

LUMINESCENCE SPECTRA OF ALKALI HALIDES.

By H. N. BOSE and J. SHARMA.

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ABSTRACT.

The luminescence spectra of some of the alkali halides, pure and impurity activated, under cathode ray excitation, have been investigated at ordinary and low temperatures. It has been found that pure specimens, which are non-luminescent under ultraviolet excitation, emit a spectra composed of a number of diffuse bands. The effect of different impurities, when added to the melts or as mechanical mixtures, has been investigated in some of the cases; the effect of concentration on the luminescence spectra has been studied for the system KI+Tl. Comparing the measurements with the ultraviolet luminescence spectra of impurity activated alkali halides, it is observed that part of the emission by ultraviolet excitation can be explained as that of pure matrix emission which is obtained under X-rays or cathode rays. The existence of an emission, similar to that of TlCl, in the luminescence spectra of alkali halides with high thallium content, indicates an identical environment for Thallium ions in these phosphors and in thallos chloride. Easy transfer of excitation energy between the centres, induced by X-rays or cathode rays, and those due to activators, occurs very frequently and it is suspected that activation of alkali halides by Thallium is a case of indirect activation, for that part of the spectrum, which is common in the activated and pure alkali halides, under u.v. and X-ray or cathode ray excitation respectively.

Pure alkali halides absorb in the far ultraviolet; but several other absorption bands can be created by incorporating foreign ions or by producing stoichiometric excess in the crystal. Irradiation with X-rays is reported to produce new absorption centres known as F , F' , R_1 , R_2 , M -bands, etc. The origin and mechanism of these centres have been discussed by several authors, viz. Mott and Littleton (1938), Mott and Gurney (1940), Tibbs (1939), Seitz (1946). The existence of these centres in emission has not been proved as yet. In the case of impurity activated alkali halides, ultraviolet excitation yields complicated emission spectra. [Hilsch (1937), Von Meyerer (1930), Pringsheim (1942, 1948).]

Both X-rays and cathode rays excite the phosphors through the intermediary of photo-electrons, primarily released by the radiation. The luminescence spectra in either case are expected to be identical. Because of the high and white nature of the energies of the excited electrons, higher energy levels of the pure or disturbed lattice, if there be any, are expected to take part in the emission process, which may not be indicated by ultraviolet excitation. Besides, there is the possibility of obtaining spectrum of recombination type.

Pure alkali halides, which are generally non-luminescent under ultraviolet radiation, can be made to fluoresce by X-ray excitation, the spectra consisting of several bands (P.R.S. dissertation, H. N. Bose, 1947). Because of the poor yield of luminescence under X-rays, it seemed possible that the full features of the spectra were not obtained there and the present investigation, on the luminescence spectra by cathode ray excitation, was undertaken in order to supplement the X-ray luminescence data, in spite of the fact that the samples are less stable under such excitation. In most cases, though not always, intensity of luminescence under cathode rays is many times greater than that under X-rays; at low temperature, the intensity is greatly enhanced. The discolouration of the sample also takes place much more quickly resulting ultimately in great reduction in intensity; the

spectra could, however, be photographed, in general, before any visible spoiling of the samples takes place.

EXPERIMENTAL TECHNIQUE.

The construction of the demountable discharge tubes used in this investigation will be clear from Figure 1. The sample holder (1A) could be rotated to bring in different surfaces of the sample holder under cathode rays, so that fresh surfaces could be used when necessary. The phosphors were rubbed directly on the flattened surface of the sample holder without any adhesive. For low temperatures, liquid oxygen could be poured into the sample holder through the opening at the top which projects outside the discharge tube. A quartz window is provided for in the wall of the discharge tube facing the sample. The voltage of the tube could be varied between 5 k.v. to 10 k.v.

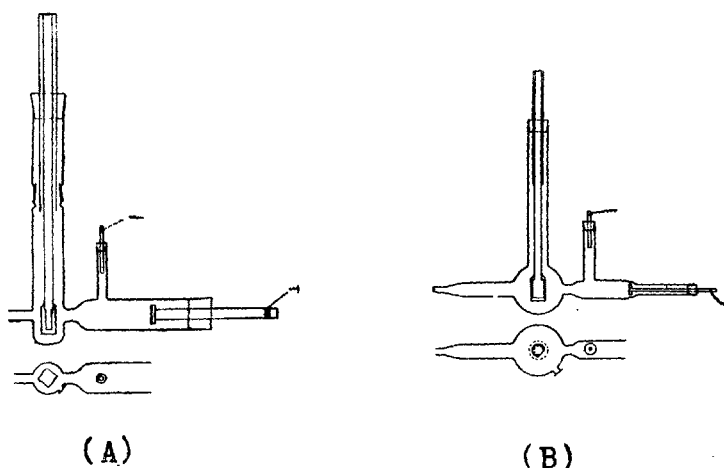


FIG. 1.
Cathode ray tube with sample holder.

