

Absorption and Emission of Thallium-Doped KBr in an External Electric Field (*).

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Summary. — The paper reports the results of measurements on the effect of an electric field on the absorption and on the luminescence for excitation in the A band of thallium-activated potassium bromide crystals. A triplet structure of the A band is found and the experimental results also show a quadratic Stark effect. The measured emission spectrum indicates that there are two different centres responsible for the luminescence.

1. — Introduction.

The alkali halide phosphors containing impurity ions with $(s)^2$ configuration such as l^+ or Pb^{++} have been investigated both experimentally and theoretically, and their excitation spectrum has been studied first by HILSCH⁽¹⁾, HILSCH and POHL⁽²⁾, and LORENZ⁽³⁾. The absorption spectrum associated with the thallium activator consists, as is well known, of three principal bands which are called A , B and C bands in order of increasing energy.

On the basis of those experimental results SEITZ⁽⁴⁾ proposed in 1938 the first detailed explanation of the absorption and emission spectra of these phosphors. His analysis was based upon the positions of the energy levels of the free Tl^+ ion and upon the expected modification of these levels when the ion is in a crystal. He explained the observed structure of the absorption spectra

(*) To speed up publication, the authors of this paper have agreed to not receive the proofs for correction.

(¹) R. HILSCH: *Zeits. Phys.*, **44**, 860 (1927).

(²) R. HILSCH and R. W. POHL: *Zeits. Phys.*, **48**, 384 (1928).

(³) H. LORENZ: *Zeits. Phys.*, **46**, 558 (1928).

(⁴) F. SEITZ: *Journ. Chem. Phys.*, **6**, 150 (1938).

by means of a model based on the intra-ionic transitions, attributing the *A*, *B* and *C* bands to $^1S_0 \rightarrow ^3P_1$ (spin-orbit allowed), $^1S_0 \rightarrow ^3P_2$ (vibration induced), and $^1S_0 \rightarrow ^1P_1$ (dipole allowed) transitions.

More recently SUGANO⁽⁵⁾, following these assignments, proposed the use of molecular orbitals $a_{1\sigma}, t_{1u}$ which are supposed to be diffused over the neighbourhood of the impurity ion. Using this model he obtained the following relation between the observed positions of the *A*, *B* and *C* absorption bands and the ratio of the dipole strength of the *C* band to that of the *A* band:

$$R = \left| \frac{(W_C - W_A) + \bar{W}}{(W_C - W_A) - \bar{W}} \right|,$$

where

$$\bar{W} = \frac{2}{3} \{ -(W_B - W_0) + [6(W_C - W_0)^2 - 2(W_B - W_0)^2]^{1/2} \}, \quad W_0 = \frac{1}{2}(W_A + W_C),$$

and W_A, W_B, W_C denote the band positions.

To verify the validity of Sugano's formula, FUKUDA *et al.*⁽⁶⁻⁸⁾ compared their experimental results (carried out for several impurity systems involving $\text{In}^+, \text{Ga}^+, \text{Tl}^+, \text{Sn}^{++}$ and Pb^{++}) with those obtained theoretically; remarkable agreement has been found in thallium- and lead-activated phosphors. They also revealed that the *A* band has doublet structure and the *C* band has a triplet one. These structures exist in other thallium phosphors and are even more pronounced in Pb^{++} and Sn^{++} phosphors. Previously, PATTERSON⁽⁹⁾ had measured the absorption and emission spectra on crystals of KCl with a wide range of thallium concentrations at various temperatures, and found that the *A* band could be resolved into Gaussian-shaped bands A_1, A_2, A_3 in order of decreasing energy.

Even more recently, several authors⁽¹⁰⁻¹²⁾ have found that the *A* band is non-elementary and shows at least two sub-bands at room temperature and a third sub-band at higher temperatures. Experimental data indicate that these results should be ascribed, in the first instance, to the splitting of the excited state of the centre due to the dynamical Jahn-Teller effect⁽¹³⁾. Upon this framework TOYOZAWA and INOUE⁽¹⁴⁾, taking account of the lattice vibrations

(5) S. SUGANO: *Journ. Chem. Phys.*, **36**, 122 (1962).

