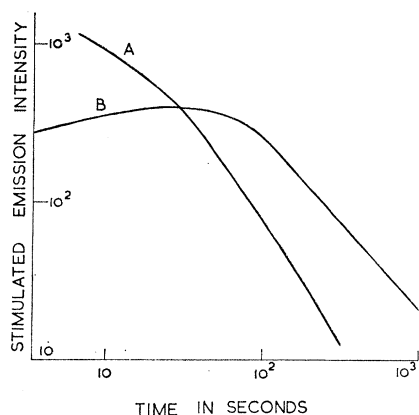


FIG. 10. The rise and decay of stimulated emission under  $0.8\text{-}\mu$  irradiation of a ZnS-Mn-Pb phosphor after excitation at  $290^\circ\text{K}$ : A, at  $290^\circ\text{K}$ ; B, at  $90^\circ\text{K}$ .

only the last peak of the glow curve (the  $1.3\text{-}\mu$  and S.W. band not being well-separated and requiring graphical resolution), the activation energy of the  $1.3\text{-}\mu$  band is  $0.07\text{ eV}$ , and that of the S.W. band ( $0.9\mu$ )  $0.031\text{ eV}$ . For SrS-Ce-Sm (standard VII) excited at  $290^\circ\text{K}$ , the activation energy for the distinct  $1.0\text{-}\mu$  band when excited at  $290^\circ\text{K}$  is  $0.07\text{ eV}$ . The strength of the S.W. band was only slightly reduced over the available temperature range. For Sr(S Se)-Eu-Sm(B1), the activation energy for the  $0.94\text{-}\mu$  stimulation band is  $0.10\text{ eV}$ . The yellow emission of this phosphor made it impracticable to investigate the S.W. band. However, for SrS-Ce-Sm, it was possible to obtain stimulation in the  $1.0\text{-}\mu$  band at  $77^\circ\text{K}$  (instead of  $123^\circ\text{K}$ ) if traps are filled below  $290^\circ\text{K}$ . This suggests that the mechanism responsible for the temperature variation of stimulability of this phosphor is different from that for the ZnS-Cu-Pb phosphors investigated, in which the  $1.3\text{-}\mu$  band could not be obtained at lower temperatures even though shallow traps were filled. (The filling of these traps only increased the strength of the  $1.3\text{-}\mu$  band within the same temperature range.) This suggests, for the ZnS-Cu-Pb phosphors, that the temperature-dependent process may be in the absorbing center or in the transfer mechanism rather than in the trap. A temperature-dependent process in the trap is easier to visualize, since a resonance transfer of energy from the center absorbing the stimulating radiation to the trapped electron might only be possible when the electron is in an excited level of the trap.<sup>6</sup>

#### VII. THE RETRAPPING IN SHALLOWER TRAPS OF ELECTRONS EJECTED FROM TRAPS BY INFRARED RADIATION

Retrapping has been observed for all phosphors when it has been found possible to create conditions suitable for a test of retrapping. The necessary conditions are that stimulation should be obtained at a temperature  $T_s$ , sufficiently below the temperature of

decay  $T_D$ , for the retrapped electrons to be clearly distinguishable from those due to the original excitation.

The probability, that an electron will be retrapped rather than give rise to stimulated emission, appears to be very high if empty electron traps exist in the phosphor. This phenomenon should be compared with the well-known one in which little fluorescence is observed from zinc sulfide phosphors until the empty traps have been filled. With single crystals of ZnS-Cu, this phenomenon is so marked that the crystals could easily be considered to be nonluminescent after a superficial inspection although they are actually highly fluorescent.

As a natural consequence of retrapping, when infrared irradiation ceases, an afterglow of considerable intensity relative to the stimulated emission intensity is observed. Thus, it is necessary to consider what proportion of the stimulated emission is a consequence of the thermal release of electrons (from shallow traps in which they have been retrapped), and what proportion is a consequence of direct recombination between free electrons and empty luminescence centers.

Also probably related to these retrapping phenomena are the considerable increases (of the order of doubling) of the stimulability in the sharp band at  $1.2\text{ }\mu$  because of irradiation of short wavelengths immediately before the  $1.2\text{-}\mu$  irradiation. This would be expected from the high stimulability found for  $1.2\text{-}\mu$  irradiation of electrons in very shallow traps.

The prevalence of retrapping as a result of stimulating radiation indicates that the traps capture the same carrier (therefore both capture holes or both electrons). It is difficult to see how thermoluminescence attributable to holes could be produced by infrared irradiation of electron traps filled by excitation. If the excitation fills deep traps with electrons, infrared irradiation might excite holes from empty luminescence centers into hole traps, but no thermoluminescence would be observed until electrons had been thermally ejected from deep traps as well as holes from shallow ones.

A slow rise of stimulated-emission intensity appears to be associated with retrapping in the same way that a slow rise in fluorescence is associated with trapping. Curves of stimulated emission intensity of ZnS-Mn-Pb (under  $0.8\text{-}\mu$  irradiation) illustrate this. If stimulated at the temperature of excitation ( $290^\circ\text{K}$ ), the rise is much more rapid than for stimulation at  $90^\circ\text{K}$ , the stimulated-emission intensities being comparable (Fig. 10).

#### VIII. THE STIMULATION PHENOMENA OBSERVED IN THE VARIOUS EMISSION BANDS OF ZINC SULFIDE PHOSPHORS

While it is, at present, difficult to attribute the bands of the stimulation spectrum to definite centers, it is of value to consider the emission bands in which the stimulated emission may occur. At  $77^\circ\text{--}90^\circ\text{K}$ , both  $1.2\text{-}\mu$  and short-wavelength bands have been observed in the emission characteristic of all the acti-

TABLE I. Apparent stimulation efficiencies at 90°K for zinc sulfide phosphors.

