

Valence-Band Structures of Lead Halides by Ultraviolet Photoelectron Spectroscopy

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(Received May 19, 1998)

Photoelectron spectra of PbF_2 and PbCl_2 have been measured with use of ultraviolet synchrotron radiation as a light source in order to clarify the electronic structures of their valence bands. It is found that the central part of the valence-band spectra of PbF_2 is remarkably decreased in intensity with irradiation time, but no similar change occurs in PbCl_2 . This decrease is likely due to the desorption of fluorine atoms from the sample surface. It is pointed out that the valence band of PbF_2 is composed of $2p$ electrons of F^- ions in the central part and an admixture of Pb^{2+} $6s$ and F^- $2p$ electrons in the upper and lower parts. The valence-band structure of PbCl_2 is almost the same as that of PbF_2 .

1. Introduction

Lead halides exhibit a variety of interesting physical properties, such as anomalously large ionic conductivity in PbF_2 ¹⁾ or self-trapping of electrons in PbCl_2 .^{2, 3)} They have also applications to high-energy particle detectors, because of the high density. For example, PbF_2 is a Cherenkov radiator suitable for electromagnetic calorimetry.^{4, 5)} Despite these interest and usefulness, the band structures of lead halides have been a controversial issue over the last quarter century, except for PbI_2 .⁶⁻⁸⁾ Especially the nature of the valence bands has not yet been understood satisfactorily in PbF_2 , PbCl_2 and PbBr_2 .

The Pb-halide crystals show in common "cationic" exciton transitions near the fundamental absorption edges. These excitons are believed to be formed from electronic states localized on the Pb^{2+} ion (intra-atomic $6s \rightarrow 6p$ transition).⁶⁻⁹⁾ This contrasts with the well-studied alkali halides where the fundamental absorption edge is due to transitions from the anion p states to the cation s states. For PbF_2 , PbCl_2 and PbBr_2 , a number of photoemission experiments have been done to investigate the nature of their valence bands. Beaumont *et al.*¹⁰⁾ and Scrocco¹¹⁾ have performed X-ray photoelectron spectroscopy (XPS) for PbF_2 and PbBr_2 , and have concluded that the top of the valence bands is built up by Pb^{2+} $6s$ orbitals. The same conclusion has been reached from ultraviolet photoelectron spectroscopy (UPS) for PbCl_2 and PbBr_2 by Kanbe *et al.*¹²⁾ and

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for PbF_2 by Cháb *et al.*¹³⁾ However, Mason and Gerenser¹⁴⁾ have pointed out from XPS studies that the valence bands in PbCl_2 and PbBr_2 are primarily halogen p like and the lead $6s$ level lies several electron volts below the top of the valence bands. Furthermore, Poole *et al.*¹⁵⁾ have attributed the highest band of XPS spectra in PbF_2 to the Pb^{2+} $6p$ orbitals that are usually assigned to the lowest conduction band. It is noticed that there are some differences between the UPS and XPS spectra in PbF_2 . For example, the XPS spectrum of ref. 11 is composed of four peaks in the valence-band region, while a five-peaked structure is observed in the UPS spectrum of ref. 13.

The crystal structure of PbCl_2 and PbBr_2 belongs to orthorhombic space group. There have been no band-structure calculations for these materials. Therefore it is not possible to compare the photoemission data of PbCl_2 and PbBr_2 with the theoretical calculations. On the other hand, PbF_2 crystallizes in two phases, one of which has a cubic fluorite lattice (β - PbF_2), and the other is orthorhombic (α - PbF_2). The former is metastable at normal conditions.¹⁶⁾ Because of the simple crystal structure, a few band calculations have been reported for β - PbF_2 , and used to interpret the photoemission data.¹⁷⁻¹⁹⁾

In the present study, we have performed UPS of PbF_2 and PbCl_2 with use of synchrotron radiation as a light source. It is found that the central part of the valence-band spectra of PbF_2 is decreased in intensity with irradiation time, but no similar change occurs in PbCl_2 . This decrease is likely due to the desorption of fluorine atoms from the sample surface. Based on this observation, we suggest that the valence band of PbF_2 is composed of $2p$ electrons of F^- ions in the central part and an admixture of Pb^{2+} $6s$ and F^- $2p$ electrons in the upper and lower parts. Furthermore it is supposed that the valence-band structure of PbCl_2 is almost the same as that of PbF_2 . A short note of this paper has been reported in ref. 20.

