Excitation and High-Temperature Absorption of KCl:Tl

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Optical measurements have been made on crystals of KCl with a wide range of thallium concentrations. Absorption measurements have been made up to 560°C and excitation spectra for luminescence have been measured from liquid nitrogen temperature to 100°C. These measurements, in conjunction with earlier work, lead to the conclusion that there are at least seven bands in KCl:Tl: three in the "*A*" band region and two each in the "*B*" and "*C*" band regions. The large shift from "*C*" band to "*B*" band at high temperatures which has been previously reported was not found here. It is noted that the addition of small amounts of Sr to KCl shifts the fundamental absorption edge to short wavelengths.

INTRODUCTION

A SMALL amount of thallium introduced into an alkali halide produces a luminescent material of considerable fundamental interest. The relative simplicity of the cubic lattice, the univalent ionic nature of the constituents and the apparent simplicity of the phosphor's optical properties have stimulated efforts to understand the fundamental processes involved for more than thirty years.

The absorption spectrum associated with the thallium activator consists of three principal bands which Seitz[1] has called the "*A*," "*B*," and "*C*" bands. In KCl:Tl their spectral positions are 247, 209, and 196 mμ, respectively, and their relative strengths are $C>A>B$. Associated with them are two main emission bands at 305 and 475 mμ. Seitz[1] has proposed a model in which the luminescent center consists of a thallium ion replacing an alkali ion in its regular lattice position. Certain optical properties of the phospher have been described with some success using this model and a configuration coordinate diagram proposed by Seitz[1] and developed quantitatively for KCl:Tl by Williams.[2]

Recent experimental results, however, tend to suggest that the apparent simplicity of the system is an illusion and that a more complex problem must be dealt with before a complete solution is obtained. Typical are the facts that both the "*A*" and "*C*" bands are quite asymmetric at room temperature but sharpen into essentially symmetric bands at low temperature[3]; that an additional emission band has been found in the "*A*" absorption band region[4]; and that excitation of the two main emission bands occurs in two separate portions of the "*A*" band rather than in a single one.[5] Also of interest are the additional facts that the "*A*" band absorption maximum shifts abruptly to shorter wave-

length at the pressure-induced phase change[6]; and that the emission bands of thallium in NH$_4$Br are affected in very different ways by the thermally-induced phase change.[7] To account for these results, some authors[3,7,8] have suggested that more than one type of center is involved while others[9] have adapted the configuration coordinate curves for the single center model to include some of the new information.

It has also been reported by Forró[10] that at high temperatures the "*C*" band decreased and the "*B*" band increased in amplitude. This thermally induced change in relative amplitudes has important implications in choosing models for the centers involved. One purpose of the present work was to reinvestigate the Forró effect and to see whether or not a similar effect occurred in the "*A*" band. In addition, it was felt that a detailed study of the absorption and excitation spectra of carefully prepared crystals both as a function of temperature and thallium concentration would be worthwhile in showing more clearly the "fine structure" in the optical spectra of KCl:Tl and in determining its properties. A careful study of this sort seemed necessary in order to be able to evaluate the extent to which various simple models describe this system.

EXPERIMENTAL TECHNIQUES

A. Crystal Growth

The crystals were grown under dry argon gas by the Kyropoulos technique. The apparatus consisted of a temperature controlled electric furnace with a cylindrical quartz liner; a close fitting Pyrex lid for the liner; a hollow, gas-cooled platinum "finger" which was raised continuously by a variable speed motor drive; and a platinum crucible containing the melt. The lid has a small central hole for the finger, two larger holes for observation ports which are closed by glass cover slides

[1] F. Seitz, J. Chem. Phys. **6**, 150 (1938).

[2] F. E. Williams, J. Chem. Phys. **19**, 457 (1951).

[3] D. A. Patterson, Phys. Rev. **112**, 296 (1958).

