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## Photoluminescence of orthorhombic and cubic PbF<sub>2</sub> single crystals

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**Abstract.** The photoluminescence of orthorhombic and cubic PbF<sub>2</sub> crystals has been studied with the use of a deuterium lamp or synchrotron radiation as the light source. The spectra of orthorhombic samples exhibit a single band at 2.07 eV, while the spectra of cubic samples show an intense band at 4.10 eV, accompanied by some other bands depending on the sample. These two main bands are stimulated only under exciton-band excitation. No luminescence is detected when both crystals are excited with photons in the band-to-band region. The present results are compared with earlier data for PbCl<sub>2</sub> and PbBr<sub>2</sub> which have the orthorhombic structure. The relaxation processes of excitons and electron-hole pairs in lead halides are discussed.

### 1. Introduction

The optical properties of lead halides have been studied extensively as an interesting subject in solid-state spectroscopy [1–15]. The reason for this seems to be threefold. First, their fundamental absorption edges are dominated in common by ‘cationic’ transitions due to excitons localized on the Pb<sup>2+</sup> ion (intra-atomic  $6s^2 \rightarrow 6s6p$  transition) [1–9]. This is in clear contrast to the case for the well-studied alkali halides, for which the fundamental absorption edge is due to transitions from the anion p states to the cation s states [16]. Second, PbI<sub>2</sub> is a semiconducting compound with a gap energy of 2.5 eV, while PbBr<sub>2</sub>, PbCl<sub>2</sub> and PbF<sub>2</sub> are insulators with gap energies greater than 4.0 eV. Third, the Pb halide crystals have three different structural modifications; hexagonal (PbI<sub>2</sub>), orthorhombic (PbBr<sub>2</sub>, PbCl<sub>2</sub> and  $\alpha$ -PbF<sub>2</sub>) and cubic ( $\beta$ -PbF<sub>2</sub>) [17].

Among the lead halides, PbF<sub>2</sub> is particularly interesting because it has two structural modifications that one can obtain under normal conditions. The  $\alpha$ -phase is more stable below 320 °C, but the  $\beta$ -phase is also metastable at low temperatures [18]. Furthermore, according to a recent study [19], both the cubic and orthorhombic modifications may appear stable under normal conditions.

In the orthorhombic structure, the lead ions are surrounded by nine halogen ions at different distances. This structure can also be thought of as a considerably distorted close packing of

halogen ions with the lead ions accommodated in the same plane as them. In the cubic structure, each lead ion is at the centre of eight halogen ions situated at the corners of a surrounding cube, and each halogen ion has around it a tetrahedron of lead ions. This is often called the fluorite-type structure, like that of  $\text{CaF}_2$  or  $\text{CdF}_2$ .

The luminescence properties of  $\text{PbBr}_2$ ,  $\text{PbCl}_2$  and  $\text{PbF}_2$  have recently regained particular interest both in fundamental [20–23] and applied [24, 25] research. This was inspired by the finding of electron self-trapping in  $\text{PbCl}_2$  [26, 27] and also by the successful growth of  $\alpha$ - $\text{PbF}_2$  single crystals [19, 28, 29]. All previous optical studies on  $\text{PbF}_2$  [10, 12, 14] have been done for the cubic structural modification of this material (the  $\beta$ -phase), except for a very recent study by Alov and Rybchenko [20]. For  $\alpha$ - $\text{PbF}_2$ , they observed a photoluminescence band at 2.2 eV. The photoluminescence was excited by a KrCl excimer laser ( $\lambda = 222.9$  nm) that falls on the low-energy side of the lowest exciton band.

In the present experiment we have investigated the luminescence properties of  $\alpha$ - and  $\beta$ - $\text{PbF}_2$  crystals with the use of a deuterium lamp or synchrotron radiation as the tunable light source. Our main aims are (1) to examine the intrinsic nature of the luminescence by observing the excitation spectra, (2) to obtain information concerning the luminescence from compounds consisting of the same elements but having different structure and (3) to compare systematically the luminescence properties of  $\text{PbBr}_2$ ,  $\text{PbCl}_2$  and  $\alpha$ - $\text{PbF}_2$  with orthorhombic structure. On the basis of these results, the relaxation processes for the photo-excited electronic states in lead halides will be discussed.

