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Some Observations on the Photoluminescence of PbFCl and PbFBr Single Crystals

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Violet, blue, yellow, and red emissions were observed for PbFBr, which correspond to similar emissions of $PbBr_2$. Contrary to results with $PbBr_2$, the luminescence is not excited in the exciton absorption region, but in low-energy absorption bands. These bands probably arise from a deviation from molecularity. PbFCl shows a blue and a red emission, which are excited in the low-energy absorption bands as well as in the exciton region. In addition a blue-green luminescence was observed which strongly depends on the quality of the crystal.

1. Introduction

The luminescence properties of single crystals of the binary lead halides, PbI_2, $PbBr_2$, $PbCl_2$, and β-PbF_2, have gained much interest (*1–6*). The number of emission bands (and lines in case of PbI_2), as well as details of the emission and excitation spectra depend strongly on the sample preparation. Five emission bands were found both for $PbCl_2$ and $PbBr_2$ (*2, 6*), and two bands for β-PbF_2 (*5, 6*). The ternary lead halides PbFCl and PbFBr have been neglected for a long time. It is the aim of our study to examine the optical properties of these compounds. This paper gives an account of the luminescence behavior of single crystals of $PbFX$ ($X =$ Cl, Br) which were grown in our laboratory during the past few years (*7*). A description of the purity and structure of the $PbFX$ single crystals and an account of the experimental setup and techniques are given in (*6*).

2. Results

2.1. Absorption Spectra

Knowledge of the absorption spectra will be helpful in understanding the luminescence spectra. For that purpose, optical density measurements were performed. The optical density, defined as $-\log T$, where T is the transmittance, is shown as a function of photon energy in Fig. 1. The spectra for $PbBr_2$ and $PbCl_2$ (curves 1 and 3, respectively) are also presented for comparison. They exhibit a steep rise only. On the contrary, curve 2 for PbFBr exhibits a maximum at 3.72 eV, whereas curve 4 suggests that also for PbFCl a band is present in the tail of the absorption edge.

Reflectance measurements were carried out on single crystals at 84°K to elucidate more structure, and the spectral dependence of the absorption coefficient was derived from the Kramers–Kronig transformation (*8*). For PbFBr, relatively weak absorption bands were observed at 3.65 eV ($\alpha = 1 \times 10^4$ cm^{-1}) and 3.95 eV ($\alpha = 3 \times 10^4$ cm^{-1}) followed by a strong exciton absorption peak at 4.55 eV ($\alpha = 0.9 \times 10^6$ cm^{-1}). Obviously, the band at 3.65 eV corresponds to the band at 3.72 eV in Fig. 1, which was measured on another specimen. A discrepancy exists, however, between their absorption coefficients. α was derived for the 3.72 eV maximum in the optical density spectrum using the relation:

$$T = (1 - R)^2 e^{-\alpha d}, \qquad (1)$$

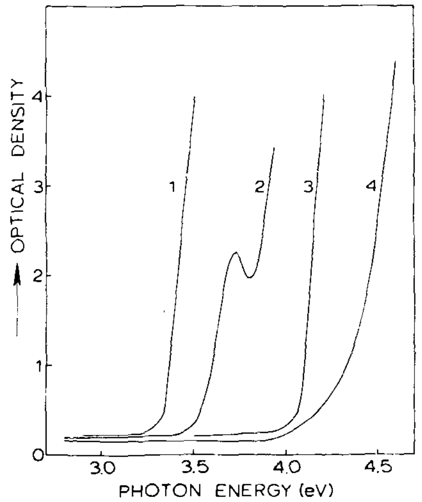

FIG. 1. Optical density vs photon energy of single-crystalline disks at room temperature. 1, $PbBr_2$, thickness $d = 236$ μm; 2, PbFBr, $d = 144$ μm; 3, $PbCl_2$, $d = 230$ μm; 4, PbFCl, $d = 63$ μm.

where R is the reflectance and d is the sample thickness. A low value of 400 cm^{-1} was obtained in this way. This discrepancy illustrates a difference in the state of perfection of different crystal specimens. It is also possible that the absorption centers are concentrated at the surface and near dislocations, so that the effective thickness d in Eq. (1) is much smaller than the crystal thickness and α therefore larger. The absorption spectrum of PbFCl (*8*) shows a strong exciton absorption peak at 5.13 eV ($\alpha = 1.1 \times 10^6$ cm^{-1}) and several weaker bands at its low-energy side near 4.1 and 4.8 eV.

2.2. *Luminescence of PbFBr*

The emission spectra at 4.2°K of PbFBr single crystals are presented in Fig. 2. Four bands were observed situated in the red, yellow, blue, and violet spectral regions. The violet band was shifted somewhat to lower energies upon excitation in the low-energy tail of the excitation band. The position of the maximum and the half-width of the blue band also depended on the excitation energy. This might be caused by the partial overlap of the yellow band. The red and yellow bands strongly overlapped. Upon excitation with 3.60 eV, both emissions had the same intensity, and the apparent band maxima were found closer to each other.

