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Citation: *J. Chem. Phys.* **6**, 150 (1938); doi: 10.1063/1.1750216

View online: <http://dx.doi.org/10.1063/1.1750216>

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Interpretation of the Properties of Alkali Halide-Thallium Phosphors

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(Received November 16, 1937)

An attempt is made to interpret the properties of alkali halide-thallium phosphors. The experimental basis of this interpretation is the work of Pohl and his numerous collaborators on these substances. It is concluded that the long wave-length absorption peaks of the phosphors which are not contained in the pure alkali halides are to be attributed to the excitation of the thallium ions. These are assumed to be distributed throughout the crystal, replacing alkali metal ions. The structure of the observed peaks is interpreted in terms of the details of the spectrum of Tl^+ and the probable effects of crystalline perturbations. The nature of the fluorescent and phosphorescent spectra is then correlated with the behavior of the normal and excited levels during the time after absorption and before optical radiation in which the crystal again comes to

mechanical equilibrium. Distinction is drawn between two cases: That in which the excited Tl ion has no thallium ions among its twelve positive ion neighbors and that in which it has one. It is concluded tentatively that excitation to the lowest excited levels, associated with a triplet in the free ion, will give rise to fluorescence in either case, and that excitation to the higher, singlet level will lead to the alternative possibility of phosphorescence in the second case, but not in the first. The theoretical justification of these tentative conclusions involves assuming that the homopolar forces between the excited ion and its neighbors depress singlet excited levels more than triplet excited levels, and that singlets are depressed more when one of the neighbors of a Tl ion is another Tl ion than when none are.

I. SURVEY AND INTRODUCTION

MANY kinds of crystals, when they contain suitable impurities, are fluorescent and phosphorescent. Such impure crystals are called phosphors, and the effective impurity element is termed the activator. Phosphors have been extensively investigated during the past forty years, and much experimental data on their properties is available.¹ A large part of this accumulated information is, unfortunately, not very useful to one who is trying to form a fairly complete picture of the mechanism of crystal fluorescence and phosphorescence. Most of the measurements have concerned only a particular phase of the behavior of a particular phosphor, such as its decay characteristic, and most of the materials studied have been intricate in composition and properties. Attention has been given, quite naturally, to those phosphors which are technically important, and these without exception are so complex as to discourage theoretical attack, as long as a detailed mechanism has not been established for simpler cases.

There is, however, one group of phosphors which are relatively simple and for which the data are fairly complete. These are the alkali halides, activated with thallium. They have been studied by Pohl^{5, 7} and his collaborators Hilsch,^{2, 5} Smakula,³ Lorenz,⁴ MacMahon,⁶ Koch,^{7, 9} F6rro,⁸ von Meyeren,¹⁰ B6niger,^{11, 12} and Flechsig.^{11, 12}

These phosphors can be obtained as large single crystals, on which unambiguous absorption measurements are possible. The light which is absorbed by the activated halide, exciting it to fluorescence and phosphorescence, is in bands fairly distinct from the absorption bands of the pure substance. Hence, the dependence of these exciting bands on such variables as temperature and concentration of activator can be conveniently studied, and the quantum efficiency of the fluorescent processes can be measured with comparative ease. Finally, since these phosphors show many characteristics common to phosphors in general, there is some reason for the hope that they may furnish a key to the understanding of the more complicated substances.

The present paper proposes a picture, based on the modern theory of the solid state, which appears to correlate practically all of the observed facts about the behavior of these thallium-activated alkali halide phosphors. The treatment is similar in some ways to that of Muto,¹⁴ which came to the author's notice while this paper was being written. We shall comment upon the differences between our picture and his in the last section.

II. PREPARATION OF THE PHOSPHORS

The experimental samples are made by dissolving a small quantity of thallous halide in a

melt of the corresponding alkali halide, and growing a crystal by the well-known Kyropoulos method. The crystal contains a smaller mole percentage of Tl than the liquid. Koch,⁹ using an optical absorption method, finds that in KCl + TlCl the ratio between the concentration in the crystal and in the melt varies from 0.5 to 0.05, depending upon unknown factors, and is not the same for all parts of the same crystal. Since most of the workers quote only the mole percentage of thallous salt added to the melt, we shall have to estimate the concentration of Tl in the final crystal. Koch shows that the absorption coefficient for one of the exciting bands, in KCl + TlCl, is practically proportional to the Tl concentration. We shall use this linear relation in estimating the Tl content in KCl + TlCl, whenever this absorption coefficient is stated.

We shall assume that the Tl is present in the lattice in the thallous (monovalent) state, since this form of the thallium salt is most stable at the high temperatures at which the crystals are grown. In addition, we shall assume that the Tl ion replaces an alkali ion of the lattice and that the Tl ions are dispersed uniformly throughout the lattice in cases in which the concentration of Tl in the crystal is small (less than 0.1 percent). Koch⁹ has presented good evidence for this in a paper which deals with the investigation of the number of dispersion electrons that are associated with the near ultraviolet absorption spectra of the phosphors. He found that for small concentrations this number is strictly proportional to the number of Tl ions present in the crystal and that the ratio of the two numbers, which is the *f* factor, is of the order of 0.1. This proportionality is not generally valid in other types of alkali halide phosphors, such as those containing Cu or Pb, but we shall not be concerned with these here.¹⁵

III. ABSORPTION SPECTRA

The absorption spectrum of an alkali halide phosphor consists of two parts, one part characteristic of the pure substance, the other part characteristic of the activator impurity. The latter component is weaker, and lies on the long wave-length side of the former (see Table I). We shall discuss these two parts separately.

(a) Characteristic absorption of pure alkali halides

These absorption spectra were initially studied by Hilsch and Pohl,⁵ and have recently been measured farther into the ultraviolet, to about 1050 Å, by Schneider and O'Bryan.¹⁶ Hilsch and Pohl interpreted the structure of the bands by supposing that when a quantum is absorbed an electron is transferred from a halogen ion to a nearby alkali ion. Using the classical theory of ionic crystals, they were able to account semi-quantitatively for the positions of the peaks. Von Hippel,¹⁷ also using classical methods, has refined these computations.