## 2. Experiment

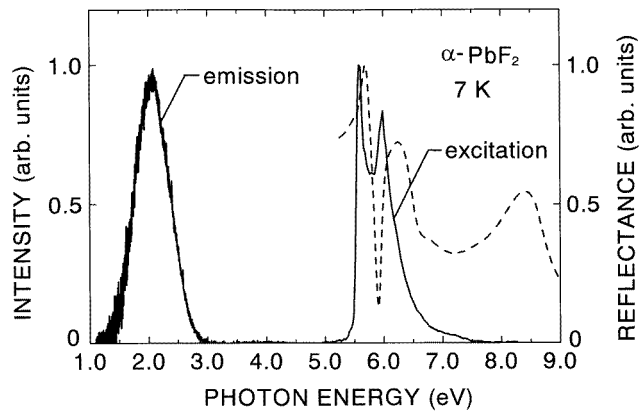
Single crystals of  $\alpha$ - $\text{PbF}_2$  were grown from an aqueous solution of perchloric acid by a slow-cooling method, the details of which have been described in [28]. The typical size of the samples was about  $2 \times 2 \times 0.1$  mm<sup>3</sup>, with the  $c$ -axis perpendicular to the platelet plane [9]. The samples of  $\beta$ - $\text{PbF}_2$  were cleaved from a single-crystal ingot, which was grown by the Stockbarger technique at the Harshaw Chemical Company. No appreciable absorption band was observed in the visible region at 7 K for both the  $\alpha$ - and  $\beta$ -samples used.

The present experiments were mainly carried out by using synchrotron radiation passed through a 1 m Seya–Namioka monochromator at beam line 1B of UVSOR in the Institute for Molecular Science, Okazaki. The specimens were mounted on the copper holder in a variable-temperature cryostat of He-flow type. The photoluminescence was dispersed through a SPEX270M monochromator equipped with a CCD camera (Princeton, LN/CCD-1152B).

Parts of the experiments were performed at Shinshu University. The light beam from a 150 W  $\text{D}_2$  lamp with a  $\text{MgF}_2$  window (HPK, L1835) was dispersed with a 0.4 m Seya–Namioka monochromator. Luminescence from the sample, mounted in a cryogenic refrigerator, was observed by means of a Nikon G250 monochromator and a photomultiplier tube (HPK, R106UH or R955). All of the luminescence spectra reported here were corrected for the dispersion of the analysing monochromators and for the spectral response of the detection systems. The excitation spectra were also corrected for the intensity distribution of the incident light.

## 3. Results

Figure 1 shows luminescence and excitation spectra of an  $\alpha$ - $\text{PbF}_2$  crystal measured at 7 K. Here, the luminescence spectrum was taken under photo-excitation at 5.61 eV, while the excitation spectrum was obtained for photons emitted at 2.07 eV. The reflection spectrum of  $\alpha$ - $\text{PbF}_2$



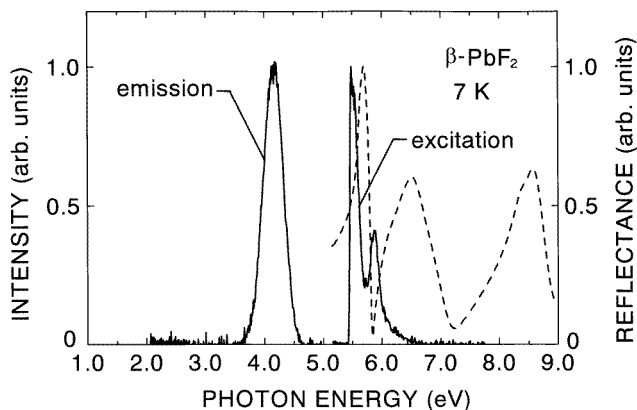
**Figure 1.** Luminescence and excitation spectra of  $\alpha\text{-PbF}_2$  measured at 7 K. The former was excited with 5.61 eV photons, while the latter was detected for the photons at 2.07 eV. Both spectra have been normalized to unity at their maxima. The reflection spectrum of  $\alpha\text{-PbF}_2$  ( $E \parallel b$ ) at 7 K is also shown by a broken curve for reference.

