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Luminescence of $PbCl_2$ and $PbBr_2$ Single Crystals

III. The Blue and Violet Luminescence; Mechanism of Energy Transport

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The results of the decay time, quantum efficiency and temperature dependence measurements of the uv, blue and red luminescence of $PbCl_2$ and $PbBr_2$ are reported. The blue luminescence is associated with a charge transfer transition of the halide ion. $PbCl_2$ crystals also show a violet luminescence at temperatures lower than 30 K. We tentatively assume that the violet emission, like the uv emission is due to recombination of $^3P_1$ cation excitons. The excitation of the blue and red luminescence of both lead halides in the energy region of the $^3P_1$ cation exciton absorption band occurs by transport of excitation energy. We arrive at the conclusion that the excitation energy is transferred nonradiatively from the $^3P_1$ state of the exciton to the excited state of the centers responsible for the blue and red emission.

1. Introduction

In previous papers we reported about the origin of the uv (*1, 2*) and red (*6, 7*) luminescence of $PbCl_2$ and $PbBr_2$ single crystals. The uv luminescence has been attributed to excitation and recombination of $^3P_1$ cation excitons. The red luminescence has been ascribed to excitation and decay of single Pb^+ ions, pairs of Pb^+ ions or of both. Both lead halides also show a blue luminescence at low temperatures. The investigation has been continued with measurements on crystals of $PbCl_2$ and $PbBr_2$ doped with monovalent or trivalent cations, to check whether the blue luminescence could be associated with anion or cation vacancies.

Further on we carried out temperature dependence, decay time and quantum efficiency measurements of the uv, blue and red luminescence of both lead halides. The excitation of the blue and red luminescence of both lead halides in the $^3P_1$ cation exciton absorption band occurs by transport of excitation energy. The transport mechanism has been studied with the aid of the aforementioned measurements in conjunction with the absorption spectra and the excitation and emission spectra of the luminescence. Additional information on the transport mechanism is obtained from the investigations of Willemsen (*16*) on rare-earth-doped $PbCl_2$ crystals.

2. Experimental Methods

2.1 *The Temperature Dependence, Decay Time and Quantum Efficiency Measurements*

All measurements described in this section were carried out on very pure single crystals of $PbCl_2$ and $PbBr_2$ (*1, 3, 4*). Platelets of about 1 mm thickness were cleaved parallel to the (001) plane from large single crystals. The decay time and temperature dependence of the luminescences were measured in the temperature region 10–200 K, and the quantum efficiencies at 77 K. The temperature of the samples was determined with a calibrated Ge diode in the region 10–80 K and a chromel alumel thermocouple in the region 75–200 K.

The temperature dependence measurements were carried out using the stainless steel cryostat described in a previous paper (*1*). The samples were excited parallel with the *c*-axis. The excitation part of the setup consisted of a high pressure xenon lamp (Osram, XBO 450 W) in combination with suitable filters or a quartz single monochromator. For the detection of the emission we used a similar monochromator with flint or suprasil prism and a photomultiplier

(EMI, 9658 QB). After amplification and synchronous detection the signal was recorded. The band pass of the emission monochromator was 0.03–0.1 eV; the peak of the emission band under study was transmitted. During the warming-up the emission monochromator was adjusted in accordance with the shift of the emission band with temperature. The heating rate of the samples was $\leqslant 1°$/min.

The decay time measurements were carried out with the aid of the TRW model 31 A nanosecond spectral source. This instrument was equipped with a deuterium or nitrogen discharge lamp for excitation with short or long wavelength uv radiation, respectively. Suitable filters were placed in the exciting beam to obtain the desired excitation wavelengths. The samples were placed in the cryostat mentioned above. The emitted radiation was detected at right angles to the exciting beam. The detection part of the setup consisted of filters absorbing the exciting radiation and a photomultiplier (Philips, type 56 TUVP). The decay signal was visualized on a sampling scope (Tektronix, type 454 B) and subsequently recorded.

The quantum efficiency measurements were carried out using a deep elliptical mirror with 2π-geometry as described by Van der Does de Bye (*5*). With a few other parts, including two quartz windows this mirror constitutes a chamber which can be evacuated in order to allow measurements at temperatures down to 77 K. The sample and the photomultiplier (EMI, type 9658 QB) were located at the two focal points. To fix the sample at the focal spot provision was made for an adjustable insertion of the sample holder using micrometer screw arrangements. The samples were excited with monochromatic radiation. For the detection of the emission we used a similar setup as described for the temperature dependence measurements. A $CaWO_4$ single crystal was used as a standard. The quantum efficiency (q) of the standard was taken from the measurements of Kröger (*29*), viz, about 90% at low temperatures. For the calculation of the q's the following formula was used:

$$q = \frac{V}{V_s}\frac{1 - r_s}{1 - r}\cdot q_s,$$

where r = reflection coefficient
s = standard
V = total amount of quanta emitted per incident photon.

