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Luminescence of Lead Chloride and Lead Bromide Single Crystals: I. The excitation and emission spectra

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The luminescence of very pure $PbCl_2$ and $PbBr_2$ single crystals has been studied at liquid nitrogen and liquid helium temperature. At 10 K, $PbCl_2$, as well as $PbBr_2$, exhibits three emission bands in the spectral region investigated, viz., one in the ultraviolet part of the spectrum, a second one in the blue and a third one in the red. In addition, $PbCl_2$ shows a violet emission at 5 K. If, at 80 K, $PbCl_2$ and $PbBr_2$ crystals were exposed to ultraviolet radiation for one hour or more, a yellow emission appeared.

Thin film absorption spectra of both lead halides are discussed. The band in the low energy region of the absorption spectra is attributed to the creation of a cation exciton.

The excitation spectra of the different emissions have been measured. The thin film absorption spectra and the luminescence excitation spectra are strongly correlated. All emissions are preferentially excited in the low energy region of the absorption spectrum, i.e., the region of the cation exciton absorption band. The ultraviolet emission of both lead halides is discussed and attributed to the recombination of cation excitons.

1. Introduction

$PbCl_2$ and $PbBr_2$ decompose under exposure to ultraviolet radiation at room temperature. Verwey (*1*) investigated the photochemical decomposition on pure single crystals and formulated a qualitative mechanism for this process. Below room temperature, however, the rate of the photolysis process decreases, and photoluminescence is observed. With reference to this phenomenon we carried out the present investigation.

The optical properties of solid $PbCl_2$ and $PbBr_2$ have not been studied thoroughly in the past. Some thin film absorption spectra (*2–5*) and luminescence measurements on powders and water-grown crystals (*5–11*) are known in the literature. The results of these investigations are not in good agreement and appear to depend on the presence of water. Because of the hygroscopic character of $PbCl_2$ and $PbBr_2$ our single crystals were prepared with special care to avoid adsorption and inclusion of water.

$PbCl_2$ and $PbBr_2$ have an orthorhombic crystal structure (*12*) with space group D_{2h}^{16} (*Pnma*) and four formula units per unit cell. The point group symmetry at the Pb^{2+} sites is monoclinic, C_s. The lead ions are surrounded by nine halide ions. Two types of halide ions exist, one is surrounded by four and the other by five Pb^{2+} ions.

In 1938 the fluorescence of solid $PbCl_2$ at low temperature was reported for the first time by Randall (*6*). Gobrecht and Becker (*7*) investigated the luminescence of water-grown crystals. The emission spectra under uv excitation at 93 K show a yellow and a green emission band for $PbBr_2$ and a blue one for $PbCl_2$. They concluded that water would be an activator for the luminescence of solid $PbCl_2$ and $PbBr_2$. Sost and Langouet (*8*) measured the excitation spectra of the phosphorescence of water-grown crystals at room and liquid nitrogen temperature. Absorption and emission spectra of water-grown $PbCl_2$ and $PbBr_2$ crystals have been studied by Bettinali and Ferraresso (*9*). The luminescence emission bands measured at 100 K were similar to those of Gobrecht. The emission was ascribed to the presence of a Pb^{2+} ion, associated to a defect. The emission spectra of $PbCl_2$ powder measured by Bohun et al. (*11*) at 78 K exhibit a blue and a yellow band. Preliminary measurements at 5 K on

$PbCl_2$ single crystals (Bridgman technique) by Liidja et al. (*5*) showed an emission in the ultraviolet region of the spectrum. Czeglédy (*10*) observed a blue luminescence on $PbCl_2$ crystals excited with X-rays at liquid nitrogen temperature.

The aim of the present study is to determine the luminescence emissions of $PbCl_2$ and $PbBr_2$ single crystals in the spectral region 220–850 nm, and to formulate the luminescence mechanisms. The main experiments, therefore, are: (a) measurements of the excitation and emission spectra, (b) EPR measurements of luminescence centers, (c) measurements of the luminescence decay time, and (d) quantum efficiency measurements.

The present paper deals with the excitation and emission spectra of lead chloride and lead bromide single crystals at liquid nitrogen and liquid helium temperature. The thin film absorption spectra and the ultraviolet emission spectra of both lead halides are discussed and interpreted.

2. Experimental

(*a*) *Single Crystals*

Single crystals of $PbCl_2$ and $PbBr_2$ were grown in this laboratory from zone-refined material by the Bridgman method. An extended report has been published elsewhere (*13*). The samples were analysed by emission spectroscopy.[1] Results are given in Table I.

TABLE I

IMPURITY CONTENT OF THE CRYSTALS (ppm)

	$PbCl_2$	$PbBr_2$		$PbCl_2$	$PbBr_2$
Li	<1	<1	Si	2	—[b]
Cu	3	<1	Ge	<10	<10
Mg	1	1	Bi	<10	<10
Ag	<0.5	<0.5	Cr	<1	5
Sr	<5	<5	Mn	<1	<1
Ba	<1.5	<1.5	Fe	<1	2
Hg	<3	<3	Co	<3	<3
Ga	<5	<5	Ni	<5	<5
Tl	<50	<50	H_2O[a]	<1	—

[a] I thank Mr. B. Willemsen of this Laboratory who kindly made available the mass spectrometric analyses.

[b] Not measured.

(*b*) *Experimental Setup*

The experimental setup to measure the excitation and emission spectra was built around a liquid helium cryostat (stainless steel). The crystal holder, cooling tubes, and top plate can be rotated around the cooling tube axis. The samples were cleaved perpendicular to and excited parallel with the *c* axis. The emitted radiation was detected at right angles to the exciting beam.

