ABSORPTION AND LUMINESCENCE IN IMPURITY-ACTIVATED ALKALI HALIDES

R. A. EPPLER

Research and Development Division, Corning Glass Works, Corning, New York

Received December 27, 1960

CONTENTS

I. INTRODUCTION

The various alkali halides, when activated by small amounts of heavy metals such as thallium or lead, constitute the simplest and most clearly understood of the many luminescent materials. Their study is, therefore, basic to an understanding of the phenomenon of luminescence.

Ever since the field was first investigated by R. W. Pohl and his numerous coworkers in the late 1920's (5, 7, 9–11, 23–25, 36, 40, 67–69, 77, 91, 96, 107, 135–136) this subject has been extensively studied, both experimentally and theoretically. In this period five conferences have been held (14, 17, 79, 110, 122), and several of the major contributors to aspects of this problem have published reviews of their work (37–39, 64, 148, 156). This review is an attempt to survey the extensive literature on this subject, both theoretical and experimental, and to summarize in one article an overall view of the subject.

II. SPECTRAL MEASUREMENTS

A. *Absorption characteristics due to ions of an impurity*

When thallium, lead, or one of certain other heavy metals is added to a melt of an alkali halide and then crystals are grown by the Kyropoulos (73) method, new absorption bands appear, due to the presence of the heavy metal (see figure 1). The positions of the bands are similar for most of the alkali halides. Nearest the visible is a small peak (designated A) and about 1 e.v. beyond this are two peaks (designated B and C), incompletely resolved (120). The B band appears only in the alkali chlorides at room temperature. It has been observed at low temperatures in potassium iodide (160). Positions of the bands vary only slightly as alkali or halide ions are changed and are tabulated in table 1 for those alkali halide phosphors which have been measured. This, plus the absence of photoconductivity during absorption, led to the conclusion that

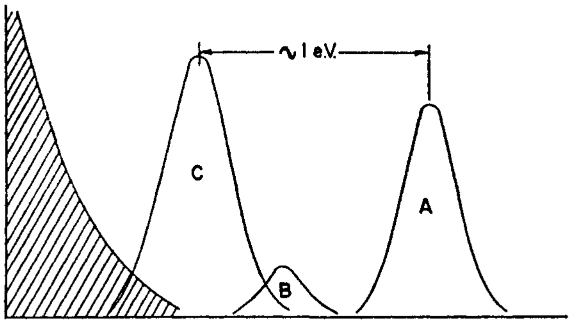

FIG. 1. Typical absorption bands in impurity-activated alkali halides (from Seitz (120)).

the absorption process is confined to the region of the ion of the impurity and is not concerned with wandering or free electrons in the lattice (31).

In the original work, the Göttingen group measured the absorption spectra of various alkali halides activated by small amounts of thallium (25, 36, 40), copper (23, 135), silver (40, 135), and lead (36). They studied the variation of the absorption with concentration of impurity (23, 67, 68) and found that, at least for low concentrations, the intensity of absorption is directly proportional to the concentration of the impurity. Koch (68) was able to predict the effects of concentration on the absorption from the number of optical dispersion electrons. They also investigated the effect of temperature on the absorption bands (23, 24, 77, 91). The bands were found to decrease in intensity with increasing temperature. In addition, it was found that the B band increases rapidly at high temperatures (over 500°C.) at the expense of the C band (24). Finally, they found that x-rays serve to decrease the intensity of the absorption bands (5, 136). This work is summarized in the reviews of Hilsch (37–39) and Stockmann (139).

B. Emission spectra

The Göttingen group also investigated the emission spectra of these phosphors (9–11, 96), concentrating almost exclusively on thallium-activated phosphors. The spectra consist of broad bands which can be resolved into one, two, or three peaks. These are all on the low-energy side of the absorption bands. The entire emission spectrum is stimulated by light in any one of the three absorption bands A, B, or C of figure 1. The relative intensity of the bands is independent of the exciting frequency (120). A strong temperature dependence is also observed.

The quantum yield was measured by Bunger (9), who found that the yield was close to unity.

C. Other phosphors

More recently, the variety of alkali halide phosphors upon which absorption and emission measurements have been made has increased considerably. Fialkovskaya (22) has studied the emission of thallium-activated mixed crystals. Extensive investigations of copper-activated alkali halides have been reported (8, 33, 43, 44, 144). Two groups have investigated tin-activated alkali halides (1, 2, 41, 53, 54), which have fine structure not present with other activators. The Lushchiks (81–90) have investigated phosphors activated by indium, gallium, and germanium, as well as thallium, lead, and tin. Two other groups (159, 161) have also studied activation by indium. Parfianovitch (98–103) has studied nickel-activated sodium chloride. Four investigations of thallium-activated ammonium

TABLE 1

Spectral location of the absorption due to impurities in alkali halide crystals

Phosphor	Peak Frequency of the		References
	A band	C band	
	A.	A.	
NaCl:Tl	2540	1990	(25)
NaBr:Tl	2670	2160	(25)
NaI:Tl	2930	2340	(25)
KCl:Tl	2475	1950	(25)
KBr:Tl	2610	2100	(25)
KI:Tl	2870	2360	(25)
RbCl:Tl	2450	1950	(25)
RbBr:Tl	2590	2120	(25)
RbI:Tl	2860	2400	(25)
CsCl:Tl	2480	1960	(25)
CsBr:Tl	2630	2140	(25)
CsI:Tl	2990	2410	(25)
0.8KI/0.2KBr:Tl	2858	—	(18, 20)
0.6KI/0.4KBr:Tl	2836	—	(18, 20)
0.4KI/0.6KBr:Tl	2810	—	(18, 20)
0.7KI/0.8KBr:Tl	2708	—	(18, 20)
KCl:In	2815	2435	(53, 84, 159)
KBr:In	2930	2430	(84)
NaCl:In	2940	2390	(84)
KBr:Bi	3712	—	(18, 20)
KI:In	3130	2620	(84)
NaCl:Pb	2740	1930	(36)
NaBr:Pb	3040	2200	(36)
NaI:Pb	3578	—	(18, 20)
KCl:Pb	2730	1960	(36)
KBr:Pb	3020	2230	(36)
KI:Pb	3542	—	(18, 20)
RbCl:Pb	2720	1980	(36)
RbBr:Pb	3004	—	(18, 20)
RbI:Pb	3541	—	(18, 20)
CsCl:Pb	2849	—	(18, 20)
CsI:Pb	3705	—	(18, 20)
NH$_4$Br:Pb	3077	—	(18, 20)
NH$_4$I:Pb	3580	—	(18, 20)
KCl:Cu	2650	—	(135)
KBr:Cu	2650	—	(135)
NaCl:Cu	2550	2200	(8, 135)
KI:Ag	2650	2540	(25)
NaBr:Cu	2590	—	(135)
NaCl:Ag	2100	—	(135)
NaBr:Ag	2190	—	(135)
KCl:Sn	2810	2250	(41)
KBr:Sn	3050	2470	(41)
KI:Sn	3510	2600	(41, 89)
KBr:Ga	2700	2260	(86)
KBr:Ge	2880	2510	(86, 87)
KCl:Ga	2600	2180	(82)
KCl:Ge	2750	2150	(82, 87)
NaCl:Ge	2820	2150	(87)
NH$_4$Br:Tl	2560	2250	(141)
NH$_4$Cl:Tl	2400	2150	(141)
NH$_4$I:Tl	2900	2600	(141)
KI:Ga	—	2300	(161)
NaCl:Ni	2400	—	(103)

halides have been reported (13, 60, 97, 141, 142), as have studies on thin films of mixed alkali halides and heavy metal halides (58, 59, 123–127, 140).

D. Luminescent decay

The phosphorescent decay properties of these materials were measured by Bunger and Flechsig (10, 11), who found that the decay followed a simple first-order kinetic equation:

$$dn/dt = -\alpha n \tag{1}$$

where n is the number of excited electrons and α is a constant which varies with temperature according to equation 2,

$$\alpha = s \exp[-E/kT] \tag{2}$$

where $s = 2.9 \times 10^9$ sec.$^{-1}$ and $E = 0.67$ e.v.

Randall and Wilkins (113) found the above measurements to be essentially correct, but detected minor (less than 1 per cent) discrepancies.

Several other authors (3, 4, 6, 42, 111) do not agree with these results or with one another.

