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Emission and Excitation Spectra of Thallium-Activated Potassium Chloride at Low Temperatures

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Measurements are reported on the emission spectrum and excitation spectrum for emission of thallium-activated potassium chloride at low temperatures. The emission spectra derived from Williams' computed configuration coordinate curves are not in close agreement with those observed experimentally. It is shown that the simple one-dimensional treatment of the configuration coordinate curves cannot account for all the absorption and emission data in a self-consistent way. At 300°K and 77°K the excitation spectra for the 3050 A emission and the 4750 A emission are found to be different. It is suggested that these two emissions may arise from different thallium centers rather than from two excited states of the same center as proposed by Johnson and Williams.

INTRODUCTION

THE introduction of a small concentration of thallium into a potassium chloride crystal produces a luminescent material with relatively simple properties. This system has been widely investigated both experimentally and theoretically and is at present probably the most completely understood luminescent system in inorganic solids. Efforts are being made in various laboratories to enlarge the information available about KCl:Tl in order to evaluate further the validity of the model of this center and the accuracy of the theoretical treatment. Experimental results of this type are presented in the present paper.

Measurements of the room temperature absorption spectrum have been made by Hilsch[1] and Forró[2] who found bands peaking at 1950 A and 2475 A. Measurements on the longer wavelength absorption band have been extended to 4°K by Johnson and Studer[3]; the short wavelength band has been measured at 80°K by Johnson.[4] A principal emission band is found at 3050 A and its spectrum has been measured in the range from 90°K to 423°K by von Meyeren.[5] Another emission band, of lower intensity, was found by Bünger and Flechsig[6] at 4750 A and was measured at 80°K by Johnson.[4] Bünger and Flechsig[6] also measured the phosphorescent decay of this material and concluded that the addition of Tl introduced a trap with an activation energy of 0.67 ev.

Seitz[7] has proposed a model for thallium-activated alkali halides and has discussed the relation of the experimental results to this model in considerable detail. In the case of Tl in KCl the 1950 A absorption is attributed to a ${}^1S_0-{}^1P_1$ transition in the thallium ion and the 2475 A absorption band to a ${}^1S_0-{}^3P_1$ transition.

More recently Williams[8] (referred to hereafter as W I) has calculated the energy of the ${}^1S_0$ and ${}^3P_1$ states of the Tl ion in KCl starting with information about the free ions. The terms investigated were those arising from the Madelung, repulsive, van der Waals, ion dipole, and Coulomb overlap forces. Exchange effects were included indirectly. The energies of these two states were computed as functions of the distance between the thallium ion and its nearest neighbor chlorine ions so that quantitative configuration coordinate curves were obtained. The results are given in Fig. 1. From these it is possible to compute the peak positions and the temperature dependence of the band widths of the 2475 A absorption and 3050 A emission bands corresponding to transitions between these two levels. Williams[9] (referred to hereafter as W II) attempted a further refinement by including effects due to the asymmetry of the wave functions in the excited state. It is generally agreed[10,11] however, that a cubic crystal field cannot resolve the degeneracy of *p*-states so that this latter calculation is not applicable. For this reason the comparison of experiment with theory in the present work will be made using the older theory (W I).

It is also possible to compute the configuration coordinate curves for simple systems from absorption and emission data.[12] A similar scheme was followed by Johnson and Williams[13] who proposed a configuration coordinate curve for the ${}^1P_1$ state using experimental data as a base; their work assumed among other things that the 4750 A emission occurred as a result of transitions from the ${}^1P_1$ to ${}^1S_0$ state. In addition, tentative configuration coordinate curves for the ${}^3P_0$ and ${}^3P_2$ states have been proposed[14] to account for observed trapping effects. These curves are, however, related to the calculations of W II. The configuration coordinate curve for the ${}^1P_1$ state obtained by application of the

