Emission Spectra of KCl:Tl, KBr:Tl, and KI:Tl at 300, 80, and 12°K*

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Emission spectra have been measured for single crystals of KCl, KBr, and KI doped with about 0.01 mole % thallium. The measurements were made at 300, 80, and 12°K. Several new bands observed at 12°K are reported. An emission band which is centered directly on the A-absorption band is shown to be present in KI:Tl and KBr:Tl as well as KCl:Tl. An energy level scheme is suggested to explain the observed emission.

INTRODUCTION

SINGLE crystals of the alkali halides doped with small concentrations of thallium are luminescent systems which are a great deal simpler than the standard phosphors. They have been the subject of considerable experimental and theoretical work. One of the first attempts to explain their optical properties was made by Seitz[1] in 1938 based on the experimental evidence of workers at Göttingen, principally Hilsch and Pohl[2] and von Meyeren.[3] The dominating experimental observation was the similarity of the impurity absorption bands introduced by the thallous ion impurity in the different alkali halide hosts. Seitz labeled the thallous ion absorption bands the A, B, and C bands. A typical absorption spectrum is shown in Fig. 1. The absorption spectra of KCl:Tl and KI:Tl resemble that of KBr:Tl with respect to the relative heights and positions of the A, B, and C bands.

Seitz suggested two possible models, both based on the assumption that the thallous ion replaces the alkali ion substitutionally. The first model was based on the excited states of a free thallous ion in a cubic field. The second model considered the transitions of the electrons from the neighboring halides to the thallous ion. Seitz considered the possibilities of the first model in describing the optical properties of the thallium-doped alkali halides and rejected the second model. Knox[4] in 1959 discussed the electron transfer model as it applies to the interpretation of the absorption spectra.

After the center is excited a relaxation takes place. The nature of the center after relaxation is at present an open question. The emission spectra yield as much information about the excited center after relaxation as the absorption spectra indicate about the center in the ground state. It has been conventional to describe the transitions on a one-dimensional configurational coordinate diagram. It is always possible to choose a single configuration coordinate that is some linear combination of the normal coordinates of the ground state near equilibrium.[5] After excitation and the resulting relaxation it may be that the proper configuration coordinate is an entirely different coordinate from the one used to describe the absorption. If this were the case, one diagram would be needed for absorption and additional diagrams would be necessary in general for the emission from each excited state. The Jahn-Teller theorem predicts that the host lattice will not remain symmetrical when the center is in the excited states. The nature of the new configuration which removes the cubic field is not yet known. The experimental results of Klick and Compton[6] on the polarization of the emission from KCl:Tl at liquid-helium temperature indicates the importance of these considerations.

The experimental data on the emission of the thallium-doped alkali halides at liquid-nitrogen and liquid-helium temperatures is very incomplete. It is essential that data be gathered on single crystals with low concentrations of the thallous ion dispersed randomly in the crystals. Concentrational effects and mechanical defects produce anomalies in the emission spectra which have added confusion to this field even up to the present time.

This experimental study compares the emission spectra of three systems KCl:Tl, KBr:Tl, and KI:Tl. Previous workers have also measured some of the characteristics of the emission spectra of these same ma-

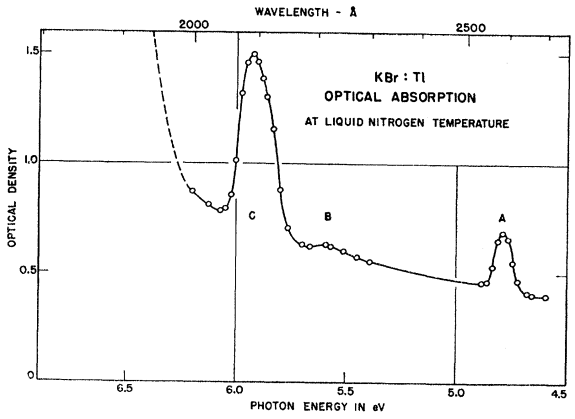

FIG. 1. Optical absorption spectrum of KBr:Tl at 80°K.