The excitation part of the setup consisted of a high pressure Xenon lamp (XBO 450 W) and a quartz single monochromator (Leiss). For the detection of the emission we used a similar monochromator with flint or suprasil prism and a photomultiplier[2] with a trialkalicathode (EMI 9558 Q and 9658 QB with extended S-20 cathode). After amplification and synchronous detection the signal from the photomultiplier was recorded.

(*c*) *Luminescence Emission Measurements*

The band pass of the emission monochromator for the different emission bands was:

yellow and red bands	0.05 eV
blue	0.02
uv and violet	0.03

The excitation monochromator bandwidth was about 0.1 eV.

A correction was made for the variation of the photomultiplier sensitivity in the range of the emission spectra. This correction was quite large for the lower energy part of the emission spectra (six times larger at 1.72 eV than at 2.41 eV). This correction may have introduced some uncertainty as to the exact shape of the red emission band; the blue and uv bands are situated in regions where the correction was very small.

The emission spectra on a frequency scale are calculated from those on a wavelength scale. For the red emission bands the difference between both plots amounts to 0.02 eV; the differences for the blue and uv bands are less than 0.01 eV.

(*d*) *Luminescence Excitation Measurements*

The excitation spectra were measured at 3.4–6 eV. The band pass of the excitation monochromator for the different excitation spectra was 0.03–0.05 eV. Preliminary experiments were point by point comparisons of the luminescence and exciting intensities. Later on we measured

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[1] Thanks are due to Dr. R. D. Schuiling of the Vening Meinesz Laboratory at Utrecht for these analyses.

[2] Thanks are due to Mr. J. A. ter Heerdt of the Physical Laboratory at Utrecht, for verifying the spectral response of the photomultiplier (9558 Q).

the luminescence intensity as a continuous function of wavelength and made a machine correction for the exciting intensity (the Xenon lamp was stabilized). The two methods supplied similar results.

The emission was detected by a monochromator–photomultiplier combination. The band width of the emission monochromator was about 0.1 eV. We adjusted the emission monochromator in such a way, that the peak of the various emission bands was transmitted.

3. Experimental Results

3.1. *Influence of Water*

Since our crystals were cleaved and prepared in air, it might be possible that hydrolysis products influence the luminescence process. Verwey (*1*) has noted that lead bromide shows a characteristic change after storage in air, which is absent in lead chloride. In the surface layer of the $PbBr_2$ crystals rods, due to hydrolysis, are formed in a distinct direction. To check this the emission of three $PbBr_2$ samples treated in a different way was compared. First, we measured the emission spectrum of a sample prepared as described above at 80 K (10^{-7} Torr), subsequently we cleaved the crystal in vacuum, in such a way that the latter part remained in its position and measured the emission again. Finally, a sample was stored at 475 K during several hours in air saturated with water, after which we measured the emission spectrum under otherwise equal circumstances. After this experiment the sample showed the rods mentioned above. The three samples showed the same emission band: the position of the maximum and the halfwidth did not differ, only the intensity varied a little. These experiments lead us to the conclusion that water vapor from the ambient neither causes nor influences the luminescence of lead bromide.

3.2. *Emission Spectra*

The emission spectra of lead chloride and lead bromide are presented in Figs. 2 and 3.

(*a*) *$PbCl_2$*. The $PbCl_2$ emission spectrum at 10 K consists of three bands (cf. Fig. 1A), viz., one in the uv part of the spectrum (~3.8 eV), a second one in the blue (~2.8 eV) and a third one in the red (~1.8 eV). At 5 K another two emission bands have been observed, viz., a violet (~3.1 eV) and a yellow (~2.2 eV) one; the violet band has not been reported before (cf. Fig. 2A.II). The uv emission is quenched in the temperature region 10–80 K.

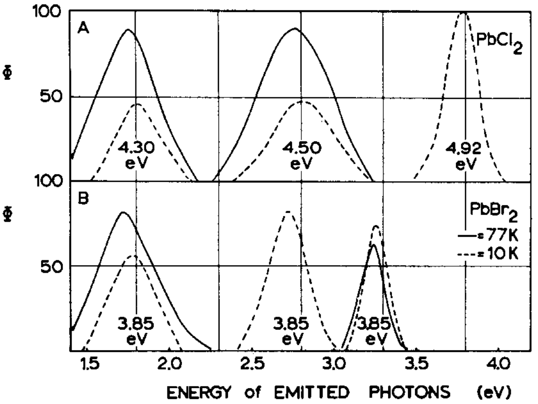

FIG. 1. Spectral energy distribution of the red, blue and uv luminescence of $PbCl_2$ (A) and $PbBr_2$ (B) at 77 and 10 K. Φ is the radiant power (per constant energy interval). The curves of the different emissions have not been plotted to the same scale. The excitation energy of the different emissions is indicated below the curves.

(*b*) *$PbBr_2$*. The $PbBr_2$ emission spectrum at 10 K consists also of three emission bands. These correspond with those of $PbCl_2$ (cf., Fig. 1B). In this case no new bands have been observed in the temperature region 10–5 K. The blue emission is quenched at about 30 K.

(*c*) If $PbCl_2$ and $PbBr_2$ crystals were exposed to uv radiation at 77 K for 1 hr or more, a new emission appeared at the high energy side of the red band (cf. Figs. 2A and 2B). The maxima of the new bands are situated in the yellow part of the spectrum. If such an irradiated $PbCl_2$ crystal was cooled to 5 K the spectrum 2A.II appeared; the intensity of the yellow band, however, was on the increase.