[4] J. E. Eby and K. J. Teegarden, University of Rochester, March, 1958 (unpublished); for discussion see R. S. Knox, Phys. Rev. **115**, 1095 (1959). F. E. Williams and P. D. Johnson, Bull. Am. Phys. Soc. **3**, 272 (1958); Phys. Rev. **113**, 97 (1959).

[5] P. D. Johnson and F. E. Williams, J. Chem. Phys. **20**, 124 (1952); K. H. Butler, J. Electrochem. Soc. **103**, 508 (1956); D. A. Patterson and C. C. Klick, Phys Rev. **105**, 401 (1957).

[6] R. A. Eppler and H. G. Drickamer, J. Phys. Chem. Solids **6**, 180 (1950).

[7] P. Brauer, Z. Naturforsch. **13a**, 1002 (1958).

[8] J. Ewles and R. V. Joshi, Proc. Roy. Soc. **254**, 358 (1960).

[9] R. S. Knox, Phys. Rev. **115**, 1095 (1959). F. E. Williams and P. D. Johnson, Phys. Rev. **113**, 97 (1959); **117**, 964 (1960). N. N. Kristoffel, Trudy Inst. Fiz. i Astron. Akad. Nauk Eston. S. S. R. **7**, 85–111 (1958).

[10] M. Forró, Z. Physik **56**, 534 (1929).

during the growth, and a gas inlet tube. The crucible, liner, and finger were cleaned before each growth in boiling HNO_3 and then in boiling HCl. A large single crystal of KCl grown by the Optovac Manufacturing Company was used as the starting material. The thallium was introduced as TlCl powder which had been triply recrystallized from aqueous solution, ground together thoroughly with a much larger amount of the Optovac KCl and placed in the bottom of the crucible. The crucible was filled with cleaved KCl sections and placed in the bottom of the liner. The lid and finger were put in place and the liner thoroughly flushed with dry argon gas. The gas was allowed to flow continuously, maintaining a small positive pressure in the liner throughout the rest of the process. The furnace was then heated to above 200°C and held there overnight before the growth. The crystals were grown with an average rate of rise of the finger of about 0.2 inch per hour and were allowed to cool slowly to room temperature in the furnace before removal. The crystals grown for these investigations had "A" band absorption maxima ranging from 0.9 cm^{-1} to over 400 cm^{-1} corresponding to thallium concentrations[11] of approximately 10^{-4} M % to well over 5×10^{-3} M %.

B. Excitation

The excitation spectra of a series of thallium doped KCl single crystals were measured between 200 mμ and 290 mμ at room temperature. Monochromatic excitation was provided by a Beckman DU Spectrometer with an Allen arc hydrogen lamp and by a Gaertner quartz prism spectrometer with a Xenon arc lamp. The crystals were mounted as shown in Fig. 1 with one face normal to the exciting light. The fluorescence excited in a 14-mm length of the crystal was observed at right angles by an RCA 1P28 photomultiplier. This arrangement minimized the reflected light reaching the photomultiplier and increased the detection probability for weak or in-
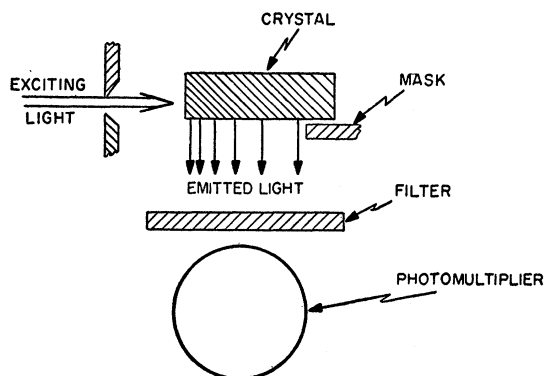

FIG. 1. Schematic arrangement for excitation measurements with crystals. The right-angle arrangement reduces stray light reaching the photomultiplier to a minimum. The filters are used to select the emission region to be studied.