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[1] F. Seitz, J. Chem. Phys. **6**, 150 (1938).
[2] R. Pohl and R. Hilsch, Z. Physik **48**, 384 (1928); **57**, 145 (1929); **59**, 812 (1930).
[3] W. von Meyeren, Z. Physik **61**, 321 (1930).
[4] R. Knox, Phys. Rev. **115**, 1095 (1959).
[5] M. Lax, J. Chem. Phys. **20**, 1752 (1952).
[6] C. Klick and D. Compton, J. Phys. Chem. Solids **7**, 170 (1958).

terials. The literature of the Göttingen group in the 1930's describes emission spectra from elevated temperatures down to liquid-nitrogen temperature. These workers did not observe the high-energy emission bands that are reabsorbed by the A band. Teegarden has previously reported the high-energy emission of[4] KCl:Tl and[7] KI:Tl at liquid-nitrogen temperature. Williams[8] has made some measurements at liquid-nitrogen temperature of the emission spectra of the three systems that we are comparing here. He predicted a high-energy emission in the region of the A band from KBr:Tl at low temperature but did not observe it. Patterson and Klick[9] have made detailed measurements of the shape of the 3000 Å emission band of KCl:Tl at liquid-helium temperature.

EXPERIMENTAL PROCEDURES

Three types of spectra could be measured on each sample in a single experimental run. Optical absorption spectra were measured by comparing the intensity of the incident beam produced by a monochromator, to the intensity of the beam transmitted through the sample. Excitation spectra were measured by recording the intensity of the luminescence observed at right angles to the exciting beam while driving the excitation monochromator. Emission spectra were measured by analyzing the luminescence with another grating monochromator.

The samples were single crystals that had been grown by the Kryropolous method with about 0.01 mole % of thallium halide added to the melt. The crystals had dimensions of 1.5 cm×1.0 cm×0.3 cm and the thallium was presumably distributed randomly throughout the sample.

In the initial investigation at room temperature and liquid-nitrogen temperature, the sample was excited with a windowless hydrogen-discharge tube (Hanovia) and a vacuum ultraviolet monochromator employing a Bausch and Lomb tripartite concave grating blazed for 1200 Å. The monochromator could be driven over the wavelength region from 1500 to 3000 Å. Slit widths were used that corresponded to a band pass of 50 Å. A lithium fluoride window isolated the Dewar containing the sample from the monochromator chamber.

The measurement of the emission spectrum employed an additional monochromator. An image of the crystal was formed with a quartz lens onto the entrance slit of a Bausch and Lomb $f/4.5$ plane grating monochromator blazed for 2600 Å. An EMI photomultiplier with a quartz envelope was used to measure the intensity at the exit slit of the monochromator. This experimental arrangement was sensitive over the range from 2000 Å, which was the lower wavelength limit of the Bausch and Lomb monochromator, to about 6000 Å, which was the cutoff of the EMI photocathode. The emission spectra were recorded by measuring the intensity as the wavelength of the emission monochromator was driven over the desired range. With an excitation bandpass of 50 Å, it was possible to obtain reliable emission spectra with the analyzing monochromator set to a bandpass of 50 Å. The recorded emission spectra have not been corrected for the transmission function of the monochromator or the relative sensitivity of the photomultiplier. It is assumed that these parameters are slowly varying over the width of a typical emission band (500 Å).

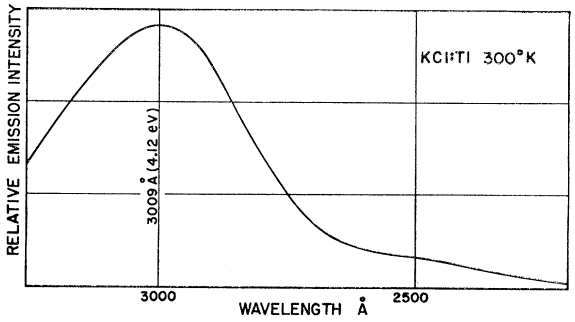

FIG. 2. Emission spectrum of KCl:Tl at 300°K.

