Effect of Pressure on the Optical Absorption of the Activator System in KCl:Tl

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The optical absorption spectrum of thallium-activated potassium chloride has been measured at 2000 atmospheres. The absorption band corresponding to the $^1S_0 \rightarrow {}^3P_1{}^0$ transition of Tl$^+$ shifts 4 A to longer wavelengths at this pressure. The spectral shift is calculated theoretically from the quantitative configuration coordinate model of KCl:Tl. The occupation probabilities of accessible atomic configurations of the activator system are dependent on pressure, whereas the transition energy for a particular configuration is independent of pressure. The pressure is considered to act hydrostatically on six pistons corresponding to the Cl$^-$ nearest neighbors. The theoretical shift in absorption under 2000 atmospheres pressure is 5 A to longer wavelengths.

I. INTRODUCTION

A QUANTITATIVE theory of solid-state luminescence has been formulated and applied to impurity-activated ionic crystals.[1] From fundamental considerations and the properties of the constituent ions, the theoretical absorption and emission spectra of thallium-activated potassium chloride have been evaluated and found to be in satisfactory agreement with experiment. The dependence on temperature of these spectra has also been successfully computed.[2]

A single parameter, the activator—nearest-neighbor distance, was found adequate for quantitative calculation of the properties considered. By measuring the effect of pressure on the optical properties of a phosphor crystal, it is possible to affect directly this important parameter and so to subject the theory to a crucial test. In the present work, the effect of pressure on the absorption spectrum of the activator system in KCl:Tl is determined experimentally and computed theoretically.

II. EXPERIMENTAL

The absorption measurements were made using an American Instrument Company high-pressure cell No. 11–550 as the sample holder and hydraulic pump No. 406–155 to provide pressures up to 2000 atmospheres. A Bourdon gauge was used for the determination of pressure. Phillips "spectro grade" isooctane was found to be a satisfactory pressure-transmitting fluid. Particular care was exercised to eliminate from the apparatus all traces of hydrocarbons exhibiting absorption and fluorescence in the spectral region from 2400 to 2600 A. The optical path-length in isooctane was 1.5 mm. Pressure has no effect on the transmission of isooctane from 2400 to 2600 A. The KCl:0.00002 Tl crystal was 4.5 mm thick and completely covered the optical opening through the sample cell. It was held in place by a stainless steel holder with a recess machined to accommodate the crystal.

The sample cell was placed at the exit slit of an ultraviolet monochromator[3] having a LiF window at the exit slit. A 1P28 photomultiplier was used as the detector of transmitted radiation. Because of the construction of the pressure cell, the detector was approximately 12 cm from the phosphor crystal. This arrangement eliminated the necessity for making any special provision to exclude from the detector, fluorescence of the phosphor or of the fused quartz windows of the high-pressure cell. With such a long optical path between monochromator exit slit and detector, the system might be expected to be sensitive to changes in geometry of the absorption cell or of the crystal. Deliberate alteration of the geometry of sample cell and detector, and use of two different exit-slit settings corresponding to band widths of 5 A and 12 A showed no detectable effect on the results.

The shift in absorption with pressure was observed by determining the intensity of transmitted radiation at various wavelengths at approximately 330-atmosphere intervals from atmospheric to 2000 atmospheres pressure. Lack of any permanent effect on the crystal or contamination of isooctane was ascertained by also measuring the transmitted radiation as the pressure was decreased to one atmosphere. Typical experimental results for two wavelengths are shown in Fig. 1, in which the ratio of intensity I_p of radiation transmitted at pressure P to that I_0 transmitted at atmospheric pressure is plotted as a function of pressure.

This ratio is given by the expression

$$I_p/I_0 = e^{-l(k_p - k_0)}, \qquad (1)$$

where l is the thickness of the crystal, k_0 is the absorption coefficient of the crystal at atmospheric pressure
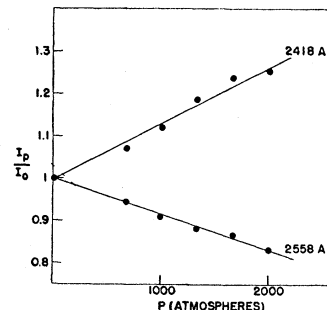

FIG. 1. Experimental data on the pressure dependence of transmission for two typical wavelengths.