The excitation spectra of the luminescence of PbFBr at 4.2°K have been depicted in Fig. 3. The red emission was observed via a low-energy pass filter absorbing all energies above 1.7 eV. In Figs. 3b and 3c the dashed curves pertain to another specimen.

The temperature behavior of the luminescence intensities is shown in Fig. 4. The emission bands were excited in a maximum of excitation and were selected via suitable filters. Upon excitation with 3.63 eV, the red and yellow emissions had about equal intensities. So the experimental curve for the intensity of the red emission vs the temperature (Fig. 4a) is influenced by the presence of the yellow emission. Upon excitation with 3.79 eV, on the contrary, the red emission was more intense than the yellow one by a factor of three, and thus the influence of the yellow luminescence was considerably less. At 80°K the emission and excitation spectra of the red and yellow bands were hardly changed with respect to 4.2°K. These emissions were quenched above the same temperature (~250°K). The blue and violet luminescence

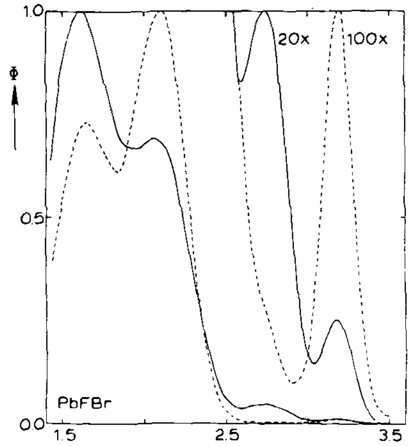

FIG. 2. Spectral energy distribution of the emission bands of PbFBr at 4.2°K. Φ gives the radiant power per constant energy interval in arbitrary units. All spectra are normalized to $\Phi = 1$. - - -, $E_{exc} = 3.67$ eV; ——, $E_{exc} = 3.87$ eV.

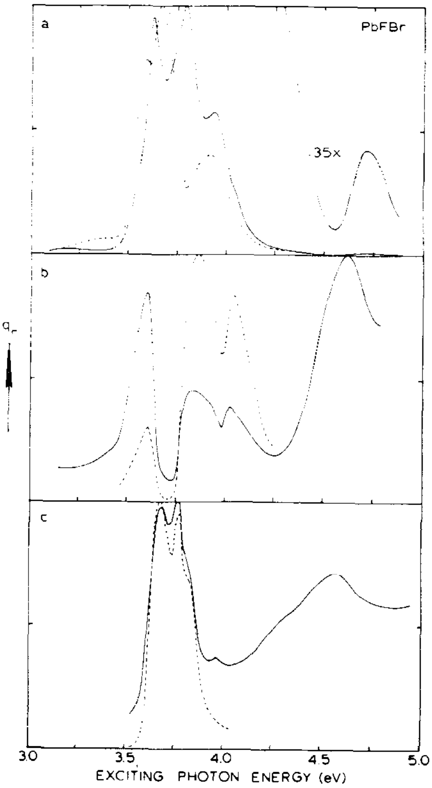

FIG. 3. Relative excitation spectra of the luminescence of PbFBr at 4.2°K. q_r denotes the relative quantum output. All spectra are normalized to $q_r = 1$. (a) ——, $E_{obs} < 1.7$ eV; ----, E_{obs} 2.10 eV. (b) ——, E_{obs} 2.75 eV; ----, E_{obs} 2.75 eV (different specimen). (c) ——, E_{obs} 3.18 eV; ----, E_{obs} 3.18 eV (different specimen).

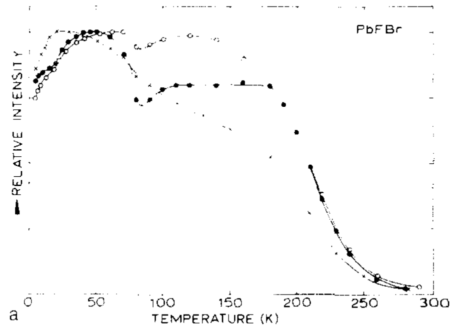

FIG. 4a. Temperature dependence of the intensities of the emissions of PbFBr. The curves are not drawn to the same scale. ×, yellow band, E_{obs} 2.10 eV, E_{exc} 3.67 eV. ○, red band, E_{obs} 1.60 eV, E_{exc} 3.63 eV. ●, red band, $E_{obs} < 1.7$ eV, E_{exc} 3.79 eV.