V was corrected for the transmittance of the filters (all filters were calibrated in the setup) and for the quantum efficiency of the photomultiplier. The reflection coefficient of $CaWO_4$ and $PbBr_2$ at 77 K was measured by Vos in this laboratory, that for $PbCl_2$ was taken from the measurements of Liidja, Plekhanov, and Malysheva (*8*).

2.2 The Measurements on $PbCl_2$ and $PbBr_2$ Crystals Doped with Tl^+ or Bi^{3+}

$PbCl_2$ and $PbBr_2$ single crystals doped with Tl^+ or Bi^{3+} were prepared by means of the Bridgman technique (*3, 4*). The concentration of the dopants was in the range 5×10^{17}–2×10^{18} cm^{-3}. The excitation and emission spectra of the luminescence of these crystals were measured at 77 and 10 K with the setup used for the temperature dependence measurements (see Sect. 2.1).

3. Experimental Results

The temperature dependence of the intensity of the red, blue and uv luminescence of $PbCl_2$ and $PbBr_2$ is presented in Figs. 1A and 2A. For these measurements the blue and red emission of both compounds were excited in the low energy bands of the excitation spectra (see Figs. 5 and 6); the uv luminescence of $PbCl_2$ was excited at 4.77 eV and that of $PbBr_2$ at 4.11 eV. For experimental reasons it was not possible to carry out these experiments under excitation with the same energy.

The results show that the blue luminescence of $PbBr_2$ is quenched at a considerably lower temperature than that of $PbCl_2$, whereas the opposite holds for the uv emission of these compounds. In the case of $PbCl_2$ the intensity of the blue emission is strongly reduced in the temperature region 30–10 K, whereas the uv emission appears in the same region; the same holds for the red and blue emission of $PbBr_2$ in the region 40–10 K. The quenching temperature of the red luminescence of $PbCl_2$ appears to depend on the irradiation intensity. For the measurement presented here (see Fig. 1A) the intensity was $\sim 10^{16}$ photons cm^{-2} sec^{-1}. The quenching temperature shifts about 30 K to higher temperature if the intensity is decreased to 10^{14} photons cm^{-2} sec^{-1}. This phenomenon has been discussed in detail in previous papers (*6, 7*).

In Figs. 2B and 1B the decay times as a function of temperature are given for the blue and red luminescence of $PbBr_2$ and the blue one of $PbCl_2$.

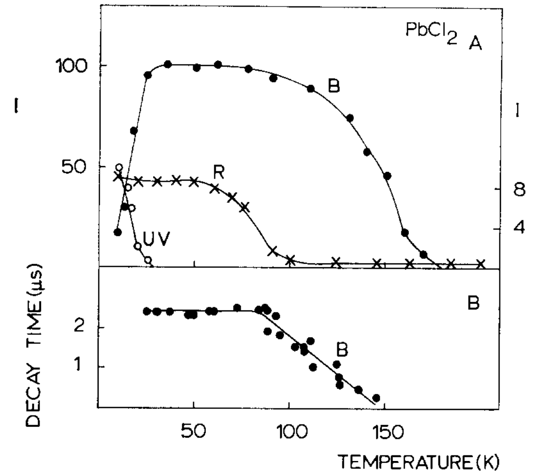

FIG. 1A. Temperature dependence of the intensity of the blue (B), red (R), and uv luminescence of $PbCl_2$. The excitation energy for the different measurements is given in the text. Along the ordinate the radiant power is given for the same intensity of the exciting radiation and after correction for the spectral response of the photomultiplier. Note that curve uv is drawn to an extended scale given on the right side. (B) Decay time as a function of temperature for the blue (B) luminescence of $PbCl_2$, excited in the cation exciton band.