(6) A. FUKUDA: *Science of Light*, **13**, 64 (1964).

(7) A. FUKUDA, S. MAKISHIMA, T. MABUCHI and R. ONAKA: *Journ. Phys. Chem. Solids*, **28**, 1763 (1967).

(8) T. MABUCHI, A. FUKUDA and R. ONAKA: *Science of Light*, **15**, 79 (1966).

(9) D. PATTERSON: *Phys. Rev.*, **119**, 962 (1960).

(10) M. F. TRINKLER and I. K. PLYAVIN: *Phys. Stat. Sol.*, **11**, 277 (1965).

(11) N. N. KRISTOFFEL: *Optics Spectr.*, **22**, 36 (1967).

(12) W. U. WAGNER: *Zeits. Phys.*, **181**, 143 (1964).

(13) H. JAHN and E. TELLER: *Proc. Roy. Soc., A* **161**, 220 (1937).

(14) Y. TOYOZAWA and M. INOUE: *Journ. Phys. Soc. Japan*, **21**, 1663 (1966).

around the impurities, have calculated the shapes of this band and have given a detailed explanation of these experimental facts.

In the present paper we study the effect of an electric field upon the *A* absorption band and on the consequent emission spectra of KBr-Tl containing a small amount of thallium ions. The measurements were performed at various temperatures and as function of the magnitude of the electric field by the modulation technique described in previous papers⁽¹⁵⁾.

We find a triplet structure of the *A* band and a quadratic Stark effect; the measurements point out also that there are two different centres responsible for the emission. Preliminary results have been published elsewhere^(16,17).

2. - Experimental techniques.

Single crystals of potassium bromide containing different concentrations of thallium were grown from the melt by the Kyropoulos method in air. The thalious ions were also introduced into the crystal by heating the latter at various temperatures in a quartz tube, previously evacuated, in the atmosphere of saturated thallium metal vapour⁽¹⁸⁾.

The size of the samples was $(10 \times 1 \times 0.5)$ mm³ for absorption measurements and $(10 \times 10 \times 1.5)$ mm³ for emission ones. Owing to their hygroscopic nature the crystals were cleaved in a dry atmosphere and then put in an evacuated chamber where they were slowly heated to 100 °C for three days before each measurement.

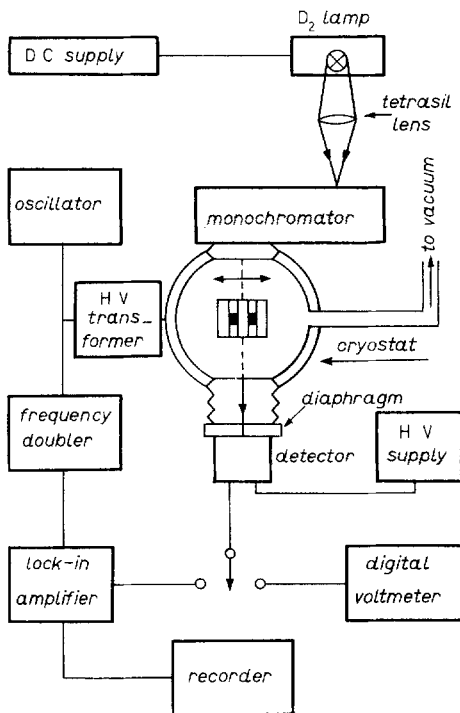


Fig. 1. - Block diagram of the experimental arrangement.

⁽¹⁵⁾ S. BALLARÒ, A. BALZAROTTI and V. GRASSO: *Phys. Lett.*, **23**, 405 (1966); *Nuovo Cimento*, **51 B**, 303 (1967).

⁽¹⁶⁾ V. GRASSO and G. SAITTA: *Phys. Rev. Lett.*, **22**, 522 (1969).

⁽¹⁷⁾ U. GIORGIANNI, V. GRASSO and P. PERILLO: *Phys. Rev. Lett.*, to be published.

⁽¹⁸⁾ T. TAMAI: *Journ. Phys. Soc. Japan*, **16**, 2459 (1961).

