

THE TETRAGONAL SYMMETRY OF THE Pb⁺⁺-CENTRE IN KCl

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Synopsis

The polarization characteristics of the KCl:Pb phosphor are investigated. The measurements are explained with a configuration coordinate model. With the assumption that the Pb⁺⁺-centre has the symmetry 4mm, the first excited state of the Pb⁺⁺-ion ³P₁ will be split into two sublevels with *E*- and *A*₂-symmetry. Absorption occurs between the ground state and the two excited sublevels at 4.49 eV and 4.53 eV. Emission occurs only from the lowest sublevel with *E*-symmetry. The model proposed here is compared with the model proposed by Trinkler.

Introduction. Alkali halides activated with the homologous series of mercury-like ions have been studied extensively, especially those with Tl⁺. A recent review can be found in ref. 1. Nevertheless the symmetry and structure of the centres is not cleared completely. It seemed therefore very useful to us to study one of these phosphors, KCl:Pb, with a differential polarimeter. With this apparatus it is possible to measure very small changes in the polarization degree of the emitted light and, as will be shown, we could detect two sublevels of the first excited state of the Pb⁺⁺-ion.

Experimental. Single crystals of KCl:Pb were obtained from Dr. K. Korth, Kiel, West-Germany. The Pb⁺⁺-concentration was according to the manufacturer 10⁻³ molar fraction. No precipitation was observed with the optical microscope. The samples had {100} faces and were cleft from a larger block.

After the preparation the samples were annealed at 630°C for 20 min and then slowly cooled down to room temperature at a rate of about 1°C/min. We used as controller a Leeds and Northrup Speedomax H recorder with a 2-action D.A.T. control unit for cam-type programme control, and as furnace a 400 W Heraeus furnace. All stresses induced during cleaving had vanished after annealing. As the faces of the crystals were thermally etched at temperatures above 600°C, special precautions had to be taken to avoid the damage of the optical surfaces. We placed the crystals with the faces on flat, polished quartz plates.

For measuring the various spectra we used a differential polarimeter. The apparatus was a slightly altered version of the differential polarimeter described by Vrehen²⁾. For further details we refer to his description.

The excitation and polarization spectra, the intensity and the polarization degree of the emitted light as a function of the photon energy of the exciting light, and the polarization diagram were made with the arrangement presented in fig. 1. The ultraviolet radiation from a deuterium lamp (Hanau D60R) passes through a monochromator and is linearly polarized by a polarizing filter (Polacoat PL40) with variable azimuth. The monochromatic radiation is focused on the sample. The luminescence is focused on the slit of the polarimeter.

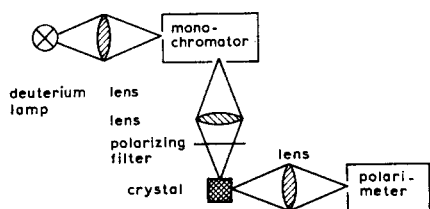


Fig. 1. Optical arrangement for measuring the excitation and polarization spectra and the polarization diagram.

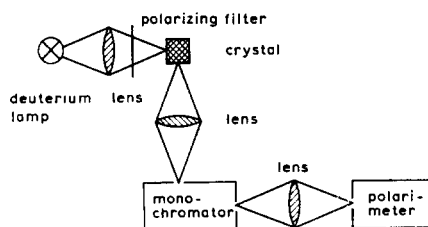


Fig. 2. Optical arrangement for measuring the emission and polarization spectra.

We also measured the emission and polarization spectra, the intensity and the polarization degree as a function of the photon energy of the emitted light, with the arrangement given in fig. 2. In this case the crystal is excited with unfiltered, linearly polarized radiation from a deuterium lamp. The luminescence radiation passes through a monochromator and is focused on the slit of the polarimeter. The results have to be corrected for the instrumental polarization of the monochromator. This influences unfavourably the accuracy of the results.

In the arrangement of fig. 1 and fig. 2 we used an optical filter (Jena UG12, 4 mm thick) in the polarimeter to eliminate possible stray light.