Impurity activated samples were prepared by mixing a measured quantity of the impurity with the pure substance and melting the mixture in furnace at about 900°C . for 15 minutes when the substance melts into a clear transparent homogeneous liquid. Same conditions as regards annealing, etc. were maintained as far as possible. Three different types of plates, viz. Ilford H.P. 3, Gevaert Pan and sensitized superchrome, were used in many cases; this is sometimes essential as characteristic spectral sensitivity of the particular plate may distort the spectrum in particular region as regards its intensity as well as its structure. Obviously the substances have been studied in high vacuum so that spurious effects, if there be any, due to the water content of the hygroscopic samples or causes of similar nature were automatically eliminated. Dark discharge must be maintained during the experiment, by proper manipulation of the pressure, otherwise the appearance of molecular bands of the residual gas, specially that of nitrogen which are obtained with great ease at low temperature, may create confusion; despite all precautions, atomic lines could not be avoided in some cases. These, however, could be used as reference lines in addition to the copper lines which have been used for calibration. With a view to avoid all possible sources of error and confusion, dummy experiments were, however, carried out without any phosphor on the sample holder under different steady conditions.

The measurements have been made on the microphotometric records but even then, it has been found that the extended nature of the emission spectra, producing a flat type of microphotometric curve limits the accuracy of measurements to about ± 20 A.U. The temperature of the bombarded sample is rather uncertain; this uncertainty of the temperature of the phosphors produces a change in some of the band positions, which further limits the accuracy of the measurements on the band maxima.

Results and discussions.

As in the case of X-ray excitation, alkali halides in the pure state, which are non-luminescent under ultraviolet irradiation, show fluorescence as well as phosphorescence under cathode rays. The luminescence spectra extend from extreme long wave-length of visible spectrum to ultraviolet region. The spectra consist of broad bands and are, in general, identical with those obtained by X-ray excitation; in some cases intensity distribution is different. On lowering the temperature of the phosphor, the intensity of luminescence is greatly increased; but no decisive change in the positions and widths of the bands could be observed even when the temperature is changed from 30° C. to -184° C.; of course, it must be remembered that temperature of the sample under cathode rays must be somewhat uncertain. Changes in the relative intensity of the different bands are, however, observed. In the following discussion the spectra at low temperature (-184° C.) have been presented.

Pure alkali halide phosphors.

