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Optical spectra and electronic structures of lead halides

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Polarized reflectivity spectra of single crystals of α-PbF_2, β-PbF_2, $PbCl_2$, and $PbBr_2$ have been measured at 10 K in the energy range up to 30 eV using synchrotron radiation as a light source. The spectra are well resolved in comparison with those reported previously. Optical constants have been derived through the Kramers-Kronig analysis. The effect of phase transition on the optical spectra of PbF_2 is also examined. With use of the discrete variational $X\alpha$ method, the electronic structures of the clusters consisting of a Pb^{2+} ion and neighboring halogen ions have been calculated for better understanding of the optical properties of Pb halides. The calculation indicates that the lowest excitons in all lead halides are attributed to the cationic transitions. The electronic structures of lead halides are discussed on the basis of a comparison of experiment and calculation.

I. INTRODUCTION

As is well known, lead halides have three kinds of structural modifications under normal conditions.[1] PbI_2 crystallizes in a hexagonal CdI_2 structure. $PbCl_2$ and $PbBr_2$ exhibit an orthorhombic structure. PbF_2 crystallizes in two phases: the orthorhombic structure of $PbCl_2$ type (α-PbF_2) and the cubic structure of CaF_2 type (β-PbF_2). In temperatures below 320 °C, α-PbF_2 is stable, but β-PbF_2 is also able to exist as a metastable phase.

The Pb halides have drawn attention of many workers because they exhibit interesting features from the standpoint of the electron-lattice interaction.[2–17] They are also attractive materials for practical use, e.g., as a scintillating substance (PbF_2) (Ref. 2) and as acousto-optical crystals ($PbCl_2$ and $PbBr_2$) (Refs. 3 and 4).

Since the earlier study by Plekhanov,[5] the fundamental absorption edges of PbF_2, $PbCl_2$, and $PbBr_2$ have been believed to be dominated by cationic excitations in the Pb^{2+} ions, which is in clear contrast to the case of well-studied alkali halides. The self-trapping of electrons was found, for the first time, to occur in $PbCl_2$.[6] In $PbCl_2$ and $PbBr_2$, two types of luminescence are observed, that is, the excitonic luminescence and the recombinational luminescence. The former is ascribed to radiative decay of an exciton self-trapped at Pb^{2+} ion site, while the latter is attributed to tunneling recombination of a shallowly trapped hole and a self-trapped electron [a $(Pb_2)^{3+}$ center].[7,8] Both α- and β-PbF_2 emit only the luminescence that corresponds to the excitonic luminescence in chloride and bromide.[9]

Recently, multiplication of electronic excitations in lead halides have been studied using synchrotron radiation as a light source.[10,11] The excitation with photons in the VUV region involves optical transitions not only from the valence band to the high-lying states in the conduction band but also from the core levels to the low-lying states in the conduction band. In order to make proper discussions on the relaxation processes after high-energy excitation, reliable optical spectra up to the VUV region and theoretical calculations on the electronic states are strongly desired.

Many works have been reported on the optical constants of PbF_2, $PbCl_2$, and $PbBr_2$.[5,12–17] There exist, however, some differences among them. One possibility for this is that the strain in thin films makes the features in absorption spectra obscure. Furthermore, in PbF_2, one should be careful of the effect of phase transition on optical spectra, because the cubic phase is transformed into the orthorhombic phase by application of pressure[18] or by exposure to water.[2] The electronic band structure has been calculated for cubic PbF_2,[19,20] but no theoretical calculation is available for orthorhombic lead halides.

In the present study, we have measured reflectivity spectra of single crystals of α- and β-PbF_2, $PbCl_2$, and $PbBr_2$ in the energy range up to 30 eV with the use of synchrotron radiation. The optical constants are derived through the Kramers-Kronig analysis. The electronic structures of these lead halides are calculated by using the discrete variational $X\alpha$ (DV-$X\alpha$) method,[21,22] which has been successfully ap-

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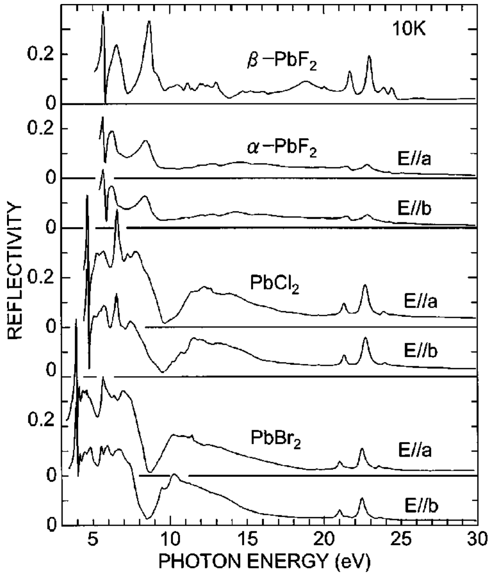

FIG. 1. Reflectivity spectra of α-PbF$_2$, β-PbF$_2$, PbCl$_2$, and PbBr$_2$ at 10 K in the 3–30 eV region. The spectra were measured for the polarization parallel to the *a* axis (**E**$\|$**a**) and *b* axis (**E**$\|$**b**), except for that of β-PbF$_2$.