measured at 7 K is also shown [30] by a broken curve for reference. The measurements for figure 1 were made with the use of synchrotron radiation with the electric vector parallel to the  $b$ -axis ( $E \parallel b$ ). There was no appreciable difference in peak position and line shape of the luminescence and excitation spectra between the excitations with  $E \parallel a$  and  $E \parallel b$ . One can see a single luminescence band centred at 2.07 eV with a full width at half-maximum (FWHM) of 0.67 eV. A similar band has been observed under KrCl excimer laser excitation in [20]. It is clear that the 2.07 eV band is strongly excited with photons in the region of the lowest exciton band peaking at 5.70 eV and exhibits a sharp decrease in intensity as the excitation energy is raised beyond the onset of the band-to-band transition. In the present experiment, no other luminescence was observed in the spectral region between 1.5 and 5.0 eV.

After several repeated rapid coolings and warmings of  $\alpha\text{-PbF}_2$  samples, there appears a weak luminescence band at around 3.0 eV. This luminescence is probably linked to some lattice imperfection induced by thermal strain.

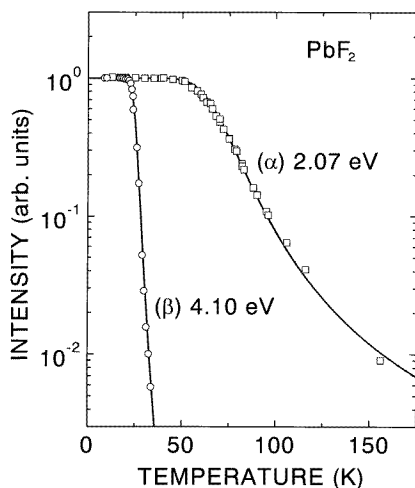
The luminescence spectra of the  $\beta\text{-PbF}_2$  crystals varied somewhat from sample to sample, in spite of the fact that they were cleaved from the same ingot. Figure 2 shows a typical example of the luminescence and excitation spectra of a  $\beta\text{-PbF}_2$  crystal, along with the reflection spectrum (broken curve), measured at 7 K. Here, the luminescence spectrum was taken under photo-excitation at 5.51 eV, while the excitation spectrum was obtained for photons emitted at 4.10 eV. This figure shows only one luminescence band at 4.10 eV with a FWHM of 0.40 eV, which is stimulated with photons in the region of the lowest exciton band peaking at 5.69 eV. In some cases,  $\beta\text{-PbF}_2$  emits two luminescence bands at 2.07 and 4.10 eV under exciton-band excitation. The 4.10 eV band is always observed, and has been assigned to the intrinsic luminescence of  $\beta\text{-PbF}_2$  in previous work [10, 12, 14, 20]. The coexistence of the 2.07 eV and 4.10 eV bands suggests that small orthorhombic inclusions are diluted in the volume of the cubic material. The appearance of these inclusions is probably due to the stress that is usual for large-volume crystals grown using the melting technique. It is known [18] that at low temperatures the orthorhombic phase of  $\text{PbF}_2$  is more stable under pressure than the cubic one.

From figure 2, one may see that the 4.10 eV band is hardly excited under the above-gap excitation. Recent experiments on  $\text{PbBr}_2$  and  $\text{PbCl}_2$  [23] have shown that the exciton luminescence induced by exciton-band excitation is enhanced again when the excitation energy



**Figure 2.** Luminescence and excitation spectra of  $\beta$ -PbF<sub>2</sub> measured at 7 K. The former was excited with 5.51 eV photons, while the latter was detected for photons at 4.10 eV. Both spectra have been normalized to unity at their maxima. The reflection spectrum of  $\beta$ -PbF<sub>2</sub> at 7 K is also shown by a broken curve for reference.

approaches double the band-gap energy. Such an enhancement is indicative of secondary-exciton production through inelastic scattering of excited electrons, and has also been observed for alkali halides [31]. Although not shown in figure 2, it is found that the intensity of the 4.10 eV luminescence is enhanced again in the region of secondary-exciton production in  $\beta$ -PbF<sub>2</sub> [32]. From comparison of figures 1 and 2, it is noticed that the onset of the 4.10 eV luminescence is situated about 100 meV lower than that of the 2.07 eV luminescence, although the exciton peaks for the two phases are located at almost the same position. And also, the 2.07 eV band is more efficiently stimulated than the 4.10 eV band on the high-energy side of the exciton band.