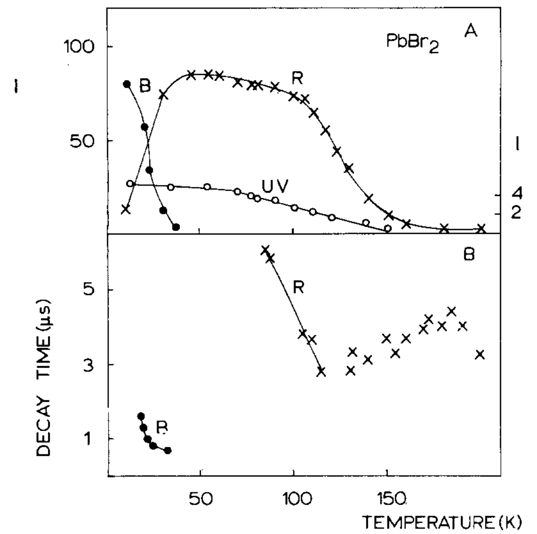

FIG. 2A. Temperature dependence of the intensity of the blue (B), red (R) and uv luminescence of $PbBr_2$. The excitation energy for the different measurements is given in the text. Along the ordinate the radiant power is given for the same intensity of the exciting radiation and after correction for the spectral response of the photomultiplier. Note that curve uv is drawn to an extended scale given on the right side. (B) Decay time as a function of temperature for the blue (B) and red (R) luminescence of $PbBr_2$, excited in the cation exciton band.

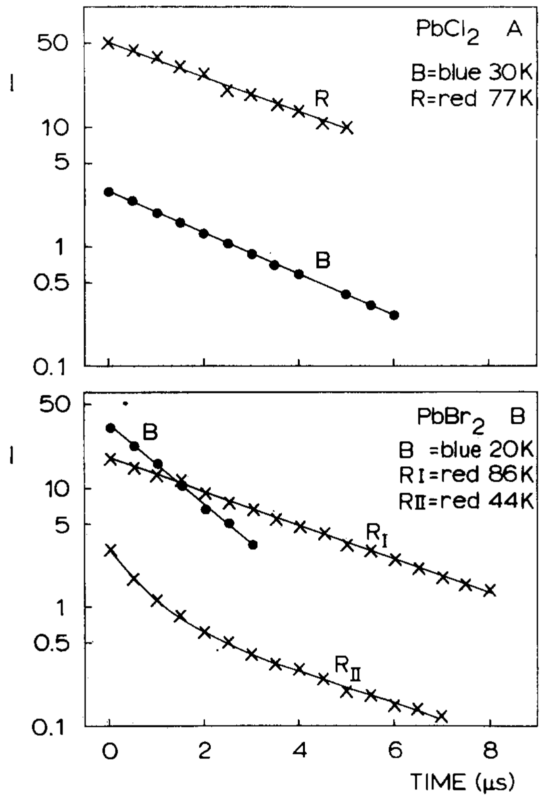

FIG. 3. Decay of the blue and red emission of $PbCl_2$ and $PbBr_2$. The emissions were excited in the cation exciton absorption band of the compounds.

The decay curves of these emissions are all exponential (see Fig. 3). In the region 20–75 K the decay curves of the red emission of $PbBr_2$ proved to be composed of two components (see Fig. 3B): a slower one with $\tau = 7$ μsec and a faster one with $\tau = 1$ μsec. Although the decay patterns appear to follow the exponential decay predicted by a monomolecular process, it is possible that individual curves could be fitted within the experimental error by a bimolecular decay form. To differentiate between these two processes neutral density filters were used to reduce the intensity of the nanosecond spectral source by a factor of 50 or 20. The lifetime of a bimolecular process varies as the $-\frac{1}{2}$ power of the intensity. We found no change in the lifetime with these changes in intensity for the emissions mentioned above. The decay time at 10 K of the uv emission of $PbCl_2$ is less than the limits of measurement ($<8 \times 10^{-9}$ sec). The decay time of the red emission of $PbCl_2$ could not be detected because of the relatively low intensity of the exciting radiation (deuterium lamp) and the small efficiency of the photomultiplier in the red energy region, that of the uv of $PbBr_2$ because of the low intensity of the emission. Preliminary measurements at 77 K have been done elsewhere[1] with a microsecond spectral source for the red and blue luminescence of $PbCl_2$ and the red one of $PbBr_2$. The decay time of the red emission of $PbCl_2$ was 3 μsec at 77 K. The decay curve appears to be exponential (see Fig. 3A.II). The measurements for the other two emissions showed the same results as measured with the nanosecond source. For these three emissions no long-living components are detected at 77 K. The value of the decay time of the red emission of both compounds seems reasonable taking into consideration that the transition involved is probably spin-forbidden. Perhaps the slower decay time of the red emission of $PbBr_2$ is associated with single Pb^+ ions and the faster one with the Pb^+ pairs (see above). The small increase of the decay time of this emission (cf. Fig. 2B) in the temperature region 120–180 K cannot be explained at the moment.

