Self-trapped states and related luminescence in PbCl$_2$ crystals

Masanobu Iwanaga
Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan

Masanobu Shirai and Koichiro Tanaka
Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan

Tetsusuke Hayashi
Faculty of Integrated Human Studies, Kyoto University, Kyoto 606-8501, Japan

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We have comprehensively investigated localized states of photoinduced electron-hole pairs with the electron-spin-resonance technique and photoluminescence (PL) in a wide temperature range of 5–200 K. At low temperatures below 70 K, holes localize on Pb$^{2+}$ ions and form self-trapping hole centers of Pb$^{3+}$. The holes transfer to other trapping centers above 70 K. On the other hand, electrons localize on two Pb$^{2+}$ ions at higher than 50 K and form self-trapping electron centers of Pb$^{3+}$. From the thermal stability of the localized states and PL, we clarify that the blue-green PL band at 2.50 eV is closely related to the self-trapped holes.

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I. INTRODUCTION

Electronic excited states relax into self-trapped (ST) states in solids where electrons strongly interact with acoustic phonons. The structure of ST states has been extensively examined with the electron-spin-resonance (ESR) technique in ionic crystals. The annihilation of the ST states often induces photons due to electron-hole (e-h) recombination via the electric dipole transition. Therefore, the luminescence study is another effective technique to investigate the ST states in highly efficient luminescent materials. A comprehensive study with the ESR technique and luminescence spectroscopy is often powerful enough to clarify the ST states and the correlation with luminescence.

Localized states of excited electrons and holes in PbCl$_2$ crystals have been studied with the ESR technique for the past few decades. In the early stage around 1970, the localized states induced by ultraviolet (uv) light irradiation at 80 K were observed around $g \approx 2$ (Refs. 4–6). Figure 1 shows ESR signals photoinduced at 80 K; a set of five resonances around $g \approx 2$ was called the “A signal” and is enlarged in the inset. In addition, the ESR signals after x-ray irradiation at 10 K were also reported around $g \approx 2$ and were called the “B signal” and “C signal.” Though some trials were performed, the localized state responsible for the A signal has been disputed and the origins of the B and C signals have not yet been identified. The next advance was reported by Nistor et al in 1993; self-trapped electrons (STEL’s) induced by x-ray and $\gamma$-ray irradiation at 80 K were observed and found to be dimer-molecular Pb$^{3+}$ centers. The ESR spectrum of Pb$^{3+}$ is also presented in Fig. 1.

Localized states in cubic PbF$_2$ (Ref. 10) and PbBr$_2$ (Ref. 11) have been revealed with the ESR technique. In PbF$_2$, only holes get self-trapped and form Pb$^{3+}$ centers. On the other hand, both electrons and holes get self-trapped in PbBr$_2$, and form electron centers of Pb$^{3+}$ and hole centers of Br$^{2-}$, respectively. The configurations of self-trapped holes (STH’s) are different between PbF$_2$ and PbBr$_2$. The difference is qualitatively explained by the components at the top of the valence bands; the 6s states of Pb$^{2+}$ are the main component in PbF$_2$, while the 4p states of Br$^{-}$ mainly constitute the valence band in PbBr$_2$ (Ref. 12). According to the cluster calculation for PbCl$_2$, the top of the valence band is composed of about half Pb$^{2+}$ (6s) and half Cl$^{-}$ (3p) ions. Therefore, the structure of localized hole centers in PbCl$_2$ is significant to clarify the relation of hole-relaxation dynamics with the electronic-band structure in PbCl$_2$ and to understand the relation in lead halides comprehensively.

Luminescence in PbCl$_2$ has been studied in parallel with the ESR. The intense photoluminescence (PL) at low temperatures below 10 K was classified as the uv PL band at 3.8

![Fig. 1. Typical ESR spectrum measured at 9 K after photodarkening at 80 K; the light source is described in Sec. II. The inset enlarges the A signal around 330 mT. The microwave frequency was 9.400 GHz. The magnetic field vector B was in the bc plane; the angle between the B and the b axis was 10°.](image-url)
eV, the blue PL band at 2.8 eV, and the blue-green (BG) PL band at 2.5 eV. The uv and the blue PL bands are mainly induced under one-photon excitation into the exciton band, and the BG PL band is dominantly induced under excitation into the energy region higher than the lowest exciton. As the origins of the uv PL band at 3.76 eV and the blue PL band at 2.88 eV, the self-trapped excitons (STEs) with the configuration of (Pb\(^+\) + hole) were proposed, and the origin of the BG PL band was attributed to the STE's of (Pb\(^2+\) + hole). The models claim that the lowest excitons and free \(e^{-}h^{+}\) pairs relax into different localized states. However, the Pb\(^+\) centers in PbCl\(_2\) have not been reported. Another interpretation on the PL bands was recently proposed; it declares that the uv and blue PL bands come from the STE's of (Pb\(^3+\) + hole) and the BG PL band originates from the tunneling recombination of the pairs of a STEL of Pb\(^2+\) and a STH of Cl\(^2-\). On the other hand, another PL study has shown that PL below 10 K under two-photon excitation into the exciton band is dominantly composed of the BG PL band, and the intensity of the uv PL band heavily saturates such that \(I_{\text{uv}} \propto J_{\text{exc}}^{0.6}\) where \(I\) is intensity of incident light. The results imply that, under the bulk excitation such as two-photon excitation, the relaxed states of \(e^{-}h^{+}\) pairs are independent of the excitation energy and yield the BG PL band. Consequently, it is possible to explain that the lowest excitons created under one-photon excitation are captured by surface defects and result in the uv and blue PL bands. Thus, the origins of PL bands are still under dispute.