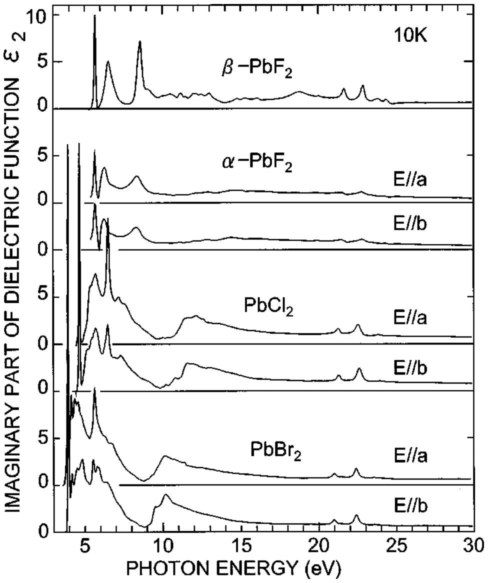

FIG. 2. Imaginary part of dielectric functions (ϵ_2) of PbF$_2$, PbCl$_2$, and PbBr$_2$ at 10 K in the 3–30 eV region. The spectra are presented for the polarization parallel to the *a* axis (**E**$\|$**a**) and *b* axis (**E**$\|$**b**), except for that of β-PbF$_2$.

plied to metals and inorganic compounds. The results of experiment and calculation are compared with each other, from which we will discuss the electronic structures in Pb halides.

II. EXPERIMENT AND RESULTS

Single crystals of PbCl$_2$ and PbBr$_2$ were grown by the Stockbarger method. They were cleaved along the *ab* plane. Single crystals of α-PbF$_2$ were grown from aqueous solution with perchroic acid.[23] They were obtained as thin flakes that have surfaces with typical size of 2×2 mm^2. The as-grown surface contained the *ab* plane. Reflectivity spectra of PbCl$_2$, PbBr$_2$, and α-PbF$_2$ were measured for the polarization parallel to the *a* and *b* axes. Single crystals of β-PbF$_2$ were obtained from the Harshaw Chemical Company. Since flat surfaces could not be obtained by the cleavage of β-PbF$_2$ crystals, their reflectivity spectra were taken for uneven surfaces cleaved.

Optical experiments were made using synchrotron radiation of UVSOR (Ultraviolet Synchrotron Orbital Radiation) Facility at the Institute for Molecular Science, Okazaki. The light beam was monochromatized through a 1-m Seya-Namioka monochromator at beam line 1B. Reflectivity spectra of near normal incidence were measured using a photomultiplier tube coated with sodium salycilate. In measurements of the low-energy region, a quartz or LiF filter was used to eliminate the higher order light.

In Fig. 1 are shown reflectivity spectra of orthorhombic α-PbF$_2$, PbCl$_2$, and PbBr$_2$ crystals in the 3–30 eV region at 10 K for the polarization parallel to the *a* axis (**E**$\|$**a**) and *b* axis (**E**$\|$**b**). The reflectivity spectrum of a cleaved surface of cubic β-PbF$_2$ crystal is also shown in Fig. 1.

The absolute values of reflectivity in the low-energy region for PbCl$_2$ and PbBr$_2$ agree well with the results of the precise measurement by Kanbe *et al.*[12,13] and are consistent with those calculated from the refractive indices.[4] The measured reflectivity of β-PbF$_2$ near the absorption edge was about one-half that calculated from the refractive index data,[24] because of the scattering of reflected light from uneven surface of the cleaved crystal. Consequently, the spectrum of β-PbF$_2$ in Fig. 1 was presented by multiplying the measured spectrum by a factor of nearly 2. The refractive index data of α-PbF$_2$ is not available in literature. We thus presented the spectrum of α-PbF$_2$ by assuming that the reflectivity in the transparent region for **E**$\|$**a** and **E**$\|$**b** is the same as that of β-PbF$_2$.

In the present study, a flat surface of β-PbF$_2$ crystal was also prepared by polishing with alcoholic paste of polishing powder. It was found that the reflectivity spectrum in the 5–10 eV region for the polished surface of β-PbF$_2$ resembles that for the as-grown surface of α-PbF$_2$, rather than that for the cleaved surface of β-PbF$_2$. This indicates that the surface of the cubic phase is transformed into the orthorhombic phase by the stress during mechanical polishing.[2,18] The spectra of the cleaved surface should be regarded as intrinsic to β-PbF$_2$.

The imaginary part of the dielectric function (ϵ_2) and the absorption coefficient of each material have been derived through the Kramers-Kronig analysis of the reflectivity spectra in Fig. 1. The ϵ_2 spectra are shown in Fig. 2. The absorption spectra in the first exciton-band region, in the 3–12 eV region, and in the 3–30 eV region are given in Figs. 3, 4, and 5, respectively.