The quantum efficiency of the luminescences of $PbCl_2$ and $PbBr_2$ at 77 K (see Figs. 1A and 2A) are given in Table I. The excitation energies mainly refer to maxima and minima in the excitation spectra of the various luminescences [see Ref. (*1*) and Figs. 5 and 6]. The maximum quantum efficiency at 77 K for $PbCl_2$ obtained from the sum of the q values of the blue and red luminescence is $(60 \pm 20)\%$ (excitation energy 4.49 eV); for $PbBr_2$ the maximum value is $(40 \pm 10)\%$ (excitation energy 3.75 eV).

TABLE I

QUANTUM EFFICIENCIES OF THE LUMINESCENCES OF $PbCl_2$ AND $PbBr_2$ at 77 K[a]

$PbCl_2$				$PbBr_2$			
Blue		Red		uv		Red	
Exc. energy (eV)	q (%)	Exc. energy (eV)	q (%)	Exc. energy (eV)	q (%)	Exc. energy (eV)	q (%)
4.31	30	4.13	9			3.44	2
4.49	50	4.27	15	3.82	2	3.75	40
4.79	40	4.42	8	4.07	1	4.13	20

[a] Standard, $CaWO_4$, $q = 90\%$.

The measurements on $PbCl_2$ and $PbBr_2$ doped with Tl^+ or Bi^{3+} indicated that the luminescence properties of the pure crystals are not influenced by the presence of the dopants.

4. The Blue Luminescence

First we want to discuss whether the blue luminescence of both $PbCl_2$ and $PbBr_2$ could be associated with anion or cation vacancies. As the intrinsic point defects in $PbCl_2$ and $PbBr_2$ are known to be of the Schottky type (*4*, *9*) anion and cation vacancies are the dominant intrinsic point defects in both lead halides. It has been shown (*4*, *10*, *12*) that upon doping with monovalent cations in a concentration well above that of the intrinsic lattice defects the anion vacancy concentration ($[V_x^{\cdot}]$) equals the concentration of the dopant, whereas the cation vacancy concentration ($[V_{Pb}'']$) decreases. The opposite holds in crystals doped with trivalent cations. Conductivity measurements on undoped $PbCl_2$[2] and $PbBr_2$ (*12*) single crystals revealed that at room temperature the vacancy concentration is determined by remaining impurities. The $[V_x^{\cdot}]$ at 300 K is $\sim 10^{17}$ cm^{-3} in $PbCl_2$ and $\sim 5 \times 10^{16}$ cm^{-3} in $PbBr_2$, while the $[V_{Pb}'']$ in both compounds is very low ($<10^{13}$ cm^{-3}). Upon cooling the crystals the $[V_x^{\cdot}]$ remains constant, if no association occurs, while the $[V_{Pb}'']$ decreases. In view of this low concentration it is very unlikely that the blue luminescence is associated with cation vacancies. The $[V_x^{\cdot}]$ in the Tl^+-doped crystals increased to $\sim 10^{18}$ cm^{-3}, whereas the $[V_{Pb}'']$ was further decreased. On the other hand, the cation vacancy concentration in the Bi^{3+}-doped crystals amounted to $\sim 10^{18}$ cm^{-3} and in this case the $[V_x^{\cdot}]$ was very low ($\ll 10^{10}$ cm^{-3} at 80 K). If the blue emission would be associated with the anion vacancies we expect this luminescence to disappear in the Bi^{3+}-doped crystals. As the measurements on the doped crystals (see Sect. 3) do not show any influence of the dopants on the luminescence it seems very improbable that the blue luminescence of both lead halides is associated with the anion vacancies.

The Blue Luminescence and Charge Transfer Transitions

The absorption band at 5.2 eV (5 K) in $PbCl_2$ and at 4.50 eV (5 K) in $PbBr_2$ (cf. Figs. 5 and 6) has been ascribed to a charge transfer transition

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[1] Thanks are due to Dr. A. Bril and Mr. J. A. de Poorter of Philips Research Laboratories at Eindhoven for these measurements.

[2] Thanks are due to Dr. J. Schoonman of this laboratory for the conductivity measurements on the $PbCl_2$ crystals.