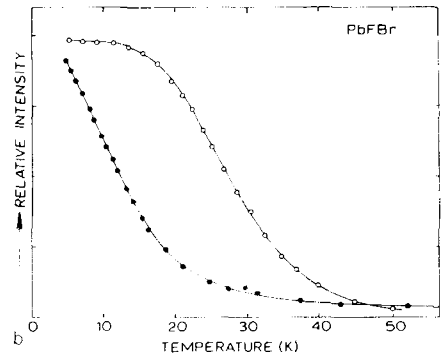

FIG. 4b. Temperature dependence of the intensities of the emissions of PbFBr. The curves are not drawn to the same scale. ○, blue band, E_{obs} 2.74 eV, E_{exc} 3.85 eV. ●, violet band, E_{obs} 3.18 eV, E_{exc} 3.67 eV.

TABLE I

QUANTUM EFFICIENCIES q OF THE LUMINESCENCE OF PbFBr AND PbFCl AT 4.2°K

	PbFBr		PbFCl	
Band	q (%)	E_{exc} (eV)	q (%)	E_{exc} (eV)
Red	25	3.79	35	4.44
Yellow	25	3.67		
Blue-green			1	4.05
			30	3.6 (specimen II)
Blue	1	3.60	5	4.27
			30	4.92 (150°K)
Violet	1	3.67		

(Fig. 4b) were quenched above ~40 and ~25°K, respectively.

The quantum efficiencies of the red and yellow luminescences were measured at 77°K. Proceeding from these values the efficiencies at 4.2°K of all emissions were derived, taking into account their temperature dependences, excitation maxima and relative intensities. The results are given in Table I.

In view of the difference in quantum efficiencies between the yellow and red emissions on the one hand, and the violet and blue emissions on the other hand, the increase of the former intensities in the intensity–temperature curves (Fig. 4a) cannot be explained by energy transfer only. Nevertheless, the violet emission band overlaps the excitation spectra of the yellow and red emissions to some extent (Figs. 2 and 3a), so that the condition for a nonradiative energy transfer is satisfied. Free carriers are probably more important in the transfer process because photoconductivity was measured (*9*) upon excitation in the low-energy absorption bands.

2.3. Luminescence of PbFCl

Single crystals of PbFCl, which were grown at different times, were not of equal quality because of still uncontrollable factors in sample preparation (*6*). The emission spectra of different specimens always consisted of three bands in the red, blue–green, and blue spectral regions, with little scatter in the position of the maxima. But in transparent crystals like the specimen I discuss below the blue–green luminescence was very weak, whereas in more or less opaque crystals, of which specimen II is a typical representative, this luminescence was clearly observable. The excitation spectra of the luminescences also varied considerably from sample to sample.

Figure 5 presents the emission spectra of the transparent specimen I. The luminescence could only be excited efficiently for $E_{\mathrm{exc}} \geqslant$ 4.0 eV. The maximum and half-width of the red emission band showed an unusual dependence on the excitation energy and the temperature. This may be indicative of a composite character. The blue–green luminescence was detected as a shoulder upon excitation with about 4.0 eV radiation. The blue luminescence was most efficiently excited with 4.27 eV radiation at 4.2°K, but with 4.92 eV radiation at 80°K.

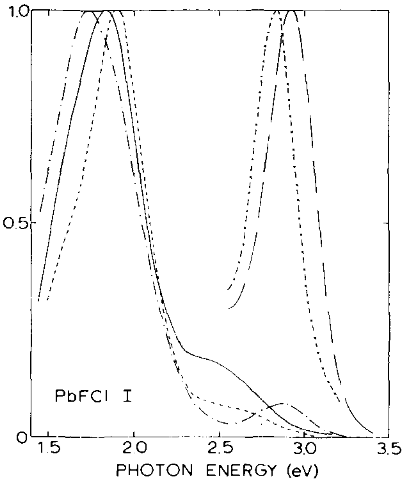

FIG. 5. Spectral energy distribution of the emission bands of PbFCl, specimen I, upon excitation with various energies and at two temperatures. ——, $E_{\mathrm{exc}} = 4.00$ eV, $T = 4.2$°K; —·—, $E_{\mathrm{exc}} = 4.12$ eV, $T = 4.2$°K; ——, $E_{\mathrm{exc}} = 4.27$ eV, $T = 4.2$°K; ---, $E_{\mathrm{exc}} = 4.00$ eV, $T = 80$°K; ×—×, $E_{\mathrm{exc}} = 4.96$ eV, $T = 80$°K.

In Fig. 6 the emission spectra of the opaque specimen II at 4.2°K are depicted. The main difference with specimen I was the fact that the blue–green luminescence could be excited for $E_{\mathrm{exc}} \leqslant 4.0$ eV and was far more efficient. Its maximum was found at 2.40 eV, and the half-width was 0.55 eV. The red emission could also be excited with energies below 4.0 eV. The blue luminescence was observed as a shoulder at 2.9 eV.