The sample orientation is illustrated in fig. 3. The crystal is excited by light incident along the [100] axis, the detection apparatus is placed along the [010] axis. The angle between the electric vector of the incident exciting light and the [001] direction of the crystal is α , the angle between the electric vector of the detected light and the [001] direction is β . The angle β is used only in connection with the polarization diagram. We define the polarization P of the detected light as:

$$P = \frac{I_{001} - I_{100}}{I_{001} + I_{100}},$$

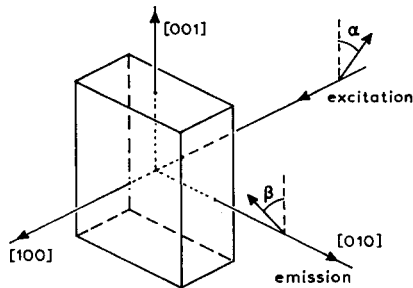


Fig. 3. The directions of the exciting and the emitted light with respect to the crystal directions. The angle between the electric vector of the exciting light and the [001] direction is α , the angle between the electric vector of the detected light and the [001] direction is β .

where I_{001} is the intensity of the light with the electric vector along [001] and I_{100} the intensity with the electric vector along [100].

Results. In fig. 4 the excitation and the polarization spectra are given. The exciting light was vertically polarized ($\alpha = 0$). As it was impossible to measure the absolute value of the polarization degree with the polarimeter, we determined at which photon energy the polarization degree of the emitted light was the same for vertically and horizontally polarized exciting light. The polarization degree was not a function of the photon energy in the

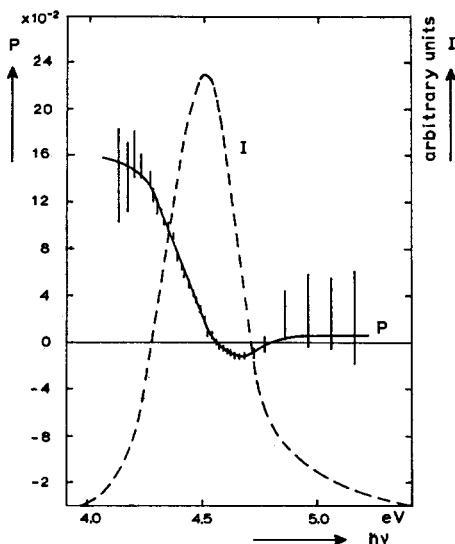


Fig. 4. The excitation and polarization spectra, the intensity and the polarization degree of the emitted light as a function of the photon energy of the exciting light.

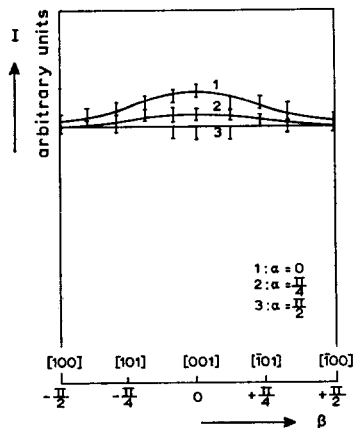


Fig. 5. The polarization diagram. The energy of the exciting light is 4.37 eV.

latter case. We therefore assume as a calibration, that the polarization degree is zero if the exciting light is horizontally polarized.

We also measured the intensity of the emitted light as a function of β with α as a parameter. The results at a photon energy of 4.37 eV are given in fig. 5. At 4.64 eV the polarization degree was too low to make reliable measurements.

The emission and the polarization spectra are given in fig. 6. The crystal was excited by vertically polarized light in this case too ($\alpha = 0$). The absolute value of the polarization degree was determined as above.

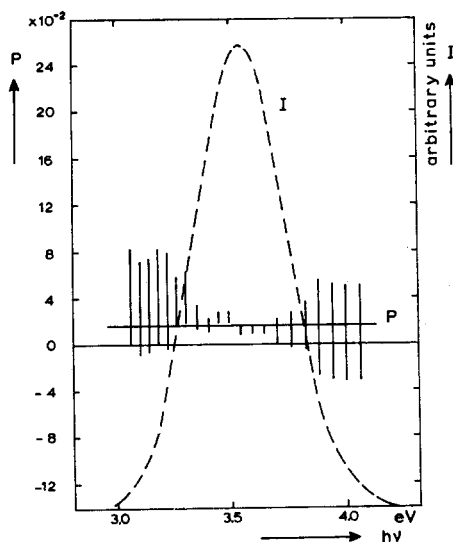


Fig. 6. The emission and polarization spectra, the intensity and the polarization degree as a function of the photon energy of the emitted light.