Color of emission		Blue					Other than blue				
Wavelength of irradiation (microns) $\mu$		1.6	1.4	1.2	1.0	0.9	1.6	1.4	1.2	1.0	0.9
Activators	Specimen number	Color									
Sn	1			0.07	0.014				2.4	<0.001	
	2			0.02	0.006				0.8	0.4	
P	1			0.10	0.08				0.9	0.8	
	2				0.17				1.2	...	
Mn	2		no blue emission						...	0.6	0.4
	3		0.16	0.15	0.13				0.6	0.6	0.4
	4		...	0.13	0.07				...	0.7	0.6
	5		...	0.13	0.08				...	0.6	0.4
	6		...	0.20	0.14				...	0.6	0.4
Cu-Pb	8								1.4		1.9
	9								0.6		0.7
Pb	1							1.5	1.0		0.5
	2								0.34		
Mn-Cu	3			0.05		0.09			0.5		0.02
Ag-Cu-Pb	1		0.13						0.5		0.4
									blue-green	0.6	
									1.5		

vators investigated, namely, Na (0.39  $\mu$ ), Zn (blue), Ag (blue), Cu (both blue and green bands), Pb (both blue-green and orange-red bands), P (yellow), Mn (orange), and Sn (red). At room temperature, peaks at 1.3  $\mu$  have been observed in the emission bands characteristic of Mn (orange), Pb (blue-green and orange bands), and probably Cu (green). The Ag emission did not appear at room temperature when conditions were favorable for its appearance.

In general, if the stimulated emission of a phosphor occurs in two emission bands, the stimulation spectra for those bands is similar in form. However, for one phosphor, ZnS-Cu-Pb (specimen 7) which has both green and yellow emission bands, the stimulation spectra for the green emission contained both the 1.2- $\mu$  and S.W. bands, while that for the yellow emission contained only a S.W. band. (The yellow emission in ZnS-Cu-Pb phosphors often behaves in a different way to other bands. For example, the yellow afterglow at room temperature in some specimens is unaffected by stimulating radiation which removes the green afterglow.)

The apparent stimulation efficiencies (ASE) at 90°K for a number of ZnS phosphors are given in Table I. The list of phosphors is limited, measurements of ASE only being made in later investigations. Efficiencies in each band are regarded as independent. For example, in a ZnS-Sn phosphor, the red- and blue-emitting systems are treated as independent.

The values of ASE obtained for the blue emission are always relatively low (of the order of 0.1). In phosphors exhibiting additional emission bands, this low efficiency might be due to transfer to other bands. However, for ZnS-Mn phosphors, the ASE for the orange band is not dependent on the presence or absence of a blue band, so that it is doubtful if energy

transfer between emission bands is the general explanation. Apparent stimulation efficiencies for other bands range from less than  $10^{-3}$  to 2.4. The value of 2.4 for ZnS-Sn (1) may be because of the optical ejection of electrons from the traps, which give rise to blue thermoluminescence at 140°K, leading to red stimulated emission rather than blue. The efficiency of 1.5 obtained for 1.6- $\mu$  irradiation of ZnS-Pb (1) is probably due to nonradiative loss during thermoluminescence as the ASE for 1.2- $\mu$  radiation decreases with decreasing irradiation intensity showing that nonradiative processes are occurring at these low temperatures.

In general, the ASE obtained for the sharp (long-wavelength) peaks tends to be greater than that for S.W. bands, although such differences are often small. Since short wavelengths tend to eject electrons from deep traps (often slowly) this may account for some of the differences observed, since very high efficiencies are usually observed when only a limited region of shallow trapping levels are emptied by irradiation. Measurements of ASE taken over various parts of the stimulation period should provide further information provided that glow curves can be reproduced with sufficient accuracy to permit reliable difference measurements to be made.

There is a general tendency in the literature to assume that S.W. bands make less efficient use of the energy of ejected electrons in producing stimulated emission than long-wavelength ones and are more likely to produce an immediate diminution in phosphorescence intensity without any initial enhancement. This is not necessarily so. For ZnS-Mn-Cu (3), the main stimulated emission is the orange (Mn) emission. The stimulation spectrum consists of a strong 1.3- $\mu$  band and a S.W. band extending from 1.0  $\mu$  into the visible. When the phosphor is irradiated with 1.3- $\mu$

radiation, the green phosphorescence decreases quickly to zero. With  $0.9\text{-}\mu$  irradiation a feeble stimulation is observed before the green emission decreases rapidly to zero. It should be noted that  $0.9\text{-}\mu$  radiation (but not  $1.3\ \mu$ ) can eject electrons from a group of traps which are thermally emptied nonradiatively at higher temperatures.

For stimulation at  $290^\circ\text{K}$ , ASE of  $10^4$  and greater are common, because of large concentrations of traps whose emptying does not give rise to thermoluminescence. However, even for ZnS-Pb (1), where the glow curve extends to above  $500^\circ\text{K}$ , an ASE greater than unity can be obtained. This indicates that the trap concentration is greater than that indicated by the thermoluminescence, even in specimens where the glow curve extends to very high temperatures.