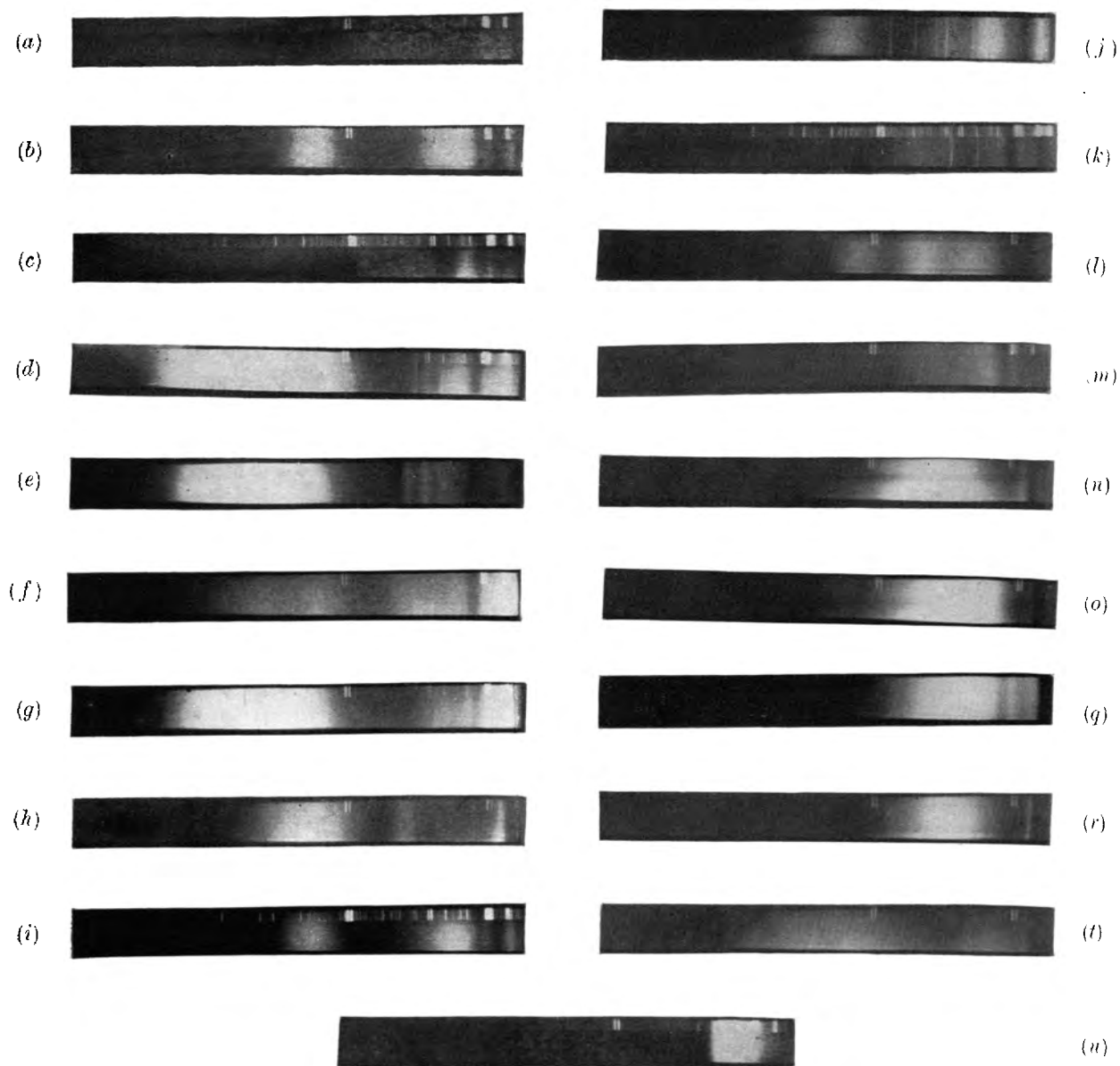
The diffuse bands, in general, superpose on each other to a great extent resulting in an extended spectrum with certain maxima; the measurements are shown in Table I. The extreme long wave-length band at λ 6500 (approx.), which is obtained in all cases, is rather sharp compared to other bands; it seems possible that the band actually extends into the infra-red region, and only a part of the band limited by the sensitiveness of the plate appears in the spectrum. The absence of the band in some cases, as shown in Table I, is due to the use of non-panchromatic plates; but visual examination always reveals its existence in the spectrum. Some of the structures in the long wave-length part are not obtained with quartz spectrograph because of less dispersion and low transmission in this region.

At low temperature colouration of the samples takes place very quickly and more intensely, release of electrons from the traps taking place less easily at low temperature. It is known that on intense exposure, deposit of alkali metal atoms takes place on the surface of the alkali halide crystals; luminescence by cathode ray being rather a surface phenomenon, the penetration of excitation energy inside the coloured crystal does not take place to the same extent as in the case of unexposed ones. Besides, the different parts of the spectrum are absorbed to a different extent so that the spectrum presents an altered appearance, so far as the relative intensities of the different bands, are concerned. In case of X-rays, excitation takes place throughout the entire volume of the crystals; this will probably explain the difference in behaviour in the two cases. The temperature effect on the luminescence spectra can also be partly explained in this way; of course, the radiative mechanism at the individual emitting centres may be responsible too. In potassium bromide and potassium chloride the samples are coloured much more quickly and intensely, than in the case of others; consequently in this case shorter wave-length parts of the spectra are very weak at room temperature and could not be obtained even at low temperature.

In the case of sodium bromide several sharp bands λ 4130, 3940, 3740, 3570 Å.U. are obtained only in the case of fresh samples while after exposure for some time

TABLE I.
Extensions and prominent peaks of the luminescence spectra.

	NaCl.		NaBr.		NaI.		KCl.		KBr.		KI.		LiCl.		TiCl.	
	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.
Extensions	6600-4900	1.87-2.52	6600-5100	1.87-2.42	6600-5100	1.87-2.42	6600-5100	1.87-2.42	6600-6250	1.87-1.97	6600-4600	1.87-2.68	6600-6100	1.87-2.02	6230-4280	1.98-2.89
Peaks	6530 5810 5520	1.89 2.12 2.24	6510	1.90	6540 5890 5430 5160	1.88 2.10 2.27 2.39	6520	1.89	6520	1.89	5920 5380 5240 4730	1.89 2.08 2.36 2.61	6460	1.91	6200 5860 5085 4680	1.99 2.11 2.43 2.69
Extensions	4900-3250	2.52-3.80	4600-3500	2.68-3.53	4000-3500	3.09-3.53	5100-?	2.42-?	6200-3360	1.99-3.67	4700-3300	2.63-3.74	6100-5100	2.02-2.42		
Peaks	3980 3550	3.10 3.48	4130 3940 3740 3570	2.99 3.13 3.30 3.46	3745	3.30			5740 5400 5140 4480 4280 3660	2.15 2.29 2.40 2.75 2.91 3.37	4130 3870	2.99 3.19	5860 5400 5170	2.11 2.29 2.39		
Extensions			3350-2500	3.68-4.94	3350-2600	3.68-4.75							5100-4060	2.42-3.09		
Peaks			Continuous		3000	4.11							4570	2.70		
Extensions													3680-2650	3.35-4.66		
Peaks													3000	4.11		



Luminescence spectra of some of the alkali halides at liquid oxygen temperature under cathode rays with quartz spectrograph. 'p' and 's' refer to panchromatic and superchrome plates respectively.