E. Thermoluminescence

Urbach (143) suggested a variation of the decay measurement wherein the phosphor is excited at a low temperature where thermal release of trapped electrons is negligible, and is then heated at a constant rate while the spectral emission is measured as a function of temperature.

If an electron is trapped in an energy level which is E e.v. below the conduction band, it must acquire this energy to escape the trap and be available for luminescence. Consequently the probability for luminescence at temperature T is (113):

$$p = s \exp[-E/kT] \tag{3}$$

Now, assuming that E is single valued and the temperature is increasing at a uniform rate,

$$dn/dt = -ns \exp[-E/kT] \tag{4}$$

where n is the number of trapped electrons at time t. Equation 4 assumes no retrapping, which has been shown (114) to be a reasonable assumption.

Then, writing $dT = \beta dt$, where β is the rate of warming, and integrating:

$$\log\left[\frac{n}{n_0}\right] = -\int_0^T \frac{1}{\beta} s e^{-E/kT}\, dT \tag{5}$$

and

$$n = n_0 \exp\left[-\int_0^T \frac{1}{\beta} s e^{-E/kT}\, dT\right] \tag{6}$$

whence, since the intensity I of luminescence is proportional to the rate of release of electrons,

$$I = C\frac{dn}{dt} = n_0 C \exp\left[-\int_0^T \frac{1}{\beta} s e^{-E/kT}\, dT\right] \tag{7}$$

where C is a constant of proportionality.

Using the values of s and E given in Section II,D and applying equation 7, Randall and Wilkins (113) were able to come within 2 per cent of the experimental glow curve for KCl:Tl, which they measured and found to have one major peak in the vicinity of 330°K.

III. THE COMPLEX-ION MODEL

In 1929 Fromherz, Lih, and Menschick (27–30) noted a strong resemblance between the spectra of impurities such as thallium and lead in alkali halides, and the spectra of solutions of these heavy metal ions. They postulated, therefore, that the impurity center in the alkali halides was the same as the structure that exists in solution. That is to say, the heavy metal anion is complexed with varying numbers of the appropriate halide ions. Three possible complexes are known in solution: $PbCl_2^0$, $PbCl_4^{2-}$, and $PbCl_6^{4-}$.

This view was supported by Koch and Pohl (69), Hilsch (39), Kato (50–52), and Pringsheim (111, 112). Kato points out that for several silver- and copper-activated alkali halide phosphors, the luminescence phenomena associated with the impurity can be explained on the basis of this model.

After Seitz published his model for the phenomenon (see Section IV below), the complex-ion model fell into disuse, primarily because of the greater simplicity of the Seitz model.

Recently, however, several observations have been made which indicate that for divalent impurities such as lead this theory is more useful. Fredericks and Scott (26, 118) have made transference measurements on lead impurity in alkali halides. They found that the transport number for lead is negative, indicating that the lead ion is complexed with sufficient halide ions to make the whole complex negatively charged.

Sears (119) has found that a few parts per million of lead chloride in an aqueous potassium chloride solution alters the growth of potassium chloride crystals in a way which is consistent with the postulate of the addition of a complex lead-containing ion at certain growth steps.

Makishima (92) has pointed out that if the spectra of Tl^+ and Pb^{++} impurities arose from a similar center one would expect the spectra to be similar in structure and shape, but quite different in wavelength. This is not observed experimentally. He has also made several optical studies and concluded that the origin of the luminescence of alkali halide phosphors is the transitions between ground and excited states of electrons in homopolar bonds between the impurity and the surrounding halide ions.

Eppler and Drickamer (18–20) have studied the effect of pressure on the absorption of lead-activated alkali halides. They found that the data are consistent with the complex-ion model, but inconsistent with the Seitz model (see Section VI,D).

Another important form of complexing is vacancy-anion complexes. In order to preserve charge neutrality (obeyed by all alkali halides) it is necessary to introduce into the crystal lattice a positive-ion vacancy for each and every divalent-ion impurity introduced into the lattice of a monovalent material. Measurements of dielectric loss on such materials (76) have shown that such vacancies are essentially 100 per cent associated with the divalent ions. Therefore, there should be a bound vacancy associated with every lead or stannous ion present as impurity in an alkali halide lattice. Studies of the excitation and emission spectra of NaCl:Pb (12, 116) have shown side bands to the A band which could be attributed to lead–vacancy or lead–lead pairs. The phosphor was also found to be sensitive to its thermal history, which may be due to the interaction with defects.

IV. THE SEITZ MODEL

A. Entry of the impurity into the alkali halide lattice

In a discussion of thallium-activated alkali halide phosphors, Seitz (120, 121) suggests that the thallium enters the lattice substitutionally as a monovalent positive ion, replacing alkali ions in the lattice in a random manner. This view is supported by the fact that solutions of thallous ions in alkali halide solutions show similar spectra (31), pure thallous salts have spectra in the same region as the thallium-activated alkali halides (31), the ionic radii of thallous and alkali ions are about the same (121), and the maximum concentration for which the observed, simple relationships between concentration and absorption (67) hold is about the same as that calculated from statistical mechanics for an energy separation of 1 e.v. between the absorption of thallium and that of the fundamental crystal (121).

B. The energy states of the thallous ion

The configuration of the valence electrons in the ground state of the thallous ion is $6s^2$, and the energy state is ${}^1S_0$. From spectroscopic studies of the free ion it is known that the excited states of lowest energy arise from the configuration $6s6p$ and are, in order of increasing energy: ${}^3P_0$, ${}^3P_1$, ${}^3P_2$, and ${}^1P_1$, each separated by a gap of the order of 1 e.v.

The transition ${}^1S_0 \rightarrow {}^3P_2$ is excluded by the general selection rule $\Delta J = 0, \pm 1$, and the selection rule against transitions from $J = 0$, to $J' = 0$ suggests that ${}^1S_0 \rightarrow {}^3P_0$ does not occur either. As the coupling is in part J—J, the selection rule $\Delta S = 0$ is not too effective and the transitions ${}^1S_0 \rightarrow {}^3P_1$ and ${}^1S_0 \rightarrow {}^1P_1$ have a certain probability.

C. The structure of the absorption bands

In order to analyze the nature of the absorption due to the impurity, it is first necessary to understand how the energy states of a free thallous ion are modified when the ion is brought into the lattice (see figure 2)

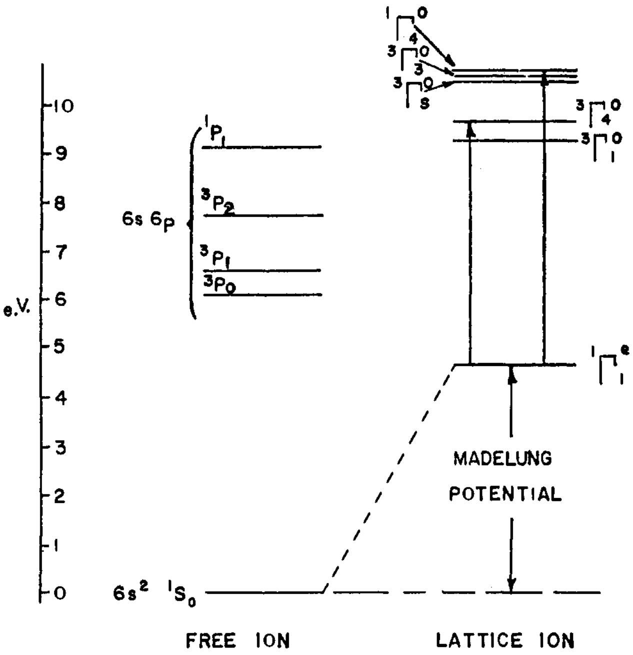

FIG. 2. Energy levels of the thallous ion (from Seitz (120)).

In the unexcited state the interaction of the Tl⁺ ion with the lattice consists of electrostatic attraction and homopolar repulsion. In the first excited state, the excited electron will be shared by several adjacent ions and the charge distribution is not the same as for the excited Tl⁺ ion in the free state. Here the electrostatic attraction remains the same, but the homopolar interaction possesses an attractive minimum. This causes the energy levels of the excited state to be closer together than in the free ion.