It thus appears that when the ASE exceeds unity, this is because of the presence of traps whose efficiency of contribution to the glow curve is small. However, these traps can be identified by the variation of optical light sum with decay temperature, so that such data can be legitimately excluded when seeking a maximum value of the utilization efficiency of the energy stored in traps and emitted as stimulated emission. Since ASE at  $77^\circ\text{--}90^\circ\text{K}$  may be as high as 0.9 for phosphors in which no anomalous effects are apparent, the stimulation process may be almost as efficient as the thermoluminescence at low temperatures. However, no reliable figure for thermoluminescence efficiency is available.

With suitable single crystals it would be possible to determine the number of quanta of stimulating radiation absorbed. In the simplest type of phosphor (in which no nonradiative processes occur), the number of stimulating quanta absorbed would equal the number of stimulated-emission quanta produced and also the decrease in the number of quanta subsequently emitted as thermoluminescence. Even an order of magnitude for such determinations would enable stimulation theory to be put on a more secure footing. Such measurements, extended to phosphors with more than one emission band would enable the extent of interaction between the emission bands to be determined.

### IX. THE EXISTENCE OF COMPLEX CENTERS IN LUMINESCENT MATERIALS

There have been fashions in luminescence theory. Complex centers have been in fashion and then have become unfashionable as the current trends of investigation have emphasized what appeared to be localized behavior or what appeared to be free motion through the crystal. The last swing to free motion from complex centers was probably in sympathy with the massive progress of semiconductor physics.

The term "complex center" merely signifies that certain of the localized levels in the phosphor (e.g., luminescence centers, traps, centers absorbing stimulating radiation) have an association greater than

that afforded by mere proximity (without interaction), or by an overwhelmingly greater capture cross section.

A simple picture of a phosphor, containing two types of luminescence center (giving rise to two easily separable emission bands) and a selection of traps of various depths not associated with the luminescence centers, would suggest that the thermal glow peaks would occur at the same temperatures for the two emission bands, the intensities of the glow peaks modified by a factor representing the capture cross sections of the two luminescence centers and also the number of each type of luminescence center remaining empty. Thus, when all luminescence centers of a given type become filled, no glow peaks at higher temperatures will be observed in the corresponding emission band.

Compare the expected result with the phenomena observed for a ZnS-Sn phosphor (1) shown in Fig. 11. (The emission bands of this phosphor, being situated in the red and blue spectral regions, are very easy to separate.) There is no trace of the sharp peak of red thermoluminescence at  $140^\circ\text{K}$  in the blue thermoluminescence although blue-emitting luminescence centers must be empty at this temperature for the peak of blue thermoluminescence at  $180^\circ\text{K}$  to be observed. Similarly, only the faintest trace of the peak of blue thermoluminescence at  $180^\circ\text{K}$  is visible in the red thermoluminescence although red thermoluminescence is observed at this and higher temperatures. Close

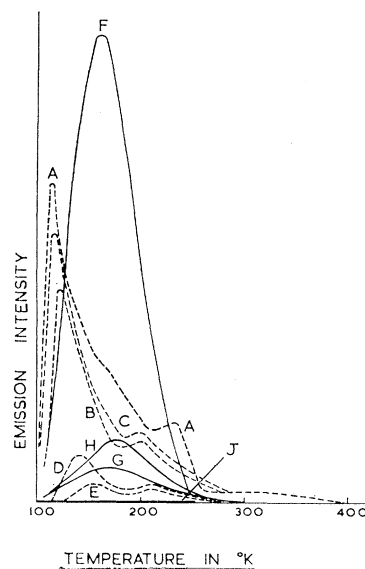


Fig. 11. Thermal glow curves for a ZnS-Sn phosphor (specimen 1) after infrared irradiation for various times (in min), as shown below. The red emission intensities should be multiplied by a factor of approximately 6 to allow for the variation of photomultiplier sensitivity with wavelength.

	Red emission	Blue emission
No irradiation	A	F
$1.0\text{-}\mu$ irradiation	B, 3.0	G, 3.0
$1.2\text{-}\mu$ irradiation	C, 4.0	H, 3.0
Heterochromatic irradiation	{D, 1.0	J, 1.0.
	{E, 3.0	

proximity, between a trap of a particular group and a luminescence center emitting a particular emission band, might account for this type of association provided that the distance traversed by the electron is sufficient to account for the conductivity observed during thermoluminescence. However, the consistent proximity of trap and luminescence center is improbable without some energy of interaction.

Similar association would account for the comparative freedom from retrapping during thermoluminescence. Although no fluorescence is observed in ZnS phosphors until deep traps are filled (suggesting a large cross section for capture by these traps), it is found that when only a small fraction of the traps are filled (instead of the traps being filled to saturation), only a small change in the form of the glow curve occurs (Fig. 12, curves B and A, respectively). However, changes in the form of the glow curve with further reductions in the fraction of traps filled, indicate that an even more complex situation exists (curve C).

Attempts made by Garlick and Gibson<sup>16</sup> to determine, quantitatively, the extent of retrapping during thermoluminescence have not been entirely successful. They have, however, shown that, in general, the probability of retrapping during the thermoluminescence of a group of traps having little variation in depth thus giving rise to a narrow glow peak is small. Certain of the data, however, require re-assessment. The SrSiO<sub>3</sub>-Eu phosphor, which appeared from the glow curve to have a very narrow distribution of traps, was found (by the stimulation techniques developed later<sup>12</sup>) to have a very wide distribution and much greater concentration of traps than could be deduced from the thermoluminescence. (The electrons from these traps lose their energy nonradiatively when thermally ejected.) The extreme narrowness of this glow curve (less than the theoretical for absence of retrapping) would then appear to be a result of the intervention of nonradiative processes and to be useless as evidence in the question of retrapping.