(a) NaCl (p); (b) NaCl+Tl 2.5% (p); (c) NaCl-Tl. mixture (p); (d) NaBr (p); (e) NaBr (p), showing fine structure peaks; (f) NaBr+Tl 2.5% (p); (g) NaBr-Tl. mixture (p); (h) NaI (s); (i) KCl-Tl 2.5% (p); (j) KCl-Tl. mixture (p); (k) KBr (p); (l) KBr-Tl 2.5% (s); (m) KBr-Tl. mixture (p); (n) KI (s); (o) KI+Tl 5% (s); (p) KI+Tl. mixture (p); (r) KI-Mn 5% (s); (t) LiCl (s); (u) TlCl (p).

these separate band maxima disappear, yielding place to a continuous extension. It is not possible to explain this behaviour without more accurate knowledge about the nature of the emitting centres; but it seems that continuous irradiation causing greater concentration of the emitting centres somehow modifies the nature of the particular centre; the effect may also be due to an uncertain rise of temperature in the immediate vicinity of the bombarded ions.

The mechanism of luminescence of pure alkali halides under X-rays or cathode rays is an involved process and the nature of the emitting centres obscure. It must be admitted that, in spite of great precaution, the samples may still contain minute traces of impurities. But samples used have been found to show no luminescence under ultraviolet irradiation in the solid state or in solution. So the method of excitation appears to be responsible for the behaviour. Most of the work of previous workers on the luminescence spectra of alkali halides, activated by impurities, deals with excitation by the wave-lengths of the new absorption region; on comparison it is found that the emission spectrum is, partly at least, composed of that due to the parent lattice, as obtained in the present investigation. Under X-rays or cathode ray excitation, energy is absorbed by the whole lattice so that emission is mostly due to the transfer of excitation energy from the parent lattice to emitting centres through the intermediary of internal photo-electrons moving through the conduction band; emission due to the direct excitation of centres, as takes place in the case of ultraviolet excitation, is rather small in this case. The electrons from the conduction band are profusely trapped inside the crystal and phosphorescence is obviously due to the electrons leaking thermally into the excited states of the emitting centres. It thus seems natural to assume that emission is due to electrons falling into the excited states of the emitting centres from the conduction band.

The exposure of alkali halide crystals to X-rays or cathode rays is known to create several absorption centres (F , F' , R_1 , R_2 , etc.) which have been discussed and elucidated by Seitz (1946); occurrence of these centres in emission has not been established; besides, no systematic agreement of the present measurements with the absorption data is obtained, and the temperature dependence of the emission spectrum is not so well marked as in the case of absorption bands. We are thus led to believe that the emission is due to centres possibly created by internal ionisation due to X-rays or cathode ray irradiation such that the excited states of the centres lie very close to the conduction band. It is interesting to note in this connection that in the valence band spectra of these compounds (Das Gupta, 1947) in the soft X-ray region, several peaks are obtained; if internal transition is assumed, some of the bands in the luminescence spectra may be explained. This mechanism is specially favourable for the emission of the long wave-length band at λ 6500 (approx.), for, the separation between the prominent peaks of the valence band is approximately 2 volts; further, this band decays so quickly that it could not be detected in the afterglow emission. The afterglow is too weak for its spectrum to be recorded, but was examined visually only.