Although not shown in Fig. 3, a spurious structure appears below 5.5 eV in the absorption spectra of α-PbF$_2$ obtained by the Kramers-Kronig analysis. The absorption measurement of an α-PbF$_2$ sample with about 0.1 mm thickness showed this region to be transparent at 10 K. Hence, the assumption concerning the reflectivity mentioned above is supposed to be somewhat crude. Some uncertainty in the absolute reflectivity affects the intensities of the structures in optical spectra, but their energy positions are hardly changed. The main structures in the valence-excitation region are numbered as 1, 2, 3, and 4 (Fig. 4). The fine struc-

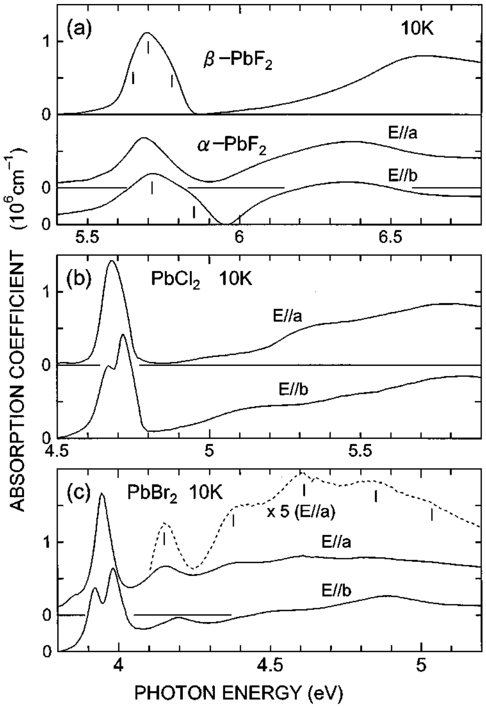

FIG. 3. Absorption spectra of PbF_2, $PbCl_2$, and $PbBr_2$ at 10 K in the first exciton-band region. The spectra are presented for the polarization parallel to the *a* axis (**E**||**a**) and *b* axis (**E**||**b**), except for that of β-PbF_2.

tures in the core-excitation region are named $c_0, c_1, \ldots$ (Fig. 5). The energy positions of these structures are summarized in Table I.

The reflectivity spectra in Fig. 1 are essentially the same as those reported previously by us.[16,17] The ϵ_2 spectra in the first exciton-band region in Fig. 2 agree well with those by Kanbe *et al.*[12,13] The optical spectra in the VUV region have been obtained by absorption,[5] reflection,[10,15] and electron energy loss experiments.[25] The present spectra are more refined than them. Beaumont *et al.* measured the reflectivity spectrum of β-PbF_2 using a polished surface of crystal and an evaporated film.[15] According to Ref. 15, both samples exhibit essentially the same spectra, at least above 8 eV. The optical spectra of β-PbF_2 in Figs. 1, 2, and 5 seem to be consistent with their results, except for the region below 10 eV.

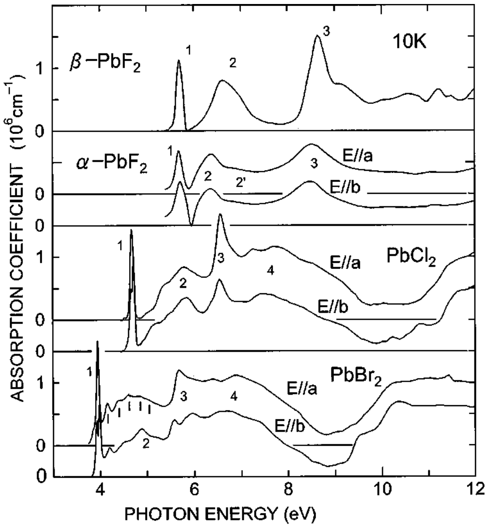

FIG. 4. Absorption spectra of PbF_2, $PbCl_2$, and $PbBr_2$ at 10 K in the energy range below 12 eV. The spectra are presented for the polarization parallel to the *a* axis (**E**||**a**) and *b* axis (**E**||**b**), except for that of β-PbF_2. The main structures in the valence-excitation region are numbered as 1, 2, 3, and 4.

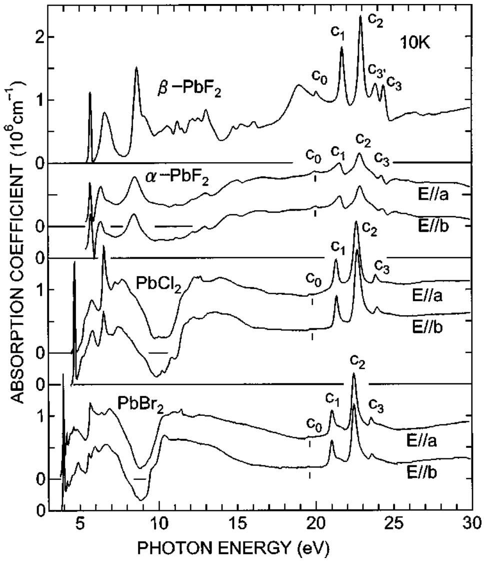

FIG. 5. Absorption spectra of PbF_2, $PbCl_2$, and $PbBr_2$ at 10 K in the 3–30 eV region. The spectra are presented for the polarization parallel to the *a* axis (**E**||**a**) and *b* axis (**E**||**b**), except for that of β-PbF_2. The fine structures around 22 eV are named c_0, c_1, c_2, $c_{3'}$, and c_3.