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[12] C. C. Klick, Phys. Rev. 85, 154 (1952).
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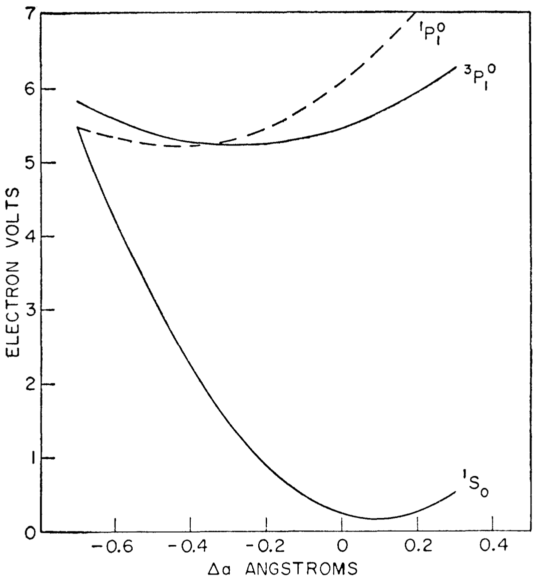

FIG. 1. Configuration coordinate curves for KCl:Tl. The ordinate represents the total energy of the system in various states; the abscissa gives the variation in the Tl^+-Cl^- distance about a zero taken as the K-Cl distance in the pure lattice. The $^1S_0$ and $^3P_1$ states were computed from theoretical considerations (after reference 8). The $^1P_1$ state is derived from experimental data using the method of reference 13 and the curves of reference 8.

method of reference 13 to the results of W I is plotted in Fig. 1.

Wave functions for thallium in potassium chloride have been published by Douglas, Hartree, and Runciman[15]; they do not, however, include exchange. No attempt has as yet been reported to repeat the calculations of Williams using these wave functions, but they have been used by Knox and Dexter[16] to investigate the problem of the oscillator strengths for the absorption bands in KCl:Tl.

Butler[17] has made room temperature excitation measurements on KCl:Tl phosphors prepared, in general, by grinding together KCl and TlCl. He reported separate excitation peaks at 2600 A and 2450 A for the visible and ultraviolet emissions respectively. Somewhat similar results had previously been reported in the work of Johnson and Williams.[13] In the model proposed by Johnson and Williams,[13] see Fig. 1, the absorption of light near 2500 A leads to the excitation of Tl from its ground state to the $^3P_1$ state. The center then relaxes to the minimum of this state. It is assumed that the curves for the $^1P_1$ and $^3P_1$ states intersect near their minima so that transitions to the $^1P_1$ state from the $^3P_1$ state are possible with little or no activation energy. As a result both the $^1P_1$ and $^3P_1$ states are populated, leading to two emission bands, although there has been only a single absorption transition. Thus the same excitation spectrum should be observed in the 2500 A region for both emission bands. The experimental results above thus cast some doubt on this model.

Butler has proposed a different set of transitions than that assumed by Seitz and extended by Williams and Johnson. The excitation peak at 2600 A and the emission peak at 4750 A are ascribed to transitions between the ground state of the thallium ion and the $^3P_1$ excited state. Excitation in the 2450 A band and emission at 3050 A are ascribed to transitions to the $^1P_1$ state. Absorption and excitation bands at wavelengths less than 2000 A are tentatively suggested as being due to higher excited states of the thallium ion or possibly due to lattice absorption in regions perturbed by the thallium ion.

The purpose of the present work is twofold. First, measurements of the emission spectrum of the 3050 A band over a range of temperature from 4°K to 300°K would provide additional data to check the configuration coordinate curves for the $^1S_0$ and $^3P_1$ states calculated by Williams. Second, the measurement at various temperatures of the excitation spectrum of low concentration KCl:Tl phosphors prepared from the melt should give more conclusive evidence concerning the $^1P_1$ state and the curve deduced for it by Johnson and Williams.