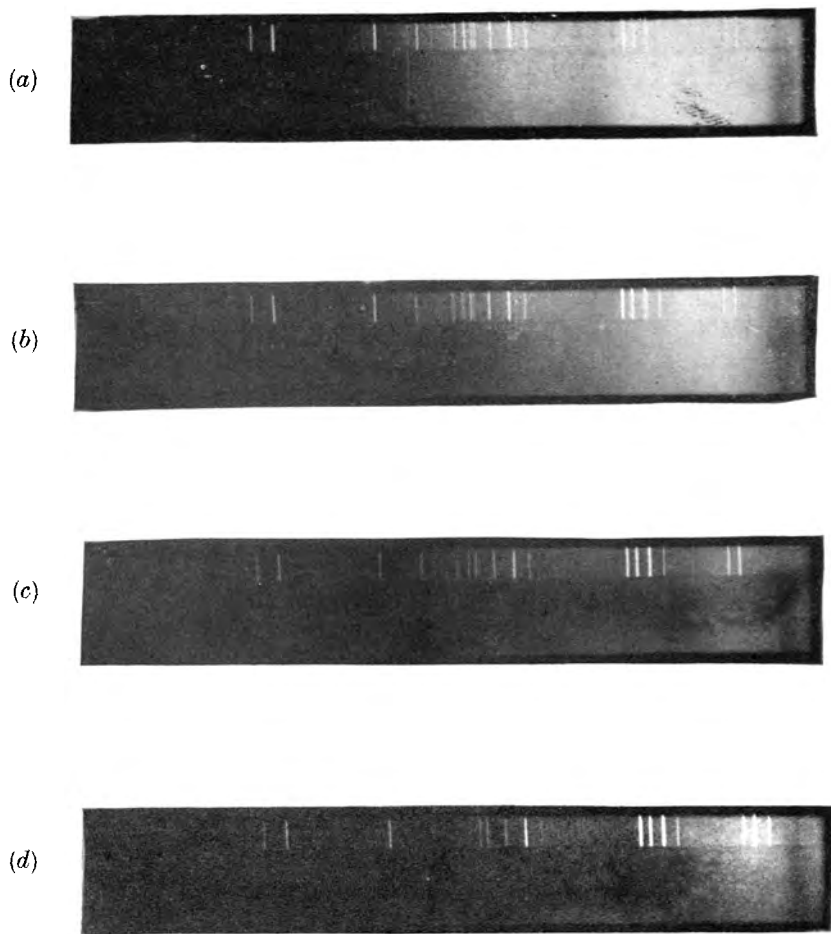
Impurity activated alkali halide phosphors.

Luminescence spectra of some of the alkali halides activated by thallium and other impurities have been measured and the measurements are given in Tables II and III. The spectrum is different from that obtained by excitation with new absorption bands created by activation (Von Meyer, 1930). It has been found that in many cases alkali halides under X-ray or cathode ray excitation, do not show the characteristic impurity band in emission which is known to be emitted when excited by the absorption band due to the activator.

Thus impurities like Mn, Cu, U, Pb, Ag, etc. are well-known activators for alkali halides under ultraviolet excitation, the corresponding emission which may be

TABLE II.
Extensions and peaks of the luminescence spectra of impurity activated alkali halides.

	NaCl+TI 2.5%		NaBr+TI 2.5%		KCl+TI 2.5%		KBr+TI 2.5%		KI+TI 0.1% 0.5%		KI+TI 5%		KI+Mn 2.5%		
	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.	
Extensions	6600- 4900	1.87- 2.52	6600- 5100	1.87- 2.42	6600- 5100	1.87- 2.42	6600- 6250	1.87- 1.97	4700- 3300	2.63- 3.74	6600- 5200	1.87- 2.37	6600- 5200	1.87- 2.37	
Peaks ..	6530 5810 5520	1.89 2.12 2.24	6510	1.90	6540 5890 5430 5160	1.88 2.10 2.27 2.39	6520	1.89	3420	3.61					
Extensions	4900- 3260	2.52- 3.80	4600- 3500	2.68- 3.53	5100- 3500	2.42- 3.53	6200- 3360	1.99- 3.67			5200- 3200	2.37- 3.86	5100- 3250	2.42- 3.80	
Peaks ..	3980 3550	3.10 3.48	4130 3940 3740 3570	2.99 3.13 3.30 3.46	4390 3910	2.81 3.16	5740 5400 5140 4480 4280 3660	2.15 2.29 2.40 2.75 2.91 3.37					3420	3.61	
Extensions	3250- 2650	3.80- 4.66	3350- 2500	3.68- 4.94	3200- 2800	3.86- 4.41	3350- 3000	3.69- 4.12							
Peaks ..	3000	4.11	3100 2780 2600	3.98 4.44 4.75	3020	4.09	3160	3.90							



Luminescence spectra of KI-phosphors with glass spectrograph at room temperature.

(a) KI pure; (b) KI+U (low conc.); (c) KI+U (high conc.); (d) KI+Pb.

of the characteristic or transfer type, occurring in each case. In the case of many of these phosphors, under cathode rays or X-rays excitation the characteristic impurity emission is absent in the luminescence spectra; the luminescence spectrum of the parent lattice is obtained, altered in intensity and sometimes partly quenched by the impurities. In some cases, of course, additional emission bands appear but emission due to the unactivated sample is always present, though the intensity distribution of the spectrum is modified. Thus the luminescence spectrum of NaCl+0.01% of Cu is practically the same as that of pure sodium chloride. With

TABLE III.