2. Experiment

The present experiments were carried out at beam line 6A2 of UVSOR, Institute for Molecular Science, Okazaki. The synchrotron radiation through a plane grating monochromator was used as a light source. It covers a wide spectral range from 10 to 130 eV by exchanging two gratings and five focusing mirrors. A typical photon flux was about 10^{10} photons/s-mm² at 90 eV. Photoelectron spectra were measured at room temperature with an angle-resolved hemispherical analyzer. The resolution of the electron analyzer was 0.20 eV, resulting in an overall instrumental resolution in the range from 0.21 to 0.25 eV, depending on photon energy. Spectral distribution of the incident radiation was determined from a photoelectric yield spectrum of gold.

Thin film samples were fabricated *in-situ* by evaporation on gold substrates in a preparation chamber, and were transferred into an analyzing chamber. Reagent-grade powders of PbF_2 (99.99% purity) and PbCl_2 (99.999% purity) from Merck were used as the starting materials. The base pressure in the analyzing chamber was better than 2×10^{-8} Pa.

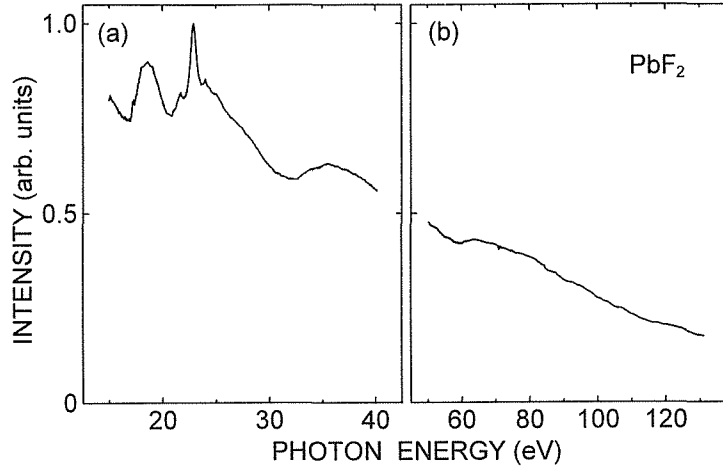


Fig.1: Total photoelectric yield spectra of PbF_2 around (a) the $\text{Pb}^{2+} 5d$ and (b) the $\text{Pb}^{2+} 5p$ excitation thresholds, measured at 295 K.

during measurements. Thickness of the specimens was maintained at about 100 \AA .

3. Results

Figure 1 shows total photoelectric yield spectra of PbF_2 around (a) the $\text{Pb}^{2+} 5d$ and (b) the $\text{Pb}^{2+} 5p$ excitation thresholds. The discontinuity present at 40–50 eV between (a) and (b) is due to lack of excitation intensity related to drop of the grating efficiency. It is well known that the total yield spectrum is similar to the photoabsorption spectrum. In fact, one can see three sharp peaks at 21.7, 22.9 and 24.0 eV in Fig. 1(a), in good agreement with the absorption spectrum obtained by Beaumont *et al.*¹⁰⁾ These peaks have been attributed to the $\text{Pb}^{2+} 5d \rightarrow 6p$ transitions leading to the final states, 3P_1 , 1P_1 and 3D_1 . A broad band around 35 eV is likely due to transitions from the $\text{F}^- 2s$ level. The spectrum of Fig. 1(b) is also similar to the result of ref. 10, and shows no clear structures due to the $\text{Pb}^{2+} 5p$ levels which lie at 83.3 and 106.4 eV below the Fermi level.²¹⁾ The missing of the $\text{Pb}^{2+} 5p$ structure is a consequence of the lowest conduction band being largely $\text{Pb}^{2+} 6p$ -like.