At first sight, this interpretation seemed to be at variance with the zone theory of solids. On this theory, the absorption of a quantum should raise an electron from a lower filled band of energy levels to an upper band in which it would be free to move throughout the crystal, not localized in the vicinity of any particular alkali ion. However, recent treatments¹⁹⁻²² of the quantum-mechanical equations for nonconducting crystals, more accurate than the Bloch-Wilson approximation which yields the zone scheme, have shown that the original interpretation probably is largely correct.

The more precise energy diagram contains, in addition to the quasi-continuous bands of the Bloch-Wilson treatment, some narrow continuous bands lying in the forbidden region between the Bloch-Wilson bands. These additional levels are a contribution from the Heitler-London

TABLE I. Position of the absorption peaks in various alkali halide-thallium phosphors in electron volts. (A, B, and C refer to the peaks of Fig. 3.)

	FIRST FUNDAMENTAL PEAK	A	B	C
NaCl	7.82 ev	4.87	5.80	6.20
KCl	7.60	4.92	5.90	6.30
RbCl	7.39	4.98	5.94	6.40
CsCl	7.63	4.90	5.90	6.30
LiBr	6.68			
NaBr	6.49	4.63		5.72
KBr	6.58	4.73		5.88
RbBr	6.43	4.77		5.82
CsBr	6.61	4.69		5.76
LiI	5.59			
NaI	5.38	4.22		5.28
KI	5.63	4.30		5.23
RbI	5.55	4.32		5.15

approximation which is used along with the Bloch approximation to give a picture that is more exact than is possible with either alone. In these states the excited electron and the hole it leaves in the filled band are closely coupled and move together. As one might expect, the electron and hole do not transport charge during this motion, so that the crystal is not made photoconducting. Because of the analogy to excited states of atoms, Frenkel has termed the states of these bands "excitation states" in contrast to "ionization states" of the Bloch-Wilson theory.

In the alkali halide crystals, the excitation state corresponds quite well with the case imagined by Hilsch and Pohl: an electron in one of them has, effectively, left a halogen ion and attached itself to neighboring alkali ions. The excited electron does not remain fixed, at least at first, but moves through the lattice with its hole.

How many such bands may be expected? Wannier²² concludes, from an approximate theoretical solution, that there will be an infinite number of them underlying the continuum of the first unfilled band, just as there are infinitely many discrete levels for a free atom, below the continuum of ionization. Wannier treats the "hole," which an excited electron leaves in the highest filled zone, practically like a point positive charge. The problem is then analogous to that of the free hydrogen atom, and an infinity of states is found to each of which corresponds a band. This view seems completely justifiable in the case of the alkali halides. The energy of attraction between the hole and the excited electron may be identified with the sum of the electron affinity of the halogen atom and the electrostatic field of the rest of the lattice. The first term, as Bethe has shown²³ in

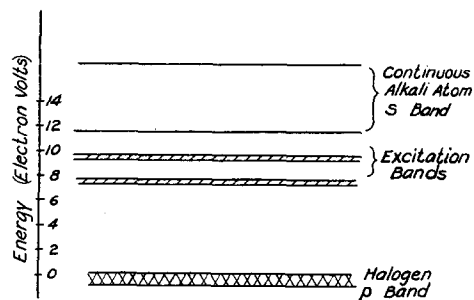


FIG. 1. Important energy levels of alkali halides for normal lattice structure. The energy scale applies, roughly, to the case of NaCl.

the case of H^- , is a correlation effect and falls off more rapidly with distance than a Coulomb force. Hence, there are not an infinite number of discrete levels in the free halogen ion. Beyond a few atomic distances from the neutral halogen atom, the other term varies as e^2/r plus a periodic potential, which is the potential of the normal lattice. The Coulomb term will give enough "assistance" to the halogen atom in holding an electron so that we may expect an infinite number of excitation bands.

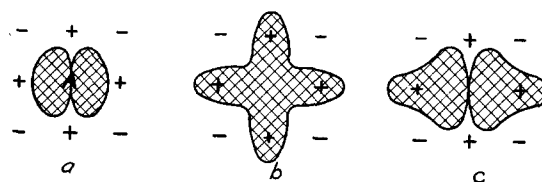


FIG. 2. Symbolic representation of charge distribution for several types of electronic states in alkali halide crystals. These are drawn for the normal lattice arrangement of atoms, which is not the most stable one for the excited states. *A* is a neutral halogen atom and the + and - correspond to alkali and halogen ions. The shaded region is that in which the electronic distribution of an additional valence electron is appreciable. (a) Distribution of additional valence electron in a normal halogen ion in the lattice. This is a *p* electron, hence the vertical node passing through *A* along which the charge distribution is zero. This *p* electron combines with the five others to form a closed-shell p^6 configuration. (b) Lowest excited electronic state in which the electron is distributed among the six neighboring alkali ions (only four shown). This is analogous to an atomic *s* function, so that the result is, effectively, a halogen ion with a p^5 configuration. (c) A higher excited electronic state having *p*-like character.

For the present, then, we shall deal with an energy spectrum such as is shown in Fig. 1. The lowest band, normally completely occupied, arises from the *p* valence levels of the halogen ion. The upper band, normally empty, arises from the *s* state of the alkali atom and is an ionization band. The levels between these bands are states in which an electron has been excited from one of the halogen ions, leaving a hole in the lower band, and is localized on the alkali ions neighboring the halogen atom which remains. The charge distribution of an electron relative to the hole in one of these states is shown symbolically in Fig. 2.²⁴ These two figures were sketched on the assumption that the ions have the same position after excitation as before. This will be true as long as the excited electron and hole are in motion, but, as Frenkel¹⁹ has pointed out, the most stable state will be one in which the electron and hole are localized at one

spot and the lattice is distorted there. Eventually the system will fall into this state.