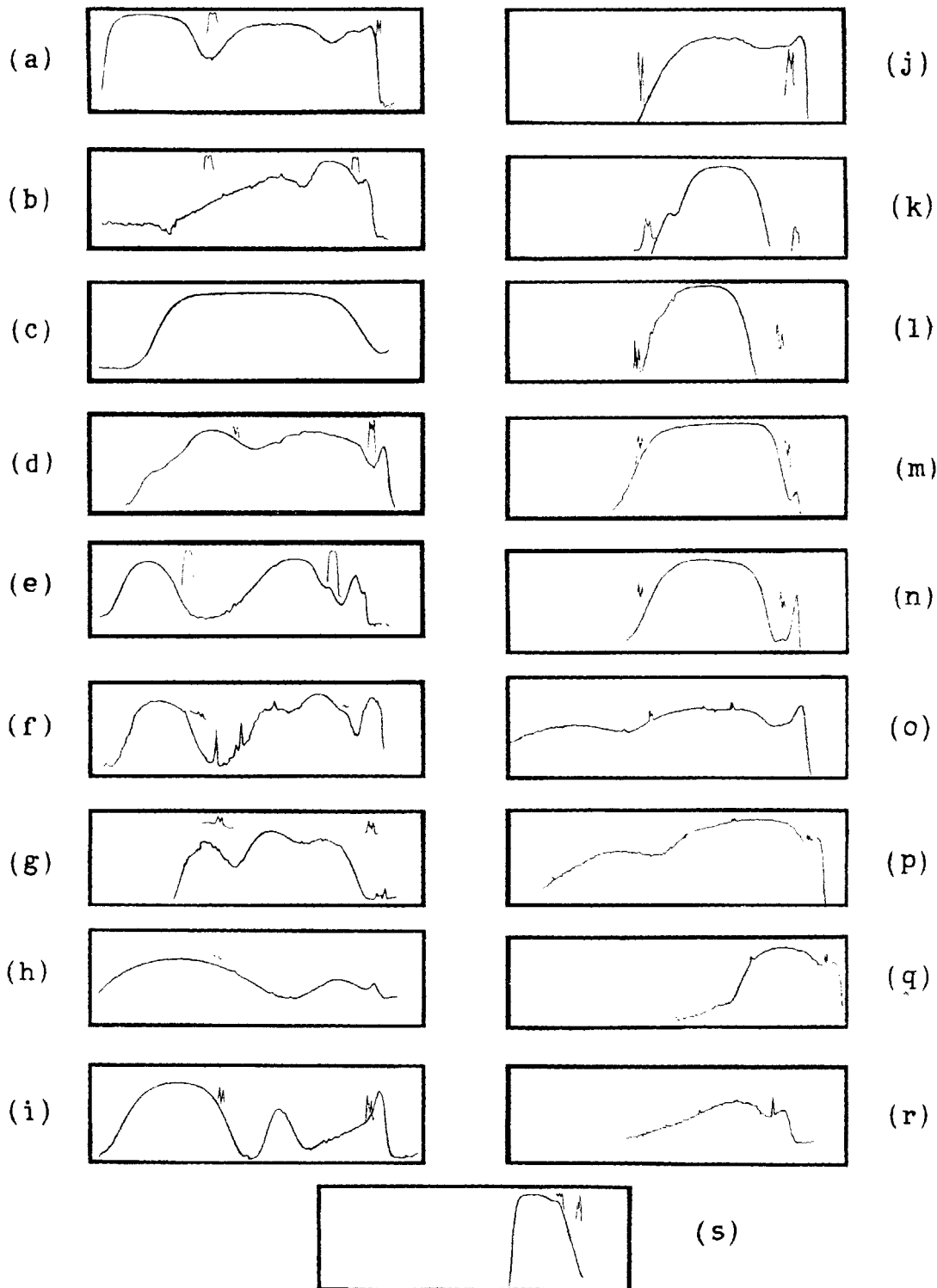
Luminescence spectra of KI with impurities at room temperature with glass spectrograph.

	KI+U low %		KI+U high %		KI+Pb	
	A.U.	e.v.	A.U.	e.v.	A.U.	e.v.
Extensions ..	6600-4700	1.87-2.63	6600-4700	1.87-2.63	6600-5200	1.87-2.37
Peaks ..	6520	1.89	6520	1.89	6520	1.89
	5920	2.09	5920	2.09	5920	2.09
	5380	2.30	5380	2.30	5380	2.30
	5240	2.36	5240	2.36		
	4730	2.61	This peak is suppressed almost completely.			

a view to study the effect of impurities on the luminescence spectrum, samples of potassium iodide activated by Pb, U, Ag, Be and Mn were prepared and its luminescence spectra under cathode rays investigated. Although the effect of concentration has not been studied in all cases, it has been found, in general, that, unlike the case of ultraviolet excitation, the effect of impurity is not very pronounced at very low concentration of the impurity; so moderately high concentration of the activators has been used throughout.