The excitation spectra of the luminescence of specimen I are shown in Fig. 7. The red emission could be excited most effectively in a broad energy region between 4.0 and 5.0 eV (Fig. 7a). The minimum at 5.15 eV coincides with the position of the exciton peak in the absorption spectra (*8*). Under observation of the luminescence at 2.5 eV the spectra in Fig. 7b were recorded. Only excitation at about 4.05 eV promoted the blue–green luminescence. The excitation spectra of th blue emission (Fig. 7c) show some interestin e features. Although these spectra are represg

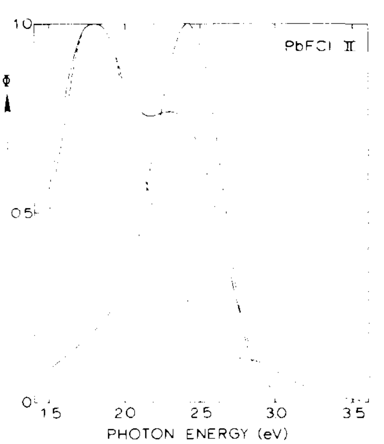

FIG. 6. Spectral energy distribution of the emission bands of PbFCl, specimen II, at 4.2°K upon excitation with various energies. —·—, $E_{\rm exc} = 3.55$ eV; ——, $E_{\rm exc} = 3.88$ eV; ---, $E_{\rm exc} = 4.27$ eV.

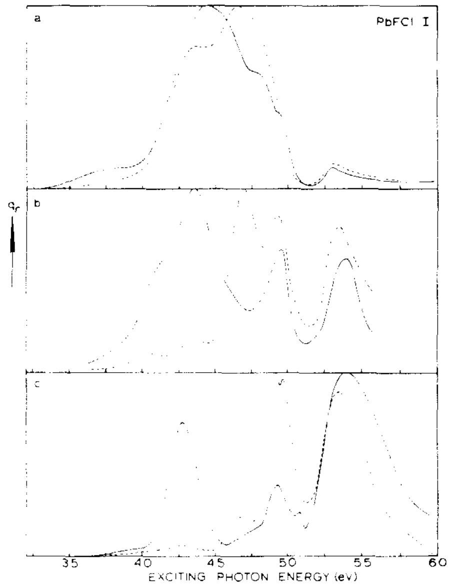

FIG. 7. Relative excitation spectra of the luminescence of PbFCl, specimen I, at 4.2°K (solid line) and 80°K (dashed line). (a) $E_{\rm obs} = 1.85$ eV; (b) $E_{\rm obs} = 2.5$ eV; (c) $E_{\rm obs} = 2.92$ eV at 4.2°K, 2.86 eV at 80°K.

ented with normalized amplitudes, they almost have the same scale. Consequently, on raising the temperature, the emission intensity decreased upon excitation in the low-energy maximum at 4.27 eV, but increased upon excitation at 4.92 eV. The minimum at 5.13 eV coincides with the exciton absorption maximum.

Figure 8 shows the excitation spectra for specimen II. The main difference with specimen I (Fig. 7) is the effective excitation of the luminescence below 4.0 eV. The spectra in Fig. 8b were obtained under observation at 2.4 eV. Only excitation in the bands with maxima at 3.6 eV and 3.9 eV promoted the blue-green emission. The quantum efficiency

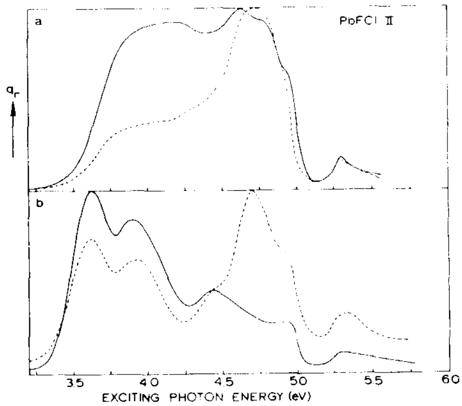

FIG. 8. Relative excitation spectra of the luminescence of PbFCl, specimen II, at 4.2°K (solid line) and 80°K (dashed line). (a) $E_{\rm obs} = 1.85$ eV; (b) $E_{\rm obs} = 2.4$ eV.

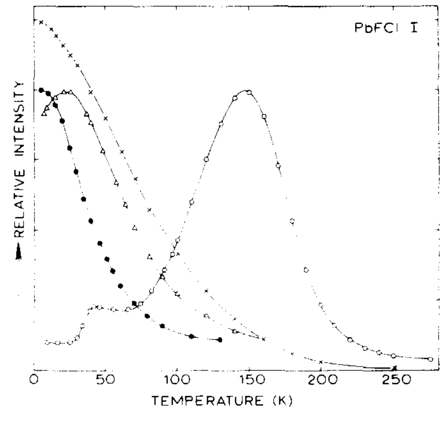

FIG. 9. Temperature dependence of the intensities of the emissions of PbFCl, specimen I, drawn on a relative scale. ×, red band, $E_{\rm obs} = 1.85$ eV, $E_{\rm exc} = 4.40$ eV. △, blue-green band, $E_{\rm obs} = 2.5$ eV, $E_{\rm exc} = 4.00$ eV. ●, blue band, $E_{\rm obs} = 3.0$ eV, $E_{\rm exc} = 4.25$ eV. ○, blue band, $E_{\rm obs} = 3.0$ eV, $E_{\rm exc} = 4.92$ eV.