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. The excitation band of the blue luminescence of $PbCl_2$ (10 K) peaking at 4.83 eV and that of $PbBr_2$ (10 K) at 4.08 eV (cf. Figs. 5 and 6) are supposed to be due to excitation in the aforementioned charge transfer bands. One would not expect that direct excitation of the blue luminescence of $PbCl_2$ in the charge transfer band results in a smaller efficiency than indirect excitation in the cation exciton band (see Table I). In fact, the efficiency of the charge transfer luminescence will be larger than 40%, as photoconductivity measurements (*15*) showed that in the energy region of the charge transfer band part of the exciting radiation is absorbed in the band edge.

The process of excitation of the blue luminescence in the $^3P_1$ cation exciton band is discussed in Sect. 6.2.

The D′ absorption band of lead-doped alkali halides has been ascribed by Fukuda (*13*) and Inohara (*14*) to a charge transfer transition from the halide ion to the bivalent lead ion. Excitation in this band at 80 K causes two emissions, one due to the transition $^3P_1 \rightarrow {}^1S_0$ on Pb^{2+}, the other one to the inverse of the charge transfer transition described above. The Stokes shift of the charge transfer luminescence appears to be considerably larger than that of the cation exciton luminescence (see Table II). In Table II we present the maxima of the charge transfer and the $^1S_0 \rightarrow {}^3P_1$ absorption bands and the maxima of the corresponding emission bands of some lead-doped alkali halides and of $PbCl_2$ and $PbBr_2$. The luminescence properties of the lead-doped alkali halides and of $PbCl_2$ and $PbBr_2$ described here agree qualitatively. The Stokes shift of the charge transfer luminescence of the doped compounds, however, is considerably larger than that of $PbCl_2$ and $PbBr_2$. The coordination number of the lead ion in $PbCl_2$ and $PbBr_2$ is 9, and in the doped alkali halides 6. It may be that the smaller Stokes shift of the charge transfer luminescence in the lead halides with respect to that in the lead-doped alkali halides is due to the change of the coordination of the lead ion. Such an effect is not unknown for charge transfer transitions of several tungstates (*29*, *30*).

5. The Violet Luminescence of $PbCl_2$

In addition to the uv emission of $PbCl_2$, a weak emission appears in the violet part of the spectrum (peak position 3.2 eV at 5 K) at temperatures lower than 30 K. The excitation and emission spectrum of the violet luminescence has been given previously (*1*). The origin of the uv luminescence has been mentioned in Sect. 1.

It is known that several alkali halides doped with Pb^{2+} or Sn^{2+} show two emission bands at low temperatures under excitation in the A (the transition $^1S_0 \rightarrow {}^3P_1$ on the impurity ion) absorption band. According to Fukuda (*11*) it is likely that the Jahn–Teller effect in the $^3P_1$ excited state causes two emission bands corresponding with two kinds of minima on the $^3P_1$

TABLE II

SOME CHARACTERISTICS OF THE CHARGE TRANSFER AND CATION EXCITON LUMINESCENCE OF SOME LEAD-DOPED ALKALI HALIDES AND OF $PbCl_2$ AND $PbBr_2$

	Maxima of the charge transfer absorption band (eV) (eV) (80 K)	Maxima of the $^1S_0 \rightarrow {}^3P_1$ absorption band (eV) (300 K)	Maxima of the $^3P_1 \rightarrow {}^1S_0$ emission band (eV) (300 K)	Maxima of the charge transfer emission band (eV) (80 K)	Stokes shift ΔE $^3P_1 \rightleftarrows {}^1S_0$ (eV)	Stokes shift of the charge transfer luminescence ΔE (eV)
NaCl:Pb (*14*, *27*)	6.70	4.55	3.89	2.67	0.66	4.03
KCl:Pb (*14*, *27*)	6.57	4.54	3.61	3.00	0.93	3.57
RbCl:Pb (*14*)	6.45	4.58	3.60	2.35	0.98	4.10
KBr:Pb (*14*, *27*)	5.75	4.12	3.38	2.28	0.74	3.47
			10 K			
$PbCl_2$	5.2	4.68	3.78	2.76	0.90	2.4
$PbBr_2$	4.5	3.98	3.27	2.72	0.71	1.8

adiabatic potential energy surface. The reflectivity spectra of $PbCl_2$ at 5 K (*8*) showed that the $^3P_1$ cation exciton band is split into two components. In this case the degeneracy of the $^3P_1$ state is expected to be lifted by the crystal field. The Pb^{2+} site shows in rough approximation trigonal symmetry (*1*). Although the violet luminescence has not been investigated thoroughly up to now, we tentatively assume that the violet emission, like the uv emission, is due to the recombination of the $^3P_1$ cation excitons.