An electron excited to the upper (ionization) band will have a charge distribution similar to that of a free electron in an alkali metal. If the excitation is by absorption of light, the crystal should be photoconducting. Experimentally, no photoconductivity is observed when the crystal absorbs light in the long wave-length end of the absorption spectrum, covered by the measurements of Hilsch and Pohl—this in itself is evidence that the excitation is to excitation levels. Absorption of quanta of greater energy should raise the electrons to the upper continuum of ionization levels. It is reasonable to expect photoconductivity in the far ultraviolet absorption region investigated by Schneider and O'Bryan. Experiments on this question have yet to be done.

We mention, incidentally, the position of the F centers in an energy level diagram such as Fig. 1. One current interpretation²⁵ is that these are discrete levels in which the electron is localized about a particular alkali ion, and the surrounding lattice is deformed. They are permitted only to "extra" electrons—that is, electrons which have come from a distance of many lattice spacings into a part of the lattice where all the halogens are still ions. Another hypothesis,²⁵ perhaps in better agreement with the observations, is that F centers are electrons trapped in vacant negative ion sites in the lattice, the lattice being supposed to contain, in its equilibrium condition, a certain concentration of sites not occupied by ions. We shall not be concerned further with F centers in the present paper.

(b) Absorption associated with the presence of thallium

The additional long wave-length absorption in the phosphors has been carefully measured by several investigators.^{2, 4, 8} Through all the alkali halides runs a characteristic pattern of three peaks (Fig. 3). Nearest the visible is a small peak A , and about 1 ev beyond this are two peaks B and C , incompletely resolved. Table I lists, for several halides, the positions of these and of the first peak characteristic of the pure substance. The positions of the three peaks shift only slightly as the alkali or halogen ions are changed. For

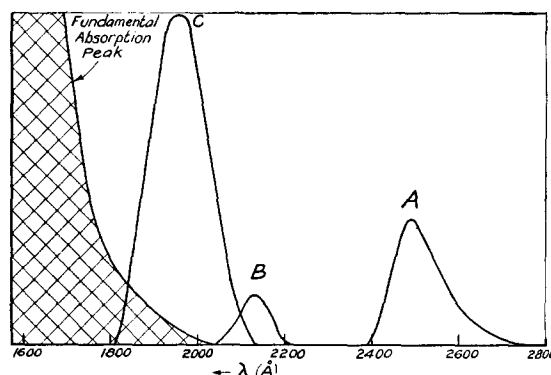


FIG. 3. Typical absorption bands of phosphors. These are adaptations of those obtained by F6rro for KCl. The doublet B - C is actually only partly resolved.

example, the shift is only about 0.7 ev, toward the red, in passing from chlorides to iodides. In contrast, the fundamental absorption peak shifts by about 2.1 ev.

This invariance almost dictates the view that these three peaks correspond to absorption by the thalious ion, and this is the hypothesis we shall use. A possible alternative is that the absorption causes the transfer of an electron from a halogen ion to a neighboring thalious ion. We reject this hypothesis, for the following reasons: (1) The peaks show none of the doublet structure which Hilsch and Pohl have associated with the doublet state of the halogen atom.²⁴ This doublet separation is 0.3 ev in Br and 0.9 ev in I, so it should be fairly conspicuous in these cases. (2) The absorption corresponding to a halogen-thallium transition should lie farther in the ultraviolet. Consider, for example, the rubidium halides. The radii of Rb^+ and Tl^+ are nearly the same, as may be seen from the table of halides in Hermann and Ewald's *Strukturberichte*, and thus a Tl ion can replace a Rb ion in the lattice without causing much distortion. The Madelung potential field, which arises from the neighboring ions, will therefore be practically unchanged; hence, in comparing the energy necessary to transfer an electron from a halogen ion to a Rb ion with the energy necessary for transfer to a Tl ion, the Madelung term can be neglected. This leaves the electron affinities of the two ions for comparison, and these can be estimated, in first approximation, from the ionization potentials of the two atoms. The ionization potential of Tl is 1.9 ev higher than

that of Rb. In the actual case, an even smaller energy difference is to be expected, for in the excited state associated with the fundamental absorption of the pure rubidium halide, six Rb ions cooperate in holding the electron, whereas only the one Tl ion will be effective in a halogen-Tl transfer. In the latter case, the electron is more localized and therefore has a greater kinetic energy. All these considerations tend to the conclusion that the halogen-thallium transition should require about the same energy as the fundamental halogen-rubidium transition. Table I shows, however, that the actual energy gap between the A peak and the fundamental absorption peak is nearly 2.5 eV in the case of RbCl, even higher than the estimated limit of 1.9 eV. This argument is not as conclusive as the first, but, in the writer's opinion, it does carry some weight.

The characteristic absorption of pure thallous halides has been measured in the near ultraviolet by Hilsch and Pohl. They find peaks at the same region of the spectrum as the low energy absorption peaks of the phosphors. If we do not associate these peaks with halogen-Tl transitions

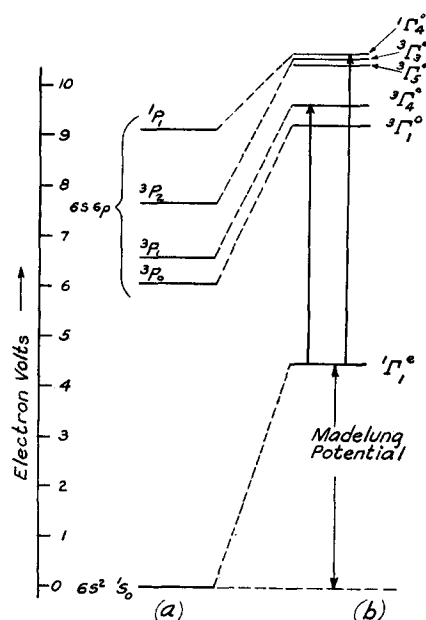


FIG. 4. (a) The energy level diagram of Tl^+ referred to the lowest state. (b) The relative disposition of levels of the ion in the solid. The position of the ground state has been adjusted relative to that of the free atom by means of the Madelung potential for a chloride and that of the upper levels as determined by use of the absorption spectra of the KCl phosphor in the manner described in the text.

in the phosphor, it is scarcely consistent to make this association in the case of the bulk thallous halide. On the other hand, halogen gas is evolved when this absorption occurs in the thallous

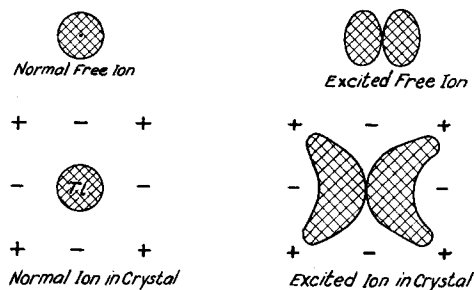


FIG. 5. Schematic representation of charge distributions of normal and excited valence electron on the Tl ion. We have assumed that the fields of the neighboring positive ions will distort the charge in such a way as to spread it in the region between the Tl and alkali ion.

halide. We hope to discuss this observation in another place; for the present we shall only state that it seems possible to reconcile it with the viewpoint adopted here.