The two main absorption bands (see figure 1) may be correlated with transitions of the Tl⁺ ion. The most probable transitions are indicated by arrows on figure 2. They are the

$$ {}^1\Gamma_1^e \rightarrow {}^3\Gamma_4^0 \text{ and } {}^1\Gamma_1^e \rightarrow {}^1\Gamma_4^0 $$

transitions, which are analogous to the ${}^1S_0 \rightarrow {}^3P_1$ and ${}^1S_0 \rightarrow {}^1P_1$ transitions of the free Tl⁺ ion, respectively, and can be identified with the A and C peaks of figure 1. Any lack of cubic symmetry due to crystal imperfections such as vacancies or dislocations will allow other weaker transitions (normally forbidden) to occur. To this is ascribed peak B of figure 1, associated with the

$$ {}^1\Gamma_1^e \rightarrow {}^3\Gamma_3^0 \text{ or } {}^3\Gamma_5^0 $$

transitions.

V. WILLIAMS' THEORY OF SOLID-STATE LUMINESCENCE

In 1945 Williams and Eyring (145, 146, 148) calculated several luminescent decay phenomena based on the ideas of Seitz (above) and the absolute rate theory (32). A few years later Williams followed this with the most quantitative theoretical treatment yet attempted in this field (48, 147, 149, 151, 153, 158, 159; see also 154, 155 and 156).

His theory is an attempt at the calculation of the absorption and emission spectra of the thallium-activated potassium chloride phosphor, starting only with the properties of the constituent ions and assuming a relatively simple configurational coördinate model for the luminescence process. (An excellent fundamental discussion of the configurational coördinate model technique is given in reference 64 and will, therefore, not be treated here.)

The assumption is made that KCl:Tl is a 100 per cent ionic crystal in which luminescence arises from the internal transitions of monovalent thallous ions substituted for potassium ions (the Seitz model). Wave functions of the free ion are used throughout and are assumed applicable to the crystalline state.

The radial charge densities of the thallous ion in the ground $^1S_0$ and excited $^3P_1^0$ states are evaluated by means of the Sommerfeld modification of the Fermi–Thomas method (137) for the core electrons ($1s^2$ to $5d^{10}$ electrons plus the nucleus) and the Hartree self-consistent field method (34, 35) for the two outermost-shell electrons. Using these wave functions and the known values of the ionic radius, the polarizability, and the repulsive energy constant for the ground state (93, 94), these parameters can be evaluated for the $^3P_1^0$ excited state of the thallous ion, interacting with chloride ions. The polarizability is determined by the Kirkwood method (55). The variation of the repulsive energy with interatomic distance is found equal to the variation of a term S^2/a, where S is an overlap integral between the thallous and chloride ions.

The total energy of the system, with thallous ions in the $^1S_0$ or $^3P_1^0$ state substituted in dilute concentration for potassium ions in the lattice, is then calculated as a function of the interatomic distance between the thallous ion and the nearest-neighbor chloride ion, with the condition that the rest of the lattice rearranges to minimize total energy. Only radially symmetric displacements of the various interatomic distances are considered. Madelung, exchange repulsion, van der Waals, and ion-induced dipole interactions are included. In addition, for the $^3P_1^0$ state, the coulomb overlap interactions are included, based upon the wave functions of the free ion. The resulting total energy is then plotted against interatomic displacement (see figure 3).

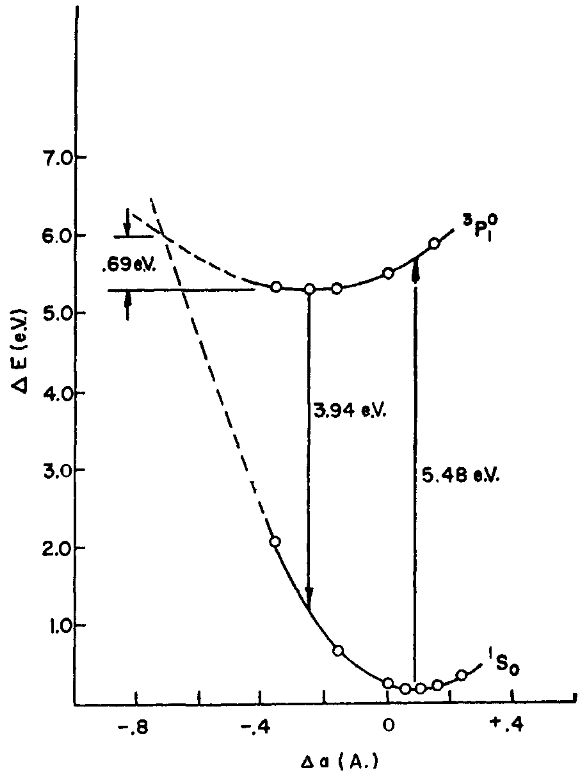

FIG. 3. Configurational coördinate diagram for KCl:Tl (from Williams (156)).

A check of the original assumption that localized wave functions and atomic rearrangements are involved in the luminescence of KCl:Tl can now be made (48, 155). The absolute energy of the $^1S_0$ state of the thallous ion embedded in the band structure of potassium chloride can be computed by a consideration of the following cycle:

$$\begin{tikzcd}
\mathrm{Tl}^+(\mathrm{g}) + \mathrm{KCl}(\mathrm{s}) \arrow[r, "I_2"] \arrow[d, "\Delta U"] & \mathrm{Tl}^{++}(\mathrm{g}) + \mathrm{KCl}(\mathrm{s}) + e \arrow[d, "\Delta U' - F"] \\
\mathrm{KCl{:}Tl}^+(\mathrm{s}) + \mathrm{K}^+(\mathrm{g}) \arrow[r, "I_2^*"] & \mathrm{KCl{:}Tl}^{++}(\mathrm{s}) + \mathrm{K}^+(\mathrm{g}) + e\,(\mathrm{s})
\end{tikzcd} \qquad (8)$$

If I_2^* for the excited state turns out to be at least several electron volts (and, therefore, a low probability for escape of electrons from the excited state into the conduction band), the assumption is justified. For KCl:Tl the values are 9.5 e.v. for the $^1S_0$ state and 4.5 e.v. for the $^3P_1^0$ state. This leads to the band theory model for KCl:Tl shown in figure 4.

The absorption spectrum is then calculated by applying a Boltzmann probability function to the various atomic configurations of the system in the ground state:

$$P(\Delta E) = [K/2\pi kT]^{1/2} \exp[-(E - E_0)/kT]\, \mathrm{d}q\mathrm{d}\Delta E \qquad (9)$$

where K is the force constant for the initial state, E is the transition energy, E_0 is the lowest energy of the ground state, and q is the displacement from equilibrium in the initial state of the nearest-neighbor chloride ions.

The emission spectrum is similarly calculated, except

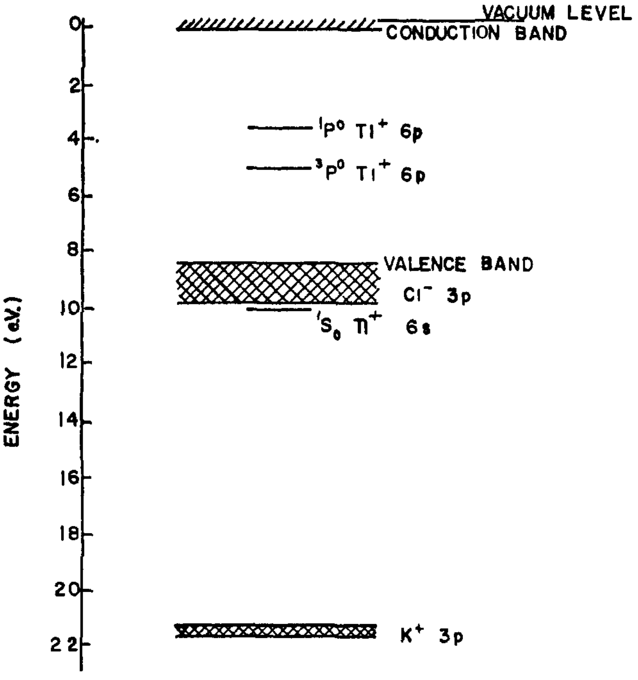

FIG. 4. Energy-level structure for KCl:Tl (from Williams (156)).

that an additional term must be added for the spin-orbit interaction (158). Data calculated by this method are within 10 per cent of the experimentally observed spectra (151) (see figure 5).

At low temperatures this equation must be modified to include the effect of zero-point energy, as described in the next section.