6. Mechanism of Energy Transport

6.1 *Transport of Energy in Rare-Earth-Doped $PbCl_2$ Crystals*

The luminescence of $PbCl_2$ crystals doped with about 50 ppm Eu^{2+} or Sm^{3+} has been investigated by Willemsen (*16*) in this laboratory. Both systems appear to luminesce at low temperatures as well as at room temperature. The emission of the rare-earth ions has been ascribed to the transition $5d \rightarrow 4f$ on Eu^{2+} and $4f \rightarrow 4f$ on Sm^{3+}. The Eu^{2+} and Sm^{3+} emission can also be excited in the $^3P_1$ cation exciton absorption band (peak position 4.69 eV at 10 K). Willemsen assumed that the excitation energy is transferred nonradiatively from the $^3P_1$ state of the exciton to the excited state of the rare-earth ion. The necessary condition of overlap of the cation exciton emission band and an absorption band related to the transition $4f \rightarrow 5d$ on Eu^{2+} is satisfied (cf. Fig. 4.II and IV). The characteristic, absorption lines related to $4f \rightarrow 4f$ transitions on Sm^{3+} are not detected in the energy region of the exciton emission band (cf. Fig. 4.III), but it is known (*28*) that some of these lines are situated in this region. The $Pb^{2+} \rightarrow Sm^{3+}$ transfer will be restricted to short distances in view of the fact that the $4f \rightarrow 4f$ transitions are forbidden. However, $Pb^{2+} \rightarrow Pb^{2+}$ transfer may occur also, as the cation exciton absorption and emission band overlap to some extent (see Fig. 4, I and IV).

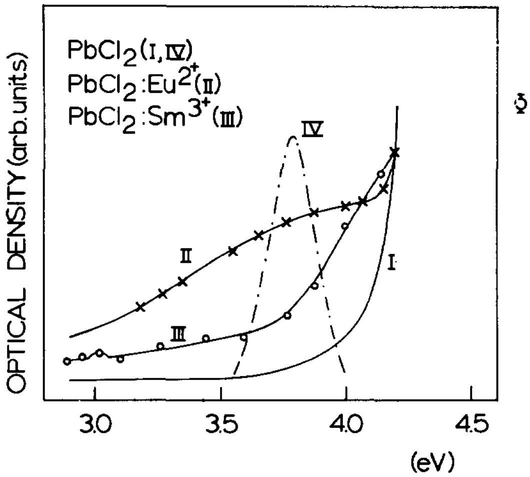

FIG. 4. Relative absorption spectra of $PbCl_2$ (I), $PbCl_2:Eu^{2+}$ (II), and $PbCl_2:Sm^{3+}$ (III) at room temperature. Spectral energy distribution of the uv luminescence (IV) of $PbCl_2$ at 10 K. Φ is the radiant power (per constant energy interval).

Finally, we note that the intensity of the blue and red luminescence under excitation in the cation exciton band is about a factor of 10 lower in the rare-earth-doped than in the pure $PbCl_2$ crystals. This phenomenon is discussed in the next section.

6.2 *Transport of Energy in Pure $PbCl_2$ and $PbBr_2$ Crystals*

The origin of the uv, blue and red luminescence has been described in Sects. 1 and 4. The absorption band related to the red emitting center has not been observed in the transparent energy region of the $PbCl_2$ and $PbBr_2$ crystals (7). As the $^1S_0 \rightarrow {}^3P_1$ (Pb^{2+}) absorption band in $PbCl_2$ and $PbBr_2$ and in lead-doped alkali chlorides and bromides is situated at about the same energy, respectively [see Ref. (*1*)], it seems reasonable to assume that the same holds for the Pb^+ absorption band of lowest energy in these compounds. The measurements of Jain and Sai (*31*) revealed that in lead-doped KCl the Pb^+ absorption band of lowest energy is situated at 4.35 eV, i.e., about 0.2 eV to lower energy with respect to the maximum of the $^1S_0 \rightarrow {}^3P_1$ band of Pb^{2+} [see Ref. (*1*)]. So, the absorption band involved in $PbCl_2$ and $PbBr_2$ is expected to be situated in the energy region of the cation exciton band. The excitation spectra (see Figs. 5 and 6) in conjunction with the absorption data indicate that the excitation of the blue and red emission of both lead halides in the energy region of the cation exciton band occurs by transport of energy to the centers responsible for these emissions.