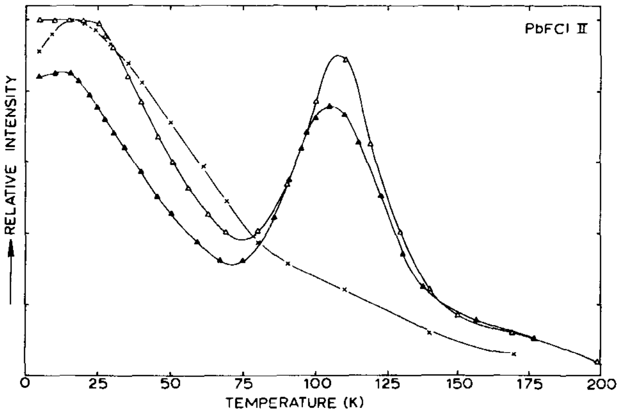

FIG. 10. Temperature dependence of the intensities of the emissions of PbFCl, specimen II, drawn on a relative scale. ×, red band, $E_{obs} = 1.85$ eV, $E_{exc} = 3.82$ eV. △, blue–green band, $E_{obs} = 2.46$ eV, $E_{exc} = 3.60$ eV. ▲, blue–green band, $E_{obs} = 2.40$ eV, $E_{exc} = 3.90$ eV.

of the blue–green emission at 4.2°K, $E_{exc} =$ 3.6 eV, was roughly 30%.

Figure 9 illustrates the thermal behavior of the luminescence intensities for specimen I. The red emission was quenched above ~150°K. The curve for the blue–green emission may be influenced by the partial overlap with the red band (cf. Fig. 5). The blue luminescence was quenched above ~100°K upon excitation in the low-energy maximum at 4.27 eV (cf. Fig. 7c). On raising the temperature, an increase of the intensity was observed, as mentioned before, upon excitation with 4.92 eV radiation. The highest intensity was reached at about 150°K with a quantum efficiency of ~30%. At room temperature, all emissions were quenched.

In Fig. 10 the intensity vs temperature curves of the red and blue–green emissions of specimen II are shown. The red emission was excited below 4.0 eV. The resulting curve is roughly the same as the one obtained for specimen I. The blue–green luminescence exhibited an unusual temperature behavior upon excitation in the maxima at 3.6 or 3.9 eV (cf. Fig. 8b). At very low temperatures, the behavior is similar to the result for specimen I (cf. Fig. 9). Above ~75°K, however, the intensity started to increase and reached a maximum at about 105°K. The emission was quenched above ~175°K. This temperature curve was measured reproducibly but the intensity and the temperature of the maximum depended on the experimental circumstances. Photoconductivity was also observed upon excitation in the maxima at 3.6 and 3.9 eV (*9*). The photocurrent is an order of magnitude higher for material like specimen II than for material like specimen I. Photoholes are the majority charge carriers (*9*). In view of the present data we can only suggest that the increase of the blue–green luminescence might be related to the migration of charge carriers.

In Table I, the quantum efficiencies of PbFCl are listed. For specimen I only the efficiency of the red emission at 77°K was measured. The other values were derived from the emission and excitation spectra and the intensity vs temperature curves.

2.4. Polarization of the Luminescence of PbFCl

For the polarization measurements a clear single crystal of PbFCl was used, referred to as specimen III hereafter, having dimensions of 10 × 5 × 1.5 mm^3. One side of the crystal was polished in a random direction perpendicular to the cleavage plane, using 0.05 μ Al_2O_3 powder. First, measurements were performed with the exciting radiation polarized $\mathbf{E} \perp \mathbf{c}$ only, while the emitted radiation was observed for $\mathbf{E} \perp \mathbf{c}$ and $\mathbf{E} \parallel \mathbf{c}$ via filters and an analyzer (*6*). The blue and red emissions appeared to be partially polarized perpendicular to the c-axis. The degree of polarization defined by

$$P = (I_{\perp} - I_{\parallel})/(I_{\perp} + I_{\parallel}),$$

where $I_{\perp}$ and $I_{\parallel}$ refer to the emission intensity for $\mathbf{E}\perp\mathbf{c}$ and $\mathbf{E}\parallel\mathbf{c}$, respectively, amounted to 4% for the blue luminescence at 4.2°K, $E_{exc} = 4.27$ eV, $E_{obs} = 2.90$ eV. For the red luminescence, P was found to be 8% at 4.2°K and 5% at 80°K, $E_{exc} = 4.30$ eV, $E_{obs} = 1.85$ eV, but this degree of polarization strongly depended on the excitation energy as shown in Fig. 11. These polarization spectra exhibit a maximum at about 4.30 eV.