The electro-absorption measurements have been done at liquid-nitrogen temperature using the experimental apparatus shown in Fig. 1.

To measure the absorption coefficient the same apparatus has been used as a normal photometer. For cooling the samples a conventional metal cryostat was used. A beam of light from a double-prism Leiss monochromator was focused onto the sample by a tetrasil lens. The crystal holder was planned with particular attention to avoid electrostrictive strains of the specimen with a resulting mechanical chopping of the light.

Light was modulated by an electric field ($2 \cdot 10^4 V_{r.m.s.}/cm$; $\nu = 80$ Hz) applied to the crystal normally to the radiation direction by a stainless-steel electrode embedded in araldite while the crystal holder acted as a second electrode. A pure KBr crystal was used as reference and the transmitted light modulated by the field was detected by a RCA 1P28 photomultiplier and the signal was fed to a lock-in amplifier tuned to twice the frequency of the field. The output of the lock-in amplifier was registered on a Varian recorder.

In emission the electric field was applied in the same direction of the excitation light by an aluminium evaporated grating electrode on a surface of the sample (10×10) mm². The intensity of emission was measured at right angles to the incident beam. The amplified modulation is detected with the same phase-sensitive technique used in absorption.

3. - Experimental results.

A typical absorption curve of the *A* band at 80 °K is shown in Fig. 2, while the modulated absorption spectrum is reported, as a function of the energy of the photons, in Fig. 3 where one can observe the structure of the *A* band. This structure is made clearer in Fig. 4 where the expression of $\Delta K + K$ is reported *vs.* photon energy. ΔK has been arbitrarily multiplied by a factor 10^4 to enable it to be compared with the absorption coefficient *K*. In this Figure the *A*-band resolution into three sub-bands can be noted clearly. These three sub-bands are already visible in the modulated absorption spectrum shown in Fig. 3, where one observes three negative peaks at 4.80, 4.86 and 4.91 eV

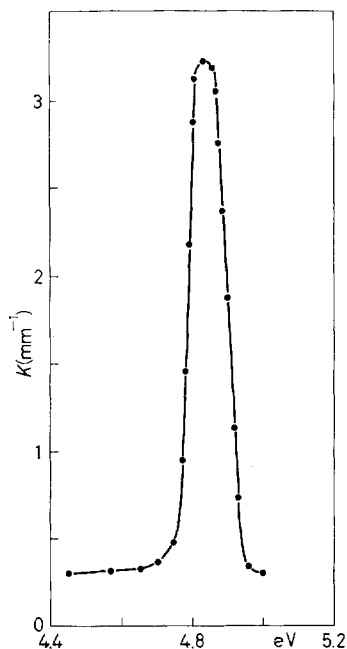


Fig. 2. - Absorption spectrum of the *A* band in KBr-Tl at 80 °K.

respectively. The origin of this strong negative change may be understood if one supposes that every Gaussian forming the *A* band, on account of the external perturbation, is subject to an increase in its half width and to a lo-

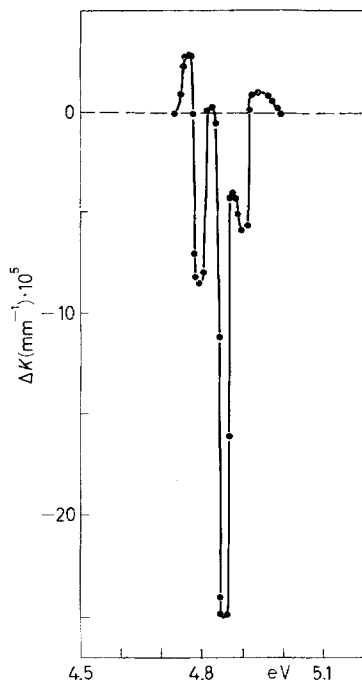


Fig. 3. — Change of the absorption coefficient of the *A* band in KBr-Tl vs. photon energy due to an applied electric field ($2 \cdot 10^4$ V_{r.m.s.}/cm).