[11] W. Koch, Z. Physik 57, 638 (1929).

efficient emissions. Sharp cutoff Wratten, Polaroid, and Corning filters were used to study selectively various regions of the emission spectrum. Some additional corroborative work with narrow band interference filters was also done. The data were reduced to the same scale and corrected to equal numbers of quanta incident by comparison with a plaque of sodium salicylate which has constant quantum efficiency in this region. No correction for photomultiplier sensitivity was applied; as a result the plotted excitation bands for the ultraviolet emission are enhanced relative to those for the visible emission. No excitation of the 247-mμ emission band separate from that of the 305-mμ band was found at room temperature. This agrees with previous reports[4] and indicates that the contribution of the 247-mμ band to the total emission at room temperature is negligible. Excitation data are presented for the visible emission alone and for both the 305 mμ and the visible emissions. It was found that the very broad visible emission could not be entirely eliminated by the use of filters.

C. Absorption

The absorption spectra of several of the thallium doped KCl crystals were measured from room temperature to 540°C. The optical ovens are described elsewhere[12] and were used with a Cary Model 14 spectrophotometer. The data were taken in the region from 185 mμ to 280 mμ with considerable accuracy and detail. Reflection corrections were applied by subtracting linear base lines drawn for each curve between the extremities of the impurity bands. No residual effects of the heating were found in comparing the spectra before and after the high-temperature run with the exception of the appearance of a small band at about 195 mμ. This band was uniform through the crystal, therefore not a surface effect, and was apparently unaffected by the presence or lack of impurities or by subsequent reheating.

RESULTS

For convenience the data will be divided into two sections. First the "B" and "C" bands will be discussed and second the data on the "A" band will be presented.

The excitation spectra for five of the thallium-doped crystals are shown in Fig. 2(a) for the combined 305 mμ and visible emission bands and in Fig. 2(b) for the visible emission alone. Comparison of the ordinate scales shows that the contribution of the weak visible emission is rather small in Fig. 2(a) so that it shows primarily excitation of the 305-mμ emission band. The absorption coefficients of the "A" band maxima of crystals 1 through 5 are 101, 415, 16, 7.3, and 0.9 cm^{-1}, respectively. Crystal 6 is the undoped control crystal. No significance is attached to the apparent decrease of excitation with increased absorption in crystal 2 relative to crystal 1.

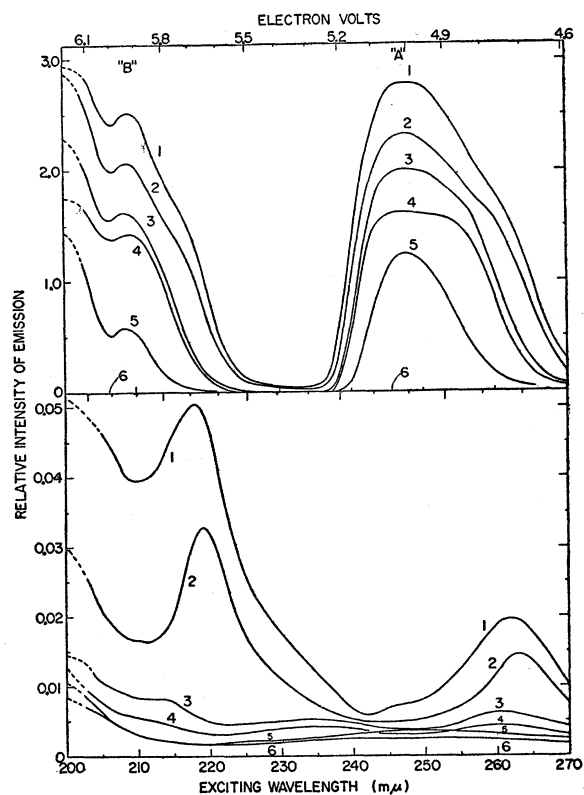[12] D. A. Patterson and H. S. Goulart, Rev. Sci. Instr. 29, 1141 (1958).