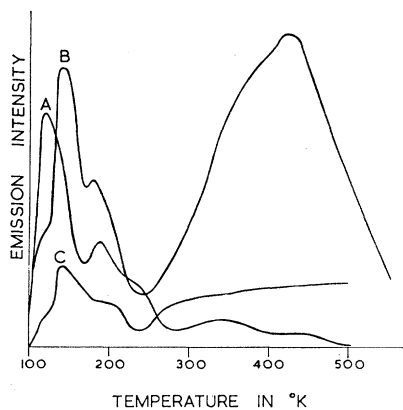


FIG. 12. Thermal glow curves of a ZnS-Pb phosphor (specimen 2) for various excitation exposures at 90°K: A, saturation curve; B, partially excited (200 times correct height); C, partially excited (1000 times correct height).

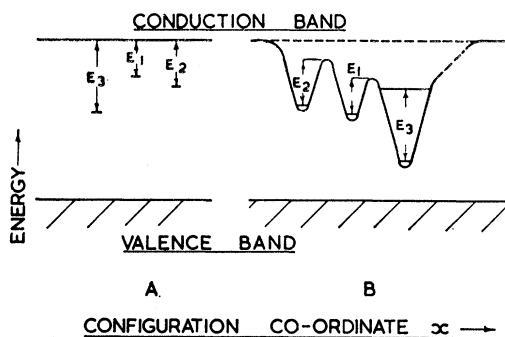


FIG. 13. Possible energy level configurations for SrSiO<sub>3</sub>-Eu: A, Conventional diagram with luminescence center (levels separated by energy  $E_3$ ) and two traps of depths  $E_1$  and  $E_2$  ( $E_2 > E_1$ ); B, Suggested energy level diagram for traps of the same depths as above. In this scheme the energy of the electron in the shallower trap is less than that of the electron in the deeper trap.

For the three phosphors considered by Garlick and Gibson, it was assumed that the linearity of the curve of  $(N/n_0 - 1)$  against the reciprocal of the excitation intensity  $J$  showed that retrapping was negligible. ( $N$  is the saturated concentration of traps and  $n_0$  the concentration of traps in equilibrium with excitation of intensity  $J$ .) However, replotting of the data for the ZnS-Cu phosphor showed that  $(N/n_0 - 1)$  is accurately proportional to  $J^{-(0.75 \pm 0.05)}$ , midway between  $J^{-1}$  for no-retrapping and  $J^{-0.5}$  for equal probabilities of capture by luminescence centers and by traps. Thus, it appears that some retrapping in the same group of traps may occur.

A different type of phenomenon, which suggests that complex centers may exist in phosphors, is found for the SrSiO<sub>3</sub>-Eu phosphor mentioned above. It is found<sup>12</sup> that traps in which electrons are stable at 362°K lose their electrons at 90°K, the traps which show thermoluminescence at 250°K becoming filled. Evidence has been given that no radiation (due to forbidden transitions or other sources) is present which could empty the deep traps and fill the shallower ones. We are thus left with the situation that an electron in the shallower trap must possess less energy<sup>18a</sup> than an electron in a deep one. Also, a transition between these states must be possible. On the normal model of a luminescent material, in which electrons are thermally activated from the trap into the conduction band, this is impossible (Fig. 13A). However, if the activation energy required by the electron is needed to surmount a barrier round the trap, this difficulty no longer remains (Fig. 13B). A luminescence center must exist within this potential configuration so that no further potential barriers have to be surmounted to reach the luminescence center after the barrier round the trap. Otherwise, the luminescence observed could not occur.

<sup>18a</sup> Although a greater value of  $T_G$  need not necessarily be associated with a greater trap depth  $E$ , since  $s$  may vary, recent work by D. Hofmann (Berlin) has shown that for ZnS, at least, this is always true. Hofmann's "fractional glow" method provides accurate values of both  $s$  and  $E$ .

At present, there is no precise picture of a complex center which can be given adequate support. Indeed, there may be several types of such center. However, the types of association found demand further investigation.

#### X. THE RELATION BETWEEN THE STIMULATION SPECTRUM AND THE ELECTRON-TRAP DISTRIBUTION

Many suggestions have been made that some direct connection should exist between groups of electron traps and peaks of the stimulation spectrum. Curie,<sup>6</sup> after describing the effect of samarium as a *sensitizer* or *auxiliary activator* in the highly infrared sensitive alkaline-earth sulfide phosphors (where the stimulation spectrum in the region of room temperature is determined by this activator), suggests that a trap might exist characteristic of samarium. While comparing Urbach's glow curves for SrS-Ce-Sm (peak at 420°K) and SrS-Eu-Sm (peak at 650°K), Curie considers that the difference between these curves may be due to a deep trapping level in the SrS-Ce-Sm phosphor which does not give rise to thermoluminescence due to nonradiative loss of energy. However, the evidence is against this theory, for although the stimulation spectrum of these phosphors is constant, the glow curve varies very considerably between various specimens both in form and in color of emission. Also, we have found that the filling of shallower traps enhances the stimulability, at least for traps with glow temperatures above 220°K. Thus the sharp peak (at 1.0  $\mu$ ) of the stimulation spectrum is not characteristic of a trap depth.

In considering the independence of the stimulation spectrum associated with Sm, of the surroundings in which the Sm is situated, we have to include several factors. Firstly, it has been found that Sm gives a (broadened) line spectrum in SrS, indicating that the luminescence center is little affected by the lattice. Secondly, however, when Sm is incorporated in a mixed lattice of SrS and SrSe (to give the B1 phosphor) instead of in SrS alone, the stimulation peak moves from 1.02 to 0.94  $\mu$  indicating some interaction with the lattice. This would indicate that the absorbing center due to Sm is more sensitive to its surroundings than the luminescence center due to Sm, and is thus not identical to it.