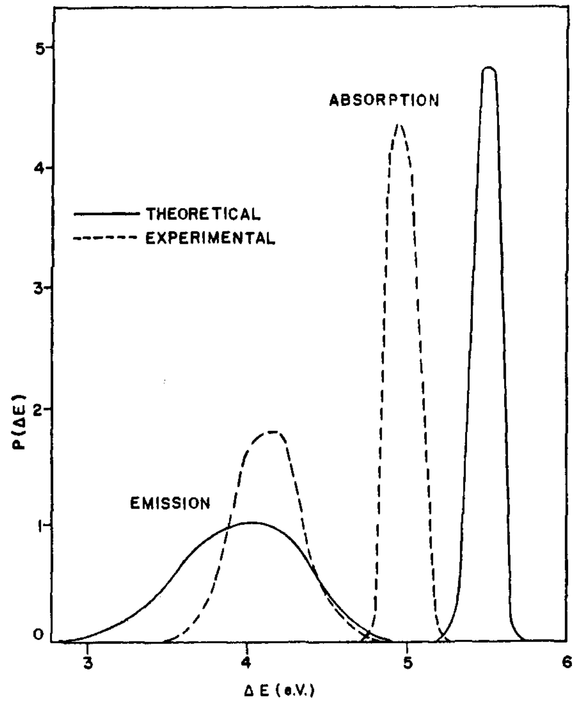

FIG. 5. Theoretical and experimental absorption and emission spectra of KCl:Ti (from Williams (151)).

A similar calculation has been made for silver-activated sodium chloride by Potekhina (108). More recently (109), Potekhina has made a quantum-mechanical treatment of the same problem, using similar assumptions but not relying on empirical parameters. The results of his two calculations are summarized in table 2 and illustrate the validity of the empirical parameters used in the Williams type of calculation.

TABLE 2

The parameters of the $4d^{10} \rightarrow 4d^{9}5s$ *transition in silver-activated sodium chloride, according to Potekhina (108, 109)*

	Williams' Type of Calculation	Quantum-mechanical Calculation
$E(^1S_0)$ in electron volts.	$4.997(\Delta a + 0.069)^2 - 0.279$	$5.475(\Delta a + 0.066)^2 - 0.079$
$E(^3D)$ in electron volts	$4.478(\Delta a - 0.107)^2 + 3.353$	$4.465(\Delta a - 0.064)^2 + 3.34$
Absorption maximum in electron volts....	3.77	3.52
Emission maximum in electron volts.......	3.477	3.32

VI. SEVERAL RECENT EXPERIMENTS

Most of the recent experimental and theoretical work has been concerned with testing the validity of the above treatments. This work is outlined in this and the next three sections.

A. Low-temperature spectra

Measurements have been made to as low as 4°K. of the absorption, excitation, and emission spectra of thallium-activated potassium chloride (46, 47, 63, 104, 106) and thallium-activated potassium iodide (160).

Spectra at 80°K. have band widths approximately one-half those at 300°K. Spectra at 4°K. are essentially the same as at 80°K., showing the existence of a zero-point energy (156). The spectra, which are asymmetric at room temperature, assume a Gaussian shape at 4°K. (104). This latter fact led Patterson (104) to propose that the crystal lattice may partially rearrange to the cesium chloride type in the vicinity of the impurity.

Yuster and Delbecq (160) observed some fine structure in the high-energy portion of the spectra at low temperatures in potassium iodide. They attributed the fine structure to normally forbidden transitions such as $^1S_0 \rightarrow {}^3P_2^0$.

Williams and Hebb (152, 157) have calculated the absorption spectra of KCl:Tl at low temperatures. The treatment is similar to that in Section V, except that a quantum-mechanical distribution is used in order to take account of the zero-point energy:

$$P(\Delta E) = [K/2\pi kT]^{1/2} \exp[-Kq^2/2k\theta \coth(\theta/T)]\, dq/d\Delta E \quad (10)$$

where

$$k\theta = \frac{1}{2}\hbar[k/m_e]^{1/2} = E_0 \tag{11}$$

and m_e is the electron mass. Results in agreement with experiment were obtained.

Patterson and Klick (106), however, object to this treatment on the grounds that p states are not radially symmetric and agreement of any theory restricted to radial effects is fortuitous.

B. X-ray studies

Runciman and Steward (115) have studied the atomic position and size of the thallium ions in KCl:Tl by x-ray techniques. By means of the application of Vegard's law with assumptions as to the relative sizes of the thallous and potassium ions in the face-centered cubic potassium chloride lattice, they arrived at the conclusion that the thallium ion is entered into the lattice substitutionally up to 15 mole per cent.

Objections to this work have been raised by Ewles and Joshi (21) and others because some other workers (42, 117, 138) have found that additions of thallous chloride to potassium chloride produce no appreciable changes in the lattice spacing, since the two materials have similar lattice constants. It should be noted, however, that identical lattice constants are the conditions most favorable to substitutional addition, as reported by Runciman and Steward.

C. Transference measurements

Fredericks and Scott (26, 118) have made transference measurements on the lead ion in potassium chloride. They found that the transport number for lead in potassium chloride is negative, indicating that the lead ion is complexed with sufficient halide ions to make the whole complex negatively charged. This is strengthened by an earlier observation of Lorenz and Ruckstuhl (78) that in fused salts of lead chloride and potassium chloride containing less than 80 per cent lead chloride, the transport number of the lead ion is negative. This is not unexpected, since with its greater charge (+2) the lead ion could pull the nearest-neighbor halide ions out of their equilibrium positions into a tighter binding (95).

D. The effect of pressure

The first measurement of the effect of hydrostatic pressure on the spectra of these materials was by Johnson and Williams (49), who found a shift of 4 A. to lower energy in the A band of thallium-activated potassium chloride at 2000 atm.

Kirs (56) has measured the shift with pressure to 2000 atm. of the A band in five tin-activated alkali halide phosphors. A shift to higher energy is observed in all cases, with the largest shifts in the iodides and the smallest shifts in the chlorides. He also (57, 61) studied the effect of the polymorphous transition on the spectra of thallium- and tin-activated ammonium iodide phosphors.

Eppler and Drickamer (18–20) have measured the effect of pressure on the spectra of the A band in several alkali halides to as high as 170,000 atm. They found that for monovalent impurities (Tl^+, In^+, etc.) the pressure shifts depend strongly on the structure of the host crystal (face-centered cubic or simple cubic) but are relatively independent of the halide ion. On the other hand, for divalent impurities (Pb^{++} for instance), the reverse is true. They also found a discontinuous shift in the spectra of the activated potassium and rubidium halides at the phase transition from the face-centered cubic to the body-centered cubic lattice (at approximately 20,000 atm. for the potassium halides and 5000 atm. for the rubidium halides). They interpret the data on the monovalent impurities to be consistent with a substitutional ion model (the Seitz–Williams treatment), and the data on the divalent impurities to be consistent with the older complex-ion model.

Johnson and Williams (49) have also proposed a theory for the pressure shift in KCl:Tl. The essential assumption is that pressure contributes the same energy to the initial and final states for any arbitrary electronic configuration. Only the probability for the various configurations is changed. This theory predicts a pressure shift approximately a factor of two greater than is observed experimentally (19).

E. Spectral measurements of higher precision

Spectral measurements at higher concentrations than those used by the Göttingen school (see Section II), and using spectrometers with higher precision, have revealed details of the spectra of these phosphors which went unnoticed in the earlier work.

Yuster and Delbecq (160), in a study of KI: Tl at low temperatures, observed several weak bands in the spectral region of the C band (associated with transition to the $^1P_1$ state) and the B band (which they associate definitely with transition to the $^3P_1$ state). One band, on the high-energy side, is associated with a transition similar to the α and β bands in colored alkali halides.

They also found three partially resolved peaks in the C band and the absence of any such resolution in the A band. These three bands could conceivably be a result of the dynamic Jahn–Teller effect (95).

Patterson (104) has made a detailed study of the shape of the A band as a function of temperature. The band is asymmetric at room temperature, but Gaussian at 4°K. On the basis of this, and the observed high-pressure discontinuity in the spectra at the phase transition in the host crystal (19), he proposed that the

A band is complex with a major peak at 2475 A. (at room temperature) and lesser peaks at 2450 A. and 2620 A. (105). He attributed one band to a substitutional thallous ion in the face-centered cubic lattice and another to a thallous ion in a localized simple cubic lattice (104).