The UPS spectra of PbF_2 were measured at various photoexcitation energies. In the course of this experiment, it was found that the spectral shape in the valence region changes seriously with irradiation time. A typical example observed under the excitation with 100-eV photons is shown in Fig. 2. Here, the measurements progressed repeatedly from (a) to (e), with a scanning time of 8 min for each spectrum. The curve (a) is the spectrum for a previously unexposed sample. The sample was exposed to 100-eV photons

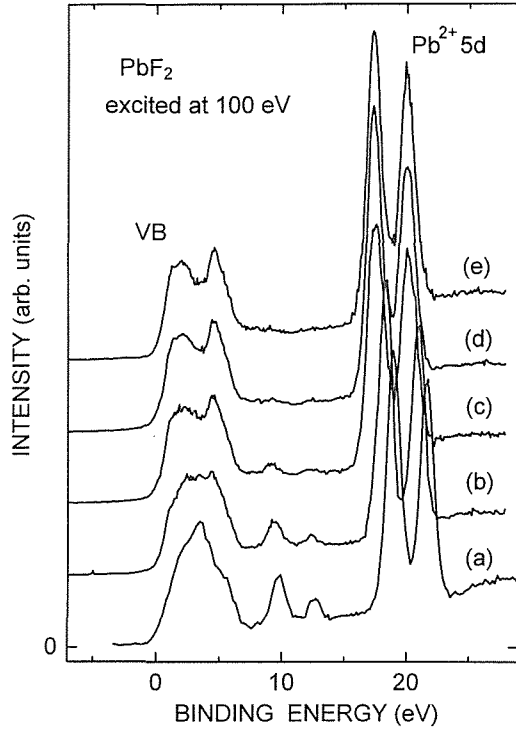


Fig.2: UPS spectra of PbF_2 measured under the excitation with 100-eV photons at 295 K. The measurements progressed repeatedly from (a) to (e), with a scanning time of 8 min for each spectrum. The curve (a) is the spectrum taken for a previously unexposed sample. The sample was exposed to 100-eV photons for 25 min before the next measurement. The binding energy is given relative to the top of the valence band.

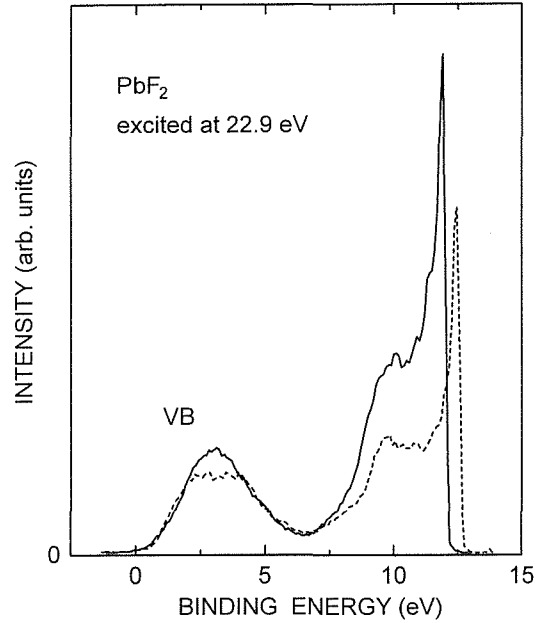


Fig.3: UPS spectra of PbF_2 measured under the excitation with 22.9-eV photons resonant to the $\text{Pb}^{2+} 5d$ level at 295 K. The solid curve was taken for a previously unexposed sample, while the broken curve was taken after 50 min of continuous irradiation. The binding energy is given relative to the top of the valence band.

for 25 min before the next measurement. The binding energy is given relative to the top of the valence band. In the spectrum (a), it may be seen that the valence band is composed of, at least, three unresolved bands; an intense band with shoulderlike structures on the low- and high-energy sides. The doublet structure around 20 eV is due to the spin-orbit-split $\text{Pb}^{2+} 5d_{3/2}$ and $5d_{5/2}$ levels. Two weak bands are also observed in the middle region between the valence band and the doublet structure. As obviously seen, the central part of the valence-band spectra is reduced remarkably with irradiation time. At the same time, the two weak bands at 10 and 13 eV are also smeared out. On the other hand, the intensity of the $\text{Pb}^{2+} 5d$ doublet around 20 eV increases slightly during the measurements, and its peaks shift toward the lower binding-energy side.