After completing a study of the excitation and emission spectra of the three systems at room temperature and liquid-nitrogen temperature, it was desired to make higher resolution emission spectra measurements at liquid-helium temperature to clarify certain questions that had come from a comparison of the emission spectra of the three systems at 80°K. To obtain a more intense emission, a hydrogen arc (Nester lamp) was focused with a quartz lens directly onto the sample without the use of a monochromator. This provided an intense excitation in all the thallium absorption bands, but also produced scattered light throughout the entire visible and ultraviolet spectrum. The sample was viewed at right angles to the excitation in order to minimize the effects of scattered light. Since the hydrogen arc produces a continuum in the near ultraviolet, the scattered light did not confuse the interpretation of the

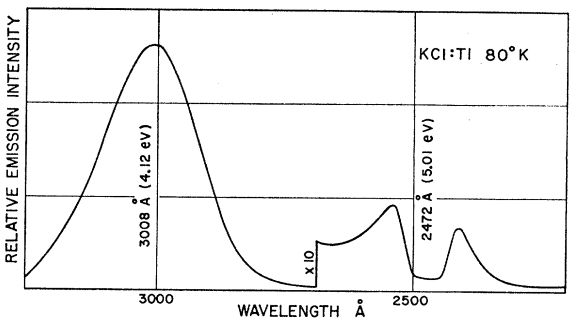

FIG. 3. Emission spectrum of KCl:Tl at 80°K.

[7] K. Teegarden, Phys. Rev. **105**, 1222 (1957).
[8] F. Williams and P. Johnson, Phys. Rev. **117**, 964 (1960); **113**, 97 (1959).
[9] D. Patterson and C. Klick, Phys. Rev. **105**, 401 (1957).

emission spectra. The bandpass of the emission monochromator was reduced to its lowest value which was 10 Å.

EXPERIMENTAL RESULTS

A. KCl:Tl

1. 300°K

Previous measurements have shown that excitation in any of the thallium absorption bands *A*, *B*, or *C* at room temperature produces the same emission spectrum. This emission consists of one broad emission band peaking at 3009 Å (4.119 eV) and having a width at half maximum of 400 Å (0.563 eV). This is shown in Fig. 2.

2. 80°K

Excitation in the *A* band produces one emission band peaking at 3008 Å (4.121 eV) with a width at half maximum of 226 Å (0.309 eV).

Excitation in the *B* and *C* bands produces an emission spectrum consisting of the above emission band

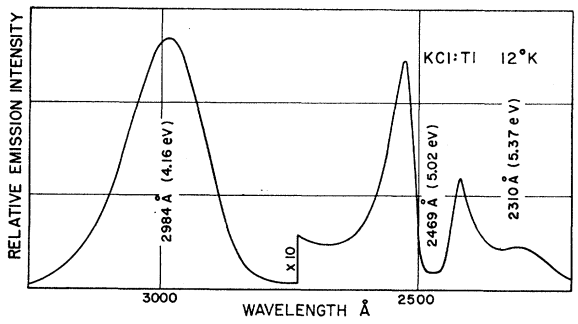

FIG. 4. Emission spectrum of KCl:Tl at 12°K.

plus an additional emission band which overlaps the *A* absorption band. The emission is reabsorbed by the crystal and the emission band has a structure similar to a self-reversed spectral line. Due to the reabsorption, one cannot measure the peak and half-maximum values for this emission band. The center of the reabsorption minimum appears at 2472 Å (5.014 eV). The data are shown in Fig. 3.

3. 12°K

The long-wavelength emission band excited by irradiation in the *A* band shifts to 2984 Å (4.157 eV) and has a width at half maximum of 174 Å (0.242 eV).

The higher energy excitation bands produce the reabsorbed emission band plus an additional emission band. The emission band that overlaps the *A* absorption band shows the reabsorption minimum centered at 2469 Å (5.020 eV). The other is a new emission band, peaking at 2310 Å (5.366 eV). This is shown in Fig. 4.

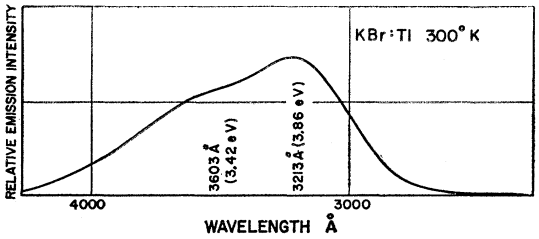

FIG. 5. Emission spectrum of KBr:Tl at 300°K.

B. KBr:Tl

1. 300°K

Excitation in any of the thallium absorption bands *A*, *B*, or *C* at room temperature produces the same emission spectrum. This spectrum has two emission bands that are broad and unresolved. The higher intensity emission band has peak value at 3213 Å (3.858 eV) and the unresolved component peaks somewhere in the region of 3630 Å (3.415 eV). This is shown in Fig. 5.