Another arrangement was used to measure the excitation spectra of the blue emission for different polarization directions of the exciting radiation, while the emitted light was observed for $\mathbf{E}\perp\mathbf{c}$ only (*6*). The results at 4.2 and 80°K are given in Fig. 12. Some features are readily recognized. At 4.2°K, the band at 3.9 eV did not show any dependence on the polarization. The maximum around 4.25 eV was lying at lower energy for $\mathbf{E}\parallel\mathbf{c}$ than for $\mathbf{E}\perp\mathbf{c}$, whereas the reverse was true for the maxima around 4.8 and 5.0 eV. At 80°K, all maxima were observed at slightly lower energy, but the same polarization dependence was found as at 4.2°K. The spectra for $\mathbf{E}\perp\mathbf{c}$ have much in common with the excitation spectra for specimen I (cf. Fig. 7c), but the band at 3.9 eV is hardly present for specimen I.

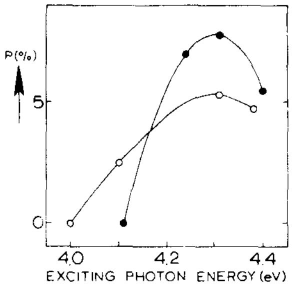

FIG. 11. Polarization spectrum of the red emission of PbFCl, specimen III. ●, E_{obs} 1.85 eV, $T = 4.2$°K; o, E_{obs} 1.85 eV; $T = 80$°K.

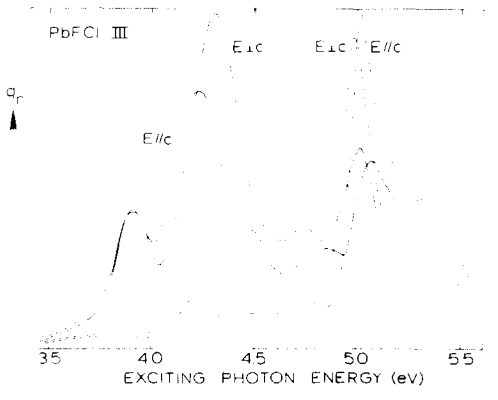

FIG. 12. Relative excitation spectra of the blue luminescence of PbFCl, specimen III, at 4.2°K (solid line) and 80°K (dashed line). $E_{obs} = 2.90$ eV. The exciting radiation is polarized parallel or perpendicular to the c-axis. Curves for the same temperature are drawn on the same scale.

3. Discussion

3.1. Comparison between the Luminescence of Binary and Ternary Lead Halides

The luminescence results on single crystals of $PbCl_2$ and $PbBr_2$ have been described in (*6*). The emission bands can be classified as follows.

(i) An ultraviolet emission is attributed to the recombination of a self-trapped exciton ($^3P_1 \rightarrow {}^1S_0$ transition on a Pb^{2+} ion). A Similar emission was observed for β-PbF_2 (*5, 6*).

(ii) Violet and blue emissions are ascribed to the recombination of an exciton bound by a defect ($^3P_1 \rightarrow {}^1S_0$ transition on a Pb^{2+} ion in the neighborhood of a defect).

(iii) Yellow and red emissions are attributed to a transition involving photocreated defects which have been generated upon ultraviolet irradiation at low temperatures.

In this connection, the emission results of PbFCl and PbFBr can be summarized as follows.

(i) An emission similar to the ultraviolet emission of the binary halides is lacking for both compounds.

(ii) PbFBr shows a violet and a blue emission with very low quantum efficiency. PbFCl shows a blue emission with a maximum efficiency at ~150°K, and a blue–green emission, the efficiency of which depends strongly on the state of perfection of the crystal.

(iii) A yellow emission was observed only for PbFBr. Red emissions were measured for both compounds.

The most striking difference between the luminescence of the binary and ternary lead halides is met with in the excitation spectra. β-PbF_2, $PbCl_2$, and $PbBr_2$ exhibit an exciton peak at the absorption edge. The exciton may either recombine and give rise to the uv emission, or transfer its energy to other centers. The excitation spectrum of the uv emission shows a minimum corresponding to the exciton absorption peak, so that the uv emission is most efficiently excited in the wings. The other luminescence bands of $PbCl_2$ and $PbBr_2$ are also excited in the exciton region.