EMISSION MEASUREMENTS

Figure 2 shows schematically the experimental arrangement for measuring the emission spectra. An *H*-6 1000-watt mercury arc mounted in fused silica was the source of exciting light. This light was passed through a quartz double monochromator and into a helium Dewar where it excited the KCl:Tl phosphor. The emitted light was observed by a 1*P*28 photomultiplier after dispersion of the emission in another quartz monochromator. The samples were prepared by melting together KCl and TlCl in a helium or HCl atmosphere and grinding the resulting solid solution to a coarse powder. The KCl was specially purified by

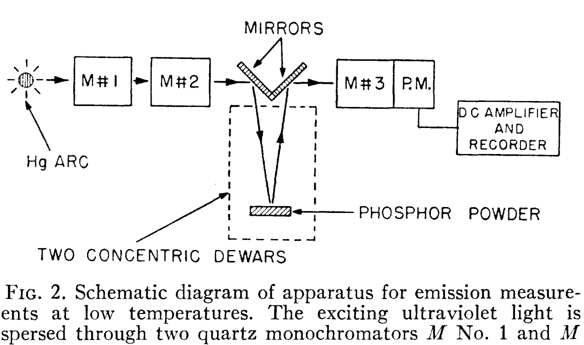

FIG. 2. Schematic diagram of apparatus for emission measurements at low temperatures. The exciting ultraviolet light is dispersed through two quartz monochromators *M* No. 1 and *M* No. 2 and then falls on a sample contained in a double Dewar. The emitted light is analyzed by a third quartz monochromator and detected by a photomultiplier (P.M.), amplifier, and recorder combination.

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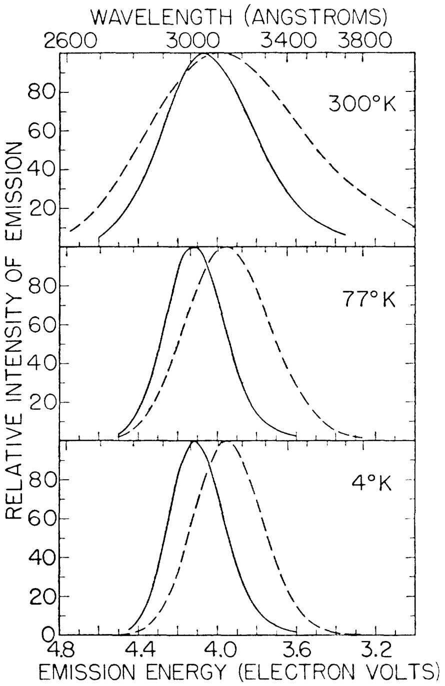

FIG. 3. Ultraviolet emission band of KCl:Tl at 300°K, 77°K, and 4°K. The dashed curve is computed from the theoretical configuration coordinate curves of reference 8; the solid curves are the results of experiment. The relative number of emitted photons is plotted as a function of energy of the emission. The curves are normalized at their peaks.

extraction with dithizone to remove heavy metal impurities.

The results of emission measurements on KCl with 0.0004 mole fraction of Tl are given in Fig. 3 for temperatures of 300°K, 77°K, and 4°K. Also given are the emission spectra computed from the configuration coordinate curves of W I. The widths of the emission spectra at half maximum at 300°K, 77°K, and 4°K are observed to be 0.54, 0.35, and 0.32 ev, respectively; those computed are 0.92, 0.50, and 0.41 ev. At 4°K the peak positions of the observed and computed emission curves differ by 0.18 ev; for the absorption spectra[3] a difference of approximately 0.47 ev had previously been found.

The simple theory of configuration coordinate curves indicates that both the absorption and emission curves should be Gaussian in shape.[18] Modifications of this theory have been suggested by Dexter[19] who concludes that simple emission and absorption spectra should be of the form

$$I = E^n G, \tag{1}$$

where I is the number of absorbed or emitted quanta, E is the energy of the quanta, G is a Gaussian function, and n is a constant which depends on the system. In the KCl:Tl case, n should be 2 for the emission spectrum and zero for the absorption curve. The experimental emission data of Fig. 3 have been compared with functions of the form of Eq. (1), but the band is so narrow that a decision between $n=0$ and $n=2$ was not possible. For simplicity the emission has been assumed to be a Gaussian of the form