2. 80°K

Excitation in the *A* band produces an emission spectrum which has two emission bands that are well resolved compared to the emission spectrum at room temperature. The peaks occur at 3106 Å (3.991 eV) and 3634 Å (3.411 eV). The 3106-Å band has width at half maximum of 216 Å (0.280 eV). This is shown in Fig. 6.

Excitation in the *C* band produces an emission spectrum with three emission bands. Two of the bands are similar to the bands excited by the *A* absorption except that the ratio of the intensities of the two bands is different. The third emission band peaks at some value which is in the region of the *A* absorption band. This emission is therefore partially absorbed by the crystal and reemitted presumably in an emission spectrum like that excited in the *A* band. This reabsorbed emission

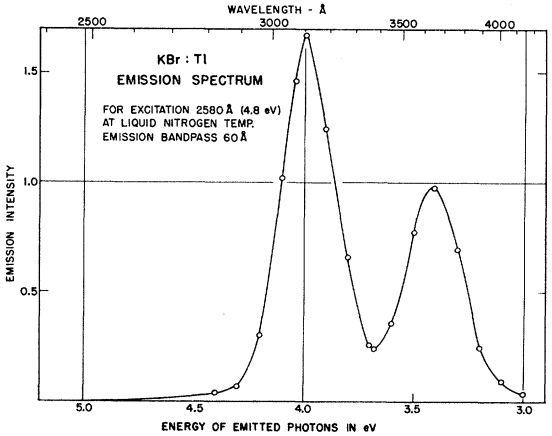

FIG. 6. Emission spectrum of KBr:Tl at 80°K, excited in the *A* band 2580Å (4.8 eV).

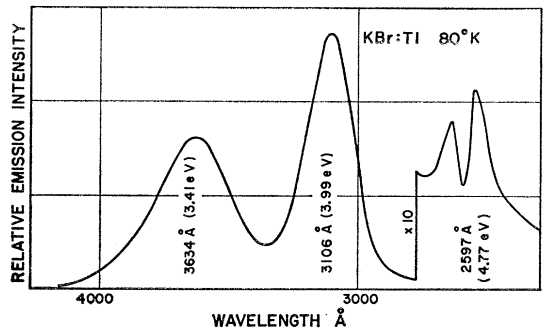

FIG. 7. Emission spectrum of KBr:Tl at 80°K.

band, therefore, also shows a shape analogous to a self-reversed spectral line. The center of the A band reabsorption minimum occurs at 2597 Å (4.773 eV). This is shown in Fig. 7 and Fig. 8.

Excitation in the B band produces the same three emission bands but with different intensities. The reabsorbed emission band is just as intense as it was with C band excitation while the other two bands are considerably weaker. This is shown in Fig. 9.

3. 12°K

The emission band, which at 80°K peaked at 3106 Å, becomes more intense as the temperature is lowered. At 12°K it peaks at 3093 Å (4.807 eV) with width at half-maximum of 157 Å (0.202 eV).

The 3634-Å band becomes very weak and peaks at 3630 Å (3.415 eV). The ratio of the intensities of the 3100-Å band to the 3630-Å band changes by a factor of 25 as the temperature changes from 80 to 12°K.

The emission in the region of the A band becomes more prominent as the temperature is lowered. The reabsorption minimum centers at 2592 Å (4.782 eV). The relative intensities of these emission bands are shown in Fig. 10.

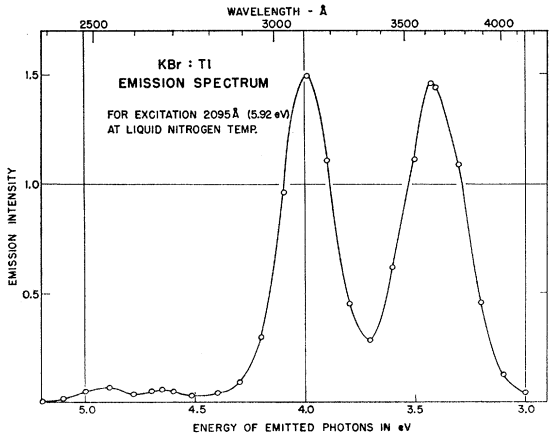

FIG. 8. Emission spectrum of KBr:Tl at 80°K, excited in the C band 2095Å (5.92 eV).