Ewles and Joshi (21) have published a series of absorption measurements on the thallium-activated potassium chloride phosphor. Their absorption measurements, however, do not agree with those of other authors, showing the A band at 2600 A. instead of 2475 A. This casts some doubt on the accuracy of their work. However, they also found a number of weaker bands at the higher thallium concentrations.

A group at the Naval Research Laboratory has shown (12) that the spectrum of NaCl:Pb is very sensitive to its thermal history, and has found auxiliary bands to the A band which they attributed to lead–lead or to lead–vacancy pairs. Opposite results were found with KCl:Pb. Since potassium and lead have similar ionic radii, unlike sodium, they suggested that lattice strain favors the aggregation of vacancies in NaCl:Pb. In both this and one other study (116) the lead spectra were found to be defect sensitive. This work points up the importance of the lead–vacancy pair (see the discussion at the end of Section III).

VII. EXPERIMENTALLY DERIVED CONFIGURATIONAL COÖRDINATE CURVES

Because of the success of Williams' treatment in the use of configurational coördinate curves to describe the optical properties of a simple system, methods have been developed to construct these curves for more complex systems, using experimental data (62, 64). Such curves give a pictorial summary of the interaction of the impurity with its environment.

The principal assumptions are analogous to those of Section V. The curves are considered to be parabolic functions of a single configurational (geometric) coördinate q. It is therefore necessary to evaluate four constants from experimental data in order to specify the two curves. They are the force constants of the ground and excited states, the displacement q_0 along the configurational coördinate of the excited state minimum relative to the ground state minimum, and the energy difference E_D between the minima for the two states (see figure 6).

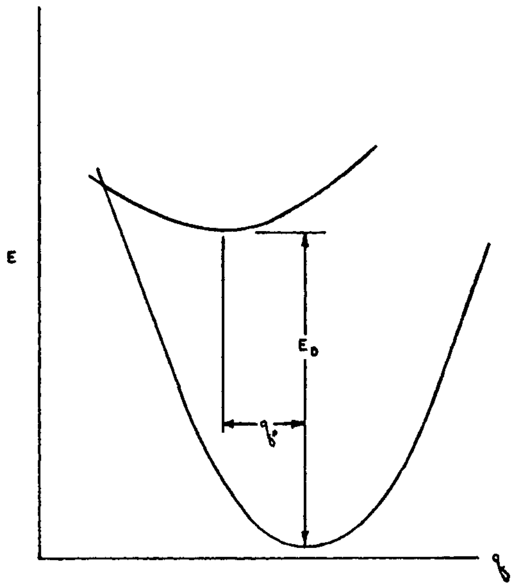

FIG. 6. Empirically derived configurational coördinate curve.

The energy of the peak of the absorption band is

$$E_{\mathrm{abs}} = E_D + K_E q_0^2/2 \qquad (12)$$

Similarly, the energy of the peak of the emission band is

$$E_{\mathrm{Em}} = E_D - K_G q_0^2/2 \qquad (13)$$

where K_G and K_E are the force constants of the ground and excited states, respectively.

From equation 10 the variation with temperature of the width of the absorption band at half maximum can be shown (64) to be

$$W_A = 2K_E q_0[1.386k/K_G]^{1/2}\left[\frac{\theta}{T}\coth\frac{\theta}{T}\right]^{1/2} \qquad (14)$$

from which it can be shown (64) that:

$$\theta = T\left[\frac{W_A \text{ at the low-temperature limit}}{W_A \text{ at any given high-temperature } T}\right]^2 \qquad (15)$$

Similarly, for the width of the emission band:

$$W_E = 2K_G q_0[1.386k/K_E]^{1/2}\left[\frac{\theta'}{T}\coth\frac{\theta'}{T}\right]^{1/2} \qquad (16)$$

from which:

$$\theta' = T\left[\frac{W_E \text{ at the low-temperature limit}}{W_E \text{ at any given high-temperature } T}\right]^2 \qquad (17)$$

Thus from an accurate measurement of the maximum energies of the absorption and emission bands, the measurements of the corresponding half-widths at room temperature and liquid helium temperature, experimentally derived configurational coördinate curves may be constructed (64). This has been done by Johnson (45) for the ${}^1S_0 \rightarrow 3P_1^0$ transition (the C band in KCl:Tl).

VIII. DISTRIBUTION OF ACTIVATORS IN ALKALI HALIDE PHOSPHORS

A group of Russian workers led by L. M. Shamovskiĭ has performed a series of experiments to investigate the distribution of impurity ions in alkali halide lattices. Their experiments included Laue photographs (131, 132), using several chemical forms of the activator material as starting materials in the phosphor synthesis (for example, using thallium metal, Tl_2O, Tl_2S, and TlI as starting materials in the synthesis of KI:Tl) (133, 134) and studies of the effect of impurities on ionic conductivity and on color centers (130, 134). They concluded (128, 129, 134) that the luminescence effect is a surface phenomenon, centered at dislocations and grain boundaries. Shamovskiĭ's theory has failed to gain wide acceptance, however, primarily because of the greater complexity of such a theory without provision for a much better insight into the phenomenon.

IX. THEORETICAL EXTENSION AND EVALUATION OF WILLIAMS' THEORY

A. Critical quantum-mechanical discussions

Williams' theory (see Section V) requires the use of several more or less restrictive approximations (74). They are as follows, in order of increasingly restrictive validity:

(*1*) A first-order perturbation treatment of the light absorption or emission, using Born–Oppenheimer wave functions.

(*2*) The same as (1) except that the dependence of the electric dipole matrix elements on nuclear positions is neglected.

(*3*) The semiclassical Franck–Condon principle: the nuclei are regarded as standing still during the optical transition. The probability of a given initial configuration is based on quantum-statistical mechanics.

(*4*) The classical Franck–Condon principle: the same as (3) except that the initial configuration is treated by classical statistical mechanics (only a portion of Williams' calculations involve this assumption).

(*5*) The quasimolecular viewpoint: a complex system is simplified by neglecting all but a small number of parameters.

Lax (74, 75) and Dexter (15) consider the range of validity of these assumptions, as applied to alkali halide and other phosphors. They conclude that for the particular case that Williams treats, the assumptions hold fairly well, but that the treatment does not have much wider validity, as had originally been hoped. In particular, it is doubtful that the treatment can be extended to those host systems which have any appreciable nonionic bonding. It is even questionable that the alkali iodide phosphors could be handled satisfactorily, because of the homopolar bonding tendencies of the iodide ion.

B. Oscillator strengths

Transitions from the ground state of the thallous ion to $^3P_1$ and $^1P_1$ states are fully allowed. The ratio of oscillator strengths (or transition probability) is around 1:5 because the spin-orbit coupling is incomplete and is the same in KI:Tl as in KCl:Tl (95). First Knox and Dexter (66) and later Williams, Segall, and Johnson (159) attempted the calculation of this ratio from atomic wave functions without taking explicit account of the anions.

Knox and Dexter began with some wave functions obtained by Douglas, Hartree, and Runciman (16) which do not include exchange terms. They obtained an oscillator strength ratio of 1:180, at wide variance with experiment. This led them to the conclusion that the then available wave functions were not sufficiently accurate to allow such a calculation with any degree of precision.

Williams, Segall, and Johnson (159), on the other hand, obtained good agreement with experiment by using the spin-orbit coupling parameters of the free thallous ion along with the singlet-triplet separation found in the crystal experimentally. Thus the impurity–crystal exchange terms were indirectly and empirically taken into account.

They also made a similar calculation for the KCl:In phosphor and found a value of 1:25, also in agreement with experiment. The very much weaker $^1S_0 \rightarrow {}^3P_1$ transition (relative to the $^1P_1$ transition) with an indium impurity center is in agreement with the much lower spin-orbit coupling constant in In^+ relative to Tl^+.

C. Electron-transfer processes in alkali halide phosphors

It has been more or less generally accepted that electron-transfer processes are not important in the consideration of the impurity absorption in alkali halides when the validity of the Seitz model is assumed (see above) (31). Knox (65) contends that this is not necessarily so. There are several details of the absorption and luminescence of these materials which are not easily explained by an excited activator model with no configuration interaction. Two of these are the growth of the B peak relative to the C peak at high temperature (24), and the appearance of a new band between A and C bands when a crystal is transformed from the NaCl structure to the CsCl structure (19). Knox suggests that perturbing electron-transfer states, or quite similar combining states, are responsible for many of the phenomena discussed above. For example, one can expect a temperature variation of the integrated absorption coefficient if the Condon approximation (approximation (2) of A above) breaks down. The appearance of a new absorption line when the lattice structure is changed from NaCl to CsCl is to be expected on the basis of electron-transfer states, where one additional singlet state exists for the CsCl structure over the NaCl structure.