$$I = I_0 \exp[-a(E-E_0)^2], \tag{2}$$

and the quantity $[\log_{10}(I_0/I)]^{\frac{1}{2}}$ was plotted as a function of E to test this relation. Figure 4 shows the 4°K emission data plotted in this way. Except for the tails of the band where the precision of the measurement is poor, the data are fitted quite well by the equation. However, it should be noted that the slopes of the two straight lines are not the same; the difference is less apparent in the 77°K and 300°K data. A similar failure to follow a single Gauss curve has been noted in the case of the F-center absorption band.[20,21] For the F-center the steeper slope is on the low-energy side of the peak, while for the KCl:Tl emission the steeper slope is on the high-energy side. No explanation of these effects has as yet been proposed.

EXCITATION MEASUREMENTS

The experimental arrangement for measuring excitation spectra is shown schematically in Fig. 5. Ultraviolet light from a hydrogen arc lamp is dispersed in a quartz monochromator and allowed to fall on a powdered sample of KCl:Tl in a Dewar. A 1P28 photomultiplier is used to record the intensity of emission as the wavelength of the exciting light is varied. The 3050 A emission was isolated by placing Corning 7740 and 9863 filters before the photomultiplier; the 4750 A emission was isolated using Corning 7740 and 3389 filters.

As before, a KCl sample with 0.0004 mole fraction of Tl was measured. The results are presented in Fig. 6.

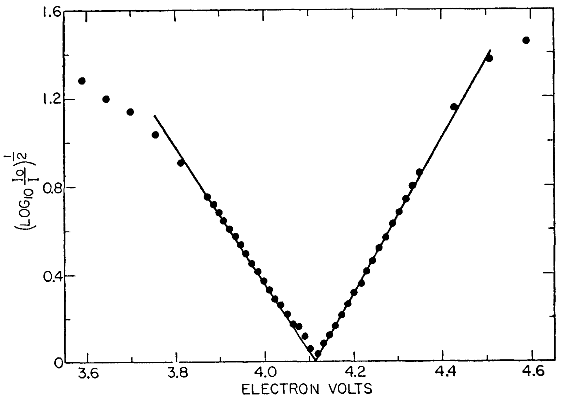

FIG. 4. Experimental data for the 3050 A emission band of KCl with 0.0004 Tl (mole fraction) at 4°K plotted as a Gaussian function of the form of Eq. (2).

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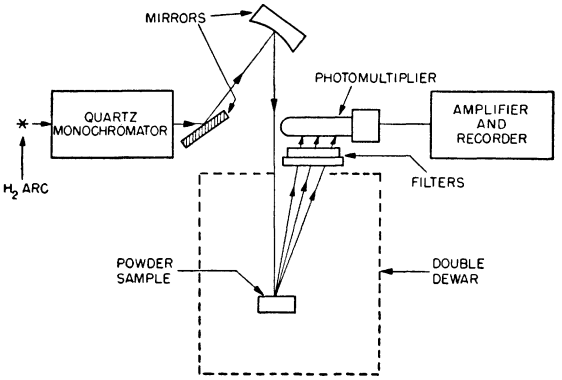

FIG. 5. Schematic arrangement of apparatus for excitation measurements at low temperatures. The filters used (see text) pass the luminescent emission and exclude the exciting light from the photomultiplier.

Excitation data for the visible emission at 4°K have been omitted since background luminescence, apparently from gases adsorbed on the sample, became so large as to make the results untrustworthy. The 77°K and 300°K results of Fig. 6 show quite clearly, however, a distinct difference in the excitation spectra for the ultraviolet and visible emissions. The excitation spectrum for the ultraviolet band peaks at 2470 A and that for the visible band peaks at 2540 A in the 77°K data.

