

${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ Transitions of Tl^0 in Alkali-Halide Crystals*

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Tl^0 has been produced in KCl-TlCl, KBr-TlBr, and KI-TlI crystals at 77°K by exposure to γ rays, and two absorption bands, which are attributed to forbidden transitions between the ${}^2P_1 \rightarrow {}^2P_3$ levels, have been measured. In KCl-TlCl, the oscillator strength, band shape, and peak positions have been determined at three temperatures: 153, 77, and 5°K.

INTRODUCTION

BÜNGER and Flechsig¹ found that a KCl-TlCl crystal, after prolonged exposure to ultraviolet light, could be stimulated to luminesce by excitation with infrared light. Upon studying the intensity of the stimulated luminescence as a function of the wavelength of the exciting light, they observed two luminescence intensity maxima at 1150 and 1550 nm. These two bands in the stimulation spectrum imply the presence of optical absorption bands at these wavelengths; however, these absorption bands are very weak and have only recently been reported by Delbecq, Ghosh, and Yuster² (DGY). DGY identified these absorption bands as arising from transitions of thallium atoms, Tl^0 , which are produced in KCl-TlCl crystals at 77°K by exposure to ionizing radiation. The present work reports additional information concerning these long-wavelength Tl^0 transitions in KCl-TlCl, KBr-TlBr, and KI-TlI.

EXPERIMENTAL PROCEDURE

Single crystals of KCl-TlCl, KBr-TlBr, and KI-TlI were grown in air by the Kyropoulos method from a melt containing the alkali halide and the corresponding thallos halide. The melts were generally prepared by adding 0.75 g of the thallos halide to about 100 g of alkali halide. Analyses of KCl-TlCl crystals grown from such a melt show the presence of about 0.01 mole % TlCl.

Tl^0 and X_2^- molecule ions were formed in these crystals at 77°K by exposure to a 2000-Ci Co^{60} γ -ray source. The infrared Tl^0 absorption bands are very weak; thus, it was necessary to make absorption measurements on crystals as thick as 24 mm with a Cary 14R spectrophotometer using the 0-0.1 absorbance slide wire.

EXPERIMENTAL RESULTS AND DISCUSSION

The infrared absorption spectrum of isolated Tl^0 is somewhat interfered with by the overlapping absorptions of two species. The first is the F' center and the second is a species we believe to consist of two substitutional thallos ions, in nearest-neighbor cation

positions, which have trapped an electron Tl_2^+ . As might be expected, the concentration of this Tl_2^+ center appears to depend on the square of the thallos-ion concentration. Details concerning this center will be presented in a later paper. The interference caused by the presence of F' centers can be readily eliminated by excitation at the appropriate wavelength, e.g., 1000 nm in the case of KCl-TlCl, resulting in removal of the F' centers. The interference resulting from the presence of Tl_2^+ centers was minimized in these experiments by limiting the Tl^+ concentration. It was possible by using several different concentrations of Tl^+ to separate the Tl^0 and Tl_2^+ spectra with reasonable accuracy.

Figure 1 shows infrared absorption spectra of Tl^0 in KCl measured at 153, 77, and 5°K. In order to obtain these spectra a KCl-TlCl crystal at 77°K was exposed to γ rays for 4 h. The crystal was then bleached for one minute at 1000 nm to eliminate F' centers. Upon warming to 153°K in the dark there was some thermal bleaching during the first 5 min. at this temperature.³ However, after the first five minutes at 153°K the intensity of the Tl^0 bands remained constant so that the spectrum of this crystal, containing a constant number of Tl^0 , could be measured at 153, 77, and 5°K. As reported previously,² these two Tl^0 bands with very low oscillator strengths are believed to arise from the forbidden ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ transition of the free atom. These levels in the free atom are separated by 0.97 eV.⁴ Table I shows the energies of the two transitions in some

TABLE I. Characteristics of the Tl^0 ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ transitions in several alkali halides.

Alkali halide	Temperature (°K)	Peak (nm)	Peak (eV)	Splitting (eV)	Oscillator strength
KCl	153	1520	0.816	0.20	11.6×10^{-5}
		1225	1.012		16.0×10^{-5}
	77	1500	0.827	0.15	8.1×10^{-5}
		1270	0.977		8.6×10^{-5}
		5	1470		0.843
KBr	5	1300	0.954	0.11	4.3×10^{-5}
		1580	0.785		0.08
	5	1430	0.867	0.07	
KI	5	1695	0.731	0.07	
		1550	0.800		

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

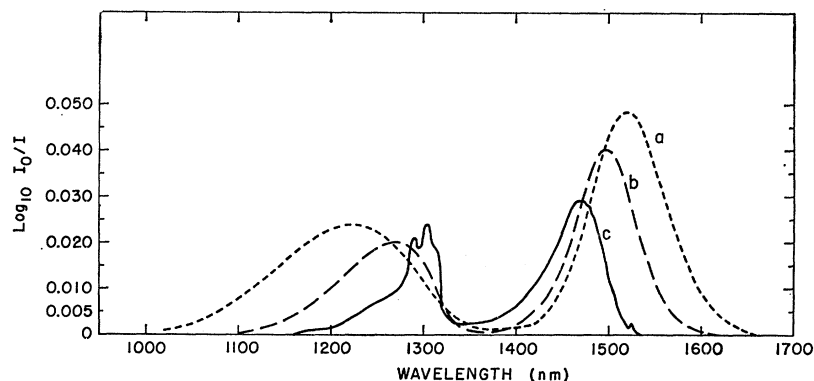
¹ W. Bünger and W. Flechsig, *Z. Physik* **69**, 637 (1931).