In Fig. 3, the exciton band 1 appears at 3.9 eV in $PbBr_2$ and at 4.7 eV in $PbCl_2$. These exciton bands have a single peak for **E**||**a**, while they have two peaks for **E**||**b**. A similar polarization dependence is also observed for exciton band 1 of α-PbF_2 at 5.7 eV. As reported in our previous paper,[17] the second-energy-derivative reflectance (2EDR) spectra exhibited the dichroism more distinctly. Exciton band 1 of β-PbF_2 appears at nearly the same position as that of α-PbF_2. The 2EDR spectrum revealed that the exciton band of β-PbF_2 consists of three fine structures.[17] They are indicated by vertical bars in the absorption spectra of Fig. 3. The broken curve in Fig. 3(c) shows the absorption spectrum of $PbBr_2$ for **E**||**a** in the 4–5 eV region on an extended scale. One may see an oscillatory structure with separation of about 230 meV, as indicated by vertical bars.

In the absorption spectra by Plekhanov, shoulder structures are observed at 6.2 eV, 4.86 eV, and 4.23 eV for PbF_2, $PbCl_2$, and $PbBr_2$, respectively, and they were assigned to the band edge.[5] In the reflectivity spectrum of β-PbF_2 by Beaumont *et al.*, a shoulder structure was found at 6.2 eV.[15] They assigned the structure to the $n=2$ exciton state. However, no particular structure was observed in the corresponding position for each material in Fig. 3. The structures found by these authors are probably due to extrinsic origin, such as strain in the thin film or phase transition by polishing the crystal.

In Fig. 4, several polarization-dependent structures are also observed below 12 eV in $PbCl_2$ and $PbBr_2$. Two broad peaks 2 and 3 and a small hump 2′ are seen in α-PbF_2, with

TABLE I. Energy positions (in eV) of the main structures in absorption spectra of lead halides at 10 K. These values contain experimental uncertainty of ±3 meV for the exciton band 1 and ±10 meV for the other bands.

Crystals	$PbBr_2$		$PbCl_2$		α-PbF_2		β-PbF_2
	E||**a**	**E**||**b**	**E**||**a**	**E**||**b**	**E**||**a**	**E**||**b**	
1	3.947	3.921	4.678	4.664	5.685	5.713	5.644
		3.982		4.716		5.854	5.698
							5.780
2		4.88	5.77	5.84	6.37	6.35	6.61
3	5.67	5.58	6.57	6.55	8.52	8.50	8.64
4	6.93	6.66	7.79	7.44			
c_0	19.50	19.48	19.61	19.68	19.95	20.02	20.04
c_1	21.02	21.01	21.31	21.34	21.53	21.55	21.70
c_2	22.45	22.45	22.64	22.69	22.85	22.86	22.92
$c_{3'}$							23.87
c_3	23.55	23.59	23.86	23.96	24.25	24.32	24.38

very weak dichroism. In β-PbF_2, two peaks 2 and 3 are observed, but their shape and position are different from those in the α phase. It should be noted that a dip is clearly observed at around 8.9 eV for $PbBr_2$ and at 10.0 eV for $PbCl_2$.

As seen in Fig. 5, broad structures with a little dichroism appear in the 10–17 eV region in α-PbF_2, while several sharp peaks are observed in β-PbF_2. A group of sharp peaks due to the Pb^{2+} 5*d* core exciton transition are recognized in the 19–25 eV region for all lead halides.[15,16] In the β-PbF_2 spectrum, an extra peak $c_{3'}$ is found between the peaks c_2 and c_3, in good agreement with the result by Beaumont *et al.*[15]

III. ELECTRONIC STRUCTURES BY THE DV-$X\alpha$ CALCULATION

No electronic band calculation has been available for the orthorhombic lead halides (PbX_2; X=F, Cl, and Br). We, therefore, calculated the electronic states of model clusters of orthorhombic and cubic lead halides by using the DV-$X\alpha$ method.[21,22] The computational details of this method have been described in Ref. 22. In the orthorhombic cluster $[PbX_9]^{7-}$, a Pb^{2+} ion is surrounded by three X^- ions in the same plane, and is sandwiched between two sets of three X^- ions lying above and below in parallel planes. The Pb-X distances are relatively short for seven X^- ions and long for two X^- ions,[26] although not all nine anions are equivalent. On the other hand, for cubic β-PbF_2, a Pb^{2+} ion is at the center of eight F^- ions at the corners of a surrounding cube; i.e., the $[PbF_8]^{6-}$ cluster. The interatomic distances in the clusters are taken from the experimental data of the crystals.[1] The basis functions included in the calculation are 1*s* to 6*d* atomic orbitals for Pb^{2+} ion and 1*s* to *np* atomic orbitals for halogen ions, where n = 2, 3, and 4 for F^-, Cl^-, and Br^- ions, respectively.

In the case of the cluster calculation for ionic compounds, some of the molecular orbitals localized on the surface atoms in the cluster are often affected by electrostatic potentials due to the ions surrounding the cluster. In fact, such electrostatic potentials shifted all the levels of Pb^{2+} and F^- ions for cubic PbF_2, but their relative energy positions remained almost unchanged. On the other hand, introduction of such electrostatic potentials resulted in unreliable band gaps for orthorhombic PbX_2. This is probably caused by the fact that it is very hard to evaluate the cation coordination correctly, because none of the neighboring nine X^- ions are equivalently situated from the Pb^{2+} ion in the orthorhombic phase. For the present results, we had not taken the influence of electrostatic potentials due to the ions outside the cluster into account.