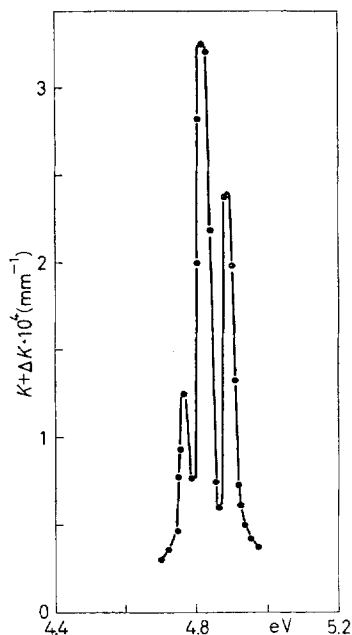


Fig. 4. — $K + \Delta K$ line shape as a function of the photon energy.

wering in the peak as shown in Fig. 5. On the basis of this assumption at the maximum of absorption corresponds a negative variation of the absorption coefficient while on the sides there are some positive changes. The resulting overlapping will give rise to the observed modulated spectrum of Fig. 3.

The emission spectra for *A*-band excitation are shown in Fig. 6. At 300 °K the emission consists of two bands centred at 3.99 and 3.54 eV, while upon cooling to 80 °K the bands at 3.99 and 3.54 eV shift to 4.06 and 3.46 eV respectively. In the latter case both bands show approximately Gaussian shape. At 300 °K the area of the lower-energy emission band (E_2) is 1.6 times greater than the area of the higher-energy emission band (E_1). At 80 °K the E_2 band area is 3 times greater than the E_1 band area. On comparing the area of the bands at the two temperatures it was noted that the E_1 area is

reduced to half when the temperature changes from 300 °K to 80 °K, while the E_2 area does not vary appreciably. The decreasing of the E_1 band area together with the temperature, found by us, is in agreement with the results obtained by TAMAI and

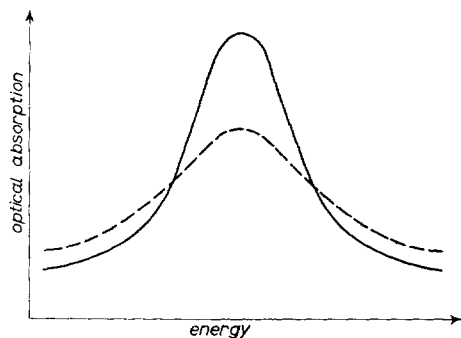


Fig. 5. - Second-order moment variation owing to an external perturbation.

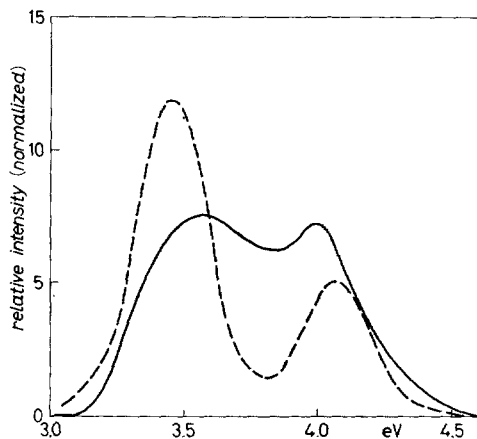
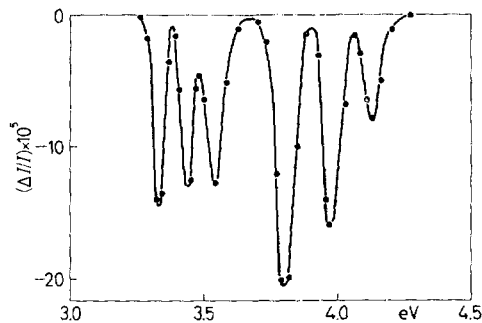


Fig. 6. - Emission spectra of KBr:Tl at — 300 °K and --- 80 °K upon excitation in the A band.

MATSUI⁽¹⁹⁾ and not with those of DONAHUE and TEEGARDEN⁽²⁰⁾.