The maxima and the half-widths of the emission bands are summarized in Table II. The following comments are noteworthy on the uv, blue and red emission bands:

(a) From Table II it appears that the half-width of the blue and the red emission band of $PbCl_2$ and the uv and the red band of $PbBr_2$ decreases and, if the crystals are cooled from 77 to 10 K, the maximum of these bands shifts to higher energy.

(b) The half-width of the uv, blue and red $PbBr_2$ emission bands is 60–40% of the half-width of the corresponding $PbCl_2$ bands at the same temperature.

(c) We observed a small shift to lower energy of the uv and blue emission bands if the crystals were irradiated in the tail of the low energy absorption band (cf. Table II).

TABLE II

MAXIMA AND HALF-WIDTHS OF THE EMISSION BANDS OF $PbCl_2$ AND $PbBr_2$ AT 77, 10 AND 5 K

Kind of emission	Excitation energy (eV)		Maxima of emission (eV)		ΔE_{max} (V – IV)	Half-width of the emission bands (eV)		ΔE (VII – VIII)
I	II	III	IV	V	VI	VII	VIII	IX
	77 K	10 K	77 K	10 K		77 K	10 K	
$PbBr_2$								
uv	—	3.70	—	3.21	—	—	0.2	—
	4.05 4.35	3.85 4.10 4.35	3.24	3.27	0.03	0.18	0.16	0.02
Blue	—	3.70	—	2.65	—	—	0.4	—
	—	3.94 4.10 4.57	—	2.72	—	—	0.28	—
Yellow	3.70 3.78 3.95 4.30	—	~2.1	—	—	~0.3	—	—
Red	3.79 3.95 4.30 4.80	3.69 3.85 4.52 4.80	1.76	1.82	0.06	0.40	~0.3	~0.1
$PbCl_2$								
uv	—	4.40	—	3.70	—	—	0.3	—
	—	4.52 4.84 4.95	—	3.78	—	—	0.26	—
Blue	4.30		2.70	—	—	0.6	—	—
	4.41 4.59 4.77	4.41 4.59 4.77	2.76	2.82	0.06	0.54	0.47	0.07
Red	4.16 4.35	4.16 4.35 4.43	1.77	1.82	0.05	0.58	~0.5	~0.1
		5 K		5 K			5 K	
Violet	—	4.26 4.35 4.90	—	~3.2	—	—	—	—
Yellow	—	4.26 4.35	—	~2.2	—	—	—	—

The tail of the low energy absorption band is known to be quite structure sensitive. Excitation in the tail excites the crystals preferentially in regions of strong disorder. It may be that the emission from these regions also shows the effects of this disorder as a shift in the emission energy.

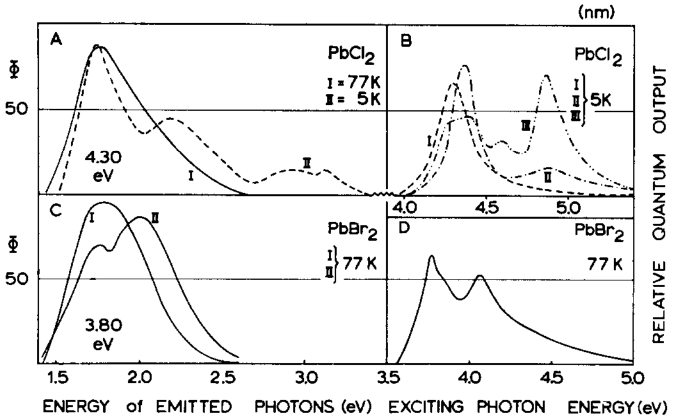

FIG. 2. (A) I. Spectral energy distribution of the red and yellow luminescence of a $PbCl_2$ crystal at 77 K, after a 1-hr uv irradiation. II. Spectral energy distribution of the red, yellow, blue and violet luminescence of $PbCl_2$ at 5 K. (B) Relative excitation spectra of the yellow (I), violet (II) and blue (III) luminescence of $PbCl_2$ at 5 K. (C) Spectral energy distribution of the red and yellow luminescence of $PbBr_2$ at 77 K, after a 1-hr uv irradiation (I) and after 2-hr irradiation (II). (D) Relative excitation spectrum of the yellow luminescence of a $PbBr_2$ crystal at 77 K, after a 2-hr uv irradiation. Φ is defined in the caption of Fig. 1. The excitation energy of the different emission spectra is indicated below the curves.

3.3. *Excitation Spectra*

The excitation spectra of the different emissions of lead chloride at 77, 10 and 5 K are presented in Figs. 2B and 3, the spectra at 77 and 10 K of $PbBr_2$ in Figs. 2D and 4. The excitation spectra were measured at 3.4–6 eV; in the region 5.5–6 eV the same luminescence was present but the intensity was very small.

Theoretically it is possible that the reflectivity anomaly associated with a sharp absorption

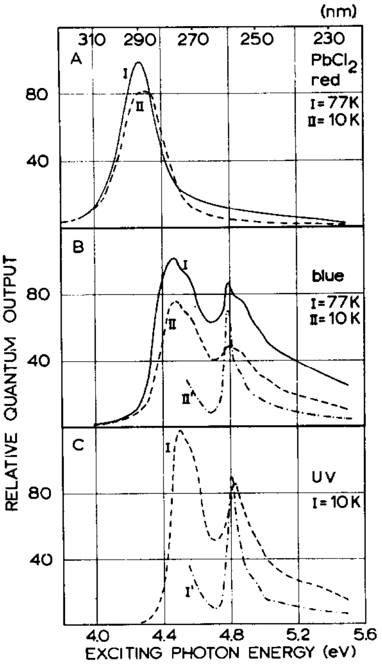

FIG. 3. Relative excitation spectra of the red (A), blue (B) and uv (C) luminescence of $PbCl_2$ at 77 and 10 K. The curves with a prime refer to the identically numbered curves after correction for reflectivity losses.