Thus the phenomena observed in these alkaline-earth sulfide phosphors show a close parallelism with those observed in ZnS-Cu-Pb phosphors, where the evidence given above suggests an infrared absorbing center separate from the trap. It further shows that some of the absorbing centers are rendered operative by the excitation of the luminescence center. The information available on the 2.4- $\mu$  band in ZnS is not sufficient to rule out the possibility that the absorption in this band might be due to a transition from a trap. However, the 1.6- and 1.2- $\mu$  peaks are associated with

more than one glow peak, and are therefore probably characteristic of an absorbing center.

The most specific effects of infrared radiation on the glow curve subsequently obtained, are in the glow peaks which are *not* removed rather than in those which are. The ZnS-Cu-Pb specimen, described above, in which shallow traps are not emptied by 0.9- $\mu$  radiation, but are rapidly emptied by 1.2  $\mu$  is a good example. The very slow reduction of the peaks at 240° and 290°K by heterochromatic irradiation of ZnS-Pb (1) is another example (Fig. 8). Thus, one might suggest that certain traps are only weakly coupled to absorbing centers of a particular type. However, no traps in ZnS appear to be completely unaffected by infrared radiation of some wavelength, i.e., coupling is never completely negligible.

#### XI. ELECTRICAL CONDUCTIVITY AND THE DETERMINATION OF THE STIMULATION PROCESS IN PHOSPHORS

Since steady electrical currents can flow through phosphors during fluorescence, it is clear that during this process either electrons must exist in the conduction band, or holes in the filled band, or both. Also, currents flow during phosphorescence, thermoluminescence, and stimulation which may be due to carrier movement in the bands or to the displacement of carriers within some system in the phosphor. Thus, valuable information may be obtained as to whether carriers are, at any given time, in the bands or in isolated levels.

We have, first, to consider what are the effects of the electrical contacts to the crystal, and under what conditions a steady current, characterized by a conductivity, can be obtained.

##### A. Conductivity—Basic Considerations

Consider an elementary volume of a uniform crystal in which a uniform electric field  $\mathbf{F}$  exists. Since the field is constant, the net charge density in the element is zero. We can consider this density of charges to be due to electrons in the conduction band, density  $n$ ; holes in the valency band of density  $p$ ; and localized charges, densities  $N$  and  $P$ , of negative and positive sign, respectively.

Thus,

$$n + p + N + P = 0. \quad (1)$$

The current density  $\mathbf{j}$  in the volume will be given by

$$\mathbf{j} = \sigma \mathbf{F}, \quad (2)$$

where the conductivity  $\sigma$  is given by

$$\sigma = ne\mu_n + pe\mu_p, \quad (3)$$

since the mobility of the fixed charges is zero;  $\mu_n$  and  $\mu_p$  are the mobilities of electrons and holes, respectively. Provided that no potential barriers exist around this element, the application of any field less than that



permitting tunnelling between levels will not change the densities of the charges of various types as new charges will flow in to replace those flowing out to maintain the neutrality expressed in Eq. (1). Thus, the densities of charges of various types will only vary in accordance with charge generation or recombination within the element. This generation may be thermal or optical or due to ionizing particles. In either generation or recombination, a change in  $n$  may produce a change in  $N$  and will be accompanied by a change in  $(p+P)$  to balance the change in  $(n+N)$ . Similarly, a change in  $p$  will change  $n$ ,  $N$  and perhaps  $P$ , so that the zero net charge density is maintained.

Consider now a volume of greater size in which potential barriers exist, the entry of electrons or holes may now be restricted. Space charges can now form. The field is no longer constant, but varies with the net charge density  $\rho$  as

$$\text{div } \mathbf{F} = 4\pi\rho/\epsilon, \quad (4)$$

where  $\epsilon$  is the dielectric constant of the crystal.

The difficulties caused by potential barriers become most acute when it is desired to bound the volume of uniform material. The significant boundaries may be:

- (1) Surfaces to vacuum or some gaseous or liquid medium.
- (2) Interfaces between parts of the crystal containing different concentrations of donors and acceptors. These interfaces will form  $p$ - $n$  or  $L$ - $H$  (light-heavy) homojunctions.
- (3) Interfaces with other materials which continue the crystal lattice and do not form surface states with the original lattice. Such interfaces will be heterojunctions.
- (4) Applied layers which form surface states and which have a crystal structure and orientation not defined by the original crystal.

These types of boundary will now be considered in detail.

### 1. *Properties of the Surface Layers of Crystals*

At a surface the crystal structure may be deformed due to the absence of the next layer of atoms. This has been clearly shown by Schlier and Farnsworth<sup>19</sup> for clean surfaces of silicon. Further detail has been added by Lander *et al.*<sup>20</sup> Thus, the work function of the material will be affected by the faulty structure, and should not be taken as characteristic of the perfect material. All normal surfaces are far from clean, the adhering atoms tending to permit the lattice to relax to its normal crystal structure. According to the nature and charge of these atoms, the surface may: (a) change its conductivity or even conductivity type; (b) form

localized states which permit recombination (perhaps with a very high surface recombination velocity) or photogeneration of a type which does not occur in the bulk material.

Conduction in layers of modified conductivity at the surface may be the most important mode of current flow between electrodes observed in near-insulators.