Figure 3 shows UPS spectra of PbF_2 excited with 22.9-eV photons which are resonant to the $\text{Pb}^{2+} 5d ({}^1P_1)$ level. The solid curve was taken on a fresh surface, while the broken

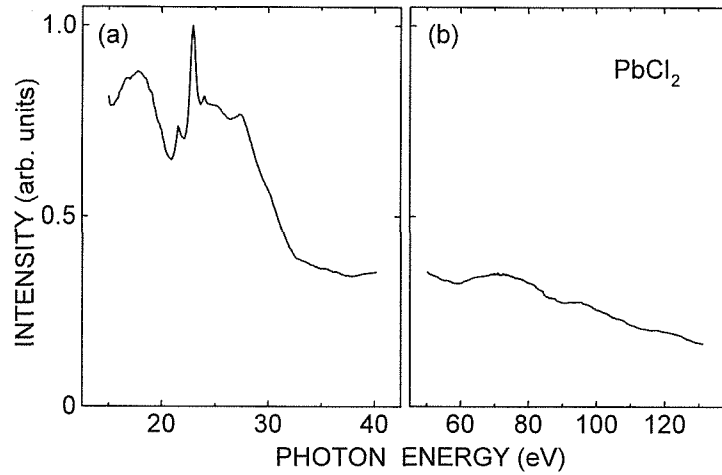


Fig.4: Total photoelectric yield spectra of PbCl_2 around (a) the Pb^{2+} $5d$ and (b) the Pb^{2+} $5p$ excitation thresholds, measured at 295 K.

curve was observed after 50 min of continuous irradiation. The strong peak in the high-energy region arises from secondary electrons. And, the 10-eV band is observed as a hump. The valence-band shape of the solid curve is almost the same as that of the curve (a) in Fig. 2, suggesting that there are no or little resonance effects. Spectral changes of the valence band were also examined by varying the photon energy in the vicinity of the Pb^{2+} $5d$ resonance. Reliable data, however, could not be obtained owing to the irradiation effect. In fact, it is seen from Fig. 3 that the valence-band shape is deformed by prolonged irradiation at 22.9 eV, as well as that at 100 eV shown in Fig. 2.

Figure 4 shows total photoelectric yield spectra of PbCl_2 around (a) the Pb^{2+} $5d$ and (b) the Pb^{2+} $5p$ excitation thresholds. One can see three sharp peaks at 21.5, 22.9 and 24.0 eV in Fig. 4(a). These peaks are in good agreement with those of the absorption spectrum obtained by Fujita *et al.*,⁹⁾ and have been assigned to the Pb^{2+} $5d \rightarrow 6p$ transitions. A hump at 27.5 eV is presumably related to transitions from the Cl^- $3s$ level. The spectrum of Fig. 4(b) shows no clear structures due to the Pb^{2+} $5p$ levels, similarly to the case of PbF_2 (Fig. 1(b)).

In contrast to PbF_2 , UPS spectra of PbCl_2 did not change seriously even when a sample was exposed to photons for more than 1 hr. Figure 5 shows UPS spectra of PbCl_2 excited at different photon energies. It is clear that the spectral shape of UPS in PbCl_2 is not sensitive to the change in excitation energies in the range 60–120 eV. The spectra consist of six bands. The lowest band is referred to the valence band. The strong doublet in the high-energy region is due to the Pb^{2+} $5d_{3/2}-5d_{5/2}$ levels. Furthermore, three weak bands are observed around 8, 14 and 16 eV. The present result of PbCl_2 is consistent with the XPS data.^{11, 22)}