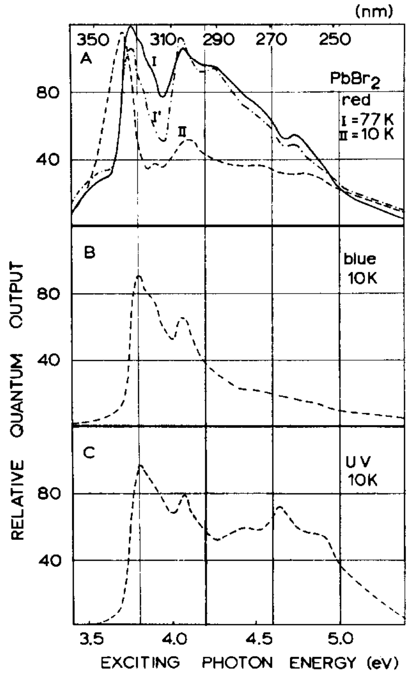

FIG. 4. Relative excitation spectra of the red (A), blue (B) and uv (C) luminescence of $PbBr_2$ at 77 and 10 K. The curve with a prime refers to the identically numbered curve after correction for reflectivity losses.

determines for a large part the excitation spectrum.

The Lorentz theory as well as a quantum mechanical treatment of the optical properties of solids predict that the reflectivity should approach 100% in the region of a strong absorption band (*14*). The excitation spectra of PbCl$_2$ at liquid helium temperature and those of PbBr$_2$[3] at liquid nitrogen temperature were corrected for reflectivity losses (*5*, *40*) (cf. Figs. 3 and 4).

The important features of the excitation spectra of both lead halides, such as the minima on the low energy side and the structure on either side of the dips are still evident.

Unfortunately, the reflectivity spectra of PbCl$_2$ at 77 K and PbBr$_2$ at 10 K are not known at the moment. We assume that the corresponding excitation spectra are also not changed essentially by the reflectivity correction, in view of the slight influence of the correction, mentioned above.

4. Discussion

4.1. Absorption Spectra

4.1.1. General

The optical absorption spectra of the lead halides in the region of the fundamental absorption bands have been investigated by a number of authors (*2–5*). For the investigation of the exciton absorption some of these measurements have been extended to very low temperatures. For the measurements of the absorption spectra very thin specimens must be used because the absorption coefficients of the samples will amount to 10^6 cm^{-1} in the region of the fundamental absorption band. In Fig. 5 we represent the absorption spectra of PbCl$_2$ and PbBr$_2$ at 293 K, at about 90 K and at 5 K (*2–5*).

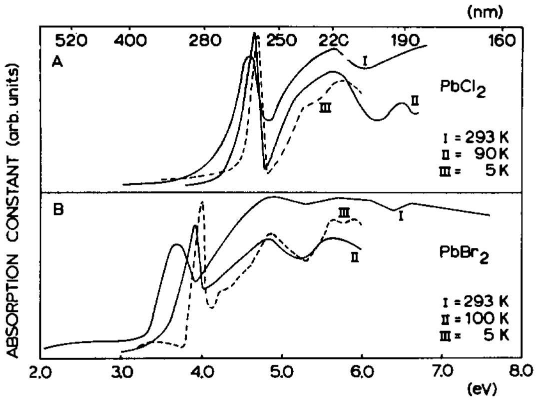

FIG. 5. Relative absorption spectra of thin layers of PbCl$_2$ (A) and PbBr$_2$ (B) at different temperatures, taken from measurements of Fesefeld (A.I and B.I), Best (A.II) and Ilmas (B.II), Liidja (A.III) and (B.III) [Refs. (*2–5*)], respectively.

The peak values of the different absorption bands of PbCl$_2$ and PbBr$_2$ are summarized in Table III up to 6.8 and 6.0 eV, respectively. Column 6 of this table gives the splitting of the peak on the low energy side of the reflectivity spectra measured by Liidja et al. (*5*) and Vos (*40*).

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[3] We are indebted to Mr. K. Vos of this laboratory who kindly made available the PbBr$_2$ reflectivity measurements (*40*).

TABLE III

THE MAXIMA IN THE ABSORPTION SPECTRA AND THE SPLITTING OF THE LOW ENERGY BAND OF THE REFLECTIVITY SPECTRA OF PbCl$_2$ AND PbBr$_2$

	Absorption maxima					Low energy reflectivity maxima
	1	2	3	4	5	6
PbCl$_2$ 90 K eV	4.65	—	5.2	5.70	6.50	—
5 K	4.69	—	5.26	5.76	—	4.716 4.672
PbBr$_2$ 100 K eV	3.90	—	—	4.80	5.64	3.910[a] 3.955
5 K	3.99	4.20	4.50	4.82	5.62 5.90	

[a] At 77 K.

4.1.2. *Exciton Absorption Band*

First we consider the absorption band in the low energy region of the spectra (cf. Table III, column 1). Liidja (*5*) attributed this band to the creation of cation excitons; Best (*3*), to that of anion excitons.

(*a*) *Anion Exciton Model.* It is well known (*16*, *17*) that the low energy absorption band of the alkali halides is ascribed to the creation of anion excitons. These bands exhibit a strong doublet structure (*18*) due to the transition, in atomic notation, $^1s_0 \rightarrow {}^1p_1$ and $^1s_0 \rightarrow {}^3p_1$ (LS coupling).