Relativistic calculations were also attempted because Pb is a heavy metal (atomic number=82). They showed the spin-orbit splitting of the 5*d* and 6*p* states of Pb^{2+} ions, as expected. However, essential features of the electronic band structures were not so different between the nonrelativistic and relativistic calculations.

For simplicity, the electronic structures obtained by the nonrelativistic DV-$X\alpha$ method are presented in Fig. 6, where the energy is referred to the top of the valence band. The total energy levels are indicated on the left side. Solid and broken lines represent occupied and unoccupied levels, respectively. The length of a line of each state indicates the partial contribution to the corresponding total one. For orthorhombic materials, anions whose distance from the central cation is less than 2.6 Å for $[PbF_9]^{7-}$, 3.1 Å for $[PbCl_9]^{7-}$, and 3.4 Å for $[PbBr_9]^{7-}$ are represented as X^-(I), and the remaining distant anions as X^-(II) in Fig. 6. For cubic β-PbF_2, the present result is in good agreement with the previous reports calculated by a tight-binding method[19] and by a periodic Hartree-Fock method.[20]

It is clear that the top of the valence band is composed of an antibonding state of Pb^{2+} 6*s* and halogen *np* orbitals. The contribution of halogen n*p* orbitals is 32%, 31%, 52%, and 65% for β-PbF_2, α-PbF_2, $PbCl_2$, and $PbBr_2$, respectively. On the other hand, the lowest valence band is a bonding state of Pb^{2+} 6*s* and halogen *np* orbitals. The middle part of the valence band is mainly built up of halogen *np* states. The lowest conduction band is almost pure Pb^{2+} 6*p* character. The higher-lying 6*d* state of Pb^{2+} ions appears at about 8 eV above the bottom of the conduction band. These features are common to all lead halides.

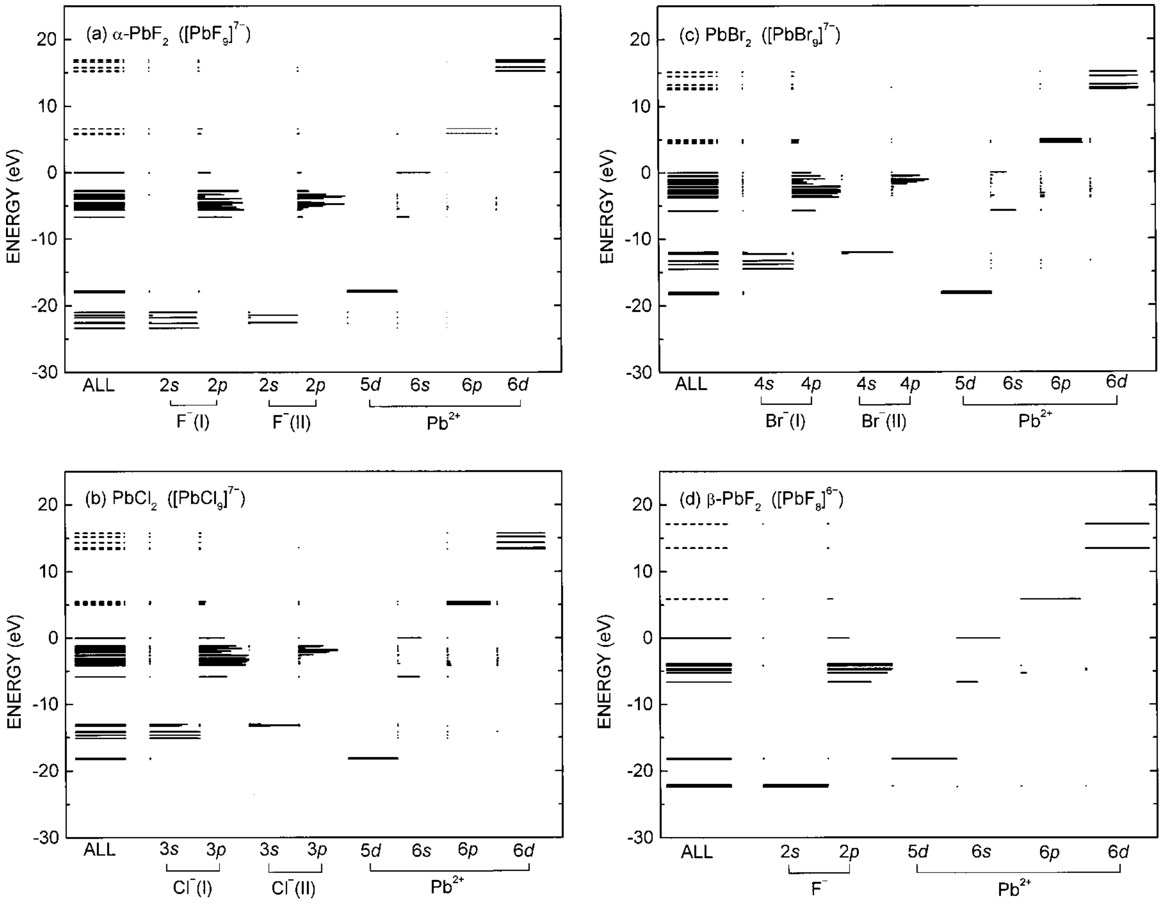

FIG. 6. Electronic structures of (a) $[PbF_9]^{7-}$, (b) $[PbCl_9]^{7-}$, (c) $[PbBr_9]^{7-}$, and (d) $[PbF_8]^{6-}$ clusters calculated by the DV-$X\alpha$ method. The energy is referred to the top of the valence band. Solid and broken lines represent occupied and unoccupied levels, respectively.