**Figure 3.** The temperature dependence of the intensities of the 2.07 eV luminescence (open squares) in  $\alpha$ -PbF<sub>2</sub> and the 4.10 eV luminescence (open circles) in  $\beta$ -PbF<sub>2</sub>, excited with photons in the region of the lowest exciton band. The intensity at low temperatures has been taken as unity. The solid curves are the best fits of the Mott formula to the data.

The intensities of the 2.07 eV band in  $\alpha$ - $\text{PbF}_2$  and the 4.10 eV band in  $\beta$ - $\text{PbF}_2$  are plotted logarithmically versus temperature  $T$  in figure 3. The excitation was carried out with photons in the region of the lowest exciton band. As is clearly seen, the intensity is constant at low temperatures, its magnitude being taken as unity, but begins to decrease rapidly at around 60 K in  $\alpha$ - $\text{PbF}_2$  and at 25 K in  $\beta$ - $\text{PbF}_2$ . These data are described well by the Mott formula based on a simple configuration coordinate diagram [33]:

$$I(T) = I(0)[1 + \tau\nu \exp(-\Delta E/k_B T)]^{-1}$$

where  $I(0)$  is the emission intensity at  $T = 0$ ,  $\Delta E$  the activation energy,  $\tau$  the radiative lifetime,  $\nu$  the frequency factor and  $k_B$  the Boltzmann constant. From the fit, we get  $\Delta E = 50$  meV and  $\nu = 4.0 \times 10^7 \text{ s}^{-1}$  for the 2.07 eV band, by using  $\tau = 100 \mu\text{s}$  [20], and  $\Delta E = 41$  meV and  $\nu = 1.3 \times 10^{12} \text{ s}^{-1}$  for the 4.10 eV band, by using  $\tau = 214 \mu\text{s}$  [14].

#### 4. Discussion

First of all we shall consider the origin of the 2.07 eV luminescence observed in  $\alpha$ - $\text{PbF}_2$ . The 4.10 eV luminescence in  $\beta$ - $\text{PbF}_2$  has already been established to be intrinsic in nature—i.e., radiative decay of self-trapped excitons (STEs) [10, 12, 14]. This conclusion is based on the fact that the 4.10 eV luminescence is stimulated with photons above the onset of the lowest exciton absorption band. As seen in figure 1, a similar situation arises in the case of the 2.07 eV luminescence as well, suggesting that this luminescence is an intrinsic feature of  $\alpha$ - $\text{PbF}_2$ . Of course, such similarity in the excitation spectra does not rule out the possibility that optically generated excitons may move about freely through the crystal and be trapped by some lattice imperfection from which the 2.07 eV photons are emitted. In figure 1, we cannot see any other luminescence. Therefore, if this possibility is realized, it has to be supposed that almost all excitons transfer their energy to imperfections before relaxing into self-trapped states. Such a supposition looks questionable, particularly in view of the strong exciton–phonon coupling in lead halides. We ascribe the 2.07 eV luminescence to the annihilation of STEs in the  $\alpha$ -phase.

The present result indicates that the intrinsic luminescence bands of  $\alpha$ - and  $\beta$ - $\text{PbF}_2$  are both stimulated in the region of the lowest exciton band. The lowest exciton bands of lead halides have been ascribed to the  $6s^2 \rightarrow 6s6p$  transition in the  $\text{Pb}^{2+}$  ions [1–9], where the ground state is  $^1\text{S}_0$ , and there exist excited-state multiplets,  $^3\text{P}_2$ ,  $^3\text{P}_1$  and  $^3\text{P}_0$ . The  $^1\text{S}_0$ – $^3\text{P}_1$  transition is spin forbidden, but partially allowed as a result of the admixture of higher energy levels (e.g.,  $^1\text{P}_1$ ) caused by spin–orbit coupling. According to a previously proposed model [4, 11, 13], the exciton luminescence bands of both  $\alpha$ - and  $\beta$ - $\text{PbF}_2$  are interpreted as arising from the partially allowed  $^3\text{P}_1$  level, with some contributions from the  $^3\text{P}_2$  and/or  $^3\text{P}_0$  levels. This is compatible with the fact that the 2.07 eV and 4.10 eV bands have long lifetimes of  $\sim 100 \mu\text{s}$  [20, 14].