FIG. 2. Excitation spectra of KCl crystals containing different amounts of Tl for emissions to long wavelengths (a) from 280 mμ and (b) from 385 mμ. No significance is attached to the fact that crystal 2 has a higher thallium concentration but a lower excitation amplitude than 1.

In Fig. 2(a), the rise toward the short wavelength "C" band is clear despite relatively large correction factors in that region. The "B" band is clearly present at 209 mμ and another band[13] is seen growing on the long wavelength side of the "B" band as the Tl concentration increases.

Figure 2(b) shows the effect of removal of the ultraviolet emission so that now the detector sees only the visible region beyond 385 mμ. The additional band at about 218 mμ is clearly associated with the visible emission and with high thallium concentrations. There is also evidence of additional asymmetry growing on the long wavelength side of the 218-mμ band. The excitation spectra for the "A" band are included here for convenience. They were taken with the same experimental arrangement as was used for the "B" and "C" bands. Additional "A" band spectra, with improved resolution, are presented later.

The absorption spectra of KCl crystals with a low concentration (19 parts per million) of thallium have previously been reported[3] for temperatures from 4°K to 295°K. In the "C" band region at low temperatures

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[13] A similar band has been reported at 214 mμ by Ewles and Joshi, reference 8.

a single sharp band at 195 mμ and a very small "B" band were found. On warming to room temperature the "B" band grew and the "C" band became asymmetric. The asymmetric "C" band can be described by adding to the 195-mμ band a band at 201 mμ with approximately half its amplitude.

In the present work absorption measurements have been extended into the high temperature region. Typical results for the "B"and "C" bands are shown in Fig. 3 for a crystal in which the amplitudes of the bands and the crystal thickness very nearly duplicate those used by Forró. The dashed curve is Forró's high-temperature data. The detailed behavior in the "B" band region is shown in Fig. 4 for another thicker crystal. Similar data were obtained with NaCl:Tl and with several different KCl:Tl crystals. No substantial growth of the "B" band with temperature was observed. In addition, as is apparent in the figures, the "B" band in the present work was completely obscured by the advancing fundamental absorption edge at the temperatures at which Forró reported measurements.

A rough estimate of the thermally broadened "C" band's contribution to the increase in the "B" band was made using the experimental changes in amplitude and half-width of the "C" band and assuming Gaussian shaped bands with constant areas. The results indicated
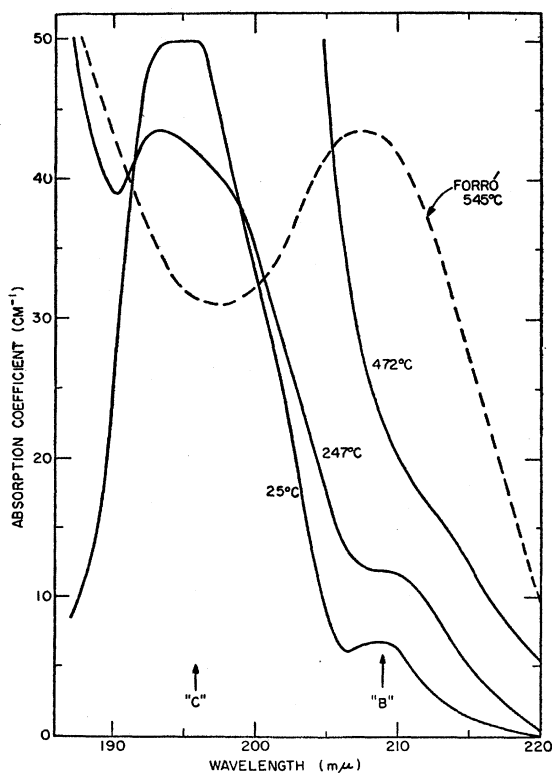

FIG. 3. Effect temperature on the absorption spectrum in the region of the "B" and "C" bands of Tl in KCl. The dashed curve of Forró[10] is shown for comparison. The curves are corrected for reflection losses by assuming zero absorption in the 26°C curve at 220 mμ. The crystal thickness is 0.036 cm.

that, in the present work, most of the increase in the "B" band region could be ascribed solely to the thermal broadening of the "C" band. Thus the present data fail to reproduce the growth in the "B" band reported by Forró. The reason for these different results is not presently understood.