Discussion. The transitions responsible for the measured effects correspond to the $^1S_0 \leftrightarrow ^3P_1$ transitions of the free lead ion¹).

The results of fig. 4 can be compared with the results of Zazubovich and coworkers³). Their results are mainly the same as ours, but as their method was not sensitive enough they could not observe any negative polarization degree at high photon energies. The excitation and emission data are in agreement with those of previous workers⁴), except for the fact that we found some indication of a very weak absorption and excitation band at about 4.95 eV.

We made an analysis⁵⁾¹⁷) of the behaviour of linear (π) and circular (σ), electric (e) and magnetic (m) dipoles in the experimental arrangement given in fig. 1 to explain the polarization diagram of fig. 5. It follows that, independent of the character, for oscillators oriented along the $\langle 100 \rangle$ axes only one curve, for oscillators along the $\langle 110 \rangle$ axes two curves, and for

oscillators along the $\langle 111 \rangle$ axes all three curves are straight lines. So it follows from fig. 5 that the oscillators are oriented along the $\langle 100 \rangle$ axes.

In table I possible symmetries of divalent cation impurities in the cubic KCl lattice are given. In addition to the nine symmetries there is also the possibility of a dynamical Jahn-Teller effect. But we think that this effect will not be pronounced at room temperature¹³). The only symmetry that seems to account for all effects is the tetragonal one caused by an associated vacancy.

TABLE I

Possible symmetries of divalent cation impurities M^{++} in the KCl-lattice				
System	Structure of the centre	Pointgroup	Oscillators	Ref.
Cubic	M^{++} substitutionally placed at a K^+ -site	$\begin{matrix} 4 & \bar{3} & 2 \\ m & & m \end{matrix}$	$\langle 100 \rangle$	
Tetragonal	M^{++} and Jahn-Teller distortion of the surrounding lattice	$\begin{matrix} 4 & 2 & 2 \\ m & m & m \end{matrix}$	$\langle 100 \rangle$	5
	M^{++} and a K^+ -vacancy at an n.n.n. site	$\begin{matrix} 4 & m & m \end{matrix}$		6
	M^{++} and a divalent anion impurity substitutionally placed at an n.n. Cl^- -site	$\begin{matrix} 4 & m & m \end{matrix}$		7
Trigonal	M^{++} and Jahn-Teller distortion of the surrounding lattice	$\begin{matrix} \bar{3} & 2 \\ & m \end{matrix}$	$\langle 111 \rangle, \{111\}$	8
	trimer consisting of three pairs of M^{++} and a K^+ -vacancy at an n.n. site	$\begin{matrix} 3 & m \end{matrix}$		9
	M^{++} and an interstitial monovalent anion impurity	$\begin{matrix} 3 & m \end{matrix}$		10
Orthorhombic	M^{++} and a K^+ -vacancy at an n.n. site	$\begin{matrix} m & m & 2 \end{matrix}$	$\langle 100 \rangle, \langle 110 \rangle$	11
Monoclinic	M^{++} near an edge dislocation	$\begin{matrix} m \end{matrix}$	$\langle 100 \rangle, \langle 110 \rangle$	12

1. From fig. 4 it is clear that within the centre there must be two inequivalent (absorbing or emitting) oscillators. This is not the case in a cubic centre.
2. A static Jahn-Teller effect is present only if the state of the ion is degenerated. During excitation the ions of the lattice have the symmetry corresponding to the ground state of the centre (Franck-Condon principle). The ground state, however, is isotropic. So there cannot be a static Jahn-Teller effect during excitation.
3. If all lead ions form complexes with divalent anion impurities, the concentration of the latter has to be as high as the concentration of the lead ions. This is unlikely.
4. The trigonal centres have no oscillators along the $\langle 100 \rangle$ axes of the crystal, according to the selection rules for optical transitions¹⁴).