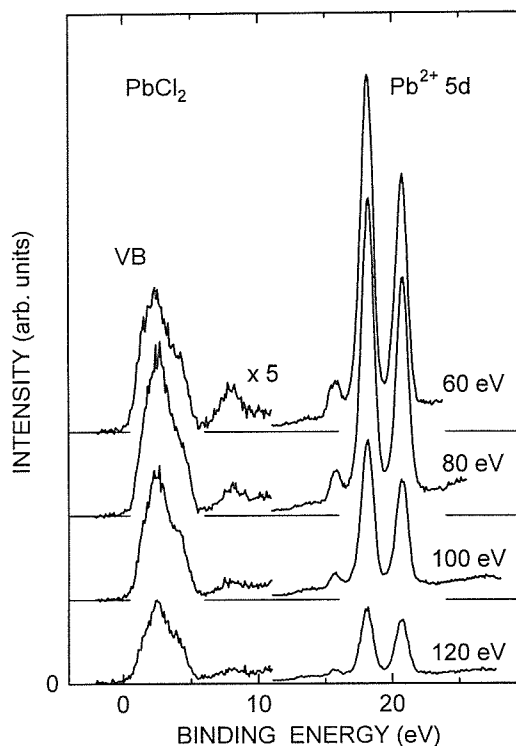


Fig.5: UPS spectra of PbCl_2 measured at 295 K. The excitation energy is indicated on each spectrum. The binding energy is given relative to the top of the valence band. The intensities in the valence region have been multiplied by 5.

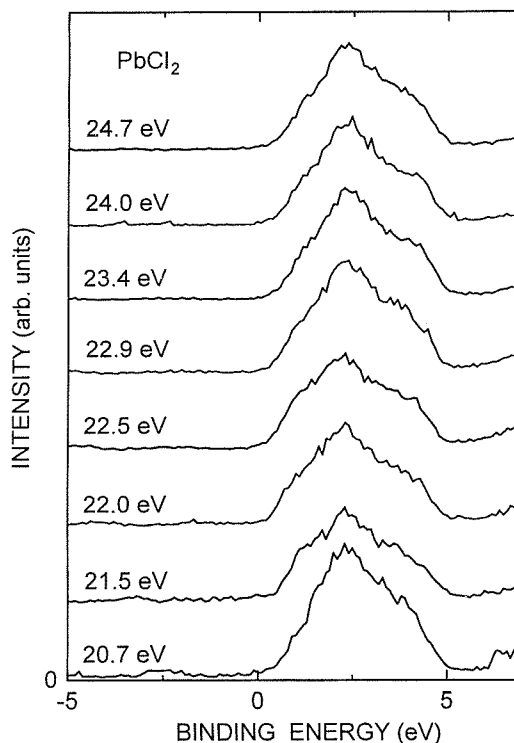


Fig.6: UPS spectra of the valence band in PbCl_2 measured at 295 K. The excitation energy is indicated on each spectrum. The binding energy is given relative to the top of the valence band.

Figure 6 shows UPS spectra of the valence band in PbCl_2 excited in the vicinity of the $\text{Pb}^{2+} 5d$ (1P_1) level at 22.9 eV. It appears that the spectral shape does not exhibit any noticeable changes in the resonance region. It should be noted that the valence-band shape of PbCl_2 is similar to that of PbF_2 shown by the curve (a) in Fig. 2; i.e., the valence band of PbCl_2 is also composed of three unresolved bands.

4. Discussion

The most striking observation in the present experiment is that the central part of the valence-band spectra in PbF_2 is reduced remarkably with irradiation time. We first have to worry about surface charging of the sample as the cause of this irradiation effect. The surface charging is known to be serious in a 1000-Å-thick sample.²³⁾ However, it is negligible in a 100-Å-thick sample like ours.

It seems most likely that the valence-band spectra of PbF_2 are deformed as a result of

photon-stimulated desorption of fluorine atoms from the sample surface. The photon-stimulated desorption of halogen atoms is a well-established phenomenon in alkali and alkaline-earth halides.^{24, 25)} In these halide crystals, it is well known that the decay of excited electronic states results in the formation of F-H defect pairs. The F center is a negative ion vacancy trapping one electron and the H center is a complementary interstitial halogen atom. The interstitial halogen atom forms a covalent bond with a lattice halide ion to form a molecular ion pair. The H center is expelled from the F center by the repulsive force between the developing F center electron and the halogen molecule ion.²⁵⁾ If this event happens near the surface, ejection of the halogen atom from the sample will occur efficiently. We suppose that the similar dynamical process of defect formation, occurring within a few atomic layers of the surface, is also responsible for the fluorine desorption in PbF_2 which has the same fluorite-type structure as alkaline-earth halides.