Assuming, for these reasons, that the absorption in the three long wave-length peaks is by the Tl^+ ion, and does not correspond to the transfer of an electron from a halogen ion to the Tl^+ , we shall next ask about the structure of this absorption. Since the position and nature of excited Tl^+ levels in the crystal must be estimated, it is necessary to inquire how the states of a free Tl^+ ion are modified when this ion is brought into the lattice, replacing an alkali ion (see Fig. 4(a)).²⁶

In the first excited state (corresponding to $6s6p$ in the free ion) the electron will be partially removed from the neighborhood of the Tl nucleus and will be shared with the neighboring alkali ions. The charge distribution of this electron about the alkali ions will, however, be nothing like the distribution in free alkali atoms. This may be seen as follows: The Madelung fields about Tl^+ and alkali ions are practically equal, so we can get a rough estimate of the positions of levels in the solid from the levels in the free atoms and ions. The Tl^+ $6s6p$ state lies about 9 eV below the normal state of an alkali atom: this energy would be required in taking an electron from the excited Tl^+ to a distant alkali ion. When the nuclei are a distance r apart,

this energy is diminished by e^2/r , roughly 3 ev for the thallium-alkali distance in the lattice. A net gap of 6 ev remains, and because of this energy difference we should not expect the wave function of the lowest excited state to contain any large atomic alkali component. We may expect some perturbation in spite of this and the charge distribution will be drawn near the positive ion to some extent. The Madelung field of the six neighbors nearest to a Tl^+ ion will be negative, and all the levels of the ion in the solid will therefore be raised above their positions in the free ion. This raising should be most pronounced for the lowest level, and should become less important as the electron goes to higher levels where it comes more and more into the field of the next-nearest positive neighbors.

In addition to this raising of the Tl^+ levels as the ion is brought into the lattice, some splitting of the levels and some changes in the distances between levels is to be expected. The splitting may be predicted qualitatively on the basis of symmetry considerations. The crystalline equivalent of the atomic p functions will not split so long as the crystalline field is cubic, as it will be during absorption. We picture the form of the s and p functions in gas and in solid as in Fig. 5. On the other hand, when these are combined to form multiplets, we may not expect any states of higher than threefold degeneracy; that is, states with $j=2$ will split. We shall not attempt to discuss this splitting quantitatively; Van Vleck and his co-workers²⁷ have done this for rare earth and iron group atoms in a number of salts.

The mean inner multiplet distances and mean intermultiplet distances may be changed for two reasons. First, the inner atomic energy terms which determine these distances in the free ion may be altered; that is, the spin orbit coupling and the electrostatic interaction terms of the Tl^+ electrons may be altered in passing from the free ion to the bound ion, because the electronic wave functions are distorted as the ion is brought into the crystal. Second, the interaction energy of the Tl ion with its neighbors will be different for states of different quantum numbers.

It is difficult to say in which way the type of inner atomic coupling will change as the ion is brought into the crystal. We mentioned in

reference 24 that the excited states of the halogen ions will probably show rather advanced $j-j$ coupling and that there is good experimental evidence to support this. Unfortunately, these excited states are not stable for the free halogen ions; hence, we have no good basis on which to make a comparison. We shall defer further comment on this matter until later in this section (see reference 28).

The interaction of the normal ion with the halogen ions is a combination of electrostatic attraction of ions and homopolar repulsion between closed-shell configurations of electrons (neglecting van der Waals forces). The electrostatic term remains unchanged for the excited states, but the homopolar term will contain an attractive minimum such as that shown in Fig. 6. These minima are sufficient to account for a depression of the excited states of the ion in the solid relative to the normal state.

In connection with the effects of interatomic interaction, it is worthwhile to estimate the difference in position of the levels of the normal halogen ion and excited thallium ion. This difference is between 10 and 11 ev for the ions in free space, because the ionization energy of a thallium ion in its first excited state is about 14 ev and the electron affinities of the halogens range between 3 and 4 ev. The halogen levels are lowered and those of the thallium ion are raised, when these ions are brought into the lattice, because of the Madelung potential. Thus, this difference is decreased by roughly 3.5 (e^2/r) which is about 16 ev for a crystal such as NaCl. This will bring the excited levels of the thallium ion and the normal levels of the halogen ion rather

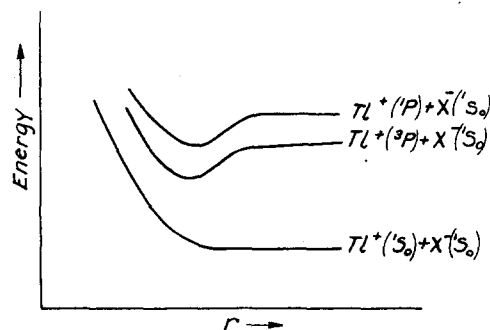


FIG. 6. Schematic representation of the homopolar part of the interaction between thallous ion and a halogen ion.

close together, and will lead to an appreciable resonance interaction. This closeness of approach is shown also by our previous estimate of the difference between the energy of an absorption process in which an electron is transferred from the halogen ion to the thallium ion, and the energy of the process in which the thallium ion is excited. We postulate that this interaction lowers the first singlet excited states of Tl more than it lowers the first triplets. One good reason for expecting this is the following.²⁸ Singlet states are usually more stable than triplets derived from the same configuration in ordinary valence or homopolar compounds in which valence conditions are satisfied. This, for example, is true of a host of diatomic molecules. The exceptions are molecules, such as O_2 , in which the interacting atoms have nearly closed p shell and with which we are not concerned. For this reason, we may expect that the states which correspond to a neutral thallium atom and a neutral halogen atom, and which lie immediately above the states of the excited thallium ion plus normal halogen ion, will have a low lying singlet level. This singlet level presumably will connect adiabatically with the normal nonpolar $^1\Sigma$ state of the free diatomic thallium halide molecule. This singlet interacts

with the upper singlet of the excited thallium ion and will depress this level relative to the triplets.