The absorption spectra of $PbCl_2$ and $PbBr_2$ do not exhibit a splitting of the low energy absorption band. In the reflectivity spectra, however, a splitting of the low energy absorption band is found, with peak separations of 0.044 eV (5 K) for $PbCl_2$ and of 0.045 eV (77 K) for $PbBr_2$ (cf. Table III, column 6). The peak separation of a "halide doublet" is about 3 times larger than the splitting mentioned above for the chloride and ^{3}11 times larger for the bromide (*17*, *18*).

In addition, we would expect two halide doublets of comparable absorption strength as a result of the existence of two types of halide ions in $PbCl_2$ and $PbBr_2$ (cf. Section 1). Neither the absorption spectra, nor the reflectivity spectra exhibit such a "double doublet" structure.

In view of these considerations it seems improbable that the low energy absorption band of $PbCl_2$ and $PbBr_2$ is due to the creation of anion excitons.

(*b*) *Cation Exciton Model.* The atomic analogue of the transition involved is $^1s_0 \rightarrow {}^3p_1$ on Pb^{2+}. This transition is spin-forbidden. As a result of the admixture of higher energy levels (e.g., $^1p_1$) by spin-orbit coupling the spin prohibition is partly removed, whereas at the same time the transition probability of $^1s_0 \rightarrow {}^1p_1$ is reduced.

Table IV gives a survey of the maxima of the $^1s_0 \rightarrow {}^3p_1$ and some $^1s_0 \rightarrow {}^1p_1$ absorption bands of lead-doped alkali halides and some other halides. Columns 1 and 2 of this table represent the coordination number of the cations in the relevant compound. The position of the $^1s_0 \rightarrow {}^3p_1$ absorption band depends only slightly on the host lattice even if the coordination number of the cations changes. The maximum of the low energy absorption band of $PbCl_2$ and $PbBr_2$ corresponds with that of the $^1s_0 \rightarrow {}^3p_1$ absorption band of the chloride and bromide salts, respectively (cf. Table IV). We conclude, therefore, that the low energy absorption band of $PbCl_2$ and $PbBr_2$ is due to the transition $^1s_0 \rightarrow {}^3p_1$ on the divalent lead ion.

Because of the low site symmetry at the Pb^{2+} ions (cf. Section 1) we expect that the three-fold degeneracy of the $^3p_1$ level is completely lifted by the crystal field. As mentioned above the reflectivity spectra exhibit a doublet structure. In fact the Pb^{2+} site shows in rough approximation trigonal symmetry. It may be, therefore, that the separation of two of the three $^3p_1$ sublevels is very small, so that this splitting could not be measured (*5*). Liidja et al. (*5*) calculated the radius of the exciton on Pb^{2+} for $PbCl_2$ (2.2 Å) and for $PbBr_2$ (~4.5 Å) by means of the exciton theory of Wannier (*23*) and Mott and Gurney (*24*).

Summarizing, we conclude that the low energy absorption band of $PbCl_2$ and $PbBr_2$ is due to the creation of Frenkel excitons localized on the Pb^{2+} ions.

TABLE IV

THE MAXIMA OF THE $^1s_0 \rightarrow {}^3p_1$ AND $^1s_0 \rightarrow {}^1p_1$ ABSORPTION BANDS OF SEVERAL LEAD-DOPED HALIDES AND $PbCl_2$ AND $PbBr_2$ AT ROOM TEMPERATURE

	Coord.	$^3p_1$ (eV)	$^1p_1$ (eV)		Coord.	$^3p_1$ (eV)	$^1p_1$ (eV)
NaCl:Pb	6	4.55 (*16*)	6.4 (*19*)	NaBr:Pb	6	4.07 (*22*)	—
KCl:Pb	6	4.54 (*16*)	6.3 (*19*)	KBr:Pb	6	4.12 (*16*)	5.6 (*19*
RbCl:Pb	6	4.58 (*19*)	6.3 (*19*)	RbBr:Pb	6	4.14 (*19*)	5.5 (*19*)
CsCl:Pb	8	4.34 (*20*)	5.8 (*20*)	CsBr:Pb	8	3.95 (*20*)	5.4 (*20*)
$CdCl_2$:Pb	6	4.60 (*21*)	5.7 (*21*)	$CdBr_2$:Pb	6	3.86 (*21*)	4.7 (*21*)
$BaCl_2$:Pb	9	4.74 (*21*)	>6.0 (*21*)	$BaBr_2$:Pb	9	4.27 (*21*)	5.2 (*21*)
$PbCl_2$	9	4.55	6.4	$PbBr_2$	9	3.70	5.4

4.1.3. *Band Edge*

Up to now the creation of free carriers in $PbCl_2$ and $PbBr_2$ has been investigated by Verwey et al. (*25*) and Liidja et al. (*5*). Verwey measured at 100 K the excitation spectrum of the photoconductivity of $PbCl_2$ and $PbBr_2$ up to 5.2 eV (cf. Fig. 6.II). Liidja measured at 5 K the spectral dependence of the ratio of the recombination luminescence yield and the creation efficiency of free carriers up to 5.7 eV (the spectral kinetic method) (cf. Fig. 6.III). From the results of both authors it appears that for $PbCl_2$ the creation of free carriers starts at about 4.7 eV. Unfortunately, no photoconductivity measurements have been done in the region 5.2–6 eV. The spectral kinetic measurements, however, suggest that the creation efficiency of free carriers increases in this spectral region. It seems, therefore, very probable that the absorption band of $PbCl_2$ peaking at 5.76 eV (5 K) (cf. Table III) is due to absorption in the band edge. For $PbBr_2$ the results of both methods agree rather well in the spectral region 4.1–5.2 eV. Consequently, we assume that the absorption band of $PbBr_2$ peaking at 4.82 eV (5 K) is also due to absorption in the band edge (cf. Table III, column 4).