It should be noted that the absorption of light near a surface of low recombination velocity which is opposite a surface of high recombination velocity will cause a diffusion current to flow in the absence of an applied electric field. In the absence of any external circuit, if only one type of carrier is free to move, a potential opposing this diffusion will be generated due to space charge. Also the absorption of light within a diffusion length of the depletion layer of a barrier (such as a  $p$ - $n$  junction) will produce a photovoltage. Thus the potential effective in any circuit may not necessarily be the applied potential or even the effective potential in the absence of irradiation.

The case of the interface with a liquid is best considered under "Other Interfaces" (Sec. 4) below.

### 2. *Homojunctions on Photoconductors*

A  $p$ - $n$  homojunction when biased in the forward direction injects minority carriers into each of the regions, the flow of each type of carrier being proportional to its concentration in the region from which it came. The current density  $j$  resulting from each of the carriers varies with the applied voltage  $V$  across the junction as

$$j = j_{0e} [\exp(eV/kT) - 1], \quad (5)$$

where  $j_{0e}$  takes the value  $j_{0p}$  for holes and  $j_{0n}$  for electrons, and  $e$  is the electronic charge. The values of  $j_{0p}$  and  $j_{0n}$  will depend on the properties of the crystal including acceptor and donor concentration. When the junction is reverse biased, the current may continue to be described by (5), approaching a limit of  $-j_{0e}$  as  $-V$  increases. If the concentration of minority carriers on one side of the junction is increased by any means, the reverse current of such carriers will be increased proportionally. However, the reverse current may, in the absence of an increased minority carrier concentration just described, be dominated by the charge carriers generated within the depletion layer and collected by the field within that layer. The reverse current will then increase as  $V^n$ , where  $n$  is less than 0.5 and depends on the distribution of donors and acceptors.

An  $L$ - $H$  junction, between material of the same conductivity type, but of very different carrier concentration, has very different properties. When biased to encourage the flow of carriers from the highly doped  $H$  region into the lightly doped  $L$  region, it only permits a very small current of minority carriers to cross the junction from the  $L$  region. When biased in the reverse direction, no minority carriers are present

<sup>19</sup> R. E. Schlier and H. E. Farnsworth, *J. Chem. Phys.* **30**, 917 (1959).

<sup>20</sup> J. J. Lander, G. W. Gobelli, and J. Morrison, *J. Appl. Phys.* **34**, 2298 (1963).

in the  $H$  region (because of the high concentration of majority carriers) to be injected into the  $L$  region. Thus, one has a junction which (for most practical considerations) conducts only by majority carrier flow, presenting little obstacle to this flow.

### 3. Heterojunctions on Photoconductors

The theory of heterojunctions is at present in an unsatisfactory state due to lack of knowledge of the effect of abrupt changes in the  $E-k$  relationship at the interface. Practical use of heterojunctions is limited by lack of knowledge of the discontinuities in valence and conduction bands at the interface. The use of gradual, rather than abrupt, junctions eases the position somewhat, but limits the materials used to those which form mixed crystals.

Many of the properties of  $p-n$  heterojunctions are similar to those of  $p-n$  homojunctions. However, for gradual junctions at least, the change in bandgap can be used to increase the proportion of carriers injected from the wider bandgap material. Thus, with equal carrier concentrations on the two sides of the junction, the injection of carriers can be overwhelmingly from the wide-bandgap material. A very large ratio of carrier concentrations may permit the injection of carriers into a material with a larger bandgap.

The behavior of the  $L-H$  heterojunction, however, will, in general, be very different from that of the  $L-H$  homojunction. Unless the discontinuity in the appropriate band is small, the virtually free flow of carriers observed in homojunctions will not occur, the junction acting as an efficient rectifier, at least for small reverse voltages (of the order of a few volts). However, even when acting as a rectifier no flow of minority carriers occurs.

### 4. Other Interfaces between a Photoconductor and another Material

In general, we have to deal in this section with interfaces which have the complexities of both the surfaces and the heterojunctions dealt with above. Since the crystal structure is not continuous, surface states may exist in large concentrations. Since the materials on each side of the junction are different, the discontinuities in conduction- and valence-band edges, observed for heterojunctions, will appear here.

#### B. The Influence of Boundary Characteristics on Circuits for Measuring Photocurrents

From the brief summaries given above, it is seen that the use of contacts employing any of the types of interface described above will not permit the observation of the electrical properties of the crystal to which the contacts are made. However, Stieltjes and Diemer<sup>21</sup> have shown that more satisfactory contacts can be

made (at least on near-intrinsic material) by providing a separate contact for electrons and for holes at each situation where an electrical contact is desired. In this way the free flow of both electrons and holes is permitted. It should be noted that the experiments of Stieltjes and Diemer were on germanium to which completely satisfactory  $p^+$ - and  $n^+$ -contacts can be made.

If the free flow of holes is not permitted, the electron current may be limited by space charge. When this occurs, the increase in applied potential may be largely used in overcoming the effects of an increase in space charge rather than in increasing the current in the way expected from the simple conductivity treatment.

The importance of surface conductivity in certain single crystals of ZnS has been shown by Alfrey by the use of guard rings minimizing the surface currents. The use of the guard ring decreased the current by two orders of magnitude at the lower applied voltages. Thus, it might be expected that a large part of the current flowing in powder layers is attributable to surface conduction. The effect of guard rings on photocurrents has not been extensively investigated. However, some preliminary measurements<sup>22</sup> in this laboratory indicate that surface currents need not be important for conductivity under  $0.365\text{-}\mu$  irradiation.