By means of these considerations we arrive at a disposition of levels in the solid such as is shown in Fig. 4(b). The term notation follows that of Bethe;²⁹ the superscripts e and o correspond to evenness and oddness in the usual spectroscopic sense; the anterior superscript, as usual, denotes the multiplicity. We have adjusted the absolute positions of the levels in this diagram to correspond with our interpretation of the transitions in the KCl phosphor. For the other alkali halide phosphors the positions will be slightly different.

The two most probable absorption transitions, indicated with heavy arrows, are from $^1\Gamma_1^e$ to the two Γ_4^o states. We shall identify these with the two strong absorption peaks A and C of Fig. 3. The $^3\Gamma_4$ state will have some strong residual triplet character, while the $^1\Gamma_4$ will be mainly singlet. Since pure singlet-triplet transitions are forbidden, C should be a stronger absorption line than A , and this difference in intensity is observed.

If the cubic symmetry is perfect, the other transitions are forbidden. They may be expected to appear with small intensity when there is any local dissymmetry, such as thermal agitation would cause. We shall attribute the peak B to a transition of this sort from the lowest state to either $^3\Gamma_3$ or $^3\Gamma_5$. The peak C is broad enough so it may possibly conceal another small peak arising from the forbidden transition to the other member of this pair. This interpretation is supported by the measurements of Lorenz⁴ and F6rro.⁸ They find that the peak B is negligible at low temperatures and increases strongly as the temperature is raised (to 550°C). C , on the other hand, broadens and becomes weaker with increasing temperature. This is to be expected, since the changes in the state $^3\Gamma_5$ which are brought about by thermal agitation would tend to add to the wave function elements for which the transition matrix components vanish.

The separation between the $^3\Gamma_4^o$ state and $^3\Gamma_1^o$ is 0.37 eV in the free atom and remains about the same in the crystal, according to our interpretation, because this separation arises from spin

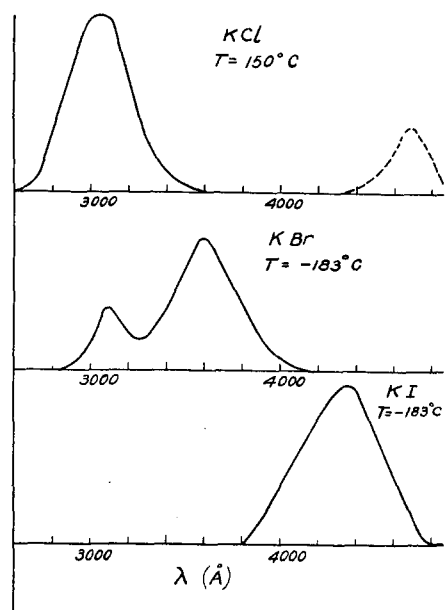


FIG. 7. Typical emission curves of phosphors (after von Meyerén). The dashed peak in KCl is qualitative.

orbit interaction, and we have not assumed that this interaction changes in going from free to bound ions. Any "forbidden" absorption from $^1\Gamma_1^e$ to $^3\Gamma_1^0$ must be under the peak *A*, if the present interpretation is correct. This peak, as measured by F6rro, does in fact show decided asymmetry at high temperatures where forbidden transitions would become prominent. (See reference 28 for discussion of an alternative possibility.)

Additional excited states appear several volts above those shown in Fig. 4(a). In the absorption spectrum, transitions to these would be masked by the much stronger fundamental absorption bands of the halides.

IV. EMISSION SPECTRA

The emission spectra have been measured quantitatively^{10, 11, 12} by von Meyeren, B6nnger, and Flechsig. KCl has received most attention, and for this reason we shall consider it most fully, remarking here that it seems to be typical of the whole group of phosphors. Fluorescence and phosphorescence will be discussed separately.

(a) Fluorescence

The following seem to be the salient experimental facts:

(1) At low concentration of the activator (e.g., less than 0.0015 mole percent in the crystal) only fluorescence, without phosphorescence, is observed. The time constant of the decay of fluorescent light is shorter than 5×10^{-5} sec.

(2) The spectra in the ultraviolet, investigated by von Meyeren between -183°C and 15°C , consist of broad bands which can be resolved into one, two, or (NaBr is the only example) three peaks. These all lie on the long wave-length side on the exciting absorption bands (see Fig. 7). KCl has only one peak in the ultraviolet, but B6nnger observed another in the visible (yellow) beyond the range of von Meyeren's apparatus, so it is possible that others, such as NaCl, which have but one ultraviolet peak may also have peaks in the visible or infra-red.

(3) The entire emission spectrum is stimulated by light in any part of the induced absorption region—the peaks *A*, *B*, and *C* of Fig. 3. The relative intensities of the different emission

bands, where more than one has been observed, do not depend on the wave-length of the exciting light.

(4) The quantum efficiency of the fluorescence in KCl was measured by B6nnger. He found that about 50 percent of the quanta absorbed in any part of the exciting region reappear in the ultraviolet emission band, and he estimated from a qualitative observation that the other emission band, in the yellow, accounts for most of the remaining 50 percent. The total quantum efficiency is thus close to unity.

These are the data which we wish to fit with our previous interpretation of the absorption spectra.