The relative change $\Delta I/I$ vs. photon energy is shown in Fig. 7 where one can observe a complex structure. The three peaks (3.33, 3.44, 3.54 eV) show a triplet structure similar to that observed in Fig. 3 for the spin-orbit allowed transition $^1S_0 \rightarrow ^3P_1$.

Fig. 7. - Relative change of KBr-Tl emission upon excitation in the A band vs. photon energy due to an applied electric field ($2 \cdot 10^4$ V_{r.m.s.}/cm), 80 °K.



4. - Discussion of the results.

TOYOZAWA and INOUE have described the electron-lattice interaction in the A band in the absence of external fields and have found that the linear interaction splits this band into three components but the quadratic A - B

⁽¹⁹⁾ T. TAMAI and E. MATSUI: *Journ. Phys. Soc. Japan*, **16**, 1489 (1961).

⁽²⁰⁾ J. M. DONAHUE and K. TEEGARDEN: *Journ. Phys. Chem. Solids*, **29**, 2141 (1968).

coupling through the T_{2g} modes superposes two components of the A band.

The triplet structure observed by us may be ascribed to electric-field-induced separation of the remaining degeneracy. The linear dependence of $\Delta K/K$ at 4.86 eV upon the square of the electric field shown in Fig. 8 seems

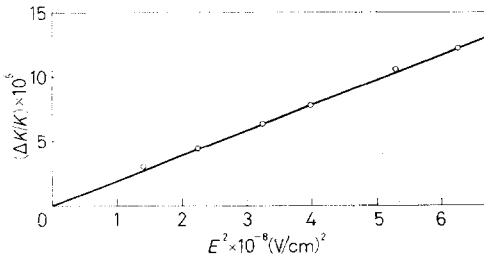


Fig. 8. — Dependence of $\Delta K/K$ on the square field strength at 4.86 eV.

to be due to a Stark effect as has been found in colour centres of alkali halides by several authors^(21,22). At variance from the latter authors' results, we observe that the zeroth moment is not conserved but in some way decreases (Fig. 3). This result is in disagreement with the theory of HENRY, SCHNATTERLY and SLICHTER⁽²³⁾, who described the changes in the optical absorption band in terms of the changes in the moments of the line-shape function that

occur when an external perturbation is applied. They found, neglecting the mixing of nondegenerate electronic states by the lattice and the applied perturbation, that the area of the band remains constant and the changes in the first and second moments are independent of the electron-lattice interaction. The moments are defined as follows:

the zeroth moment (« area ») is $A = \int f(E) dE$;

the first moment (« centre of gravity ») is $\langle E \rangle = \bar{E} = A^{-1} \int E f(E) dE$.

All higher moments, measured about \bar{E} , are defined by

$$\langle E^n \rangle = A^{-1} \int (E - \bar{E})^n f(E) dE.$$

The second moment $\langle E^2 \rangle$ measures the spread of the band. In the presence of an external electric field, perturbation theory shows that the zeroth and the first moments remain unchanged. On the other hand, our experimental results of Fig. 3 and Fig. 7 indicate a remarkable decrease of area. This result can be explained by the assumption that an oscillator strength transfer between the

⁽²¹⁾ G. CHIAROTTI, U. M. GRASSANO and R. ROSEI: *Phys. Rev. Lett.*, **17**, 1043 (1966).

⁽²²⁾ C. R. RHYNER and J. R. CAMERON: *Phys. Rev.*, **169**, 710 (1968).

⁽²³⁾ C. H. HENRY, S. E. SCHNATTERLY and C. P. SLICHTER: *Phys. Rev.*, **137**, A 583 (1965).

A band and the other absorption bands *B* and *C* occurs. Such interpretation seems the most convincing and measurements in this direction are being done.

Concerning the decrease of area in the modulated emission spectrum another explanation is possible as due to the quenching of luminescence by electric field. In fact DENKS⁽²⁴⁾, investigating conductive and nonconductive electronic excitations in thallium-activated alkali iodide crystals, has found that the influence of an external electric field produced a transient suppression of the emission. He attributed such an effect to the removal of the quasi-free electron cloud by the field, decreasing therefore the number of radiative recombinations, when one considers the small penetration depth of the exciting radiation into the crystal and the remarkable mobility of quasi-free electrons compared to the mobility of quasi-free holes. This is in agreement with POLOGRUDOV⁽²⁵⁾, who observed that an alternating electric field affects the luminescence of a KI-Tl phosphor excited in the activator absorption bands.