X. THE KRISTOFEL' TREATMENT

Kristofel' (70–72) has recently made a calculation of the absorption and emission spectra of thallium-activated potassium chloride. His assumptions are similar to those of Williams' treatment discussed above. However, the calculation procedure does not require the use of empirically determined values of the various properties, such as polarizability, in order to calculate the luminescence spectra. Instead only a model and the mathematical techniques of quantum mechanics are required.

A Seitz model (see Section IV) is assumed for the system and the electrons are assumed to interact only with local vibrations (72). The single-oscillator approximation is made, which takes account only of the interactions of the activator with totally symmetric local vibrations. Wave functions are then chosen for the $^1S_0$ ground (71) and the $^3P_1$ excited (72) states.

From these wave functions, the energy of the system as a function of the interatomic displacement is determined, in a manner similar to Williams' treatment. Equation 18 results:

$$\Delta E = 4.23 + 7.08q - 9.7q^2 \qquad (18)$$

Also in a manner analogous to Williams' treatment, the semiclassical probability function is applied to calculate the absorption and emission spectra. These are compared with experiment in figure 7. The correspondence is of the same order as with Williams' treatment. Thus the chief value of this treatment lies in the elimination of the dependence upon experimentally derived data and the establishment of a purely theoretical approach. This opens up the possibility of a more detailed and exact description of the luminescence process.

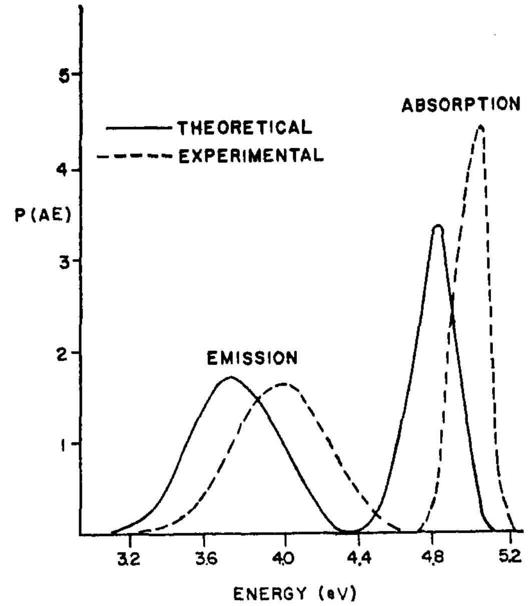

FIG. 7. Theoretical and experimental absorption and emission spectra of KCl:Tl (from Kristofel' (72)).

XI. COPPER-ACTIVATED ALKALI HALIDES

The early work on copper as an activator of alkali halides assumed that the copper was dispersed in the cuprous state and, consequently, that the process was similar to that with other heavy metal activators (23, 135). Boesman and Dekeyser (8) have presented evidence that the copper responsible for the 2500 A. absorption in NaCl:Cu is in the cupric, rather than the cuprous form. They prepared a sample activated with roughly 50 per cent Cu^+ and 50 per cent Cu^{++}. It had peaks at 3300 and 2500 A. and a doublet at 2200 A. Addition of CuCl to the sample removed only one peak of the doublet at 2200 A. It was therefore concluded that the other three peaks, including the one at 2500 A., are due to cupric-ion impurity.

Other investigators (18, 44) have also noticed that the 2500 A. band is probably due to cupric ion.

On the other hand, Lushchik and Lushchik (90) think that this band is a result of the $^1S_0 \rightarrow {}^1P_1$ transition of the cuprous-ion impurity, due to the similarities with optical phenomena associated with heavy metal and noble metal impurities.

XII. SUMMARY

The calculations of F. E. Williams have provided a basis for further investigation into the properties of the thallium-activated alkali halides.

The results of several authors (15, 74, 75, 108, 109) have served to elucidate further the significance theoretically of this work. The assumptions made in the treatment are quite restrictive. However, they have the great virtue that they permit the calculation of quantitative spectra which agree well with the observed values. In addition, further calculations (70–72, 109) of a purely quantum-mechanical nature, based upon similar assumptions, have been made and have given similar results.

Recent experiments, however, have shown details in the optical spectra which cannot be predicted from theories as restrictive as Williams' treatment. These second-order effects will probably not be predictable until the tools of quantum-mechanical calculation have been materially improved (65).

In addition, the new evidence supports the view that the states of the lead ion in alkali halides are more intimately mixed with the lattice states than with thallium (95). Thus a quantum-mechanical calculation based upon the complex-ion theory appears to be a current need in this field at this time.

The author wishes to thank the Editor of the *Journal of Chemical Physics* for permission to reproduce figures 1, 2, and 5, and the Editor of the *Journal of the Optical Society of America* for permission to reproduce figures 3 and 4.

XIII. REFERENCES

(1) ANDRIANOV, A. S., AND KATS, M. L.: Doklady Akad. Nauk S.S.S.R. **96**, 253 (1954).

(2) Andrianov, A. S., and Kats, M. L.: Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. 21, 552 (1957).

(3) Antonov-Romanovskiĭ, W. W.: Bull. acad. sci. U.R.S.S., Sér. phys. **5**, 523 (1941).

(4) Antonov-Romanovskiĭ, W. W.: J. Phys. (U.S.S.R.) **7**, 153 (1943).

(5) Arsenjewa, Agnes: Z. Physik **57**, 163 (1929).

(6) Birus, K., and Zierold, H.: Naturwissenschaften **30**, 63 (1942).

(7) Blau, M.: Nachr. Ges. Wiss. Göttingen. Math.-phys. Kl. **1933**, 401.

(8) Boesman, E., and Dekeyser, W.: Physica **24**, 52 (1958).

(9) Bunger, W.: Z. Physik **66**, 311 (1930).

(10) Bunger, W., and Flechsig, W.: Z. Physik **67**, 42 (1931).

(11) Bunger, W., and Flechsig, W.: Z. Physik **69**, 637 (1932).

(12) Burstein, E., Oberly, J. J., Henvis, B. W., and Davisson, J. W.: Phys. Rev. **81**, 459 (1951).

(13) Butler, K. H.: J. Electrochem. Soc. **103**, 508 (1956).

(14) Conference on the Conduction of Electricity in Solids held at Bristol, July, 1937, Proc. Phys. Soc. (London) **49**, extra part (1937).

(15) Dexter, D. L.: Nuovo cimento Suppl. **7**, No. 2, 245 (1958).

(16) Douglas, A. S., Hartree, D. R., and Runciman, W. A.: Proc. Cambridge Phil. Soc. **51**, 486 (1955).

(17) Electrochemical Society, One Hundred and Seventeenth Meeting, May 1–5, 1960, J. Electrochem. Soc. **107**, 58C (March, 1960).

(18) Eppler, R. A.: Doctoral Dissertation, University of Illinois (1960).

(19) Eppler, R. A., and Drickamer, H. G.: J. Phys. Chem. Solids **6**, 180 (1958).

(20) Eppler, R. A., and Drickamer, H. G.: J. Phys. Chem. Solids **15**, 112 (1960).

(21) Ewles, J., and Joshi, R. V.: Proc. Roy. Soc. (London) **A254**, 358 (1960).

(22) Fialkovskaya, O. V.: Doklady Akad. Nauk S.S.S.R. **60**, 575 (1948).

(23) Forro, M.: Z. Physik **56**, 235 (1929)

(24) Forro, M.: Z. Physik **56**, 534 (1929)

(25) Forro, M.: Z. Physik **58**, 613 (1930)

(26) Fredericks, W. J., and Scott, A. B.: J. Chem. Phys., **28**, 249 (1958).

(27) Fromherz, H.: Z. Physik **68**, 233 (1931).

(28) Fromherz, A., and Lih, K. H.: Z. physik. Chem. (Leipzig) **153A**, 321 (1931).

(29) Fromherz, H., and Menschick, W.: Z. physik. Chem. (Leipzig) **3B**, 1 (1929).

(30) Fromherz, H., and Menschick, W.: Naturwissenschaften **17**, 274 (1929).

(31) Garlick, G. F. J.: *Luminescent Materials.* Clarendon Press, Oxford, England (1949).