First, it is necessary to recognize a point emphasized by von Hippel¹⁷ in his discussion of the photoelectronic properties of pure alkali halides: the lattice in the neighborhood of an excited Tl^+ ion will not be in equilibrium immediately after the quantum has been absorbed. The redistribution of electronic charge causes a change in the interatomic forces and the atoms will shift about to new equilibrium positions in the new force field, radiating away the excess energy in the form of elastic waves. A complete description of this rearrangement would obviously require energy contours in a configuration space having three times as many coordinates as there are atoms involved in the change. For a crude qualitative picture, we shall symbolize these many coordinates by a single "configuration parameter." As a convenience, the Tl ion and the group of neighboring ions which are involved in the changes following absorption of a light quantum, and whose coordinates are specified by the configuration parameter, will be called a "center." (Lenard has used this term in a similar but less precisely defined way.) The center is, in effect, a large molecule containing fifty or a hundred ions. The energy states to be discussed can conveniently be called energy states of the center.

According to a general theorem,³⁰ all degeneracy of each of the levels is removed in the equilibrium position. The neighbors of the Tl ion will not be distributed about it with cubical symmetry: some of the twelve neighboring alkali ions will be nearer than others to the Tl ion. The equilibrium configurations will be different

for the different excited states, of course—the minima of the energy curves will lie at different values of the configurational parameter.

It is not possible to give a precise description of the stable arrangement of atoms for the excited

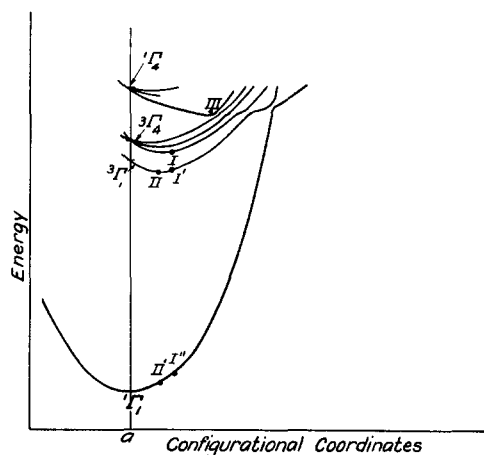


FIG. 8. Diagrammatic representation of behavior of the energy levels of Tl ion in crystal as a function of atomic coordinates. For clarity, the upper triplet states are omitted. The point going with the minimum of the lowest curve corresponds to the normal lattice arrangement.

states without more experimental or theoretical work than is available. Fig. 8 shows, however, what we may plausibly expect for the behavior of the various levels as functions of the configurational parameter. The minimum of the lowest curve is the normal energy state of the center. The point a represents the normal configuration of the ions in the center. The positions of the upper energy surfaces at a are as illustrated in Fig. 4(b). As we go away from this point,³⁰ the state $^3\Gamma_1^0$ remains singly degenerate; the $^3\Gamma_4^0$ and $^3\Gamma_5^0$ split into three states each; and Γ_3^0 breaks into a doublet. We assume that the states arising from $^3\Gamma_4$ and $^3\Gamma_1$ have their minima inside the valley of the lowest state, while those arising from $^1\Gamma_4$ do not have minima before they cross the rising portion of "progeny" of $^3\Gamma_4$. Actually, there will be no true crossing, but two cusps, more or less as shown in Fig. 8, will be formed. The progeny of $^3\Gamma_3$ and $^3\Gamma_5$ are omitted for simplicity. It is assumed that they (figuratively speaking) "cross" $^1\Gamma_4$ and rise. This, of course, will not be true crossing.

It seems reasonable to suppose that the energy terms which displace the minima of the excited

states from a are connected with the difference in the homopolar term of the interaction of the normal and excited Tl ion with the halogen ion. We referred to this in the preceding section when discussing the change in relative position of excited and normal states at a (see Fig. 6).

In order to explain the comparatively large depression of the singlet state, we apparently must invoke once again the influence of the higher singlet which corresponds to the neutral atomic states. It is possible that this higher singlet actually drops and "crosses" the progeny of this $^1\Gamma_4$ and that the lower singlet curves of Fig. 8 correspond to the offspring of the upper singlet. We cannot decide between these alternatives on the basis of available work.

Absorption in the A band, on this view, excites a center to the $^3\Gamma_4$ state. The system then passes, in about 10^{-13} sec., to the minimum I of the lowest member of the triplet, meanwhile losing the excess energy as elastic waves. If the system initially runs along one of the higher members of the triplet into which $^3\Gamma_4$ splits, it will fall to the lowest level, with elastic radiation, in a time short compared with the 10^{-8} sec. required for optical radiation. This sort of transition will be very probable²⁰ when the energy to be dissipated is of the order of the energy of lattice vibrational quanta.

From I the system may proceed by an optical transition either to I' in the next lowest state or to I'' in the ground state. These transitions occur vertically, in accordance with the Franck-Condon principle. The transition $I \rightarrow I'$ presumably gives light in the infra-red (possibly this transition also occurs with radiation of elastic waves, since the time required is of the same order as for radiation of a light quantum). From I' the system goes to the minimum II and radiates optically to reach II' —this radiation will be identified with one of the peaks in the fluorescent spectrum. The optical transition $I \rightarrow I''$ will be assumed to account for another emission peak. Without additional experimental evidence or refined computations, it cannot be predicted which of these quanta has the longer wave-length.

If the absorption takes place in either B or C , we shall assume that the system shifts to III , which is at the upper cusp associated with the crossing of the singlet and the lower levels of the

triplet. From here it proceeds to *I* by a sequence of non-optical transitions. Since the two Γ_4 states are only 1 ev apart at *a* and draw together, all the energy gaps between cusps in the crossing region will be of the order of fractions of volts, and non-optical transitions will be probable. Having arrived in the state *I*, the system goes on to the ground state by the course outlined above. The optical emission spectrum is thus independent of which of the three peaks is used for excitation.

Von Meyeren seems to find three emission peaks for the NaBr phosphor. The third peak might be explained by assuming that some of the centers which are excited to the lowest Γ_4 manage to stay in one of the higher levels of the three into which this splits, long enough to radiate a light quantum. There is an obvious difficulty, however, with this interpretation. The transition from *III* to *I*, as we have outlined it, involves several jumps through the upper states of the progeny of $^3\Gamma_3$. If the third emission peak in NaBr arises because the center can exist in one of the higher levels of $^3\Gamma_4$ long enough to radiate, we should expect the relative intensity of this peak to depend on the wave-length of the exciting light, since there is no *a priori* reason for supposing that absorption in the peak *A* will populate the three states of $^3\Gamma_4$ in the same way as an absorption in *B*—*C*. This point will require additional experimental work.