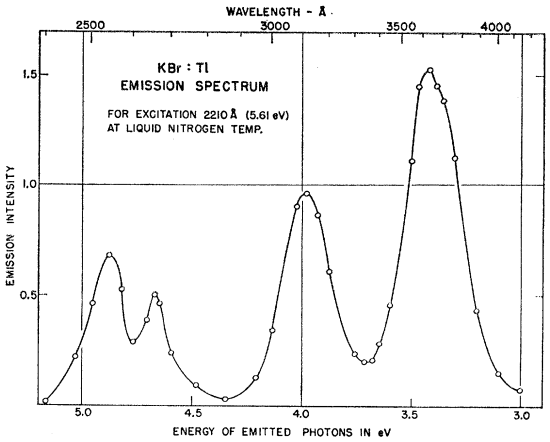

FIG. 9. Emission spectrum of KBr:Tl at 80°K, excited in the B band 2210Å (5.61 eV).

C. KI:Tl

1. 300°K

Excitation in any of the thallium absorption bands, A, B, or C produces a single broad emission band peaking at 4140 Å (2.994 eV) and having a width at half-maximum of 932 Å (0.535 eV). This is shown in Fig. 11.

2. 80°K

Excitation in the A band produces a single emission shifted to 4264 Å (2.907 eV) and having a width at half-maximum of 408 Å (0.279 eV).

Excitation in the B and C bands produces two emission bands with the new emission band peaking at 3044 Å (4.072 eV). The high-energy tail of this emission band overlaps the wavelength region of the A absorption band. The emission is reabsorbed and the reabsorption minimum is centered at 2817 Å (4.400 eV). Details of the emission spectrum in this region are masked by the reabsorption process. This is shown in Fig. 12.

3. 12°K

As the crystal is cooled to 12°K, two new emission bands appear that are not present at 80°K. One of these

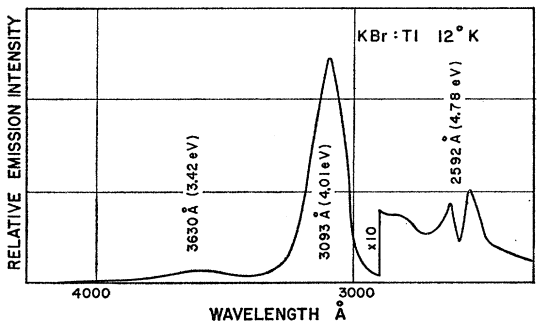

FIG. 10. Emission spectrum of KBr:Tl at 12°K.

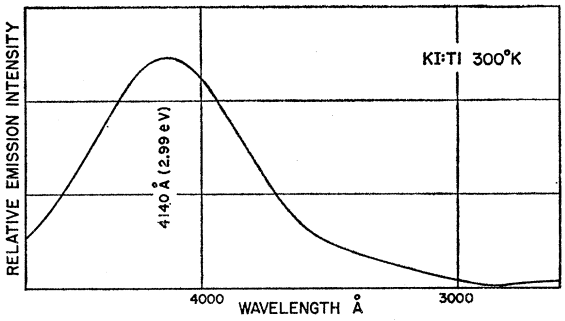

FIG. 11. Emission spectrum of KI:Tl at 300°K.

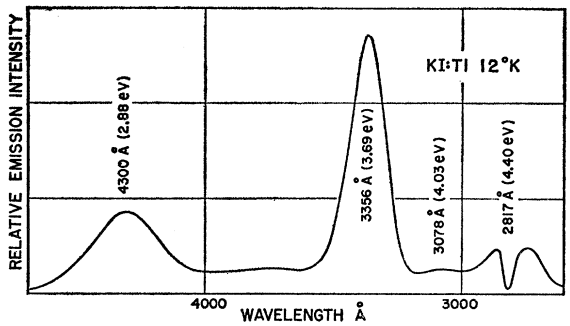

FIG. 13. Emission spectrum of KI:Tl at 12°K.

bands peaks at 3356 Å (3.693 eV) with width at half maximum of 164 Å (0.180 eV). The other new emission band is observed in the region of the A absorption band. It shows the same self-reversed structure as the corresponding emission bands in the other two materials. The center of the reabsorption minimum occurs at 2817 Å (4.400 eV). This is shown in Fig. 13.