On the other hand, PbCl_2 crystallizes in orthorhombic structure, where the interstitial space is not so open as PbF_2 . Accordingly, the defect formation process leading to the chlorine desorption may not be easy to occur in PbCl_2 . Furthermore, photoconductivity studies of PbCl_2 and PbBr_2 have revealed that the photoholes have a larger mobility than the photoelectrons in both materials,^{26, 27)} which suggests the hole to be nearly free or shallowly self-trapped at a halide lattice site. Therefore, the driving force for the defect formation is supposed to be considerably weak in PbCl_2 even if the self-trapping of holes takes place. These facts explain the experimental result that the valence-band shape of PbCl_2 is kept well during the irradiation with synchrotron radiation. The above explanation of the cause of the difference in halogen-desorption yield between PbF_2 and PbCl_2 is still speculation, which will require further studies to solve this problem.

From Fig. 2, it appears that the valence band of PbF_2 has a composite structure consisting of three unresolved parts. The central part is interpreted as being predominantly fluorine $2p$ in character. This interpretation is based on our argument that the central part of the valence band in PbF_2 is reduced as a result of the photon-stimulated desorption of fluorine atoms. On the other hand, the upper and lower parts, which almost keep their intensities even after prolonged irradiation, are supposed to originate from $6s$ electrons of lead ions. The existence of an s -like state at the top of the valence band has also been postulated to explain anomalous pressure shifts of the band gap excitons in Pb-halides.²⁸⁾ However, the present result does not rule out the possibility of small contribution of fluorine p electrons to both the upper and lower parts. From theoretical considerations of the electronic structures,¹⁷⁻¹⁹⁾ it has been pointed out that, in PbF_2 , the Pb^{2+} $6s$ states should sink into the occupied band from F^- $2p$ states, and therefore, the s - p hybridization becomes much more important than in other fluorides like CaF_2 or CdF_2 . Évarestov, Murin and Petrov¹⁷⁾ have shown that the upper valence band includes a 20% contribution of the F^- $2p$ states, while the lower band is mainly formed by the Pb^{2+} $6s$ states. Velický and Mašek¹⁸⁾ and Nizam *et al.*¹⁹⁾ have suggested that both the upper and lower bands are an admixture of Pb^{2+} $6s$ and F^- $2p$ states. All these calculations have revealed the central part of the valence band in PbF_2 to be almost pure F^- p character. Our experimental

result is fairly consistent with the above theoretical calculations, though it is hard to evaluate the degree of an admixture of lead $6s$ and fluorine $2p$ electrons in the upper and lower parts. From Figs. 2 and 5, one can recognize the similarity in the valence-band shape between PbF_2 and PbCl_2 . Although both materials have different crystal structures, it is supposed that the electronic structure of the valence band in PbCl_2 is almost the same as that in PbF_2 ; i.e., the central part is predominantly $\text{Cl}^- 3p$ in character, and the upper and lower parts are mainly built up by lead $6s$ state with some contributions from chlorine $3p$ state.

From the spectra in Figs. 2 and 5, the valence-band widths are estimated to be about 7 eV for PbF_2 and 5 eV for PbCl_2 . The present value of PbF_2 is very close to the band width of 7 eV estimated by a tight-binding method,¹⁸⁾ but somewhat smaller than the value of 9 eV calculated by a periodic Hartree-Fock method.¹⁹⁾ No theoretical calculation of the valence-band width has been available for PbCl_2 . It is interesting to note that the valence-band widths of PbF_2 and PbCl_2 are 2–3 times larger than those of alkali and alkaline-earth halides.^{29, 30)} This is primarily because the valence bands of lead halides include two contributions of lead $6s$ and halogen np states, where $n = 2$ and 3 for PbF_2 and PbCl_2 , respectively.

In many systems,³¹⁾ it has been found that the Auger decay process following the resonant excitation from the core to the unoccupied orbital enhances the emission of photoelectrons. We tried to observe such enhancement in PbF_2 and PbCl_2 . However, the intensity and shape of the valence bands did not exhibit any noticeable changes in the $\text{Pb}^{2+} 5d \rightarrow 6p$ resonance region in PbCl_2 (and also probably in PbF_2), indicating a minor role of the Auger transitions in the decay of the corresponding excitation.