Another interesting difference between the present work and that of Forró is found in the high-temperature positions of the edge of the fundamental absorption band. In Forró's KCl crystals it lies 8 mμ to shorter wavelengths than in those used in the present work. The same difference is found in NaCl crystals, with the exception of Forró's pure synthetic crystal in which the edge position agrees with that found here. The care taken in preparing the present crystals makes it seem likely that their impurity content is small and that the displacement of the absorption edge to shorter wavelengths may be produced by the presence of certain imperfections. Another possibility is suggested by recent work[14] in which it has been found that addition of some divalent positive ions to alkali halide crystals may substantially improve their optical quality in the far ultraviolet. A brief investigation of this as a possible explanation of the discrepancies noted above showed that Ca had no large effect on the high-temperature position of the fundamental edge in NaCl but that Sr in KCl did shift the edge to shorter wavelength and very nearly to the position for synthetic KCl reported by Forró. Further work on this interesting effect is planned.

In the following paragraphs the experimental data on the optical properties of the "A" band will be briefly reviewed and new results will then be presented. In previous work[3] it was shown that the single symmetric absorption band found at low temperatures became

FIG. 5. (a) Effect of temperature on the absorption spectrum in the region of the "A" band of Tl in KCl. Crystal thickness in 0.073 cm. (b) Other experimental data for comparison with Figs. 5(a) and 5(b). The curves are all normalized at their peaks. (c) Resolution of the complex "A" band [curve 5 in Fig. 5(a)] into Gaussian shaped bands A_1, A_2, and A_s using assumed A_s peak position at 261 mμ.

quite asymmetric upon warming to room temperature. This appeared to be due to the growth of a second band at 253 mμ. From the abrupt shift of the "A" band which accompanys the change in structure from NaCl-type to CsCl-type at high pressures,[6] it was suggested that the 247-mμ band might arise from single Tl$^+$ ions surrounded by Cl ions in a CsCl arrangement while the 253-mμ band might be due to an isolated Tl$^+$ ion in an NaCl arrangement. In addition to these bands which appear in absorption, an additional band at 262mμ appears in the excitation spectrum for the visible emission.[5] Since this emission increases faster than linearly with thallium concentration, it has been suggested that this band arises from thallium ions in pairs or larger aggregates. The three bands at approximately 247, 253, and 262 mμ will be referred to as the A_1, A_2, and A_3 bands.
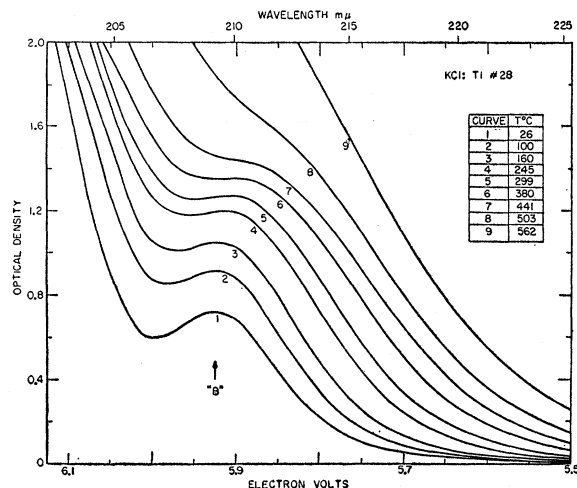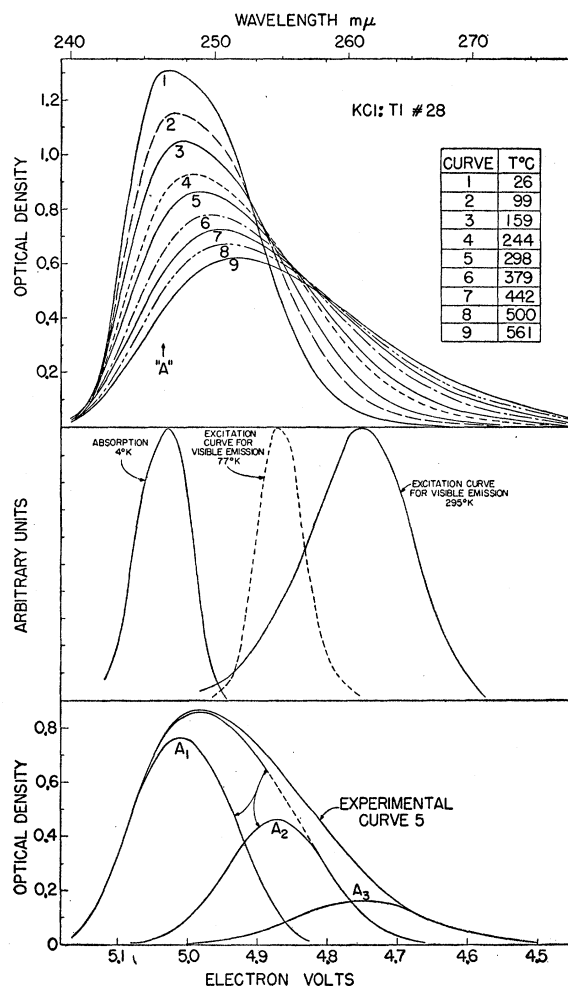