5. The orthorhombic centre cannot have a piezospectroscopic effect (which has actually been observed¹⁵) for the degeneracy of the levels is lifted, and the centre cannot orient itself at room temperature under the action of an uniaxial stress field¹¹)¹⁶).
6. Only 6 ppm lead can produce saturation of the occupation of sites near the dislocations¹²). As the lead concentration in our crystals is much higher, most Pb⁺⁺-centres must have another symmetry.

Thus the Pb⁺⁺-centre should have the tetragonal symmetry that is caused by a K⁺-vacancy on a next-nearest neighbour place. The pointgroup is 4mm, and six different orientations in the lattice are possible.

From the polarization characteristics and knowing the symmetry of the centre we may conclude to the multipole character of the luminescing oscillators¹⁷). The polarization diagram of fig. 5, determining the low-energy absorption, can be explained in two different ways. The absorbing and emitting oscillators can be linear electric dipoles ($\pi_e\pi_e$) or they can be circular electric dipoles ($\sigma_e\sigma_e$). The negative polarization degree at photon energies near 4.65 eV (fig. 4) leads to four possibilities for the multipole character: $\sigma_e\pi_e$, $\pi_e\sigma_e$, $\pi_e\pi_m$ or $\sigma_e\sigma_m$. A combined magneto-electric oscillator, however, is not likely¹⁴). So the high-energy absorption must have the character $\sigma_e\pi_e$ or $\pi_e\sigma_e$. The emission and polarization spectra of fig. 6 seem to indicate that all emitting oscillators within a centre have the same character.

From these conclusions we arrive at a model for the Pb⁺⁺-centre in KCl. The Pb⁺⁺-ion is substitutionally placed in the KCl-lattice. On a next-nearest neighbour place there is a K⁺-vacancy. In this tetragonal symmetry the degenerated ³P₁-state is split into a doublet state with *E*-symmetry and into a singlet state with *A*₂-symmetry. Which of these states is the lowest cannot be concluded from the measurements. But in this excited *P*-state one of the two electrons is in a *p*-orbital. In the singlet state this orbital lies along the axis through the Pb⁺⁺-ion and the vacancy, in the doublet state the orbital lies in the plane perpendicular to the axis, fig. 7. The K⁺-vacancy is negatively charged with respect to the lattice and repulses the electron. Therefore it is likely that the doublet state is the lowest one. Moreover, the curves representing the states in the configuration coordinate model, should cross each other near the minimum of the highest state. Now if the centre is excited to the *E*-state, the centre retains its symmetry and it falls back to the ground state under the emission of light with the same polarization as the exciting light. On the other hand, if the centre is excited to the *A*₂-state it relaxes to the minimum of the *E*-state and the polarization of the centre is not preserved, as has been found. The configuration coordinate model is schematically drawn in fig. 8.

The polarization degree of the emitted radiation is in the case of the $\sigma_e\sigma_e$ oscillator $P_1 = \frac{1}{3}$, and of the $\pi_e\sigma_e$ oscillator $P_2 = -1$, as follows from a

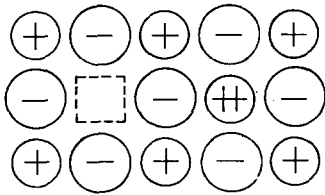


Fig. 7. Model of the Pb⁺⁺-centre in KCl. The charge compensation is afforded by a K⁺-vacancy on a next nearest neighbour place.