The two emission bands which were prominent at 80°K are reduced in intensity at 12°K and peak at 3078 Å (4.027 eV) and 4300 Å (2.883 eV). The width at half maximum of the 4300 Å band is 282 Å (0.188 eV).

DISCUSSION

In discussing the data presented in the previous section, we will refer to Seitz's paper and use his notation.[1] In his paper the A absorption band is assumed to be due to transitions from the $^1\Gamma_1{}^e$ ground state of the thallous ion to the $^3\Gamma_4{}^o$ state, while the C band is assumed to be due to transitions to the $^1\Gamma_4{}^o$ level. The B band is attributed to the "forbidden" transition to $^3\Gamma_3{}^o$ or $^3\Gamma_5{}^o$. In our interpretation we will assume that these two levels lie too close to one another to be resolved. Transitions from $^1\Gamma_1{}^e$ to $^3\Gamma^o{}_1$ are assumed to be "forbidden" and no absorption band has been observed with could be associated with $^3\Gamma_1{}^o$. The splitting between $^3\Gamma_4{}^o$ and $^3\Gamma_1{}^o$ should be resolvable as indicated by Seitz. Our energy-level diagram thus appears as is shown in Fig. 14. In order to explain the emission spectra presented above, we also assume that there is a finite probability for a nonradiative thermal transition between $^1\Gamma_4{}^o$ and $^3\Gamma_3{}^o$, $^3\Gamma_5{}^o$; and between $^3\Gamma_4{}^o$ and $^3\Gamma_1{}^o$. This is indicated in Fig. 14 by a conventional configuration coordinate diagram. This diagram has been constructed using the experimental values of the absorption and emission bands of KI:Tl at 12°K. The positions and curvatures of the parabolas were arbitrarily chosen to be reasonable and consistent, qualitatively, with the temperature dependencies of the various emission bands.

At 12°K excitation in the C band leaves the system in the $^1\Gamma_4{}^o$ state. Luminescence occurs since the probability for a thermal transition to lower states is small at this temperature. The transition $^1\Gamma_4{}^o \rightarrow {}^1\Gamma_1{}^e$ gives rise to the emission which is centered on the A absorption band in all three of these materials. Similarly excitation in the A band leaves the system in the $^3\Gamma_4{}^o$ state and the transition $^3\Gamma_4{}^o \rightarrow {}^1\Gamma_1{}^e$ gives rise to the emission band which lies at 4.16 eV in KCl:Tl, 4.01 eV in KBr:Tl, and 3.69 eV in KI:Tl. At 80°K thermal transitions from $^1\Gamma_4{}^o$

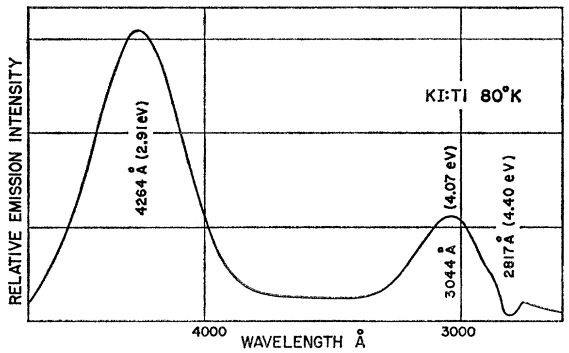

FIG. 12. Emission spectrum of KI:Tl at 80°K.

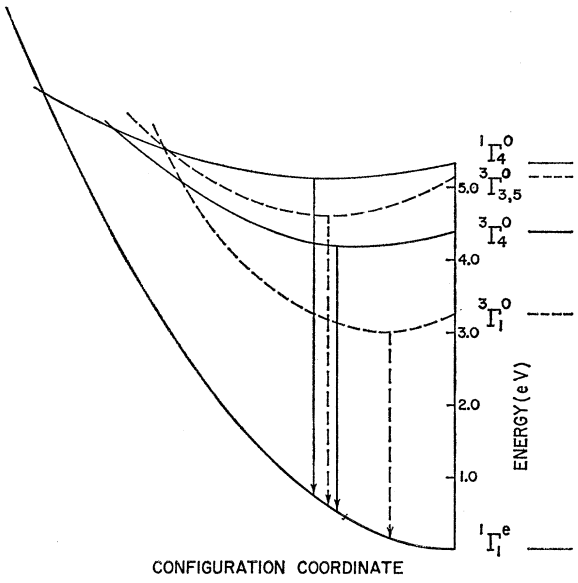

FIG. 14. Energy levels of thallous ion in a cubic field. Configuration coordinate model consistent with the absorption and emission energies of KI:Tl.