PbFCl and PbFBr exhibit a similar exciton peak at 5.13 and 4.55 eV, respectively (*8*, *10*). On the low-energy side of these peaks some weaker absorption bands occur (cf. Section 2.1 and Fig. 1). All emissions are effectively excited in the region of these low-energy absorption bands (Figs. 3, 7, and 8). No emission bands were recorded which were exclusively excited in the exciton absorption peak. The position of such exciton emission bands may be estimated from an interpolation of the absorption and emission data for the excitons of PbF_2, PbFCl, $PbCl_2$, PbFBr, and $PbBr_2$. A value of 3.7 eV is estimated for PbFBr, and of 3.9 eV for PbFCl. These emission bands overlap or even coincide with the additional absorption bands (cf. Fig. 1), so that the exciton emission is quenched due to efficient energy transfer, either nonradiative or even radiative, to other centers. In the case of PbFCl these may be luminescent centers, because the emissions are relatively well excited in the exciton region (Figs. 7 and 8). In the case of PbFBr, however, excitation in the exciton region hardly brings about luminescence (cf. Fig. 3 and the quantum efficiencies in Table I).

3.2. *The Nature of the Low-Energy Absorption Bands of PbFX*

The absorption coefficients of the low-energy absorption bands amount to several percent of the exciton absorption coefficients, as mentioned before in Section 2.1. These additional absorption bands may be assigned to transitions involving Pb^{2+} ions with a deviating coordination. This deviation might be caused by the presence of an O^{2-} ion on a F^- or X^- site (*10*). More probably, however, the deviation is due to an excess of either PbF_2 or PbX_2 in PbFX, because the phase diagrams (*11*) and the work of Banashek *et al.* (*12*) reveal that several percent of the binary lead halides can dissolve into the ternary compound during the crystal growth. Ionic conductivity measurements (*9*) confirm such an excess in our crystals. The differences between the excitation spectra of several PbFCl specimens thus refer to a different coordination for part of the Pb^{2+} ions. Segregation of a second phase, however, may also obscure the absorption and excitation spectra.

3.3. *The Excitation Spectra of PbFBr*

The excitation spectra in Fig. 3 need further attention. The maxima at 3.67 and 3.90 eV for the yellow emission correspond with the additional absorption maxima. On the contrary, these absorption maxima manifest themselves as minima in the excitation spectra of the red, blue, and violet emissions. The exciton transition at 4.55 eV appears as an excitation minimum for the red luminescence, but as an excitation maximum for the blue and violet luminescence. The coincidence of excitation minima with absorption maxima is a well-known feature (*13*) which may occur if the absorption coefficient is high enough to confine the exciting radiation to a thin layer, in which surface recombination diminishes the luminescence yield. The surface condition of the crystal is decisive for the occurrence of either excitation minima or maxima (*13*). The results in Fig. 3 indicate therefore that the different luminescent centers are not distributed homogeneously over the crystal. This conclusion is supported by two observations: First, the yellow luminescence of a PbFBr crystal is particularly visible near cracks and other discontinuities. Second, some specimens show blue-luminescent spots upon excitation of certain irregular parts of the crystals. In one case, an excitation spectrum of the blue emission was obtained showing maxima at 3.7 and 3.9 eV, and a minimum at 4.6 eV, in fact the reverse situation of Fig. 3b. It is not understood why the absorption maxima give rise to excitation maxima for the yellow emission, but to minima for the red emission. An interesting analogy was found in the literature (*14*) for the red and yellow–green luminescence of HgI_2 single crystals.

3.4. The Nature of the Luminescent Centers of PbFX

The red luminescence of $PbCl_2$ and $PbBr_2$ has been attributed by De Gruijter and Kerssen (*3*) to radiative decay of Pb'_{Pb} centers (Pb^+), or pairs of them, created by uv irradiation. The formation of Pb^+ ions can be considered as a first step to the photochemical decomposition which occurs above about 200°K (*15*). We observed that PbFCl and PbFBr also exhibit photolysis upon uv irradiation at room temperature. The red emissions of $PbFX$ and PbX_2 have comparable band positions and half-widths. In addition, they are quenched at relatively high temperatures (*4*). Because of these correspondences the red emissions of $PbFX$ are also considered to be due to Pb'_{Pb} centers.

According to De Gruijter and Kerssen (*3*), the yellow luminescence of PbX_2 is due to excitation and decay of hole centers. Halide ions near dislocations are trapping sites for holes, so the hole centers are possibly $X_X^{\cdot}$. The yellow emission of PbFBr is also attributed to a hole center in view of the corresponding spectral characteristics. No separate yellow emission band was detected for PbFCl, but the unusual shift of the red emission band with temperature and excitation energy (Fig. 5) suggests a composite character for this band. We assume that the yellow band is weak and hidden under the red band.

The maxima and half-widths of the blue and violet emissions of the lead halides are collected in Table II. There is some evidence that the violet and yellow emission of PbX_2 occur simultaneously (*6*). A similar observation is made for $PbFX$: PbFBr shows both a violet and a yellow emission, whereas for PbFCl the violet emission is absent and the yellow one weak. In analogy to PbX_2 we attribute the 3.19 eV band of PbFBr to a transition on a Pb^{2+} ion in the neighborhood of a photohole.