Here, it should be noted that the  $\alpha$ - and  $\beta$ - $\text{PbF}_2$  crystals exhibit their lowest exciton peaks at nearly the same energy position, but their intrinsic luminescence bands appear at quite different energies. This fact indicates that the difference between the interactions of excited  $\text{Pb}^{2+}$  with neighbouring  $\text{F}^-$  ions in the two crystals is very important in the formation of STEs. Therefore, the ‘cationic’ exciton model mentioned above seems to be valid only in a first and rather crude approximation. Indeed, some systematic studies, such as Raman scattering [34], reflection spectra [35] and luminescence spectra investigations [22], on mixed  $\text{PbCl}_{2(1-x)}\text{Br}_{2x}$  crystals have suggested that the excited  $\text{Pb}^{2+}$  state involves a fairly substantial influence of the neighbouring halogen ions due to the formation of covalent bonds. Furthermore, recent photoelectron spectroscopy for  $\text{PbF}_2$  and  $\text{PbCl}_2$  [36, 37] has revealed the valence bands to be composed of a considerable mixture of lead 6s and halogen  $np$  orbitals ( $n = 2$  and 3 for  $\text{PbF}_2$

and  $\text{PbCl}_2$ , respectively), in fairly good agreement with the theoretical band calculations for  $\text{PbCl}_2$  and  $\alpha\text{-PbF}_2$  [38] and for  $\beta\text{-PbF}_2$  [39–41].

**Table 1.** Characteristic energies (in eV) and lattice constants (in Å) of  $\text{PbBr}_2$  (orthorhombic),  $\text{PbCl}_2$  (orthorhombic) and  $\text{PbF}_2$  (orthorhombic and cubic).  $E_{\text{ex}}^{\text{R}}$ : the lowest exciton peak in the reflection spectra.  $E_{\text{ex}}^{\text{L}}$ : the exciton luminescence band induced by exciton-band excitation.  $E_{\text{re}}^{\text{L}}$ : the recombination luminescence band induced by band-to-band excitation. All of the optical data were taken at 7 K.

Crystals	Lattice constant <sup>a</sup>	$E_{\text{ex}}^{\text{R}}$	$E_{\text{ex}}^{\text{L}}$	$E_{\text{re}}^{\text{L}}$
$\text{PbBr}_2$	$a = 4.767$ $b = 8.068$ $c = 9.466$	3.98 <sup>b</sup>	2.75 <sup>c</sup>	2.62 <sup>c</sup>
$\text{PbCl}_2$	$a = 4.525$ $b = 7.608$ $c = 9.030$	4.68 <sup>b</sup>	3.78 <sup>c</sup>	2.62 <sup>c</sup>
$\alpha\text{-PbF}_2$	$a = 3.891$ $b = 6.427$ $c = 7.636$	5.70	2.07	Nothing
$\beta\text{-PbF}_2$	5.927	5.69	4.10	Nothing

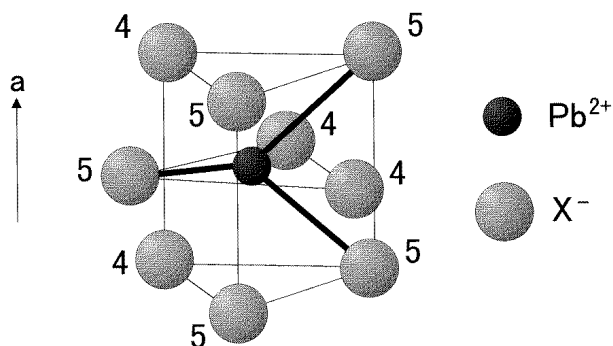
<sup>a</sup> From [42].