In each material, the Pb^{2+} 5d core level lies at -18 eV. The Br^- 4s and Cl^- 3s core levels are situated above the Pb^{2+} 5d core level, while the F^- 2s core level is below the Pb^{2+} 5d level.

The calculated band-gap energies are 5.88, 5.83, 5.03, and 4.47 eV for β-PbF_2, α-PbF_2, $PbCl_2$, and $PbBr_2$, respectively. Although exact values of the band-gap energies in lead halides are still disputable, as discussed later, the agreement between experiment and calculation seems qualitatively good. The widths of the valence bands are estimated to be 6.63, 6.72, 5.87, and 5.73 eV for β-PbF_2, α-PbF_2, $PbCl_2$, and $PbBr_2$, respectively. They are also consistent with the results determined experimentally from the photoelectron experiments.[15,27,28]

IV. DISCUSSION

The present results of calculation indicate that the top of the valence band consists of Pb^{2+} 6s and halogen np orbitals, and the contribution of halogen wave function increases on going from fluoride to bromide. The lowest conduction bands are almost pure Pb^{2+} 6p character. Therefore, the lowest exciton transitions of Pb halides are mainly attributed to the $6s \rightarrow 6p$ $({}^1S_0 \rightarrow {}^3P_1)$ excitations in Pb^{2+} ion. Based on this cationic excitation picture, the dichroism of the exciton bands of orthorhombic lead halides in Fig. 3 has been explained in terms of the crystal-field splitting of the Pb^{2+} 6p levels.[12,29]

The exciton band of β-PbF_2 in Fig. 3(a) has three fine structures. They are more clearly observed in the 2EDR spectra in the previous paper.[17] The origin of the structures remains still unclear. As was discussed in Ref. 17, there is a possibility that the interaction between an electron and a hole at inequivalent critical points in the Brillouin zone splits the exciton levels,[19,30] followed by an LO-phonon sideband.[31,32]

It should be noted that the contribution of halogen np states to the top of the valence band is comparable to that of the Pb^{2+} 6s state, according to the cluster calculation. In fact, it has been pointed out that the hole state extending on the halogen sites plays an important role in the relaxation process of the exciton in lead halides,[8,9] though the cationic excitation model explains well the lowest absorption spectra of the orthorhombic phase.

Here, let us discuss the band-gap energies of lead halides. When the crystals of $PbCl_2$ and $PbBr_2$ are excited with photons in the energy region higher than the first exciton band, they emit the luminescence due to the recombination of electrons with holes, which is called the BG luminescence.[7] The excitation spectrum measured at 10 K for the BG luminescence shows a sharp threshold at 4.75 eV for $PbCl_2$ and at 3.99 eV for $PbBr_2$.[33] Furthermore, photoconductivity spectra of these two crystals have been measured at 77 K by Verwey and Westerink[34] and at 8 K by Halff and Schoonman.[35] The spectrum of $PbCl_2$ in Ref. 34 arises at 4.8 eV, while that of $PbBr_2$ in Ref. 35 increases gradually from 4.0 eV. These energy positions are in fairly good agreement with the corresponding threshold of the excitation spectra for the BG luminescence. In the absorption spectra in Fig. 3, however, no clear structures that are suggestive of band gaps are seen at the threshold of the excitation and photoconductivity spectra. The reason is not yet clear. If we assume that the excitation threshold mentioned above corresponds to the band gap in each material, the binding energies are evaluated as $E_b = 0.086$ eV for the lowest exciton component at 4.664 eV in $PbCl_2$ and $E_b = 0.069$ eV for the lowest exciton component at 3.921 eV in $PbBr_2$. These exciton binding energies are considerably smaller than those in typical ionic compounds, e.g., $E_b = 0.5$–0.9 eV in alkali halides.[36] As is well known, the strongest dependence of exciton binding energy is on the square of the optical dielectric constant ϵ_∞; $E_b = E_0\mu/\epsilon_\infty^2$, where E_0 is the hydrogen Rydberg constant and μ is the exciton reduced mass in units of the free electron mass. We suppose that the small values of E_b in $PbCl_2$ and $PbBr_2$ may be reasonable, because their optical dielectric constants are 6.27–6.74 for $PbCl_2$ and 8.31–8.59 for $PbBr_2$,[37] which are larger than the values in alkali halides and are comparable to those in thallous halides[30] and some semiconducting materials like CdS or ZnS.[38]

In the photoconductivity spectra of $PbBr_2$ (Ref. 34) and $PbCl_2$ (Ref. 35), strange structures have been observed in the energy region below the exciton band. These structures are not seen for $PbBr_2$ in Ref. 35 and for $PbCl_2$ in Ref. 34; there is a discrepancy between the data by the two groups. Photoconductivity experiments on lead halides including PbF_2 should be reexamined. Furthermore, other optical studies such as two-photon spectroscopy are needed to get more detailed information on the band gaps and electronic structures in these materials.