4.1.4. *Charge Transfer Band*

The charge transfer band of lowest energy of the system $KCl:Tl^+$ (six-coordination) has been measured at 7.35 eV (*19*), while the corresponding band of $NH_4Cl:Tl^+$ (eight-coordination) is situated at 5.24 eV (*26*). In TlCl (eight-coordination) a corresponding band appears at about 5.0 eV (*27, 28*). It is striking that the lowest charge transfer band shifts considerably ($\Delta E = \sim 2$ eV) to lower energy if the coordination number of the cations increases from 6 to 8. The same holds for the system $KBr:Tl^+$ (6.50 eV) with respect to TlBr (4.30 eV).

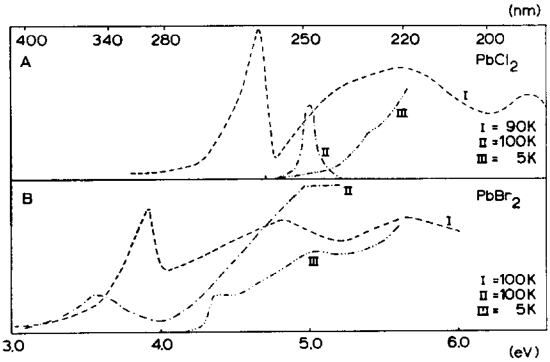

FIG. 6. Comparison between the absorption spectra (I) and the spectral kinetic measurements (III) and the photoconductivity spectra (II) of $PbCl_2$ and $PbBr_2$. Curves II and III are taken from the measurements of Verwey (*1*) and Liidja (*5*), respectively. The curves have been plotted in arbitrary units.

It is known from investigations on transition metal ions that the lowest charge transfer band shifts to higher energy if the number of ligands decreases (*29, 30*). It seems reasonable to expect from these two facts that the lowest charge transfer band of nine-coordinated lead systems ($PbCl_2$ and $PbBr_2$) shifts considerably to lower energy with respect to the position of the corresponding band in six-coordinated lead-doped alkali halides.

The charge transfer band of lead-doped alkali halides (*D′* band) has been investigated by Fukuda (*31*) and Inohara (*19*). They ascribed the *D′* band to a charge transfer transition from the halide ion to the heavy metal ion. The absorption spectra of $PbCl_2$ at 90 and 5 K and of $PbBr_2$ at 5 K exhibit a shoulder on the low energy side of the band edge (cf. Table III, column 3). In Table V the maxima of these bands are compared with the maxima of the *D′* bands (*19*) of some Pb^{2+}-doped alkali halides. This comparison raises the objection that the position of the *D′* bands of the alkali halides doped with divalent lead may be affected by the charge compensating cation vacancy. Since, according to the investigations of Koeze (*32*), this vacancy is located at a next-nearest neighbor position, we assume that the position of the *D′* band is only slightly influenced by the presence of the cation vacancies.

The absorption bands of $PbCl_2$ and $PbBr_2$ at 5.2 and 4.50 eV, respectively, are situated about 1.4

TABLE V

MAXIMA OF THE LOWEST CHARGE TRANSFER BAND OF SOME LEAD-DOPED ALKALI HALIDES AND OF $PbCl_2$ AND $PbBr_2$ AT 80 K

Coordination		Position of the lowest charge transfer band		Position of the lowest charge transfer band
6	NaCl:Pb	6.70 eV		
6	KCl:Pb	6.57	KBr:Pb	5.75 eV
6	RbCl:Pb	6.45	RbBr:Pb	5.70
9	$PbCl_2$	5.2	$PbBr_2$ (5 K)	4.20 4.50

eV lower, with respect to the *D′* bands of the six-coordinated alkali chlorides and bromides doped with lead. Consequently, we suggest that this absorption band of $PbCl_2$ and $PbBr_2$ is due to a charge transfer transition in which an electron is transferred from the $^1s_0$ (p^6) ground state of the halide ion to an excited state composed of lead orbitals and halide orbitals of higher energy. In addition to the absorption band at 4.50 eV, the $PbBr_2$ absorption spectrum at 5 K exhibits a band at 4.20 eV (Table III, column 2). Since two types of halide ions exist (cf. Section 4.1.2), it may be that the 4.20 eV absorption band is associated with a charge transfer transition from the ground state of the second type of halide ions to an excited state described above. For $PbCl_2$ only one absorption band is observed in the spectral region involved.

4.1.5. $^1s_0 \rightarrow {}^1p_1$ *Exciton Absorption Band*

We now turn to the interpretation of the absorption band of $PbCl_2$ at 6.5 eV (90 K) and of $PbBr_2$ at 5.7 eV (100 K) (cf. Table III, column 5). The positions of the maxima of the $^1v_0 \rightarrow {}^3p_1$ absorption bands of the lead-doped halides represented in Table IV, agree rather well. This agreement is less satisfactory in the case of the $^1s_0 \rightarrow {}^1p_1$ absorption bands of the same compounds (cf. Table IV). The absorption band of $PbCl_2$ and $PbBr_2$ under consideration, is also situated in the spectral region of the $^1s_0 \rightarrow {}^1p_1$ bands of the lead-doped chloride and bromide compounds, respectively. We suggest, therefore, that the $PbCl_2$ and $PbBr_2$ band involved is due to the exciton transition $^1s_0 \rightarrow {}^1p_1$ on divalent lead.