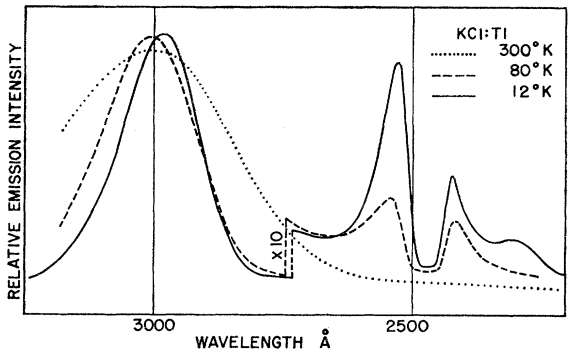

FIG. 15. Comparison of emission spectra of KCl:Tl at 300, 80, and 12°K.

to $^3\Gamma_3^o$, $^3\Gamma_5^o$ and from $^3\Gamma_4^o$ to $^3\Gamma_1^o$ become quite probable so that the states $^3\Gamma_3^o$, $^3\Gamma_5^o$ and $^3\Gamma_1^o$ are populated. In KI:Tl transitions from $^3\Gamma_1^o$ and $^3\Gamma_3^o$, $^3\Gamma_5^o$ give rise to the emission bands at 2.91 and 4.07 eV. In KBr:Tl transitions from $^3\Gamma_1^o$ to $^1\Gamma_1^e$ gives rise to the emission at 3.41 eV. As the temperature is raised from 12 to 80°K, the intensity of this emission increases with respect to the intensity of the 4-eV emission. The separation of the $^3\Gamma_3^o$, $^3\Gamma_5^o$, and the $^1\Gamma_4^o$ in KBr:Tl apparently is too small to show an additional emission band. In KCl:Tl no new distinct emission bands appear at temperatures higher than 12°K. However, the temperature dependence of the peak and shape of the 3000 Å emission, as shown in Fig. 15, does indicate that there might be two components involved. At 12°K the emission from the $^1\Gamma_4^o \rightarrow {}^1\Gamma_1^o$ and $^3\Gamma_4^o \rightarrow {}^1\Gamma_1^e$ is located at 5.02 and 4.16 eV, respectively, in KCl:Tl. As the temperature is raised it appears that a lower energy component becomes predominant such that at 80°K the peak shifts slightly to 4.12 eV. The separation of the $^3\Gamma_3^o$, $^3\Gamma_5^o$, and the $^1\Gamma_4^o$ is again apparently too small to give rise to additional emission bands. A small emission band appearing in KCl:Tl at 12°K at 5.37 eV, an energy greater than the *A* band, has not been included in this interpretation.

SUMMARY

At high temperatures the emission spectrum of each of the three materials is independent of the excitation wavelength. KCl:Tl and KI:Tl have a single broad emission, and KBr:Tl has two broad emission bands that are not well resolved.

As the temperature is lowered through the liquid-nitrogen temperature region to the liquid-helium temperature region, some of the emission bands decrease in intensity and others increase. If we extrapolate these trends, we can say that at extremely low temperatures only two emission bands would predominate in each system.

One of these emission bands overlaps the same energy values as the *A* absorption band and is partially reabsorbed by it. This was previously known in KCl:Tl, and it is now found to occur in KBr:Tl and KI:Tl also. This high-energy emission band is excited by irradiation in the *C* band.

The other emission occurs at a lower energy and is excited with irradiation in the *A* band. Since irradiation in the *C* band produces an emission which is reabsorbed in the *A* band, this lower energy emission band is also produced when the sample is irradiated in the *C* band.

The model based on the excited states of the thallous ion that we have used to interpret the emission bands assumes that the higher temperature emission bands are forbidden transitions from states that are populated to a high degree by a thermal process. We are planning to measure the lifetimes of these emission bands and compare them to the lifetimes of the low-temperature emission bands.

Klick and Compton[6] have found that the onset of polarized emission from KCl:Tl occurs between the temperatures of liquid nitrogen and liquid helium. It is interesting to compare this with the dramatic changes observed in the emission spectrum of KI:Tl as the temperature is lowered from 80 to 12°K.