FIG. 4. Effect of temperature on the absorption spectrum in the region of the "B" band of Tl in KCl. A constant reflection correction which brings the 26°C curve to $OD=0$ at 230 mμ has been subtracted from all the curves. The data of Fig. 5(a) were also obtained with this crystal (thickness=0.073 cm).

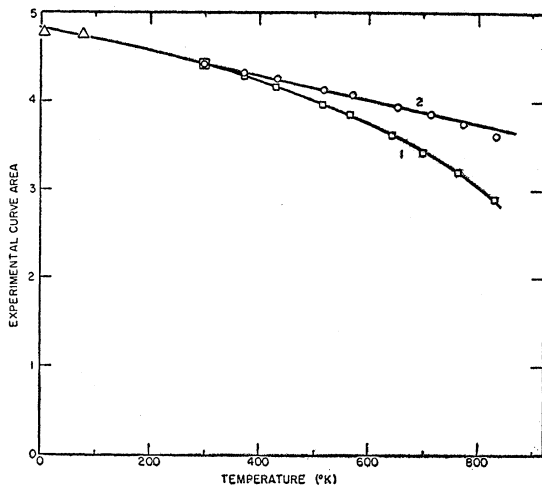[14] H. W. Etzel and D. A. Patterson, Phys. Rev. 112, 1112 (1958).

FIG. 6. Effects of temperature on the "A" band absorption curve areas in two KCl:Tl single crystals with thallium contents differing by a factor of 16. Curve 1 is for the lower concentration and curve 2 for the higher concentration [from data of Fig. 5(a)]. The two low-temperature points are adjusted data from reference 3. The areas are normalized at room temperature.