[1] F. E. Williams, J. Chem. Phys. **19**, 457 (1951); J. Phys. Chem. **57**, 780 (1953).
[2] F. E. Williams and M. H. Hebb, Phys. Rev. **84**, 1181 (1951).
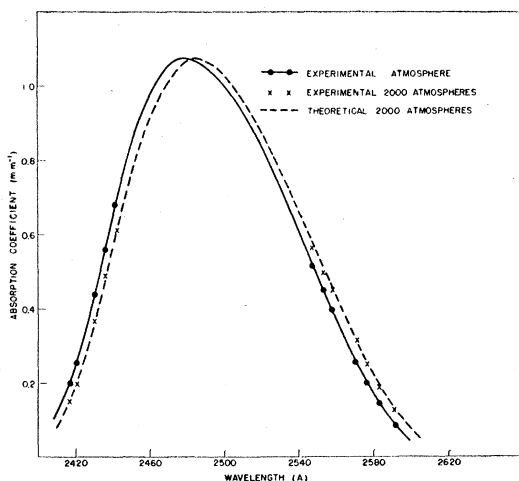[3] P. D. Johnson, J. Opt. Soc. Am. **42**, 278 (1952).

FIG. 2. Theoretical and experimental dependence on pressure of the $^1S_0 \rightarrow {}^3P_1{}^0$ absorption spectrum of KCl:Tl.

for the wavelength in question, and k_p is the absorption coefficient for this wavelength at pressure P. The quantity k_0 was determined from separate absorption measurements, using apparatus permitting accurate comparison of incident and transmitted radiation.[3]

At absorption coefficients above about 0.6 mm^{-1}, the small amount of transmitted radiation reduced the accuracy of the measurements. No strongly anomalous behavior was observed at these higher absorption values. On the more accurate portions of the curve, indicated by the experimental points, there is a substantially uniform shift of the absorption band 4 A to longer wavelengths.

III. THEORETICAL

The potential energies of the activator system in the $^1S_0$ and $^3P_1{}^0$ states of Tl$^+$ in KCl have been determined as a function of the symmetric radial displacement of the six nearest-neighbor Cl$^-$ ions from the Tl$^+$ ion.[1] The resulting parabolic dependence of potential energy on configuration permits the calculation of luminescent spectra. Since potential energy is a markedly different function of the configuration coordinate for the different electronic states, the transition energy is strongly dependent on the configuration. The classical formula for the absorption or emission spectrum with no applied pressure is

$$Q_0(\epsilon) = (K/2\pi kT)^{\frac{1}{2}} \exp(-Kq^2/2kT)(dq/d\epsilon), \quad (2)$$

where q is the displacement in the configuration coordinate from the minimum for the initial state; ϵ is the transition energy at q, in accordance with Franck-Condon principle; and K is the force constant for the initial state.

The effect of pressure is to shift the spectrum by modifying the occupational probability of any arbitrary configuration of the activator system in the initial state. Pressure contributes the same energy to the initial and to the final states for any arbitrary configuration; hence, the net effect on the transition energy is zero. The spectrum with the applied pressure P is therefore

$$Q(\epsilon,P) = Q_0(\epsilon)e^{W/kT}, \quad (3)$$

where W is the work done on the system by the pressure in going from a reference configuration to the configuration in question and is given by the expression

$$W = -\int_{V_0}^{V} PdV = -P(V_q - V_0). \quad (4)$$

The quantity V_q is the volume of the activator system with the arbitrary configuration q, and V_0 is the volume with the reference configuration determined by normalization of $Q(\epsilon,P)$.

The volume difference $(V_q - V_0)$ is equal to the volume displacement from the reference configuration q_0 to the configuration q of six pistons, each with cross-sectional area equal to the cross-sectional area of the nearest-neighbor Cl$^-$, since it is the displacement of these Cl$^-$ ions which corresponds to q. The spectrum is therefore

$$Q(\epsilon,P) = Q_0(\epsilon)e^{-A(q-q_0)P/kT}, \quad (5)$$

where A is the total cross-sectional area of the six Cl$^-$ ions and q_0 is the configuration corresponding to V_0. At the configuration q_0, it is evident from Eq. (5) that $Q(\epsilon,P) = Q_0(\epsilon)$. The substitution of Eq. (2) in Eq. (5) reveals that the activator system with the applied pressure P is characterized by the same force constant K but with a new equilibrium configuration q_e. The spectrum can, therefore, be written:

$$Q(\epsilon,P) = \left(\frac{K}{2\pi kT}\right)^{\frac{1}{2}} \frac{dq}{d\epsilon} \exp\left[\frac{-K}{2kT}(q-q_e)^2\right]. \quad (6)$$

The force applied to the activator system by the pressure must equal the restoring force at the equilibrium configuration,

$$PA = Kq_e. \quad (7)$$

By combining Eqs. (5) and (6) and by substituting for q_e according to Eq. (7), we obtain:

$$q_0 = \frac{1}{2}q_e = PA/2K. \quad (8)$$

From Eqs. (5) and (8) for the absorption band corresponding to the $^1S_0 \rightarrow {}^3P_1{}^0$ transition of Tl$^+$, and using the experimental $Q_0(\epsilon)$, the absorption under 2000 atmospheres pressure can be calculated. A shift of absorption approximately 5 A to longer wavelengths is calculated, in excellent agreement with experiment as shown in Fig. 2.