The presence of Pb or U, results in a quenching of the emission spectrum on the short wave-length side; if the activator concentration is increased quenched region extends further on the longer wave-length side. The total intensity of luminescence is not increased perceptibly. In the case of KI+Be, the band with a peak at λ 3420 A.U. becomes rather prominent without affecting the spectrum in any other way; this band, though suspected in the emission of KI alone, is very weak so that it appears there only as an extension continuous with the preceding ones. Similar effect is obtained also in the case of KI+Mn and KI+Ag, in which, further, additional emission bands in the visible region are superposed on the emission due to KI alone, thereby obliterating the peaks in this region. The longest wave-length part of the emission spectrum, however, remains unaffected in all these cases.

A large amount of work has been done by previous workers (Von Meyer, 1930, Pringsheim, 1942, Hutton and Pringsheim, 1948, etc.) on the emission and absorption spectra of Thallium activated alkali halides under ultraviolet irradiation. Some of these measurements are given in Table IV for comparison. The behaviour of single crystals containing small percentage of thallium concentration is not identical with that of powders containing higher concentration (Pringsheim, 1942). It is found that the luminescence spectra of alkali halides activated by thallium consist of a band obviously due to the activator in addition to the parent lattice emission and the relative intensities of the different bands in the spectra are modified by its inclusion. It also seems obvious that part of the emission spectra generally assigned to thallium, is obtained even for the pure alkali halides without any thallium.



Microphotometric records of the luminescence spectra of some of the alkali halides under cathode rays.

(a) NaCl+Tl 2.5%; (b) NaCl+Tl mixture; (c) NaBr, last band only is shown; (d) NaBr+Tl 2.5%; entire spectrum is given, the last band beginning from the reference lines on the left; (e) KCl+Tl 2.5%; (f) KCl+Tl mixture; (g) KBr+Tl 2.5%; (h) LiCl; (i) NaI; (j) KI; (k) KI+Tl .1%; (l) KI+Tl .5%; (m) KI+Tl 5%; (n) KI+Mn 5%; (o) KI; (p) KI+U, low conc.; (q) KI+U, high conc.; (r) KI+Pb; (s) TiCl; figures (o) to (r) refer to room temperature with glass spectrograph.

Thallium bands are known to be highly sensitive to temperature (Von Meyer, 1930); so accurate agreement is not expected.

The band due to thallium is obtained in NaCl+Tl and NaBr+Tl in the extreme short wave-length part of the spectrum. The same band is absent in the case of mechanical mixtures which yield spectra composed of independent mixture of thallos chloride and the halide. The luminescence spectrum of pure sodium bromide is characterized by a very strong band in the ultraviolet, extending continuously from λ 3350 to 2500 A.U. (perhaps even beyond); with thallium, the short wave-length part of the band is quenched up to λ 3000 and other bands with peaks at λ 2780 and 2600 A.U. are obtained; the spectrum in this region thus shows two distinct maxima with probable weak components. These are obviously the two peaks obtained in the luminescence spectrum of NaBr+Tl under ultraviolet excitation. At room temperature, i.e. 30° C., the shorter wave-length peak is the stronger of the two, while at -184° C., the longer wave-length maxima becomes more prominent.

Seitz (1939, 1938) has described the mechanism of absorption and emission process of thallium activated alkali halides in terms of the energy levels of thallium ions modified by lattice influence; the absorption is due to the transition $^1S_0 \rightarrow ^3P_{1,2}$ and $^1S_0 \rightarrow ^1P_1$ while $^3P_{1,2} \rightarrow ^1S_0$ occurs in emission. Working with powdered crystals Pringsheim (1942) has observed that visible luminescence is also shown by those phosphors, specially with higher thallium content. Thus the mechanism suggested by Seitz cannot explain the whole of the spectrum. The present measurements indicate that for NaCl+Tl and NaBr+Tl, only the shortest wave-length band should be taken as that due to thallium ions. Considering all these results, we are thus led to believe, for thallium activated alkali halides, that just as energy absorbed by the parent lattice is transferred to the impurity levels where recombination and emission occurs, the excitation energy from the thallium centres may also be transferred to the emitting centres of the parent lattice. It seems that in NaBr+Tl, energy is transferred to the thallium centres from a part of the excited states responsible for the short wave-length band of sodium bromide; and the amount of transferred energy depends on temperature. Thus this emission seems to be predominantly of the transfer type. The temperature dependence of the relative intensity will depend also on the dissipative mechanism at each centre and its dependence on temperature.

Such interdependence of the two emission bands makes us believe that the particular excited states of thallium is close to the excited states responsible for the extended band of sodium bromide and radiationless transition occurs from the upper part to the excited state of thallium. A possible energy level scheme is shown in Fig. 2.