(32) Glasstone, S., Laidler, K. J., and Eyring, H.: *The Theory of Rate Processes.* McGraw-Hill Book Company, Inc., New York (1941).

(33) Gross, E. F., and Kaplyanskiĭ, A. A.: Optika i Spektroskopiya **2**, 204 (1957).

(34) Hartree, W.: Proc. Cambridge Phil. Soc. **24**, 89 (1928).

(35) Hartree, W.: Proc. Cambridge Phil. Soc. **24**, 111 (1928).

(36) Hilsch, R.: Z. Physik **44**, 860 (1927).

(37) Hilsch, R.: Z. angew. Chem. **49**, 69 (1936).

(38) Hilsch, R.: Physik. Z. **38**, 1031 (1937).

(39) Hilsch, R.: Proc. Phys. Soc. (London) **49**, extra part, No. 274 (1937).

(40) Hilsch, R., and Pohl, R. W.: Z. Physik **48**, 384 (1928).

(41) Huniger, M., and Rudolph, J.: Z. Physik **117**, 81 (1940).

(42) Hutten, E. H., and Pringsheim, P.: J. Chem. Phys. **16**, 241 (1948).

(43) Ishiguro, M., Okuno, T., and Ueda, A.: Mem. Inst. Sci. and Ind. Research, Osaka Univ. **13**, 69 (1956).

(44) Ivanova, N. I., and Shvist, P.: Optika i Spektroskopiya **3**, 399 (1957).

(45) Johnson, P. D.: J. Chem. Phys. **22**, 1143 (1954).

(46) Johnson, P. D., and Studer, F. J.: Phys. Rev. **82**, 976 (1951).

(47) Johnson, P. D., and Williams, F. E.: J. Chem. Phys. **20**, 124 (1952).

(48) Johnson, P. D., and Williams, F. E.: J. Chem. Phys. **21**, 125 (1953).

(49) Johnson, P. D., and Williams, F. E.: Phys. Rev. **95**, 69 (1954).

(50) Kato, M.: Sci. Papers Inst. Phys. Chem. Research (Tokyo) **41**, 113 (1943).

(51) Kato, M.: Sci. Papers Inst. Phys. Chem. Research (Tokyo) **42**, 35 (1944).

(52) Kato, M.: Sci. Papers Inst. Phys. Chem. Research (Tokyo) **42**, 95 (1944).

(53) Kats, M. L., and Nikol'skiĭ, V. K.: Optika i Spektroskopiya **4**, 354 (1958).

(54) Kats, M. L.: Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. **22**, 1347 (1958).

(55) Kirkwood, J.: Physik. Z. **33**, 57 (1932).

(56) Kirs, Y. Y.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **4**, 108 (1956).

(57) Kirs, Y. Y.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **6**, 178 (1957).

(58) Klement, F. D.: Doklady Akad. Nauk S.S.S.R. **46**, 295 (1945).

(59) Klement, F. D.: Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. **9**, 411 (1945).

(60) Klement, F. D.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **1**, 3 (1955).

(61) Klement, F. D.: Abstract 54, J. Electrochem. Soc. **107**, 58C (March, 1960).

(62) Klick, C. C.: Phys. Rev. **85**, 154 (1952).

(63) Klick, C. C.: J. Phys. Chem. **57**, 776 (1953).

(64) Klick, C. C., and Schulman, J. H.: Solid State Physics **5**, 97 (1957).

(65) Knox, R. S.: Phys. Rev. **115**, 1095 (1959).

(66) Knox, R. S., and Dexter, D. L.: Phys. Rev. **104**, 1245 (1956).

(67) Koch, W.: Z. Physik **57**, 638 (1929).

(68) Koch, W.: Z. Physik **59**, 378 (1930).

(69) Koch, W., and Pohl, R. W.: Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl. **1929**, 6.

(70) Kristofel', N. N.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **7**, 85 (1958).

(71) Kristofel', N. N.: Proceedings of the Eighth All-Union Conference on Luminescence, Kiev, 1959; see also reference 72.

(72) Kristofel', N. N.: Optika i Spektroskopiya **7**, 45 (1959).

(73) Kyropoulos, S.: Z. anorg. u. allgem. Chem. **154**, 308 (1926).

(74) Lax, M.: J. Chem. Phys. **20**, 1752 (1952).

(75) Lax, M.: *Photoconductivity Conference*, pp. 111–45. John Wiley and Sons, Inc., New York (1954).

(76) Lidiard, A. B.: Handbuch der Physik **20**, 246 (1957).

(77) Lorenz, H.: Z. Physik **46**, 558 (1928).

(78) Lorenz, R., and Ruckstuhl, W.: Z. anorg. Chem. **52**, 41 (1907).

(79) Luminescence (with particular reference to solid inorganic phosphors), a Symposium held at the Cavendish Laboratory, Cambridge, April 7–10, 1954; Brit. J. Appl. Phys. **6**, supplement 4 (1955).

(80) Lunden, A.: J. Chem. Phys. **30**, 323 (1959).

(81) Lushchik, C. B.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **3**, 3 (1955).

(82) Lushchik, C. B., and Lushchik, N. E.: Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. **22**, 1351 (1958).

(83) Lushchik, C. B., Lushchik, N. E., and Shvarts, K. K.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **8**, 3 (1958).

(84) Lushchik, N. E.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **6**, 149 (1957).

(85) Lushchik, N. E.: Izvest. Akad. Nauk S.S.S.R., Ser Fiz. **21**, 754 (1957).

(86) Lushchik, N. E.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **7**, 119 (1958).

(87) Lushchik, N. E.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **7**, 134 (1958).

(88) Lushchik, N. E.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **10**, 68 (1959).

(89) Lushchik, N. E., and Lushchik, C. B.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **6**, 5 (1957).

(90) Lushchik, N. E., and Lushchik, C. B.: Optika i Spektropiya **8**, 441 (1960).

(91) MacMahon, A. W.: Z. Physik **52**, 336 (1928).

(92) Makishima, S.: Private communication to Dr. R. S. Knox (to whom the author is indebted for a copy).

(93) Mayer, J. E.: J. Chem. Phys. **1**, 270 (1933).

(94) Mayer, J. E.: J. Chem. Phys. **1**, 327 (1933).

(95) McClure, D. S.: Solid State Phys. Advances in Research and Applications **9**, 399 (1959).

(96) Meyeren, W. von: Z. Physik **61**, 321 (1930).

(97) Pae, A. J.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **6**, 169 (1957).

(98) Parfianovitch, I. A.: Acta Physicochim. U.R.S.S. **6**, 263 (1937).

(99) Parfianovitch, I. A.: Zhur. Eksptl. i Teoret. Fiz. **9**, 163 (1939).

(100) Parfianovitch, I. A.: Zhur. Eksptl. i Teoret. Fiz. **19**, 605 (1949).

(101) Parfianovitch, I. A.: Zhur. Eksptl. i Teoret. Fiz. **21**, 1389 (1951).

(102) Parfianovitch, I. A.: Zhur. Eksptl. i Teoret. Fiz. **25**, 614 (1953).

(103) Parfianovitch, I. A.: Optika i Spektroskopiya **4**, 692 (1958).

(104) Patterson, D. A.: Phys. Rev. **112**, 296 (1958).

(105) Patterson, D. A.: Bull. Am. Phys. Soc. **5**, 201 (1960).

(106) Patterson, D. A., and Klick, C. C.: Phys. Rev. **105**, 401 (1957).

(107) Pohl, R. W., and Rupp, E.: Ann. Physik **81**, 1161 (1926).

(108) Potekhina, N. D.: Optika i Spektroskopiya **2**, 388 (1957).

(109) Potekhina, N. D.: Optika i Spektroskopiya **8**, 437 (1960).

(110) *Preparation and Characteristics of Solid Luminescent Materials, Symposium held at Cornell University, October 24–26, 1946.* John Wiley and Sons, Inc., New York (1948).

(111) Pringsheim, P.: Rev. Mod. Phys. **14**, 132 (1942).

(112) Pringsheim, P.: *Fluorescence and Phosphorescence.* Interscience Publishers, Inc., New York (1949).

(113) Randall, J. T., and Wilkins, M. H. F.: Proc. Roy. Soc. (London) **A184**, 366 (1945).

(114) Randall, J. T., and Wilkins, M. H. F.: Proc. Roy. Soc. (London) **A184**, 390 (1945).