In Fig. 2, the ϵ_2 spectra of $PbCl_2$ and $PbBr_2$ show a clear dip at around 5 eV higher than the respective absorption edges. Since the valence-band widths of these crystals are about 5 eV, the structures below the dip are attributed to the transitions from the valence band to the bottom of the conduction band formed by Pb^{2+} $6p$ orbitals. The structures above the dip are mainly due to the transitions from the valence band to the high-lying Pb^{2+} $6d$ states in the conduction band. A weak dip at 14 eV in the absorption spectra of β-PbF_2 may correspond to such a dip of chloride and bromide, while no distinct dip is observed for α-PbF_2. Since the valence-band width in fluoride is wider than that in chloride and bromide,[15,27,28] it is supposed that the transitions to the upper conduction band overlap with those to the lower conduction band.

The oscillatory structure, which appears between 4 and 5 eV in the spectrum of $PbBr_2$ for $\mathbf{E}\|\mathbf{a}$ in Figs. 3 and 4, is not ascribed to the interference effect due to surface contamination, because the same structure appears in the reflection spectrum of the sample cleaved in vacuum[14] and of the sample immersed in liquid helium.[13] The structure seems to be intrinsic. The origin is not vibronic, since the energy separation of 230 meV is one order of magnitude greater than a typical value of the lattice phonon energy. This interesting structure is still an open problem.

The energy positions of the peak 3 in $PbCl_2$ and $PbBr_2$ in Fig. 4 almost coincide with those of the *C* band in the absorption spectra of Pb^{2+}-doped alkali chlorides and bromides, respectively.[39] This may indicate that the peak 3 is attributed to the $^1S_0 \rightarrow {}^1P_1$ excitation in Pb^{2+} ions, based on the localized excitation picture. There is a question of whether the origin of the peak 3 of α- and β-PbF_2 is the same as those in $PbCl_2$ and $PbBr_2$, since this band is broad and the separation between peak 1 and peak 3 in PbF_2 is more than 1.5 times larger than that in $PbCl_2$ and $PbBr_2$. It would be a promising experiment to measure the absorption spectra of Pb^{2+} ions doped in fluoride crystals, in order to get information on the correspondence between the *C* band of Pb^{2+} impurities and peak 3 of PbF_2 crystals.

The α- and β-PbF_2 exhibit different spectral features in the 10–17 eV region (Fig. 5); broad structures are seen in the former, while several sharp peaks are observed in the latter. Because of the lower symmetry of crystal structure, the valence band in α-PbF_2 is more complicated, as recognized from Figs. 6(a) and 6(d). The difference in the valence-band structure would result in the different spectra in this region.

Sharp peaks c_0–c_3 are due to the excitonic transitions from the 5*d* core level to the 6*p* level in Pb^{2+} ions.[15,16] The peaks c_1, c_2, and c_3 have been assigned to the allowed transitions from the $^1S_0$ ground state to the $J=1$ excited states of $^3P_1$, $^1P_1$, and $^3D_1$ based on the atomic excitation picture of $5d^{10}6s^2 \rightarrow 5d^9 6s^2 6p$ transition in Pb^{2+} ions. The relative intensity and splitting of these structures have been explained well by this model.[16] It should be noted that the spectral features of cubic β-PbF_2 resemble those of TlCl and TlBr.[40] This is reasonable because the Pb^{2+} and Tl^+ ions are isoelectronic and a cation is situated at the center of a cube whose corners are occupied by eight halogen ions in both the β-PbF_2 and TlCl structures. Some of the $J \neq 1$ excited states, to which the optical transition is forbidden in a free ion, can couple with the $J=1$ states through the crystal-field potential in the orthorhombic or cubic crystal.[40] The additional peaks c_0 and $c_{3'}$ are probably assigned to the transitions to such excited states. Details of the core exciton structures in heavy metal halides will be reported elsewhere.

V. SUMMARY

We measured polarized reflectivity spectra of α-PbF_2, β-PbF_2, $PbCl_2$, and $PbBr_2$ in the 3–30 eV region. Optical constants were derived through the Kramers-Kronig transformation. The spectra of single crystals were well resolved in comparison with those obtained by use of thin films or polished surfaces in the earlier studies. The electronic structures of the simple model clusters for orthorhombic and cubic PbX_2 were calculated by the DV-$X\alpha$ method. The calculated results explained well the experimental data. The absorption spectra near the band edges were examined in detail, but no clear structure that was previously assigned to the $n=2$ exciton state or band-to-band transition was observed in the present experiment. The band gaps of lead halides have remained unresolved, though tentative assignment was made for $PbCl_2$ and $PbBr_2$ from the onset of the excitation spectra for the BG luminescence. It was found that the exciton band of β-PbF_2 has fine structures, and that the oscillatory structure appears below 5 eV in the spectra of $PbBr_2$. Further investigations using external field effect, such as a magneto-optical experiment, should be done to reveal these structures.