## XII. THE SYSTEMS USED IN MEASUREMENTS OF PHOTOCURRENTS IN ZINC SULFIDE PHOSPHORS

Measurements of photocurrents in zinc sulfide phosphors have either been made of powder layers between electrodes, or of single crystals with suitably processed contact electrodes. However, in view of the very great complexities and difficulties described in the last section (Sec. IX), the lack of detail in papers describing such photocurrent measurements is remarkable. Kallmann, with various collaborators, has published a series of papers referring back for experimental method to Kallmann and Kramer.<sup>23</sup> Here, the photoconductivity which is measured is that of an aggregation of phosphor particles forced together and against aluminum foil and conductive glass electrodes by the electrostatic field created by the applied voltage. From their data, it can be deduced that the photocurrent  $I$  is related to the applied voltage  $V$  by the relation,

$$I = cV^n, \quad (6)$$

where  $n$  is 4.5 for powder  $K$ , and 5.2 for powder  $L$ . For powder  $L$ , it was shown that a thickening of the layer produced the same current for the same average field strength, suggesting that the contact to the electrodes was not more important than the contact between grains. A high-power law of this type suggests that the current is space-charge-limited, possibly due

<sup>21</sup> F. H. Stieltjes and G. Diemer, Phillips Res. Rept. 18, 95 (1963).

<sup>22</sup> D. Colman (private communication).

<sup>23</sup> H. Kallmann and B. Kramer, Phys. Rev. 87, 91 (1952).

to the nature of the contacts between phosphor particles. Also, there is no evidence that surface currents do not predominate. However, even with a system of this nature, valuable qualitative results can be obtained. A similar system, using a phosphor powder in castor oil between a transparent conducting coating on glass and a copper weight, was used by Bube.<sup>15</sup>

On single crystals of ZnS, contacts of indium (applied by suitable heat treatment) have been used. These appear to be reasonably satisfactory, but no adequate test of their characteristics appears to have been made, because of the nonavailability of low resistivity ZnS. In general, tests of electrode performance have been dominated by the bulk resistance of the ZnS crystal. Even on the low-resistivity surface layers we have prepared, no adequate test of electrode performance has been possible. Reliance appears to have been placed in the assumption that indium, as a Group III impurity, should form donors in ZnS by replacing Zn atoms. As the luminescence phenomena due to the indiffusion of In into ZnS are highly complex, both in single crystals<sup>22</sup> and powders,<sup>24</sup> this simple assumption should not be accepted too readily. If a high concentration of donors is formed by the indium diffusion, the contacts will be of  $n-n^+$  or  $\nu-n$  type, and will not allow the passage of holes. Thus, the presence of free holes can only be detected by a displacement current or by a change in the lifetime of electrons due to the increased probability of recombination. The presence of holes, whether free or not, will serve to neutralize the electron space charge and hence increase the current.

#### The Photoconduction of Powder Layers of Zinc Sulfide

In most studies of conductivity in ZnS, the phosphor has been excited by 0.365- $\mu$  radiation, which will produce free electrons but bound holes, rather than 0.30  $\mu$  which will produce free holes and electrons.

Luchner, Kallmann, Kramer, and Wachter<sup>1</sup> have explained the absence of any considerable increase in conductivity during stimulation by postulating that electrons do not have to move through the conduction band to reach the luminescence centers. If our views on the release of holes during S.W. irradiation at room temperature (as deduced from the data of Broser and Schulz) are correct, the small increase in conductivity could be due to a hole current, since we estimate that six times as many holes are released as electrons. Some of these holes may be trapped, but others may recombine (via intermediate levels) with electrons in the conduction band, thus reducing the current for some period after the stimulating radiation has been shut off. If the holes only move an infinitesimal distance, the current due to their movement will be negligible, but the effect on the concentration of electrons in the conduction band may be considerable. Thus, the immediate

response to infrared radiation may be an increase or a decrease in current. It should be noted that hole traps (other than luminescence centers) may exist, and that the release of holes from these traps due to thermal energy may increase the conductivity temporarily. This release will also tend to decrease the electron concentration in the conduction band by making possible non-radiative transitions between conduction-band electrons and valence-band holes. This could greatly distort the trap distribution deduced from either the thermoluminescence or the conductivity during thermoluminescence.

#### The Photoconductivity of Single Crystals of ZnS

Relatively few measurements have been made on single crystals of ZnS. However, Broser and Schulz<sup>11</sup> and Broser and Broser-Warminsky<sup>9</sup> have reported some measurements on the same crystal of ZnS, accidentally contaminated with copper, described in Sec. III.

Broser and Schulz find an increase in photoconductivity as the absorption edge is approached. However, they show that this could be due to the absorption corresponding to the transition from the lower level of the [2] center to the conduction band.

Broser and Broser-Warminsky have found that the photoconductivity observed under ultraviolet excitation at 83°K is enhanced when the crystal is also irradiated with infrared radiation. This enhancement is temporary, the conductivity returning to a steady value. However, no reduction in the conductivity is observed due to infrared irradiation. The luminescence and conductivity show maximum enhancement at 1.2  $\mu$ , in a sharp band similar to that found for many ZnS powder phosphors at 77°–90°K.

### XIII. CONCLUSION

We have shown that the model of Luchner, Kallmann, Kramer, and Wachter can be used (when suitably extended) to account for many of the properties of zinc sulfide phosphors reported by a large number of workers. However, it will have become evident that the major difficulty in interpreting the reported results is in the uncertain nature of the systems investigated. This difficulty is even more pronounced for electrical measurements than for optical ones.