<sup>b</sup> From [8].

<sup>c</sup> From [21].

In table 1 are summarized the characteristics of  $\text{PbBr}_2$ ,  $\text{PbCl}_2$  and  $\text{PbF}_2$ : the lowest exciton peak in the reflection spectra, the exciton luminescence band induced by exciton-band excitation and the recombination luminescence band induced by above-gap excitation, along with the lattice constants [42]. From the table it follows that the lowest exciton peak shifts progressively to higher energies in the sequence from bromide to fluoride. Such regularity, however, does not hold for the exciton luminescence: the  $\text{PbCl}_2$  band is higher in energy than the  $\text{PbBr}_2$  band, but the  $\alpha\text{-PbF}_2$  band is the lowest among them. The magnitude of the Stokes shift in  $\alpha\text{-PbF}_2$  (3.63 eV) is significantly larger than that in  $\beta\text{-PbF}_2$  (1.59 eV), despite the fact that the interstitial space in the former is less than that in the latter (the  $\alpha$ -phase is  $\sim 10\%$  more dense than the  $\beta$ -phase [43]). This is in contrast to the situation for alkali halides [44, 45], where the Stokes shift becomes larger when the interstitial space becomes more open. That is, the STEs in alkali halides with large interstitial spaces are much more easily relaxed toward an off-centre configuration, resulting in a large Stokes shift. The situation for lead halides demonstrates that such a simple analogy has its limitations, and some other factors, such as the number of ions involved in the formation of the STEs and the construction of the wave functions of these ions, should be taken into account.

In the orthorhombic phase [17, 46], the coordination number is 9 for lead ions and 4 (for site 4) or 5 (for site 5) for halogen ions. The configuration of halogen ions situated around a lead ion in orthorhombic Pb halides is shown in figure 4. By referring to the band calculation for orthorhombic Pb halides [38], we suppose that the  $6s6p$  orbitals of the excited  $\text{Pb}^{2+}$  are mixed with the  $np$  orbitals of the surrounding halogen ions, and form a bonding-type molecular orbital as a result of the  $sp^2$  hybridization. In a first approximation, three surrounding halogen ions at site 5 in the same plane as the central  $\text{Pb}^{2+}$  will be involved in the formation of a STE; see figure 4. This model has been proposed for  $\text{PbBr}_2$  and  $\text{PbCl}_2$  in [22]. In the case of  $\alpha\text{-PbF}_2$ , the lattice constant is considerably smaller than those of  $\text{PbBr}_2$  and  $\text{PbCl}_2$ , as seen from table 1. It is, therefore, reasonable to suppose that the hybridization is stronger in  $\alpha\text{-PbF}_2$ .



**Figure 4.** The configuration of halogen ions situated around a lead ion in orthorhombic  $PbX_2$ . The coordination number (4 or 5) is indicated next to each  $X^-$  ion. Three thick lines indicate the bonds forming a STE.

$\beta$ - $PbF_2$  has a cubic structure, so its direct comparison to the others with orthorhombic structure is rather difficult. The theoretical calculations for  $\beta$ - $PbF_2$  [39–41] have revealed that the anionic and cationic states are mixed with each other due to the covalency, but the integral quantities, e.g., the excess charge ( $0.95e$ ) at the fluorine ions, still support ionic character. Consequently, the covalent bonds between excited  $Pb^{2+}$  and the surrounding  $F^-$  ions are expected to be relatively weak in  $\beta$ - $PbF_2$ .

It is supposed that a large part of the hole composing an exciton is situated on the  $Pb^{2+}$  ion in  $PbBr_2$ ,  $PbCl_2$  and  $\beta$ - $PbF_2$ . This configuration will induce a small displacement of the surrounding halogen ions, resulting in the relatively small Stokes shifts in these materials. On the other hand, the hole component in  $\alpha$ - $PbF_2$  moves, to a considerable extent, from  $Pb^{2+}$  to the surrounding  $F^-$  ions, due to the strong hybridization. This will make a more complicated STE configuration including both lead and halogen ions possible, in place of the simple on-centre configuration. This will lead to an extremely large Stokes shift in  $\alpha$ - $PbF_2$ .