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[1] R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Wiley, New York, 1963), Vol. 1. Though the notation of space group for $PbCl_2$ structure is *Pbnm* in this reference, we use the notation *Pmnb* following previous optical studies in Refs. 12–14,16, and 17.

[2] D. L. Alov and S. I. Rybchenko, J. Phys.: Condens. Matter **7**, 1475 (1995).

[3] A. V. Zamkov, I. T. Kokov, and A. T. Anistratov, Phys. Status Solidi A **79**, K177 (1983).

[4] Q. Ren, L. Ding, F. Chen, R. Cheng, and D. Xu, J. Mater. Sci. Lett. **16**, 1247 (1997).

[5] V. Plekhanov, Phys. Status Solidi B **57**, K55 (1973).

[6] S. V. Nistor, E. Goovaerts, and D. Schoemaker, Phys. Rev. B **48**, 9575 (1993).

[7] M. Kitaura and H. Nakagawa, J. Electron Spectrosc. Relat. Phenom. **79**, 171 (1996).

[8] M. Kitaura and H. Nakagawa, J. Lumin. **72-74**, 883 (1997).

[9] M. Itoh, H. Nakagawa, M. Kitaura, M. Fujita, and D. L. Alov, J. Phys.: Condens. Matter **11**, 3003 (1999).

[10] R. Kink, T. Avarmaa, V. Kisand, A. Lõhmus, I. Kink, and I. Martinson, J. Phys.: Condens. Matter **10**, 693 (1998).

[11] M. Kitaura, M. Itoh, Y. Bokumoto, and M. Fujita, UVSOR Activity Report 1998 (unpublished), p. 62.

[12] J. Kanbe, H. Takezoe, and R. Onaka, J. Phys. Soc. Jpn. **41**, 942 (1976).

[13] J. Kanbe, Ph.D. thesis, Kyoiku University, 1977.

[14] A. J. H. Eijkelenkamp and K. Vos, Phys. Status Solidi B **76**, 769 (1976).

[15] J. H. Beaumont, A. J. Bourdillon, and J. Bordas, J. Phys. C **10**, 761 (1977).

[16] M. Fujita, H. Nakagawa, K. Fukui, H. Matsumoto, T. Miyanaga, and M. Watanabe, J. Phys. Soc. Jpn. **60**, 4393 (1991).

[17] M. Fujita, M. Itoh, H. Nakagawa, M. Kitaura, and D. L. Alov, J. Phys. Soc. Jpn. **67**, 3320 (1998).

[18] G. A. Samara, Phys. Rev. B **13**, 4529 (1976).

[19] B. Velický and J. Mašek, Solid State Commun. **58**, 663 (1986).

[20] M. Nizam, Y. Bouteiller, B. Siliv, C. Pisani, M. Causà, and R. Dovesi, J. Phys. C **21**, 5351 (1988).

[21] D. E. Ellis and G. S. Painter, Phys. Rev. B **2**, 2887 (1970).

[22] H. Adachi, M. Tsukada, and C. Satoko, J. Phys. Soc. Jpn. **45**, 875 (1978).

[23] A. B. Kulakov, A. A. Zohkov, G. A. Emel'chenko, and N. V. Klassen, J. Cryst. Growth **151**, 107 (1995).

[24] J. D. Axe, J. W. Gaglianello, and J. E. Scardefield, Phys. Rev. **139**, A1211 (1965).

[25] R. A. Abreu, Phys. Lett. **100A**, 375 (1984).

[26] A. F. Wells, *Structural Inorganic Chemistry*, 4th ed. (Oxford, Clarendon, 1975), p. 221.

[27] T. Matsukawa and T. Ishii, J. Phys. Soc. Jpn. **41**, 1285 (1976).

[28] M. Itoh, T. Shiokawa, K. Sawada, and M. Kamada, J. Phys. Soc. Jpn. **67**, 2140 (1998).

[29] K. Wada, Sci. Light (Tokyo) **26**, 77 (1977).

[30] K. Kobayashi, in *Excitonic Processes in Solids*, edited by M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura (Springer-Verlag, Berlin, 1986), p. 370.

[31] T. Miyata, J. Phys. Soc. Jpn. **31**, 529 (1971).

[32] M. H. Dickens and M. T. Hutchings, J. Phys. C **11**, 461 (1978).

[33] M. Kitaura (unpublished).

[34] J. F. Verwey and N. G. Westerink, Physica (Utrecht) **42**, 293 (1969).

[35] A. F. Halff and J. Schoonman, Phys. Status Solidi A **40**, 511 (1977).

[36] K. S. Song and R. T. Williams, *Self-Trapped Excitons* (Springer-Verlag, Berlin, 1993), p. 147.

[37] C. Carabatos-Nédelec, F. Bréhat, and B. Wyncke, Infrared Phys. **31**, 611 (1991).

[38] R. E. Halsted, M. R. Lorenz, and B. Segall, J. Phys. Chem. Solids **22**, 109 (1961).

[39] A. Fukuda, Sci. Light (Tokyo) **13**, 64 (1964).

[40] M. Fujita, N. Ohno, Y. Kiyama, and K. Nakamura, J. Electron Spectrosc. Relat. Phenom. **79**, 59 (1996).