As mentioned in § 1, the UPS and XPS spectra of PbF_2 reported previously are not in full agreement with each other.^{10, 11, 13, 15)} This discrepancy may be explained by assuming that the samples are more quickly and seriously damaged by X-ray irradiation.

As seen in Fig. 2, the doublet structure due to $\text{Pb}^{2+} 5d$ levels shifts gradually to the low-binding-energy side, with a slight increase in intensity, when the sample is continuously irradiated. This is likely to be caused by environmental changes around Pb^{2+} ions, introduced by the desorption of fluorine atoms from the surface layer. That is to say, the upper surface layer becomes increasingly lead enriched.

There appear several weak peaks in the middle region between the valence band and the $\text{Pb}^{2+} 5d$ doublet. From Fig. 5, we can recognize three peaks at 8, 14 and 16 eV for PbCl_2 . The 8-eV band has been assigned to the mixed states of $\text{Pb}^{2+} 6s$ and $\text{Cl}^- 3p$, and the 14-eV band to the $\text{Cl}^- 3s$ states.^{11, 12, 14)} The 16-eV band has not been observed in the XPS by Mason and Gerenser,¹⁴⁾ but can be seen as a shoulderlike structure on the low-energy side of the $\text{Pb}^{2+} 5d$ doublet in the XPS by Scrocco.¹¹⁾ The origin of this band is not clear at present. On the other hand, there are two peaks at 10 and 13 eV in PbF_2 , as seen in Fig. 2. In the UPS spectrum of ref. 15, they have been ascribed to the satellites of the $\text{Pb}^{2+} 5d$ lines, being generated by He(II) radiation. However, since the spectra of Fig. 2 were recorded with monochromatized radiation, none of the peaks can be attributed to

satellites. These two bands were found to decrease in intensity after prolonged irradiation, with a rapid rate compared to the central part of the valence band. Therefore, they may be ascribed to the electronic states originating from fluorine ions located in the surface layer, presumably having a small contribution of lead ions.

Finally, a brief comment is made on the exciton transitions in lead halides. The present experiment strongly suggests that the valence bands of PbF_2 and PbCl_2 are composed of lead $6s$ and halogen np states. This feature is quite different from that of other halide crystals, in which the valence bands have almost pure halogen nature. Since the conduction band of lead halides is formed by the Pb^{2+} $6p$ state, their fundamental absorption spectra must deeply reflect the character of the intra-atomic transitions. Indeed, the excitonic structures in PbCl_2 and PbBr_2 resemble the absorption bands due to Pb^{2+} impurities in alkali halides.^{9, 32)}

5. Concluding Remarks

In UPS of PbF_2 it was found that the central part of the valence band is remarkably chipped off with irradiation time. Based on this observation, we suggested that the middle of the valence-band region in PbF_2 is dominated by F^- $2p$ state, and the remaining upper and lower parts have Pb^{2+} $6s$ character with small participation of F^- $2p$ state. Furthermore, there existed the similarity in the valence-band shape between PbF_2 and PbCl_2 . Although this fact is not definitive evidence, it was pointed out that the electronic structure of the valence band in PbCl_2 is almost the same as that in PbF_2 .

Recent experimental studies^{33, 34)} have revealed that the intrinsic luminescence of lead halides arises from radiative annihilation of self-trapped excitons. In wide-gap ionic crystals, an exciton becomes localized by deforming the lattice around itself. This self-trapping process is closely related to the nature of the electronic states of the valence band and/or the conduction band. The mixed character of the valence bands in Pb-halides will play an important role for the self-trapping process of excitons. Therefore, it is expected that the present result promotes further studies on the luminescence properties of lead halides. Detailed investigations along this line are now in progress.

Acknowledgments

The author is grateful to Mr. T. Shiokawa (Shinshu University), Professor K. Sawada (Shinshu University) and Professor M. Kamada (Institute for Molecular Science) for their cooperation in this work. Thanks are also due to Professor T. Matsukawa (Naruto University of Education) for communicating new XPS spectra of PbF_2 and PbCl_2 and Mr. Y. Bokumoto (Shinshu University) for his assistance.

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