In Fig. 5(a) the "A" band absorption of a KCl:Tl crystal measured from room temperature to 561°C is shown. It appears that there is a general broadening and shift to long wavelengths as the temperature is increased. In Fig. 6 the "A" band areas measured with a planimeter are plotted against temperature for two crystals with different thallium concentrations. Their room temperature absorption maxima, which are related to thallium concentration,[11] differ by a factor of 16. Curve 1 is for the lower concentration and curve 2 is for the higher concentration [from data of Fig. 5(a)]. The areas have been normalized at room temperature and the low-temperature points are from reference 3. It is apparent that the area of the "A" band decreases as the temperature increases and that the rate of this decrease in
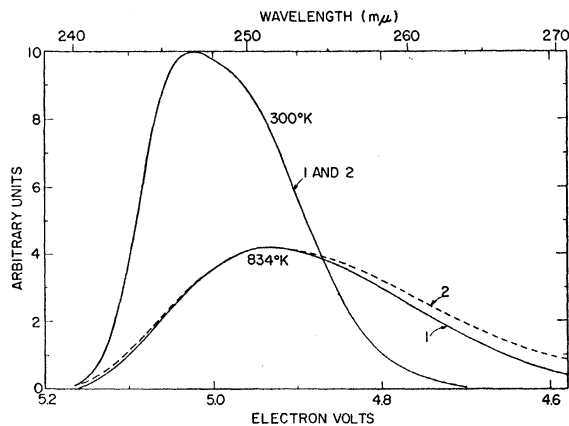

FIG. 7. The "A" band absorption at room temperature and at 834°K for the two KCl:Tl crystals used in Fig. 6. The curves are normalized at their peaks. The peak absorption coefficients at room temperature are 2.6 cm^{-1} for crystal 1 and 41 cm^{-1} for crystal 2.

area is dependent on the thallium concentration in the crystals.

A likely reason for the dependence of the curve area on the thallium content of the crystal is shown in Fig. 7. In this figure the "A" bands for the two crystals in Fig. 6 are shown normalized at their peaks and plotted at room temperature and at 834°K. Their shapes are identical at room temperature despite the different thallium contents of the crystals. This shape actually remains unchanged over the entire range of thallium concentrations investigated. This indicates that the relative amplitudes of the A_1 and A_2 absorption bands are essentially independent of thallium concentration. However, a significant difference in shape is found in the high-temperature "A" bands of the two crystals. This is due to the more rapid growth of the long wavelength tail in the higher concentration crystal number 2. Thus the dependence on thallium concentration of the area versus temperature curves in Fig. 6 is apparently due to the concentration-dependent growth of the long
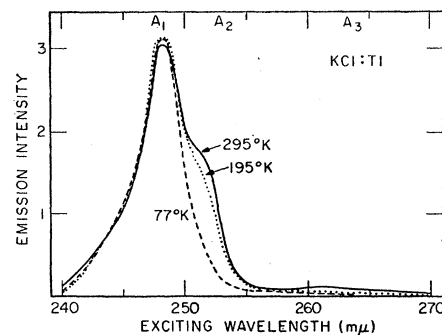

FIG. 8. Effect of temperature on the excitation spectrum for uv emission of a KCl:Tl single crystal with low thallium content. The absorption coefficient at the peak of the "A" band is 7.3 cm^{-1}. The data are uncorrected.

wavelength tail of the "A" band. This tail is in the wavelength region to be expected for the A_3 band at high temperatures. Also the increase in this region with thallium concentration is in agreement with the interpretation of the A_3 band mentioned above.

In Fig. 5(c) it is shown that the "A" band absorption curve at 298°C can be resolved analytically into three components having maxima at the A_1, A_2, and A_3 positions. The analysis used here assumed only that the bands were Gaussian in shape and that the A_3 band peaked at 261 mμ. The positions and magnitudes of the other bands were derived from the data.

Thus the absorption data indicate that; (1) at low temperature there is a single, symmetric A_1 band; (2) at room temperature there is an overlapping A_2 band at longer wavelength which has the same dependence on thallium concentration as the A_1 band; and (3) at higher temperature there is an overlapping A_3 band which increases with thallium concentration.

Further evidence for the existence of the three component bands indicated above is found in excitation

spectra taken with improved resolution. Figure 8 shows the excitation spectrum for uv emission of a KCl:Tl crystal with a low Tl concentration. The emission observed in this case is almost exclusively the 305-mμ band. The primary effect of increasing temperature is an increasing asymmetry at about the position of the A_2 band. It is also found that the A_1/A_2 ratio at room temperature is essentially independent of Tl concentration. These facts, similar to those found in absorption spectra, indicate that the A_1 and A_2 centers vary in the same way with concentration but have different temperature dependences.