(b) Phosphorescence

The phosphorescent properties of the phosphors have been examined by Büniger and Flechsig. Most of the work was done on KCl, but some experiments were made with other phosphors in the group. The characteristics listed below seem to be common to the group:

(1) Phosphorescence is stimulated only in the region of the absorption bands *B* and *C* of Fig. 3, not by the long wave-length band *A*. The ratio of phosphorescent light (total light sum) to absorption in this region is roughly proportional to the concentration of Tl for brief illumination with light that is not too intense. Since the absorption itself, from Koch's work, is proportional to the concentration, it follows that the absorption leading to phosphorescence varies as the square of the concentration. In Büniger's measurements of efficiency, the Tl content of the

melt is given. Assuming that the concentration in the crystal is 10 percent of this, the phosphorescent quantum efficiency turns out to be of the order of twenty times the mole fraction of Tl in the phosphor.

(2) The phosphorescent emission spectrum is identical with the fluorescent spectrum.

(3) The natural decay follows the same simple law as a radioactive disintegration:

$$dN/dt = -\alpha N,$$

where *N* is the number of quanta yet to be emitted, and α is a constant which varies¹¹ with temperature according to the relation

$$\alpha = s e^{-\epsilon/(kT)}.$$

For KCl, *s* is $2.9 \times 10^9 \text{ sec.}^{-1}$ and ϵ is 0.67 ev. The value of α is the same for all parts and peaks of the emission spectrum—the “color” does not change during decay.

(4) The release of the phosphorescent light can be accelerated, at a given temperature, by irradiating the crystal with additional light of suitable wave-length. The total yield is not altered by this process, and the stimulating light has no observed enduring effect, being influential only during the exposure. The effectiveness of the stimulating light varies with wave-length (Fig. 9); quanta with less energy than about 0.67 ev are not effective.

The quadratic dependence of the phosphorescent yield on Tl concentration shows that two Tl ions are involved in the phosphorescence process, and the most plausible assumption is that they lie in adjacent positive ion sites. If the Tl ions are randomly distributed among positive ion sites, the probability that another Tl ion will

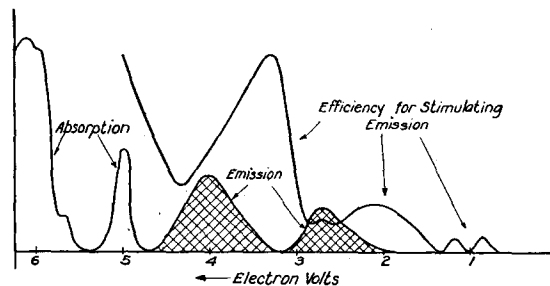


FIG. 9. Curves showing absorption and emission bands along with curve of relative efficiency for stimulating emission of phosphorescent light (after Büniger and Flechsig).

be beside a given one is 12 times the ratio of Tl to alkali metal ions. This is in fair agreement with the phosphorescent efficiency estimated from Büniger's data. The difference is in a direction

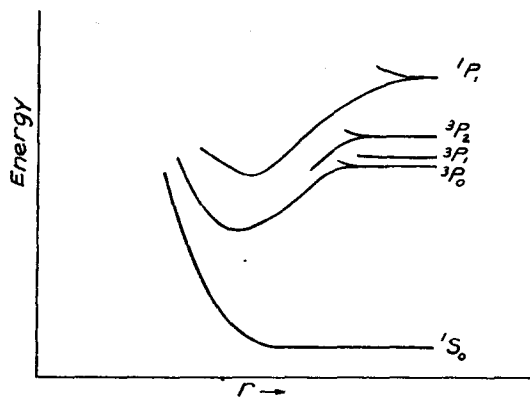


FIG. 10. Schematic representation of the homopolar interaction between two thallous ions.

which indicates that the probability of occurrence of pairs is somewhat higher than for a random distribution.

The presence of another Tl ion among the neighbors of a given one will alter the energy surfaces in the configuration space of the center. In particular, the homopolar interaction term of these two ions will be attractive in the excited state, as shown in Fig. 10, because of resonance phenomena. Fig. 10 is actually based on Finkelburg's³¹ diagram for the interaction of normal and excited mercury atoms, which have the same configuration as Tl^+ ions. There is no evidence which would lead one to conclude that the excited singlet level crosses the lowest level for a diatomic molecule of this type, and it is very unlikely that it does. This does not rule out the possibility that crossing will occur in the solid however. It must be remembered that the excited Tl^+ ion also has an attractive interaction with the neighboring halogen ions of the solid, and we shall assume that the total combination of attractive terms gives the center a metastable state in some region of configuration space. This region will undoubtedly be considerably different from that in which the minima of Fig. 8 occurred, of course, and probably corresponds to an arrangement in which the two Tl^+ ions have drawn closer together than in the normal arrangement.

In connection with these views, one should

bear in mind the fact that nonpolar states are believed to be lower than ionic states in diatomic molecules of the type InCl , TlCl , AlH , etc., in contrast with alkali halide molecules. If this be true, the ionic state must "cross" the nonpolar state as one forms the crystal of TlCl adiabatically from molecules. It is not unreasonable to suppose that the metastable center of which we are speaking is analogous to the nonpolar state of the diatomic molecule.

We shall assume, in addition, that there is no great shift in the level for the normal configuration (*a* of Fig. 8), and that the minima in the lowest excited levels in Fig. 8 are preserved. Absorption in the band *A* of Fig. 3 will then have the same consequences for a center containing two Tl ions as for a center containing but one. That is, the same fluorescent spectrum will be produced, and there will be no phosphorescence.