Two more data on these bands are known from the literature:

(a) The temperature shift of this $PbCl_2$ absorption band measured from 20 to 290 K by Best (*3*) appears to be of equal magnitude (25×10^{-5} eV/K) like the shift of the low energy exciton band, while the temperature shift of the band edge is twice as large.

(b) The $^1s_0 \rightarrow {}^1p_1$ exciton absorption band of $PbBr_2$ is single at 100 K, whereas at 5 K a doublet splitting is found with maxima at 5.62 and 5.90 eV. Unfortunately, the complete structure of the band at 5 K is not known as the absorption spectrum is only measured up to 6.0 eV (cf. Fig. 5).

For a complete interpretation of the bands involved it will be necessary to do further investigations, especially related to the splitting of the bands.

4.2. Excitation Spectra

In Table VI the maxima and minima in the low energy region of the absorption spectra and the luminescence excitation spectra of $PbCl_2$ and $PbBr_2$ are presented. From an inspection of this table it appears that the absorption maxima and the excitation minima practically coincide. This holds also for the absorption minima and the excitation maxima at higher energy. Apparently a strong correlation exists between the excitation and absorption spectra. A similar correlation has been noted for KJ and RbJ (*15*). This phenomenon can be understood if one realizes that the penetration depth in the region of $^1s_0 \rightarrow {}^3p_1$ cation exciton absorption band is reduced as a result of the strong absorption in that region. Nonradiative recombination transitions are favoured in the surface layer involved, e.g., due to a relatively high imperfection concentration.

Except for the excitation spectra of the red and yellow emission of $PbCl_2$ the low energy region of the excitation spectra exhibits two maxima. In addition these maxima practically coincide for the uv and blue spectra. Due to the strong correlation between absorption and luminescence excitation spectra the maxima of lowest energy (~4.50 eV for $PbCl_2$ and ~3.82 eV for $PbBr_2$) are situated 0.2 eV lower than the $^1s_0 \rightarrow {}^3p_1$ cation exciton absorption peaks. Consequently, we attribute these excitation bands to the creation of $^1s_0 \rightarrow {}^3p_1$ cation excitons. Tentatively we attribute the higher energy maxima (~4.83 eV for $PbCl_2$ and ~4.08 eV for $PbBr_2$) in the low energy region of the excitation spectra of $PbCl_2$ and $PbBr_2$ to the charge transfer transition described in Section 4.1.4.

Contrary to the results of the photoconductivity measurements on $PbCl_2$, $PbBr_2$ (cf. Fig. 6) shows a small photoresponse in the spectral region of the $^1s_0 \rightarrow {}^3p_1$ cation exciton band. This photoconductivity has been ascribed (*25*) to free hole production as a result of the decomposition of the created exciton at a lattice imperfection. The spectral kinetic measurements (*5*) do not exhibit any emission response due to the trapping and recombination of free carriers. In addition, all emissions are excited by preference in the spectral region of the $^1s_0 \rightarrow {}^3p_1$ cation exciton absorption band, while the relative quantum output for excitation into the region of the fundamental absorption band is relatively small. We conclude,

TABLE VI

THE MAXIMA AND MINIMA IN THE LOW ENERGY REGION OF THE ABSORPTION AND LUMINESCENCE EXCITATION SPECTRA OF $PbCl_2$ AND $PbBr_2$ AT 77 AND 10 K

$PbCl_2$	77 K			10 K		
Absorption maxima and minima (eV)		max 4.66	min 4.79		max 4.69	min 4.81
Excitation maxima and minima (eV)	max	min	max	max	min	max
uv	—[a]	—	—	4.50	4.71	4.83
Blue	4.47	4.70	4.79	4.49	4.72	4.81
Red	4.27	—	—	4.30	—	—
					5 K	
Violet	—	—	—	4.36	4.67	4.86
Yellow	$\not-$[b]	$\not-$	$\not-$	4.30	—	—
$PbBr_2$	77 K			10 K		
Absorption maxima and minima (eV)		max 3.92	min 4.04		max 3.98	min 4.10
Excitation maxima and minima (eV)	max	min	max	max	min	max
uv	*[c]	*	*	3.82	4.01	4.08
Blue	—	—	—	3.81	4.01	4.07
Yellow	3.74	3.93	4.04	$\not-$	$\not-$	$\not-$
Red	3.5 3.76	3.95	4.06	3.71	3.96	4.10

[a] — = not present.

[b] $\not-$ = not measured.

[c] * = luminescence is present, but very weak.

therefore, that in the region of the ${}^1s_0 \rightarrow {}^3p_1$ cation exciton excitation band of $PbCl_2$ and $PbBr_2$, free carriers do not transport the exciting radiation to the luminescence centers. It appears from the excitation spectra in conjunction with the photoconductivity and spectral kinetic measurements that the process of energy transport mentioned above may occur in the region of the band edge, especially for the red, yellow and uv luminescence of $PbBr_2$.

Upon cooling the $PbCl_2$ crystals from 20 to 5 K the blue luminescence is partly quenched, especially in the excitation region of the ${}^1s_0 \rightarrow {}^3p_1$ cation exciton band. This phenomenon will be discussed in more detail in a next paper.