The first development needed to produce simpler systems is probably the production of single crystals of optical quality, uniformly activated with desired impurities. It will then become possible to measure two quantities of basic importance for any theory of stimulation. The first is the number of quanta of stimulating radiation which are absorbed for each quantum of stimulated emission at various stages of the excitation and of the stimulated decay. The second is the number of quanta of infrared radiation absorbed for the loss of each quantum from the thermoluminescence obtained after irradiation.

<sup>24</sup> H. Koelmans, *J. Phys. Chem. Solids* **17**, 69 (1960).

The quality of the crystals of zinc sulfide investigated at present is very poor indeed compared with that of, say, the silicon crystals readily available. Addamiano and Aven<sup>25</sup> have reported that the density of the vapor-grown crystals normally investigated is several percent lower than that deduced from crystal spacing and atomic weights, or that obtained for melt-grown crystals. Similarly, most specimens are polytypes

<sup>25</sup> A. Addamiano and M. Aven, *J. Appl. Phys.* **31**, 36 (1960).

or are heavily twinned. Methods of growing more perfect crystals are therefore vital to progress in this field. One approach being made in this laboratory<sup>26</sup> is to grow zinc sulfide epitaxially on silicon. Present results indicate that the first layers of zinc sulfide are almost as perfect as the silicon substrate, suggesting that the use of silicon as a seed may be valuable in the growing of good quality crystals of ZnS.

<sup>26</sup> P. L. Jones, C. N. W. Litting, D. E. Mason, and V. A. Williams (private communication).

## On the Areas of Equivalence of the Bogoliubov Theory and the Prigogine Theory of Irreversible Processes in Classical Gases\*

J. STECKI,† H. S. TAYLOR

*Department of Chemistry, University of Southern California, Los Angeles, California*

The irreversible equations of evolution of classical gases, as obtained by Prigogine and Résibois from a study of the Liouville equation, in the limit of the system being very large, are examined, and the structure of the Markovian equation of evolution of the velocity distribution function is studied for homogeneous systems. It is then shown that the Markovian equations completely contain the Bogoliubov theory.

### I. INTRODUCTION

Much of the recent work on irreversible statistical mechanics has been concerned with derivations of kinetic equations for the probability densities describing the time evolution of the system. For the case of classical systems, the most general kinetic equations ever derived have been given by Prigogine and his collaborators.<sup>1-3</sup> These authors have also shown how the general kinetic equations can be reduced to a set of Markovian equations<sup>4</sup> and how these can be further simplified in the so-called instantaneous collision approximations<sup>5</sup> (ICA). In doing this, these authors have demonstrated, under very general conditions, how the irreversible equations of evolution are obtained by appropriate asymptotic procedures from (reversible) mechanical equations of motion of the system under consideration.

In view of this generality and of the rigor of deriva-

tion of the results of Prigogine and his co-workers, it is imperative to compare other approaches with the Prigogine theory. In this paper such a comparison and evaluation is presented, of a kinetic theory of classical gases advanced by Bogoliubov<sup>6</sup> in 1946.

The Bogoliubov theory is worth particular attention for several reasons. It is a strictly statistical-mechanical theory; it does not make recourse to thermodynamic arguments or concepts; and the kinetic equations are obtained by a systematic and well-defined procedure. On the other hand, it does not attempt complete generality nor any discussion of the question of how the irreversible equations can be obtained from the reversible ones; it starts from simplifying assumptions. We also note in passing that recent applications to specific problems have been most often based on either of the two theories, and that in some cases identical kinetic equations were obtained (e.g., for classical electron plasmas.<sup>7-9</sup> The final result of a study of the Bogoliubov theory is presented below; it is shown how the Bogoliubov prescription results in a well-defined approximation to the Markovian kinetic equations of

\* Financial support of this work by the U.S. Office of Naval Research, Physics Branch, under contract Norn. 228(23)NR013-307, is gratefully acknowledged.

† On leave from the Polish Academy of Sciences, Institute of Physical Chemistry, Warsaw, Poland.

<sup>1</sup> I. Prigogine, *Non-equilibrium Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1962).

<sup>2</sup> R. Balescu, *Statistical Mechanics of Charged Particles* (John Wiley & Sons, Inc., New York, 1963).

<sup>3</sup> I. Prigogine and P. Résibois, *Physica* **27**, 629 (1961); Ref. 1 Chap. 11.

<sup>4</sup> No "memory effects"—the time evolution of probabilities at time  $t$  depends on values at time  $t$  only; in the non-Markovian case it depends on values at earlier times  $t' < t$ .

<sup>5</sup> F. Henin, P. Résibois, and F. C. Andrews, *J. Math. Phys.* **2**, 68 (1961); F. C. Andrews, *ibid.* **2**, 91 (1961); Ref. 1, Chap. 11, p. 242, par. 6.

<sup>6</sup> N. N. Bogoliubov, *Problems of a Dynamical Theory in Statistical Physics* (1946). [English translation in *Studies in Statistical Mechanics*, edited by J. de Boer and G. E. Uhlenbeck (North-Holland Publishing Company, Amsterdam, 1962).]

<sup>7</sup> R. Balescu, *Phys. Fluids* **3**, 52 (1960); R. Balescu and H. S. Taylor, *ibid.* **4**, 85 (1961).

<sup>8</sup> A. Lenard, *Ann. Phys. (N. Y.)* **10**, 590 (1960); R. L. Guernsey, thesis, University of Michigan (1960) [Office of Naval Research Technical Report Nonr. 1224(15), unpublished].

<sup>9</sup> This led one of us to make a preliminary study of the relationship between these two theories in an unpublished work (H.S.T., 1961).