When the center containing two Tl ions absorbs in the band *C* or *B*, however, there enters the possibility of trapping the electron in a metastable level, at the minimum of the singlet

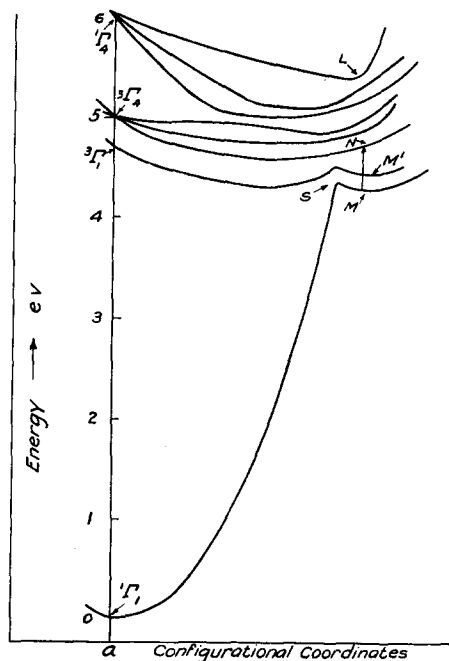


FIG. 11. Same as Fig. 8 for a center in which two Tl ions are neighbors. We have again omitted $^3\Gamma_2$ and $^3\Gamma_6$ for simplicity. Only one minimum, namely *L* of the higher states is drawn above the valley containing *M*, but there may be others which arise in a way that could not be drawn in a two-dimensional diagram without having the lines cross.

state which we have postulated as a characteristic property of these double-thallium centers. In some region of configuration space the three singlet levels will attempt to cut through the lower excited levels in some such way as is sketched in Fig. 11. Since the levels do not actually cross, the state 1T_4 of Fig. 9, which will be the state directly after absorption in $B-C$, does not lead directly into M , the metastable state. We assume, however, that some of the higher states have minima such as L which overlie the valley containing M , so that some of the excited centers, after shifting from I to L , may make a transition which finally places them at M . As there are three singlet levels, it does not seem unreasonable to suppose that the state immediately overlying M , which connects with ${}^3T_1^0$, will be a singlet with a minimum M' .

These centers which arrive in the state M must now wait for some activation process before they can return to the equilibrium configuration a . The activation energy may be furnished either by thermal fluctuations or by optical radiation. In the former case there are two possibilities:

(a) The system may pass adiabatically over the saddle point S and reach a without emission of an optical quantum.

(b) There may be electronic excitation to a state such as N , after which the system runs downhill to I of Fig. 8, and proceeds to the ground state with the emission of the same spectrum as in fluorescence. We assume, as stated above, that the system will not pass adiabatically from M' to II of Fig. 8 before jumping to M , because M' is a relative minimum. Thus, the system will return to M after excitation to the second level.

We wish to compare the relative probabilities of the two processes (a) and (b). The rates will be given by expressions of the type $A_a e^{-(\epsilon_a)/(kT)}$ and $A_b e^{-(\epsilon_b)/(kT)}$, respectively, where A_a and A_b are practically independent of temperature. The activation energy ϵ_a , equal to the energy difference between M and the saddle point S , will obviously be appreciably less than ϵ_b , the energy difference between M and N . However, the coefficient A_a may be expected to be much smaller than A_b . This expectation follows in part from the theory of reaction rates developed by Pelzer and Wigner³² and Eyring,³³ the system,

even when it has sufficient energy to reach the saddle point S , will have a small probability of finding this point out of a large region in a multidimensional space. Hence, we shall assume that at ordinary temperatures the electronic excitation is much more probable. This implies that the activation energy of 0.67 eV found by Büniger and Flechsig is the energy gap between M and N . At low temperatures, where the exponential factor will dominate in determining the statistical probability, the two rates should be reversed in relative magnitude, and the quantum efficiency of phosphorescence should be less than at room temperature. This prediction would probably be hard to check, since the decay rate at low temperatures is so low.

Suppose the metastable centers are activated by optical absorption. The energy of the lowest frequency quantum that is effective should be

$$\epsilon_b = N - M,$$

and, in fact, from the data of Büniger and Flechsig, the energy associated with long wavelength limit of the light which accelerates decay agrees well with the activation energy of 0.67 eV deduced from the natural decay rate. The stimulating bands at higher energies (Fig. 9) correspond, on this view, to transitions from M to states above N .

V. GENERAL REMARKS

Muto,¹⁴ in discussing the behavior of phosphors, has recognized the part played in the absorption process by both the continuous and nearly discrete states, but has neglected to include the effect of atomic rearrangement after absorption. For this reason, he finds it necessary to assume that the metastable state involved in phosphorescence owes its life to ordinary atomic selection rules. This view seems scarcely plausible, for the phosphorescent light can remain trapped for hours or days, whereas, under the perturbing conditions that exist in solids, the emission time even for quadrupole radiation should not be longer than seconds.

It may be remarked that the exponential form of the decay curve for these phosphors is that characteristic of a monomolecular reaction. This is in agreement with the basic assumption of our

picture, that the absorption which produces fluorescence and phosphorescence does not result in dissociation or ionization. We should not expect any photoconductivity to accompany this absorption. On the other hand, many phosphors have a decay curve of the type

$$(1/\sqrt{I}) \sim at + b,$$

where I is the intensity, a and b are constants, and t is the time. It has been pointed out elsewhere³⁴ that such a decay rate, characteristic of a bimolecular reaction, can be explained on the basis of a recombination of dissociated electrons and holes. Absorption resulting in phosphorescence having this sort of decay should, therefore, give rise to photoconductivity. The experimental data on photoconductivity of phosphors are too meager to allow a test of this prediction.

In addition to the thallium-activated alkali halides, halides activated with Hg, Cu, and Pb have been investigated to some extent by the Göttingen school. So far as can be judged from the less complete data presented for these phosphors, their behavior will also fit into a picture of the general type outlined here.

In conclusion I wish to express my indebtedness to Dr. S. Dushman, Mr. C. G. Found, and, especially, to Dr. R. P. Johnson for many helpful discussions and suggestions during the course of preparation of this paper. In addition I wish to thank Dr. Mulliken, who refereed this paper, for a number of comments and suggestions (cf. reference 28).

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