4.3. Impurities

The samples were purified and grown under special circumstances to prevent an excess of divalent lead ions. The analyses by emission spectroscopy demonstrate the high purity (cf. Table I). It seems improbable that the different emissions are produced by excitation and decay of impurity centers. Additional evidence can be obtained from the following: for the preparation of the $PbBr_2$ single crystals lead bromide precipitated from lead nitrate and hydrobromic acid (Merck) was used. $PbCl_2$ powder obtained from a different supplier (Baker Chemical Co.) served as the starting material for the $PbCl_2$ crystals. $PbCl_2$ and $PbBr_2$ crystals show four corresponding emissions (cf. Figs. 1 and 2). If one of these emissions would originate from an impurity, both lead halides would have to contain comparable concentrations of the same impurity.

4.4. Comparison Between the Luminescence Results of Water-Grown Crystals and the Results of Our Crystals

As mentioned in Section 1.3 the emission spectra of water-grown crystals measured at about 100 K show a yellow and a green emission for $PbBr_2$ and a blue one for $PbCl_2$ [Gobrecht (*7*); Bettinali (*9*)]. If the water content was reduced by warming the samples, the low temperature luminescence disappeared completely (Gobrecht). This process appeared to be reversible. So, water forms the essential intermediate for the luminescence of these samples.

Comparing these results with ours we note that:

(1) For the water-grown crystals of $PbCl_2$ a blue emission band was measured at 100 K with the maximum at 2.82 eV and a half-width of 0.75 eV (*9*). The maximum of the blue emission band of our $PbCl_2$ crystals is situated at 2.76 eV and the half-width amounts to 0.54 eV (77 K). Our $PbBr_2$ crystals did not show a green emission band and a yellow emission band was only measured at 77 K after a long time of irradiation.

(2) The red luminescence of our $PbCl_2$ and $PbBr_2$ crystals has not been measured on the water-grown crystals.

(3) In section 3.1 we arrived at the conclusion that water did not cause the luminescence of our crystals. Since the luminescence process of the water-grown crystals is strongly influenced by water it is improbable that the blue luminescence of the differently prepared $PbCl_2$ crystals is caused by the same mechanism.

(4) From these considerations it appears that the luminescence of $PbCl_2$ and $PbBr_2$ depends strongly on the crystal preparation method.

4.5. Ultraviolet Luminescence

Each of the systems $KCl:Tl^+$ and $KBr:Tl^+$ (*16*) shows two uv emissions at 300 K for excitation in the $^1s_0 \rightarrow {}^3p_1$ absorption band (*A* band). The emission of lowest energy is quenched at low temperature. At room temperature thermal transitions are assumed to be rather probable (*16*) so that the systems excited in the $^1s_0 \rightarrow {}^3p_1$ absorption band may end up in the $^3p_0$ state from which luminescence occurs. At low temperature these thermal transitions become less probable and allow luminescence to occur directly from the $^3p_1$ state. In view of these considerations in conjunction with the results of the decay–time measurements (*16*), the emission of lowest energy

TABLE VII

THE MAXIMA OF THE $^1s_0 \rightarrow {}^3p_1$ ABSORPTION BANDS AND THE MAXIMA AND HALF-WIDTHS OF THE UV EMISSION BANDS OF SOME LEAD-DOPED HALIDES AND OF $PbCl_2$ AND $PbBr_2$

	Maxima of the $^1s_0 \rightarrow {}^3p_1$ absorption bands	Maxima of the uv emission bands	Stokes shift (ΔE)	Half-width of the uv emission bands
		300 K		77 K
NaCl:Pb (*16, 19*)	4.55 eV	3.89 eV	0.66 eV	0.4 eV
KCl:Pb (*16, 19*)	4.54	3.61	0.93	0.3
RbCl:Pb (*19*)	4.58	3.60	0.98	0.3
$BaCl_2$:Pb (*21*)	4.74	3.94	0.80	
KBr:Pb (*16, 19*)	4.12	3.38	0.74	0.2
RbBr:Pb (*19*)	4.14	3.20	0.94	0.2
$BaBr_2$:Pb (*21*)	4.27	3.28	0.99	
		10 K		
$PbCl_2$	4.69	3.78	0.91	0.26
$PbBr_2$	3.99	3.27	0.72	0.16

is ascribed to the transition $^3p_0 \rightarrow {}^1s_0$ and the other one to $^3p_1 \rightarrow {}^1s_0$ on Tl^+.

The maxima of the $^1s_0 \rightarrow {}^3p_1$ absorption bands and the maxima and half-widths of the uv emission bands of some lead-doped halides are summarized in Table VII. The measurements of Inohara (*19*) on several lead-doped alkali halides at 300 and 80 K show that for excitation in the $^1s_0 \rightarrow {}^3p_1$ absorption band only one emission at the same energy is produced at both temperatures. In addition, the investigations of Koeze on $KCl:Pb^{2+}$ (*32*), Trinkler on $KCl:Pb^{2+}$ and $KBr:Pb^{2+}$ (*37*) and Fukuda (*31, 38*) on lead-doped KCl, KBr and NaCl, indicated that the emission involved occurs only from the $^3p_1$ level.

From Table VII it appears that the features of the uv emission of $PbCl_2$ and $PbBr_2$ correspond with those of the lead-doped chlorides and bromides, respectively. The uv emission of $PbCl_2$ is quenched in the temperature region 10 → 30 K, and the $PbBr_2$ emission in the region 50 → 150 K. In addition the decay time of the uv emission of $PbCl_2$ is $\leqslant 8 \cdot 10^{-9}$ sec (*41*) which agrees with the expected decay time of the transition $^3p_1 \rightarrow {}^1s_0$ on Pb^{2+}.

We conclude that the uv emission of $PbCl_2$ and $PbBr_2$ is due to the recombination of the $^3p_1$ cation excitons (*35, 36*).

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