(115) Runciman, W. A., and Steward, E. G.: Proc. Phys. Soc. (London) **A66**, 484 (1953).

(116) Schulman, J. H., Ginther, R. J., and Klick, C. C.: J. Opt. Soc. Am. **40**, 854 (1950).

(117) Schultz, L. G.: Acta Cryst. **4**, 487 (1951).

(118) Scott, A. B.: J. Chem. Phys. **30**, 324 (1959).

(119) Sears, G. W.: J. Chem. Phys. **29**, 979 (1958).

(120) Seitz, F.: J. Chem. Phys. **6**, 150 (1938).

(121) Seitz, F.: Trans. Faraday Soc. **35**, 74 (1939).

(122) Seventh Conference on Luminescence (Crystal Phosphors), Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. **21**, Nos. 4 and 5 (1957); Bull. Acad. Sci. U.S.S.R., Phys. Ser. (English translation) **21**, Nos. 4 and 5 (1957).

(123) Shalimova, K. V.: Doklady Akad. Nauk S.S.S.R. **66**, 625 (1949).

(124) Shalimova, K. V.: Doklady Akad. Nauk S.S.S.R. **66**, 851 (1949).

(125) Shalimova, K. V.: Zhur. Eksptl. i Teoret. Fiz. **19**, 753 (1949).

(126) Shalimova, K. V.: Doklady Akad. Nauk S.S.S.R. **70**, 225 (1950).

(127) Shalimova, K. V.: Doklady Akad. Nauk S.S.S.R. **71**, 651 (1950).

(128) Shamovskiĭ, L. M.: Optika i Spektroskopiya **1**, 407 (1956).

(129) Shamovskiĭ, L. M., Dunina, A. A., and Zhvanko, Y. N.: Optika i Spektroskopiya **2**, 599 (1957).

(130) Shamovskiĭ, L. M., Dunina, A. A., and Zhvanko, Y. N.: Optika i Spektroskopiya **3**, 267 (1957).

(131) Shamovskiĭ, L. M., and Rodinova, L. M.: Doklady Akad. Nauk S.S.S.R. **99**, 381 (1954).

(132) Shamovskiĭ, L. M., Rodinova, L. M., Sidorenko, G. A., and Zhvanko, Y. N.: Doklady Akad. Nauk S.S.S.R. **99**, 235 (1954).

(133) Shamovskiĭ, L. M., and Zhvanko, Y. N.: Doklady Akad. Nauk S.S.S.R. **111**, 140 (1956).

(134) Shamovskiĭ, L. M., and Zhvanko, Y. N.: Izvest. Akad. Nauk S.S.S.R., Ser. Fiz. **21**, 557 (1957).

(135) Smakula, A.: Z. Physik **45**, 1 (1927).

(136) Smakula, A.: Nachr. Ges. Wiss. Göttingen, Math.-phys. Kl. **1929**, 110.

(137) Sommerfeld, A.: Z. Physik **78**, 284 (1932).

(138) Staisw, O., and Saur, E.: Verhandl. deut. physik. Ges. **19**, 4 (1938).

(139) Stockmann, F.: Landolt-Börnstein Tables **1**, No. 4, pp. 981–1007.

(140) Terenin, A., and Klement, F. D.: Acta Physicochim. U.S.S.R. **1**, 941 (1935).

(141) Uibo, L. Y.: Trudy Inst. Fiz. i Astron., Akad. Nauk Eston. S.S.R. **7**, 227 (1958).

(142) Uibo, L. Y., and Yalk, I. V.: Doklady Akad. Nauk S.S.S.R. **105**, 1212 (1955).

(143) Urbach, F.: Sitzb. Akad. Wiss. Wien, Abt. IIA **139**, 353 (1930).

(144) Vitovskiĭ, B. V., and Anikin, I. I.: Trudy Inst. Krist. Akad. Nauk S.S.S.R. **11**, 200 (1955).

(145) Williams, F. E.: Paper 20 in *Solid Luminescent Materials, Symposium held at Cornell University.* John Wiley and Sons, Inc., New York (1948). See reference 110.

(147) Williams, F. E.: Phys. Rev. **73**, 1257 (1948).

(148) Williams, F. E.: J. Opt. Soc. Am. **39**, 648 (1949).

(149) Williams, F. E.: Phys. Rev. **80**, 306 (1950)

(150) Williams, F. E.: Science **112**, 428 (1950).

(151) Williams, F. E.: J. Chem. Phys. **19**, 457 (1951)

(152) Williams, F. E.: Phys. Rev. **82**, 281 (1951).

(153) Williams, F. E.: J. Phys. Chem. **57**, 780 (1953).

(154) Williams, F. E.: Advances in Electronics **5**, 137 (1953).

(155) Williams, F. E.: Brit. J. Appl. Phys. **6**, 597 (1955).

(156) Williams, F. E.: J. Opt. Soc. Am. **47**, 869 (1957).

(157) Williams, F. E., and Hebb, M. H.: Phys. Rev. **84**, 1181 (1951).

(158) WILLIAMS, F. E., AND JOHNSON. P. D.: Phys. Rev. **113**, 97 (1959).

(159) WILLIAMS, F. E., SEGALL, B., AND JOHNSON, P. D.: Phys. Rev. **108**, 46 (1957).

(160) YUSTER, P. H., AND DELBECQ, C. J.: J. Chem. Phys. **21**, 892 (1953).

(161) ZHVANKO, Y. N., MORGENSHTERN, Z. L., AND SHAMOVSKIĬ, L. M.: Optika i Spektroskopiya **2**, 821 (1957).

XIV. ADDENDUM[1]

A group at the Naval Research Laboratory (162) has made a correlation of the high-pressure spectral data (18–20) based upon a simple configurational coördinate model. They showed that the data fit an equation of the form:

$$\frac{\Delta E_P}{P} = K_E q_0 \left(\frac{A_G}{K_G}\right) - \frac{1}{2}(K_G - K_E)\left(\frac{A_G}{K_G}\right)^2 P \qquad \text{(A1)}$$

Leutz and Muuss (163) have made an extensive study of the spectra of potassium bromide activated by thallium, lead, copper, and silver, and mixtures thereof. In doubly activated phosphors the spectra are additive combinations of the spectra of the separate activators. This suggests separate, isolated activation centers. Tamai (166) made a similar study and reported that a B band was present in KBr:Tl at liquid-nitrogen temperature, and that the C band was asymmetric and might have structure.

A group of Russian workers (165) has studied the effects of a high-temperature (∼600°C.) annealing treatment upon the spectra of some lead-activated phosphors. In NaCl:Pb they found no effect, but in KCl:Pb they found an increase in general intensity and the appearance of a B-type band at the expense of the C band.

The Lushchiks (164) have recently published a very important study of the emission spectra, absorption spectra, and quantum yield of luminescence from impurity-activated alkali halide crystals. They studied the dependence of the emission spectra on the frequency of the exciting light and found no dependence in most cases. In a study of the relationship between the shapes of the absorption and the emission spectra of impurity centers due to thallium and lead they found that theoretical predictions based upon Williams' theory (see above) held for thallium-activated phosphors, but did not hold for lead-activated phosphors.

The Lushchiks have also studied the quantum yield (per cent of absorbed quanta which are emitted radiatively) as a function of exciting frequency. They found that it has a stepwise dependence and is independent of exciting frequency in the neighborhood of absorption bands of the individual impurity.

Vitol and Plyavin (167) have discussed the kinetics of the luminescent decay in a series of activated potassium iodide phosphors. They found that the decay is exponential to a fair degree of accuracy.

REFERENCES

(162) DOLECEK, R. L., AND ALERS, P. B.: Rep. NRL Prog., October and November, 1960.

(163) LEUTZ, H., AND MUUSS, H.: Z. Physik **155**, 531 (1959).

(164) LUSHCHIK, C. B. LUSHCHIK, N. E , AND SHVARTS, K. K.: Optika i Spektroskopiya **9**, 215 (1960).

(165) MELIK-GARKAZYAN, I. Y., ZAVADOVSKAYA, E. K., AND TRESKINA, M. N.: Optika i Spektroskopiya **9**, 83 (1960).

(166) TAMAI, T.: J. Phys. Soc. Japan **15**, 2116 (1960).

(167) VITOL, I. K., AND PLYAVIN, I K.: Optika i Spektroskopiya **9**, 365 (1960).

---

[1] Added June 5, 1961.