The behaviour of thallium activated potassium compounds is somewhat different from those of sodium. In potassium chloride, bromide and iodide, identical spectra are obtained for mechanical mixtures and the phosphors prepared from melts. As has been shown by Pringsheim, in these cases complex formation takes place very easily. On activation by thallium, the visible luminescence specially on the long wave-length side is considerably diminished in intensity for potassium bromide and chloride while the short wave-length part becomes more prominent; in both cases the band of shortest wave-length seems to be due to thallium centres. In order to study the effect of thallium in detail, samples of KI+Tl phosphors were prepared with different concentrations and their luminescence spectra investigated. At low concentration of thallium (up to 0.5%) the long wave-length bands λ 5920, 5380, 5240, 4730 Å.U. of the parent lattice, diminishes in intensity, while the short wave-length part of the spectrum increases in intensity, and band λ 3420 Å.U. (found also in the case of KI+Mn, KI+Be, etc.) becomes prominent. At higher concentration the short wave-length bands are gradually weakened, while the long wave-length bands are intensified. It is further found that at higher concentration the emission due to pure thallos chloride is superimposed on the main

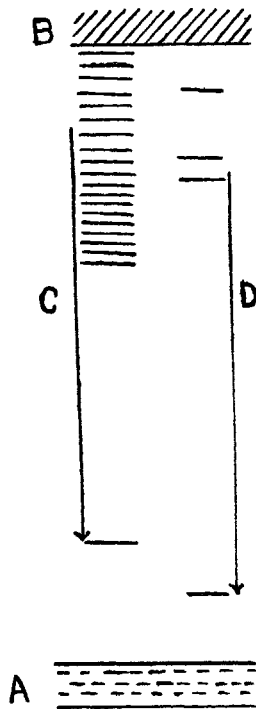


FIG. 2.

- A—Filled band.
 B—Conduction band.
 C—Levels of unactivated NaBr.
 D—Levels of Thallium ion.

pattern; thallos chloride yields, under cathode rays, intense band systems in the visible region. It has been observed by Hutten and Pringsheim (1948) that thallos chloride in the presence of traces of moisture re-acts with potassium iodide. The present phosphor, therefore, contains traces of potassium chloride (according to Hutten and Pringsheim, traces of KCl is essential for the visible luminescence of KI+Tl under ultraviolet excitation). But the additional emission that is obtained at high concentration is that of thallos chloride. This indicates that most of the added material remains as such or in a configuration similar to that of thallos chloride. Besides, in the spectrum of KI+Tl, the intensity of visible luminescence is greatly increased possibly by the emission of a strong band in the blue region (peak at λ 4200 approx.); exact measurement of this peak is not possible for, the superposition of this band on the emission spectrum of pure potassium iodide makes the band maxima indistinguishable.

Unlike other alkali halides, in KI+Tl there is no band in the ultraviolet which can be unequivocally assigned to Tl-centre; increased visible emission is possibly due to complex formation and thallos chloride as such. In the case of KCl+Tl and KBr+Tl also an emission band at about (λ 4500–4600) is suspected; it should be remembered that absorption due to F-centres in these crystals may reduce the intensity of an emission band in this region. Thus there is indication of an emission mechanism, which may be due to complex formation in the case of K-halide+Tl, besides those in the case of Na-halides+Tl. The relative intensity of the band

system in the pure and thallium activated crystals may be explained by an energy level scheme similar to that suggested in the case of NaBr+Tl.

Although the exact nature of the emission centres in alkali halides is still obscure, some general ideas can be obtained from the present investigation. Absence of luminescence by ultraviolet excitation indicates that the emitting centres are absent in pure crystals, and they are created by X-ray or cathode ray irradiation. In view of the fact that inclusion of foreign impurities results in an emission of X-ray or cathode luminescence spectrum of pure alkali halides in most cases, it is natural to suppose that the emitting centres are sometimes induced also by activation by impurities. Besides, easy transfer of energy takes place between the two types of centres in all cases; since the samples are known to be non-conducting under these conditions, transfer of energy takes place either by quantum mechanical resonance process or by self-absorption. But as the same emitting centres are created by X-rays or cathode rays and impurity inclusion, it is natural to suppose that parent matrix emission is due to the energy states of the ions perturbed by the presence of the impurity ions and it is a case of indirect activation. Further the luminescence spectrum under X-rays or cathode rays being due to the re-combination of free electrons from the conduction band with the different emission centres, only those centres which have excited states near to the conduction band, will be naturally more effective than those having excited states far below the conduction band. This may be the explanation why the impurities, which are very effective activators in ultraviolet excitation, do not play as important a rôle in the case of X-ray or cathode ray excitation.

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