² C. J. Delbecq, A. K. Ghosh, and P. H. Yuster, *Phys. Rev.* **151**, 599 (1966).

³ Those Tl^0 centers which decay do so by recombination with nearby Cl_2^- molecule ions.

⁴ *Atomic Energy Levels*, edited by C. F. Moore, Natl. Bur. Stds. (U. S.), Circ. No. 467 (U. S. Government Printing and Publishing Office, Washington, D. C., 1949).

FIG. 1. Absorption spectra showing the ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ Tl^0 transitions in KCl at (a) 153°K, (b) 77°K, and (c) 5°K.



alkali halides. M. H. Cohen has suggested to us that two bands, rather than one, arise from a splitting of the ${}^2P_{3/2}$ excited state, caused by a dynamical Jahn-Teller effect. In an accompanying article Knox has developed a semiclassical theory of the infrared absorption of Tl^0 in KCl, and has been able to account for the temperature dependence of the oscillator strengths and splittings of the Tl^0 absorption bands. As shown in Fig. 1 and Table I, both the splitting and the oscillator strengths of these two transitions increase with increasing temperature. These facts are in qualitative agreement with the above interpretations of the nature of these transitions. The importance of the vibrational interactions is further brought out by the vibrational structure observed in the high-energy band at 5°K. Some structure also occurs at 5°K in the low-energy band at about 1480 and 1520 nm; however, it is not

certain that this structure is associated with the Tl^0 band. Although vibrational structure is evident in the higher energy band, the resolution⁵ is very poor, and, therefore, accurate details of the vibrational splittings cannot be obtained from the data. However, some approximate splittings obtained in KCl-TlCl are 90 and 50 cm^{-1} . In KCl-TlCl no change in structure was observed over the temperature range 2–20°K.

The corresponding Tl^0 infrared absorption bands have also been investigated in KBr and KI, and are shown in Figs. 2 and 3, respectively. Figures 1–3 and Table I indicate that qualitatively the spectra are very similar; however, the wavelengths, splittings, and structure of these bands depend somewhat on the host crystal.

Further confirmation of the origin of the reported transitions is obtained by studying Pb^+ , which is isoelectronic with Tl^0 . The spin-orbit interaction in Pb^+ is almost double that in Tl^0 and gives a splitting of 1.75 eV between the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ levels in the free ion.⁴ We believe that we have produced Pb^+ in KCl-PbCl₂ crystals by irradiation at 77°K with γ rays. We observe one absorption band at about 910 nm and evidence of another band at about 750 nm. These bands are about at the predicted positions for Pb^+ , considering the increased spin-orbit splitting. It is very difficult to study the transitions as quantitatively as in the case of Tl^0 because of the strong interference of the long-wavelength absorption of Cl_2^- .^{6,7} However, in spite of the difficulties, our experiments indicate that Pb^+ , as well as Tl^0 , has two very weak absorption bands which can be associated with the forbidden transitions between the ${}^2P_{1/2}$ and ${}^2P_{3/2}$ levels.

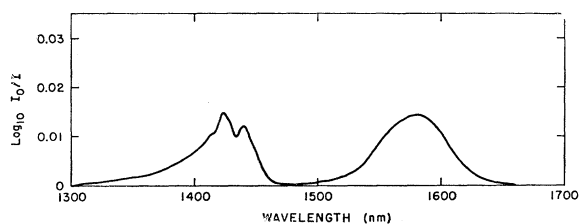


FIG. 2. Absorption spectrum showing the ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ Tl^0 transitions in KBr at 5°K.

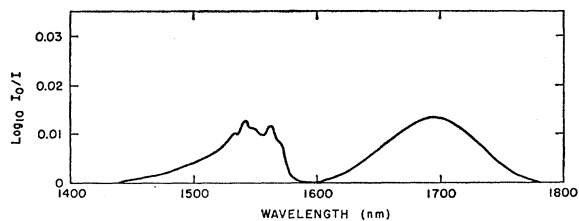


FIG. 3. Absorption spectrum showing the ${}^2P_{1/2} \rightarrow {}^2P_{3/2}$ Tl^0 transitions in KI at 5°K.

⁵ The resolution of our equipment is sufficient to bring out finer detail if it were present.

⁶ C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958).

⁷ C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).