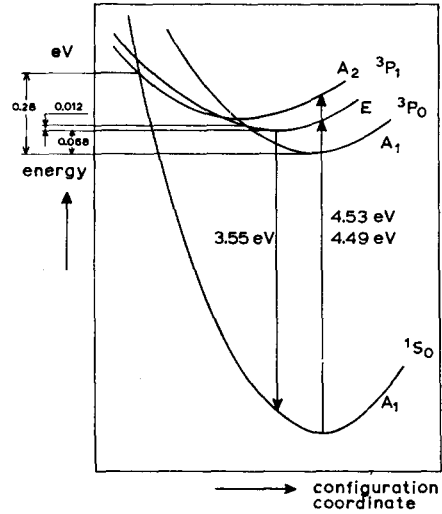


Fig. 8. Configuration coordinate model of the Pb⁺⁺-centre in KCl. The metastable ³P₀-level does not follow from our measurements, but was found by Trinkler. The energy barrier of 0.28 eV between the excited levels and the ground state was determined by Kaifu.

simple computation. The polarization degree of the emitted light at a fixed photon energy is:

$$P = \frac{P_1 I_1 + P_2 I_2}{I_1 + I_2} = \frac{\frac{1}{3} I_1 - I_2}{I_1 + I_2} \tag{1}$$

where I_1 is the intensity of the emitted light after the transition $A_1 \rightarrow E$ and I_2 the intensity of the emitted light after the transition $A_1 \rightarrow A_2$ (followed by $A_2 \rightarrow E$).

It follows:

$$I_1 = \frac{3}{4}(P + 1)(I_1 + I_2) \tag{2}$$

P and $(I_1 + I_2)$ are given by the measurements, so it is possible to compute the absorption band $A_1 \rightarrow E$. The second absorption band follows immediately from $(I_1 + I_2)$. In fig. 9 the excitation spectrum is decomposed into the two bands. The bands have a Gaussian shape and are symmetrical. The characteristic of the bands are given in table II.

The configuration coordinate model proposed by us can be compared with the model proposed by Trinkler¹⁸). In Trinkler's there are at least two excited levels: the ³P₁ and the ³P₀ level. The latter is a metastable one and acts as a trap for the ions. Within the lifetime of the excited state there

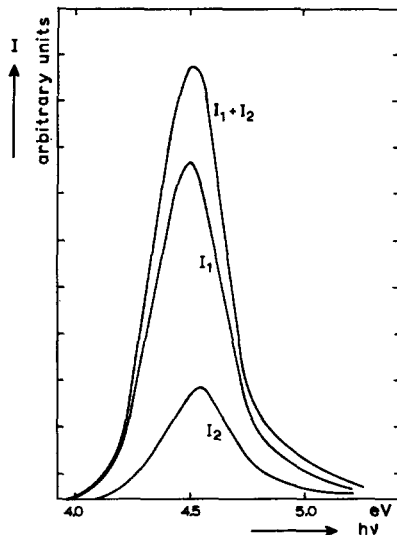


Fig. 9. The excitation band, taken from fig. 4, decomposed into two bands with peaks at 4.49 eV and 4.53 eV.

TABLE II

Band characteristics of the two bands, composing the A -band in $\text{KCl} : \text{Pb}$		
Optical transition	Peak energy (eV)	Half-width (eV)
$A_1 \rightarrow E$	4.49	0.36
$A_1 \rightarrow A_2$	4.53	0.33

is a rapid redistribution of the ions over the 3P_1 - and 3P_0 -levels according to the temperature. Emission occurs only from the 3P_1 -level. Trinkler could not detect any splitting of the 3P_1 -level, but suggested that the level may be split significantly such, that both levels will cross each other near the minimum of the highest sublevel, and emission occurs from the lowest level only. However, the splitting may also be very small.

Our model and Trinkler's model supplement each other. The results of Trinkler are also shown in the configuration coordinate model of fig. 8.

Conclusions.

1. The optical properties of a centre are not fully described by the absorption, excitation and emission data alone. The polarization characteristics are shown to yield useful additional information.
2. The Pb^{++} -centre in KCl should have the tetragonal symmetry $4mm$, caused by a K^+ -vacancy on a next-nearest neighbour place.

3. The 3P_1 -level of the Pb^{++} -ion in KCl is split in the tetragonal symmetry into a E - and a A_2 -state.
4. The main absorption band (A -band) of KCl : Pb is composed of two Gaussian and symmetrical bands with maximum absorption at 4.49 eV and 4.53 eV.

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