It is not clear whether the blue emission of PbFBr has a composite character. Its quantum efficiency is very low. In some cases the excitation was most efficient on irregular sites of the crystal. On the contrary the blue emission of PbFCl was not confined to certain parts of the crystal. We assume that the blue luminescence of $PbFX$ and PbX_2 are similar, and ascribe it to a transition involving Pb^{2+} in the neighborhood of an unknown defect which might be an anion impurity like I^- (*16*).

The blue–green emission of PbFCl which has no analog for PbFBr was mainly observed in opaque crystals, and is associated with excitation bands around 3.6 and 3.9 eV. This luminescence may be attributed to a transition on a Pb^{2+} ion with a deviating coordination like the low-energy absorption bands discussed in Section 3.2.

TABLE II

MAXIMA AND HALF-WIDTHS OF THE VIOLET AND BLUE EMISSIONS OF PbX_2 AND $PbFX$ AT 4.2°K

	Violet emission		Blue emission	
	Maximum (eV)	Half-Width (eV)	Maximum (eV)	Half-Width (eV)
PbFCl	—	—	2.92	0.36
$PbCl_2$	3.15	0.25	2.88	0.44
PbFBr	3.19	0.22	2.73	0.32
			2.67	0.23
$PbBr_2$	2.94	0.18	2.74	0.26

3.5. *The Temperature Dependence of Blue-emission Intensity of PbFCl*

Figures 7c and 9 reveal that the intensity vs temperature curve for the blue emission upon excitation in the exciton peak is different from the curve for excitation in the low-energy band. The following explanation may be proposed: The higher-energy excitation creates excitons in a thin surface layer of the crystal because the absorption coefficient is high. At 4.2°K some energy transfer takes place to the red-emitting (Pb^+) and blue-emitting centers in addition to a considerable amount of non-radiative recombination. At 80°K and especially at 150°K, the exciton mobility is higher, allowing the excitons to diffuse from the surface layer with its killer centers and Pb^+ centers to the bulk. In this way, an enhanced energy transfer to the blue-emitting center is possible. The model proposed in Section 3.4 admits this center in the bulk of the crystal.

3.6. *Polarization of the Luminescence of PbFCl*

In spite of the difficulties encountered in polishing a crystal of a layer compound perpendicular to the layers, there are reasons to believe that the polarization results are reliable and not just the consequence of experimental circumstances: Different degrees of polarization were measured for the blue and the red luminescence; in the latter case, the polarization depended on the excitation energy (Fig. 11) in a way resembling the excitation spectrum (Fig. 7a) and the polarization decreased on raising the temperature. It is likely that some depolarization occurred because of the imperfect polishing of the crystal side. Liidja and Plekhanov (*17*) have observed that the blue luminescence of a polished $PbCl_2$ crystal was polarized for 8% at 4.2°K.

The polarized excitation spectra of the blue emission of PbFCl (Fig. 12) are of more importance. As discussed above, the maxima around 5.0 eV do not correspond to absorption maxima. At 5.0 eV, absorption takes place in the low-energy side of the exciton peak. The exciton absorption can be described as the $^1S_0 \rightarrow {}^3P_1$ transition on a Pb^{2+} ion in a crystal field of C_{4v} site symmetry. The $^3P_1$ level will be split in a nondegenerate state of A_1 symmetry and a doubly degenerate state of symmetry E. The splitting of the exciton was not measured in reflectance (*8*), because the incident radiation was polarized with $\mathbf{E} \perp \mathbf{c}$ only. From Fig. 12, a splitting of the exciton peak of about 0.03 eV may be inferred as indicated in Fig. 13. This value is comparable to the splitting observed for $PbCl_2$ (*18*) and $PbBr_2$ (*8*, *18*).

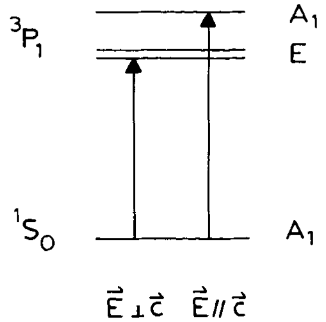

FIG. 13. Energy level diagram for the exciton transitions of PbFCl.

The sign of the splitting can be understood as follows: A lead ion in PbFCl is surrounded by four fluoride ions on one side in the direction of the *c*-axis, and by five chloride ions on the other side in the form of a pyramid. One orbital component of the antibonding $^3P_1$ state will lie along the *c*-axis, so that σ-type bonding is possible with a chloride *p*-state. The other two orbital components lie in a plane perpendicular to the *c*-axis, in which no σ-type bonding can occur. The A_1 level is therefore expected to have the higher energy.

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