DISCUSSION

There appears to be reasonably good agreement between the measured peak position of the 3050 A emission curve and that derived from the computed configuration coordinate curves of W I. The half-widths of the emission bands are in less satisfactory agreement. A more specific comparison between theory and experiment may be made by using the one-dimensional treatment of configuration coordinate curves and determining the vibrational frequency which leads to the broad emission band at low temperatures through a zero-point vibrational energy. The width of the emission band at half-maximum, H is of the form[18]

$$H = C[(h\nu/2k)\coth(h\nu/2kT)]^{\frac{1}{2}}, \tag{3}$$

where C is a constant, ν is the frequency in question, T is the absolute temperature, and h and k are Planck's and Boltzmann's constants, respectively. By measuring H at various temperatures it is then possible to obtain the frequency of vibration characteristic of the system in its excited state. This quantity may also be obtained from the $^3P_1$ curve of W I since it is of the form

$$E = KX^2/2, \tag{4}$$

where E is an energy, X is a distance, and K is a force constant. Using this force constant and an appropriate mass the vibrational frequency may be obtained. In a similar computation involving the ground state Williams[22] takes the mass to be that of the six nearest neighbor chlorine ions plus a correction factor for second nearest neighbors which amounts to 20% of the mass of the chlorine ions. The experimentally determined frequency for the system in its excited state is 4.6×10^{12} using the 300°K and 4°K data; from the $^3P_1$ curve of W I it is 2.6×10^{12} using the mass employed by Williams. A similar comparison may be made using the absorption spectra[3] and the computed $^1S_0$ curve of W I. For the ground state the experimental frequency is 3.6×10^{12} and that from the computed curves is 4.0×10^{12}. These results would seem to indicate that the ground state curve of W I is in good agreement with experiment while that for the first excited state is considerably less precise.

In addition, it is of interest to inquire whether or not a one-dimensional configuration coordinate curve treatment can account for the full range of optical data now available for KCl:Tl. To this end, the ratio of the frequencies of vibration of the excited and ground states may be taken. If one uses the results obtained

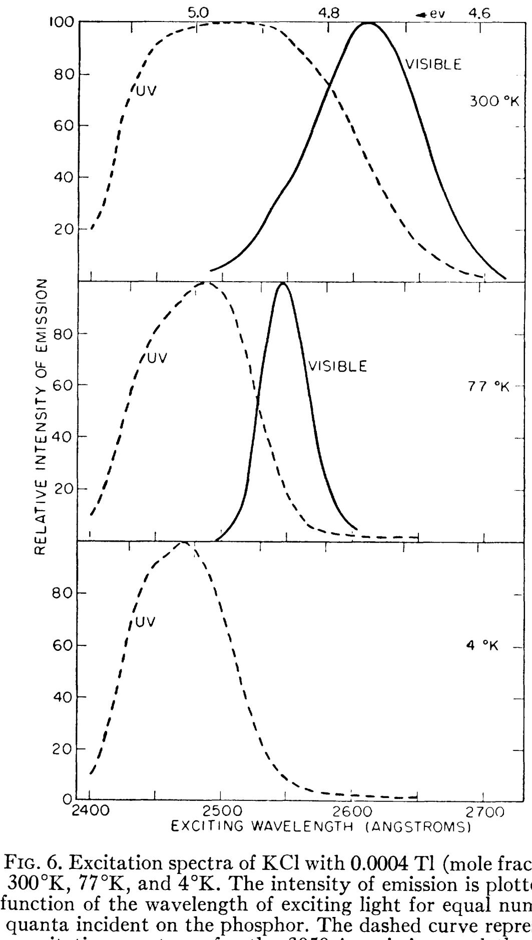

FIG. 6. Excitation spectra of KCl with 0.0004 Tl (mole fraction) at 300°K, 77°K, and 4°K. The intensity of emission is plotted as a function of the wavelength of exciting light for equal numbers of quanta incident on the phosphor. The dashed curve represents the excitation spectrum for the 3050 A emission, and the solid curve that for the 4750 A emission. The curves are normalized at their peaks.