For the visible emission, both the temperature effect on A_2 and the A_1/A_2 ratio depend on Tl concentration. For low Tl concentrations, the shape of the spectrum is unaffected by temperature. At higher concentrations, as shown in Fig. 9, the A_2 band becomes quite prominent at low temperature and strongly temperature dependent. This is just the opposite of the uv case and might
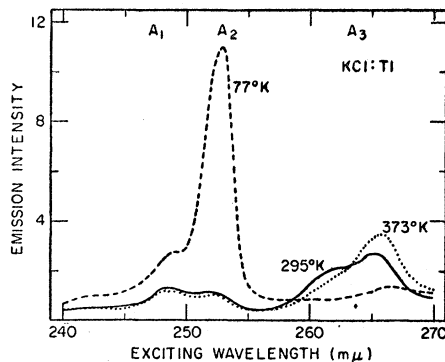

FIG. 9. Effect of temperature on the excitation spectra for visible emission of a KCl:Tl single crystal with high thallium content. The absorption coefficient at the peak of the "A" band is greater than 400 cm^{-1}. The data are uncorrected.

reasonably be ascribed to an increasingly efficient energy transfer from A_2 to A_3 (visible emitting) centers as the number of centers and their proximity to one another increase. On the other hand, the A_3 band at 265 mμ grows at a rate which seems to be consistent with the increase of absorption in this region as shown in Fig. 5.

Although the above effects are somewhat complex it seems clear that there are again at least three bands in the A_1, A_2, and A_3 positions. Each of the bands will apparently show both uv and visible luminescence under certain circumstances. It seems likely that this is partly due to the closeness of the bands in energy and, for high concentrations, of the centers in space which would allow for easy resonance transfer of energy from one center to another. In the low concentration case, where this complexity is least troublesome, it

seems clear that excitation in the A_1 and A_2 bands gives rise to uv emission and in the A_3 band to emission in the visible region.

SUMMARY

It is felt that little doubt remains about the complexity of the "A" band in KCl:Tl and that there are at least three component bands involved. These are called the A_1, A_2, and A_3 bands in this paper. The high-temperature absorption curve can be analytically resolved into three Gaussian bands whose peak positions match those of bands observed in low-temperature absorption and excitation spectra.

The A_1 band at 247 mμ is the strongest and is most clearly seen in low-temperature absorption and excitation spectra. It increases with thallium concentration, decreases with increasing temperature and leads primarily to the 305-mμ emission band. Its suggested origin is a center composed of a substitutional Tl$^+$ in a local CsCl-type environment.

The A_2 band at about 253 mμ is seen most clearly in low-temperature excitation spectra. Absorption data indicate that its dependence on thallium concentration is the same as that of the A_1 band. It apparently increases with temperature and produces primarily uv emission. The responsible center has been suggested[3] as being a substitutional Tl$^+$ ion in a local NaCl-type environment.

The A_3 band (or bands) between 262 and 266 mμ is seen in excitation at room temperature and indirectly in its effect on the shape of the absorption curve at high temperature. It increases with thallium concentration and with temperature and produces visible emission. It is probably due to an interaction-type center (e.g., pairs or aggregates).

The "C" band is also complex and, from absorption measurements, is composed of at least two bands at 195 and 201 mμ. There are also the "B" band at 209 mμ and an additional maximum at 218 mμ in high concentrations.

Thus it seems clear that there are at least seven excitation and absorption bands in thallium-doped KCl.

The Forró effect (growth of the "B" band absorption with increasing temperature) has not been observed in KCl:Tl or NaCl:Tl in the present investigation. In addition, a considerable difference exists between the high-temperature positions of the fundamental absorption edge observed in the present work and in that reported by Forró, except in synthetic NaCl. This difference is removed by the addition of Sr to KCl but Ca in NaCl has no apparent effect.