Now we want to discuss various transport processes. The creation of free carriers in $PbCl_2$ and $PbBr_2$ as a function of wavelength has been investigated at low temperatures by Verwey and Westerink (*15*) and Liidja, Plekhanov, and Malysheva (*8*). The results of these experiments in conjunction with the excitation spectra of the blue and red luminescence indicate that in the region of the cation exciton band free carriers do not transport the excitation energy to the luminescence centers. In the energy region of the band edge, however, this transport process occurs, but is inefficient (*1*).

The transport of energy due to the diffusion and trapping of excitons has been the subject of several investigations (*18–22*). In alkali halide crystals the exciton–lattice interaction is strong, so that the excitons are strongly localized (*23*, *24*). Up to now no clear experimental evidence has been presented that excitons are mobile in alkali halides. Our investigations on $PbCl_2$ and $PbBr_2$ do not give information on the mobility of the cation excitons. Liidja, Plekhanov, and Malysheva (*8*) calculated the radius of the cation exciton in $PbCl_2$ (2.2 Å) and in $PbBr_2$ (~4.5 Å). These results could indicate that the excitons are localized as is the case in the alkali halides. On the analogy of the alkali halides we assume that energy transport by diffusion and trapping of excitons in $PbCl_2$ and $PbBr_2$ is improbable.

Radiative energy transfer requires a significant overlap of the emission spectrum of the excited center and the absorption spectrum of the reabsorbing center. For both lead halides the exciton emission band and the excitation spectrum of the blue and red emission overlap to some extent (see Figs. 5 and 6). As mentioned above the absorption bands related to the red emission of both compounds are probably situated in the energy region of the cation exciton band. In view of these considerations it seems likely that the absorption bands of the red and blue centers also overlap the cation exciton band, albeit to a small degree. In view of this poor overlap the so-called cascade process cannot be important in energy transfer to the blue and red centers.

Nonradiative transfer may occur even if a poor overlap exists (*25*, *26*). It may be, therefore, that in both lead halides the excitation in the cation exciton band of the blue and red emission occurs by radiationless transfer from the $^3P_1$ state of the exciton to the excited state of the blue and red emitting centers. The absorption strength of the blue and red centers is not known. The exciton emission in $PbCl_2$ shows a short decay time ($<8 \times 10^{-9}$ sec), taking into consideration that the transition involved is spin-forbidden. Although the spin prohibition is removed by spin-orbit coupling, this can be an indication for nonradiative transfer from the $^3P_1$ level of the exciton. The transfer from the cation exciton center (U) to the centers responsible for the blue (B) and red (R) emission will be restricted to

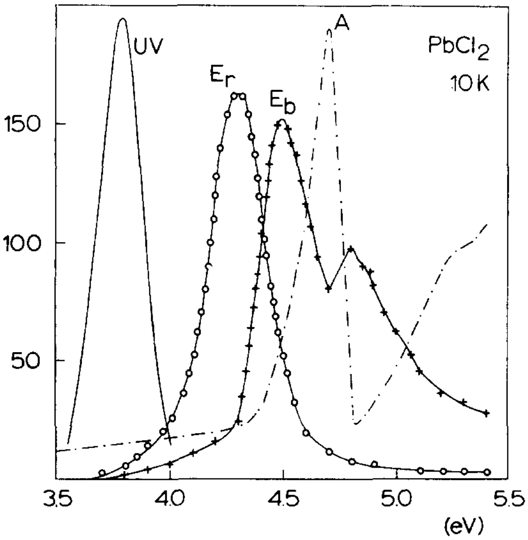

FIG. 5. (uv) Spectral energy distribution of the uv luminescence of $PbCl_2$ at 10 K. (E_b, E_r) Relative excitation spectra of the blue and red luminescence of $PbCl_2$ at 10 K. (A) Relative absorption spectrum of a thin layer of $PbCl_2$, taken from the measurements of Liidja, Plekhanov, and Malysheva (*8*). The curves have been plotted in arbitrary units.