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above from an analysis of the temperature variation of emission and absorption band widths, this ratio is

$$\nu_{\text{excited}}/\nu_{\text{ground}}=4.6\times 10^{12}/3.6\times 10^{12}=1.28. \quad (5)$$

This ratio may also be obtained from the ratio of the low temperature band widths of the absorption and emission bands.[12] This relation is

$$\begin{aligned}\nu_{\text{excited}}/\nu_{\text{ground}}&=(H_{\text{abs}}/H_{\text{emis}})^{2/5}\\ &=(0.108\text{ ev}/0.32\text{ ev})^{2/5}=0.65. \quad (6)\end{aligned}$$

It appears that different sets of data give widely different results so that the data themselves are not internally self-consistent on a one-dimensional configuration coordinate curve basis. This may result either from the approximations introduced in using such a simple model[23] or it may be due to complications in the optical properties of the center.

In the excitation spectra of Fig. 6 there are well-separated peaks for the 3050 A and 4750 A emissions at both 300°K and 77°K, thus confirming and extending the work of Butler.[17] In addition, Johnson and Williams[13] and Butler[17] have found that the ratio of the emission peak heights varies with Tl concentration. These facts appear to be difficult to understand for transitions characteristic of a single isolated center, and suggest that the 4750 A emission and the 3050 A emission may not arise in the same center.

In constructing a configuration coordinate curve for the $^1P_1$ state, Johnson and Williams used experimental data rather than extending the calculations used in determining the $^3P_1$ curve. They assumed that the 1960 A absorption band is due to a transition from the $^1S_0$ to the $^1P_1$ state and that the 4750 A emission corresponds to the inverse transition. In addition they assumed that the observed variation of the ratio of the intensity of the 4750 A emission to the 3050 A emission as a function of temperature arises from an activation energy relating the minima of the $^1P_1$ and $^3P_1$ curves. It is possible, however, to postulate other explanations of the variation of emission intensities with temperature which do not require that both emission bands arise from the same center. One such explanation is that temperature quenching occurs in the center responsible for the 4750 A emission but not in the center giving rise to 3050 A emision for temperatures below room temperature. The efficiency of the 4750 A emission would then be given by the expression of Gurney and Mott[24] as

$$I_{4750}=[1+A\exp(-E/kT)]^{-1}, \quad (7)$$

and the efficiency of the 3050 A emission is assumed to be independent of temperature so that

$$I_{3050}=K. \quad (8)$$

Then the ratio is

$$I_{4750}/I_{3050}=[K+AK\exp(-E/kT)]^{-1}. \quad (9)$$

Equation (9) is of the same form as that fitted by Johnson and Williams to their data.

Another possible explanation of the temperature dependence of the ratio of the two emission bands observed by Johnson and Williams[13] is that their measurements were made with excitation by 2537 A light from a low-pressure mercury arc. Reference to Fig. 6 will show that at 77°K this wavelength is near the peak of the excitation band for the 4750 A emission but on the side of the excitation band for the 3050 A emission. As the temperature increases, the excitation spectra shift and broaden so that the 3050 A emission is more efficiently excited. This effect will also change the emission ratio in the direction observed.

Another objection to the proposed $^1P_1$ curve has been raised by Knox and Dexter.[11] They point out that a computation of the $^1P_1$ curve using the same mathematical methods by which Williams obtained the $^3P_1$ curve[8] would lead to a curve similar in shape to the $^3P_1$ curve but displaced upward in energy by about 3 ev. Such a curve would be radically different from that proposed by Johnson and Williams.[13] When one uses the $^1S_0$ and $^1P_1$ curves of Fig. 1, the computed widths at half-maximum of absorption and emission curves at 80°K are 0.27 and 0.64 ev, respectively; Johnson[4] gives experimental values of 0.33 and 0.50 ev for the 1960 A absorption and 4750 A emission bands at the same temperature.

The energy level assignments proposed by Bulter have a number of attractive features. There appear, however, to be two objections that might be raised. First, it fails to account for the dependence of the ratio of the emission band intensities on activator concentration; and second, states which differ by about 3 ev in the free ion would lead to excitation spectra differing by only 0.14 ev in the solid.