The activation energy  $\Delta E$  for the thermal quenching of the 2.07 eV band is not so different from that of the 4.10 eV band. On the other hand, there is a big difference in the frequency factor  $\nu$  between these two bands. According to a simple configuration coordinate model [33], the frequency factor corresponds primarily to the rate of transfer of the population from the excited-state potential curve to the ground-state curve at their crossing point, and is usually of the order of the lattice vibration ( $\sim 10^{13} \text{ s}^{-1}$ ). The present value of  $\nu$  for the 4.10 eV band is quite reasonable. The reason that the value of  $\nu$  is very small for the 2.07 eV band is not clear, but there are two possibilities for explaining it. One is that a tunnelling effect may play an important role when the population of the 2.07 eV luminescent state is transferred to the ground state over the energy barrier  $\Delta E$ . The other is that the Mott formula is not applicable to the 2.07 eV state with the complicated relaxed configuration.

A very interesting fact found in the present experiment is that no luminescence appears under the band-to-band excitation for both  $\alpha$ - and  $\beta$ - $PbF_2$  crystals. When  $PbBr_2$  and  $PbCl_2$  are excited with photons in the band-to-band region, they emit recombination luminescence bands at 2.62 eV (which happen to be coincident with each other). The origin of these luminescence bands has been discussed by several authors [13, 15, 21, 23], but still remains disputable.

In connection with the above, there is an important experimental finding for  $PbCl_2$ . From ESR measurements [26, 27], it has been confirmed that the electron is self-trapped at a pair of nearest-neighbour  $Pb^{2+}$  ions, forming the  $(Pb_2)^{3+}$  centre. Although similar experiments have not been done for  $PbF_2$  and  $PbBr_2$ , the self-trapping of electrons may be a typical feature of



the lead–halogen compounds. Assuming that a hole is also trapped shallowly at some lattice site, Kitaura and Nakagawa [21] have suggested that the 2.62 eV luminescence is produced by tunnelling recombination of a pair composed of an adjacent self-trapped electron (a  $(\text{Pb}_2)^{3+}$  centre) and shallowly trapped hole.

No definitive evidence of self-trapped holes in  $\text{PbCl}_2$  and  $\text{PbBr}_2$  has been found, though several complex resonance spectra have been ascribed to a hole trapped at halogen-ion sites [47, 48]. We guess that the self-trapping of the hole is very much possible in  $\beta$ - $\text{PbF}_2$  because it has the same fluorite-type structure as alkaline-earth halides [45]. In  $\alpha$ - $\text{PbF}_2$ , the halogen-to-halogen distance is the shortest among those of the orthorhombic lead halides, so there also seems to be a strong possibility of hole self-trapping on the fluorine pair in this material. As one plausible explanation for the absence of the recombination luminescence in  $\text{PbF}_2$ , we suppose that the adjacent self-trapped electron and self-trapped hole recombine nonradiatively with each other by radiating heat or by converting to any other defect with a more stable configuration. Such nonradiative tunnelling will be possible if an electron and a hole are both self-trapped by making a large lattice deformation around themselves. The absence of recombination luminescence is very rare, and should be studied further as an interesting problem in more detail.

## 5. Summary

We have studied the luminescence properties of  $\alpha$ - $\text{PbF}_2$  and  $\beta$ - $\text{PbF}_2$  single crystals. It is pointed out that the 2.07 eV luminescence in the  $\alpha$ -phase is intrinsic in nature. An important finding is that no appreciable luminescence is excited in the band-to-band region. From the analysis of the experimental data, it is suggested that there are a variety of relaxed configurations of excitons, or electron–hole pairs, in lead halides. More detailed investigations, e.g., using the optically detected magnetic resonance technique, should be done to determine the structural configuration of the STEs. Direct experimental proof of the existence of self-trapped holes by ESR measurements is also desirable. Finally, we want to stress again that the  $\text{PbF}_2$  system is unique in many fields of solid-state research because two different structures exist under normal conditions.

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