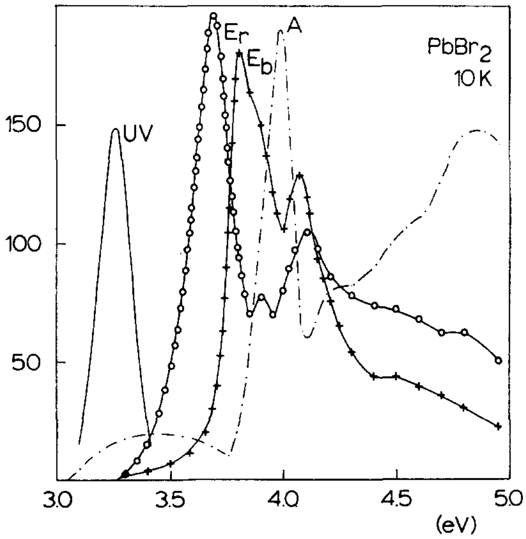

FIG. 6. (uv) Spectral energy distribution of the uv luminescence of $PbBr_2$ at 10 K. (E_b, E_r) Relative excitation spectra of the blue and red luminescence of $PbBr_2$ at 10 K. (A) Relative absorption spectrum of a thin layer of $PbBr_2$, taken from the measurements of Liijda, Plekhanov, and Malysheva (*8*). The curves have been plotted in arbitrary units.

short distances as the overlap is rather poor in both cases. For the blue luminescence (U → B transfer) the excitation energy only needs to be transferred over short distances as the centers involved form part of the host material. For the U → R transfer the situation is quite different. EPR measurements (*6*, *7*) showed that the concentration ratio

$$[U]:[R] \text{ is } \sim 2000:1 \text{ in } PbCl_2 \text{ and } PbBr_2.$$

In view of the efficiency measurements about 20% of the excitation energy in $PbCl_2$ and ~40% in $PbBr_2$ is transferred to the R centers. Comparing the foregoing data with the estimations of Dexter (*26*) we doubt whether U in $PbCl_2$ and $PbBr_2$ is able to sensitize the R centers with the efficiencies involved, even in the case of electric dipole–dipole interaction. The absorption and emission band of U, however, overlap to some extent in both lead halides (see Figs. 5 and 6). So, U → U transfer can occur also. We conclude, therefore, that the excitation energy can be transferred to the R centers via U → U transfer (compare the discussion on $PbCl_2:Sm^{3+}$).

From the temperature dependence measurement of the blue luminescence of $PbCl_2$ in conjunction with the excitation spectra at low temperatures it appears that the intensity of this luminescence excited in the center itself decreases by a factor of 4 in the temperature region 30–5 K. In this region, however, the intensity of the blue luminescence excited in the exciton band is reduced by a factor of 10 (see Fig. 1A). We assume that the "extra decrease" in intensity under excitation in the exciton band is due to the appearance of the uv and violet luminescence (see Sect. 5) or, in other words, the probability for uv radiative emission becomes larger than the transfer probability. The decrease in intensity measured under excitation in the blue center may be due to the fact that energy is transferred from the blue to the yellow center. This center ($Cl_{Cl}^{\cdot}$) is only present at temperatures lower than 50 K [see Refs. (*1*, *6*, *7*)]. The same would be expected for the red emission of $PbCl_2$. The temperature dependence measurement of this emission, however, was carried out under excitation in the very tail of the cation exciton band. In this energy region the uv luminescence is excited inefficiently. The temperature dependence curves of the red and blue luminescence of $PbBr_2$ show an opposite path in the temperature region 40–10 K, while the intensity of the uv luminescence is constant and low. This phenomenon may be due to the fact that the probability for U → U transfer decreases and becomes smaller than the U → B transfer probability. Since the red center can only be excited via U → U transfer it seems that the blue emission will replace the red emission. In view of the difference in overlap of the U-absorption and -emission band at 100 K and 5 K [see Ref. (*1*)] it seems likely that the U → U transfer probability decreases in the temperature region involved.

In Sect. 6.1 we mentioned the fact that the intensities of the blue and red luminescence under excitation in the cation exciton band are reduced by a factor of ten due to the presence of Eu^{2+} or Sm^{3+} in $PbCl_2$. Since the blue and the red emission as well as the emission of the Eu^{2+} and Sm^{3+} ions are all excited by nonradiative transfer, the probability for the transfer to the rare-earth ions will be larger. The transition involved in Eu^{2+} is allowed ($4f \rightarrow 5d$), whereas that on Sm^{3+} is forbidden ($4f \rightarrow 4f$). So, it is unlikely that the reason for this effect can be found in the differences of absorption strength of the centers. The reduction of the intensities of the blue and red luminescence will be due to the large difference in overlap of the U emission band and the absorption bands of Eu^{2+} and Sm^{3+} (cf. Fig. 4) with respect to the overlap with the absorption bands of the B and R centers.

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