Sample preparations were made incorporating trace amounts of Cu and Pb in addition to the Tl in order to determine whether the center responsible for the 4750 A emission might be due to traces of these activators which are common impurities in KCl. No increase in the 4750 A emission was observed. It appears, then, that if there are two centers from which the two emission bands arise, both are due to Tl with the type responsible for the 3050 A emission probably being the more numerous. If this center is assumed to be an isolated thallium ion in a realtively perfect part of the lattice, then the center responsible for the 4750 A emission might be due to thallium clusters as is suggested by its dependence on thallium concentration or it might be due to a thallium ion in a region where crystalline imperfections alter its optical porperties.

CONCLUSIONS

The measurements of emission and excitation spectra described here yield further evidence concerning the $^1S_0$ and $^3P_1$ configuration coordinate curves calculated by Williams for Tl in KCl. It appears from a com-

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parison of theory and absorption spectra that the $^1S_0$ curve of W I is fairly accurate. The observed emission spectra are in much less satisfactory agreement with those computed using the $^3P_1$ curve W I; nor is it possible to derive one-dimensional configuration coordinate curves which include all the experimental data on absorption and emission in a self-consistent manner. This may indicate either the presence of unsuspected complications in the absorption or emission properties of KCl:Tl, or it may indicate the limitations in the use of a one-dimensional configuration coordinate curve model for the center. The excitation spectra also casts some doubt as to the validity of the assumptions made by Johnson and Williams in obtaining the $^1P_1$ configuration coordinate curve from experimental data. It appears that the experimental results could also be interpreted as indicating the presence of two thallium centers in slightly different environments. It is probable that more certain conclusions concerning this state will arise from a detailed investigation of the 1960 A absorption band and the emission spectra associated with it.

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Optical and Electrical Properties of Silver Chloride[*]

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Simultaneous measurements of absorption, fluorescence, and photoconductivity have been investigated for AgCl as functions of exciting radiation and temperature. Excitation in the range of 250 to 400 millimicrons with temperatures from -180°C to room temperature were employed. Frequency-sensitive apparatus was used throughout the measurements with the light beam chopped at 37.5 cps. An ac electrometer circuit was employed to measure currents in the range 10^{-16} to 10^{-11} ampere.

The temperature dependence of the absorption edge has been extended to lower temperatures and the coefficient of absorption observed to be an exponential function of wavelength. It was also observed to be an exponential function of $1/T$°K in the range 387 to 400 millimicrons. The fluorescence of AgCl at -175°C was 482 millimicrons for an exciting wavelength in the region of 270 millimicrons. A second weaker fluorescence peak of undetermined wavelength was observed at temperatures in the neighborhood of -150°C for an exciting radiation of 390 millimicrons. Photocurrents proportional to the intensity of the exciting radiation were observed in the saturation current region for low applied voltages. Photoconductivity was observed in each of two different regions of the temperature range and wavelength range of exciting radiation employed. There were large photocurrents for wavelengths of exciting radiation less than 270 millimicrons in the temperature region of -175°C and smaller photocurrents at temperatures of -55°C for exciting radiation of 398 millimicrons. The spectral distribution of photoconductivity was also investigated.

I. INTRODUCTION

RECENT investigations[1,2] on the properties of AgCl have made evident the importance of measurements on crystals at shorter wavelengths and lower temperatures. Limited studies of AgCl have previously been reported, both in the edge region and at higher absorptions.[3-5] Many factors enter to make such measurements difficult. The steepness of the absorption edge requires crystals covering a wide range of thicknesses. In absorption measurements, fluorescence at low temperatures must be corrected for along with any fluorescence of the supporting quartz materials for thin samples. However, photoconductivity measurements impose the requirement that thick crystals be used in order that as much light be absorbed as possible.

It appears to be necessary to study simultaneously these properties of AgCl before an interpretation of the electronic processes can be attempted.

II. EXPERIMENTAL

A. Materials

The samples used in these experiments ranged in thickness from 0.55 cm to 5×10^{-4} cm. Two single crystals,[6,7] 0.23 cm and 0.55 cm thick, were used in the low-absorption region. Also AgCl, 0.1 cm thick, ob-

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