The observed temperature dependence shown in Fig. 6 seems to indicate that the centre responsible for the high-energy emission consists of a level which is populated at higher temperatures by thermal transition from another excited state.

DONAHUE and TEEGARDEN base their suggested identification of the two emitting centres essentially on their observed temperature dependence of the two emission bands. This is in disagreement with the present results. The emission mechanism is probably the same as proposed by DONAHUE and TEEGARDEN, except that, on the basis of our observed temperature-dependence of the intensities and of our electro-absorption and electro-emission results, we believe that the lower-energy emission must be attributed to the $^3P_1 \rightarrow ^1S_0$ transition on the thallos ion. The high-energy structure, whose origin is not yet clear, probably arises from a centre different from the centre responsible for the low-energy emission. Furthermore, following DONAHUE and TEEGARDEN⁽²⁰⁾, it is possible to attribute the high-energy emission to an exciton state perturbed by an adjacent thallos ion. Indeed, as reported by WOOD⁽²⁶⁾, account of the coincidence of two emission lines of alkali halide crystals containing V_K centres with exciton luminescence of the corresponding pure crystals, one can suppose that the V_K centre, capturing an electron, forms a centre which has states indistinguishable from those of the exciton. So, an ionic crystal, excited into an exciton state, relaxes to a final state, before emission, consisting of a V_K centre plus a bound electron. The V_K centre is a halogen molecule-ion, X_2^- , oriented along the $\langle 110 \rangle$ axes of the crystal. V_K centres are normally

(24) V. P. DENKS: *Sov. Phys. Solid State*, **8**, 1177 (1966).

(25) V. V. POLOGRUDOV and E. E. PENZINA: *Izv. Akad. Nauk. SSSR, Ser. Fiz.*, **29**, 497 (1965).

(26) R. F. WOOD: *Solid-State Comm.*, **4**, 39 (1965).

produced by X-ray irradiation at low temperatures and the rate of production is strongly increased if the crystals contain additional impurity ions such as Pb^{++} , Tl^+ , etc. There is, however, a difference, as pointed out by DONAHUE and TEEGARDEN (²⁰), between a $V_{\mathbf{x}}$ centre located randomly in an alkali halide crystal and a $V_{\mathbf{x}}$ centre which has a Tl^+ ion immediately adjacent to it. In fact, the former case leads to intrinsic emission due to the normal exciton states, and the latter leads to the emission due to perturbed exciton states.

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RIASSUNTO

Usando la tecnica delle piccole modulazioni, si è studiato l'effetto di un campo elettrico esterno sulla banda A di assorbimento e sull'emissione luminescente per eccitazione nella stessa banda del KBr drogato con tallio. Si è osservata una struttura di tripletto e una dipendenza lineare della variazione del coefficiente d'assorbimento dal quadrato del campo elettrico, dovuta ad un effetto Stark. Lo spettro di emissione ha mostrato l'esistenza di due centri differenti responsabili dell'emissione. È stata anche osservata, sia in assorbimento che in emissione, una diminuzione del momento di ordine zero, che può essere attribuita ad un trasferimento della forza dell'oscillatore dalla banda A alle altre bande di assorbimento oppure ad un'estinzione della luminescenza dovuta al campo elettrico.

Поглощение и излучение KBr с присадкой таллия во внешнем электрическом поле.

Резюме (*). — В статье сообщаются результаты измерений влияния электрического поля на поглощение и на люминесценцию из-за возбуждения в A зоне кристаллов KBr , активированных таллием. Поличена триплетная структура зоны A , и экспериментальные результаты также обнаруживают квадратичный Штарк-эффект. Измеренный спектр излучения указывает, что существуют два различных центра, ответственных за люминесценцию.

(*) *Переведено редакцией.*