Excitons in PbBr\(_2\) crystals, which belong to the same crystallographic group with PbCl\(_2\) and have similar electronic-band structures, undergo uncommon relaxation; they spontaneously dissociate and relax into spatially separated STEL's and STH's. The recent ESR study supports the relaxed state of excitons structurally. A similar relaxation in PbCl\(_2\) has been pointed out, but the structures of the localized states have not been explored fully as already described.

We have comprehensively examined the localized states of photoinduced \(e^{-}h^{+}\) pairs and PL properties in a wide temperature range of 5–200 K. As a result, the localized states of holes at low temperatures below 70 K have been found to form STH centers of Pb\(^{3+}\); the structure of STH's is different from that inferred from the ESR spectrum at 80 K as shown in Fig. 1 and from the recent study on PbBr\(_2\) (Ref. 11). We present the low-temperature ESR signals photoinduced below 10 K in Sec. III A and the PL properties in Sec. III B. The STH's are analyzed with spin Hamiltonian in Sec. IV A. We discuss the correlation between ESR signals and PL properties in a wide temperature range in Sec. IV B, the origin of the A signal in Sec. IV C, and the relaxation dynamics of \(e^{-}h^{+}\) pairs in comparison with PbBr\(_2\) in Sec. IV D.

II. EXPERIMENTS

Single crystal of PbCl\(_2\) was grown with the Bridgman technique from 99.999% powder. The crystal of orthorhombic \(D_{2h}^{10}\) (Ref. 21) was cut in the size of \(3 \times 3 \times 3\) mm\(^3\) along the right-angled crystallographic \(a, b,\) and \(c\) axes.

The sample was photoirradiated with the second harmonic (pulsed 120-fs-width, 1-kHz, and 3.10-eV light) generated from a regeneratively amplified Ti:sapphire laser; average power of the incident light was about 20 mW/cm\(^2\) on the sample surface. The incident photons induce two-photon interband transition, create \(e^{-}h^{+}\) pairs almost uniformly in the crystal, and produce measurable ESR signals within 1 min. The samples were typically photoirradiated for five minutes. The irradiated sample was measured below 12 K with the ordinary ESR technique in \(X\)-band range; the resonant microwave frequency was 9.400 GHz. The details of ESR and thermoluminescence (TL) measurements were previously reported in Ref. 11. Raising and lowering rates of temperature in measuring TL were 0.5 K/s. In the pulse-annealing measurement, the sample was kept for about 1 s at the annealing temperature.

PL was induced with the second harmonics (pulsed 5-ns-width, 10-Hz, and 2.33-eV light) generated from a Nd:YAG (yttrium aluminum garnet) laser; the incident light causes exciton-resonant two-photon excitation. The PL properties are essentially the same as those induced under one-photon excitation with uv light (\(h\omega \approx 4.8\) eV). PL was detected with an intensified charge-coupled device (CCD) camera with a grating monochromator, and time-resolved PL spectra were measured by gating the CCD camera; the temporal resolution was 5 ns.

III. EXPERIMENTAL RESULTS

A. ESR spectra and thermoluminescence

Figure 2 shows typical ESR spectrum measured at 7 K after photoirradiation at 6 K; the ESR signals at 326, 522,
1400, and 1480 mT are readily induced together, while the signal at 1180 mT appears even in measuring empty capillary. Therefore, as reported in Ref. 26, the signal at 1180 mT is ascribed to oxygen molecules in the capillary. The photoinduced four signals show similar thermal profiles; besides, they saturate for microwave power higher than 0.01 mW below 7 K, while keeping a linear response up to 0.1 mW at 10 K. Consequently, the four signals are ascribed to the same origin. The intense ESR signal at 326 mT, which is enlarged in the inset, consists of one broad resonance with 6-mT width; the structure differs from the fivefold-split A signal in Fig. 1. The signals at 326 and 522 mT are almost independent of rotation angles. Though the two signals around 1400 mT depend on rotation angles, they degenerate when the magnetic field vector is parallel to the crystallographic axes. The reason for the split and the rotation-angle dependence is discussed in Sec. IV A. The intense line at 326 mT was induced by x-ray irradiation at 10 K and was called the C signal in Ref. 5. The small signal at 336 mT in the inset of Fig. 2 is the B signal named in Ref. 5; it is far weaker than the C signal and hardly depends on rotation angles. From now on, we focus on the main A and C signals and the satellite signals.

Except for the 1180-mT resonance, the ESR spectrum in Fig. 2 is very similar to that of Pb\(^{3+}\) in KCl:Pb\(^{2+}\) therefore, the ESR signals in Fig. 2 are ascribed to hole centers of Pb\(^{3+}\). The hole centers are analyzed with the spin Hamiltonian and are compared with Pb\(^{3+}\) centers in other host crystals in Sec. IV A.

Figure 3 displays the ESR spectra measured at 9 K after photoirradiation at various temperatures. They are displayed with a vertical offset. The ESR spectrum at 8 K is doubly enlarged. The microwave frequency was 9.404 GHz. The magnetic field vector B was in the bc plane; the angle between the B and the b axis was 10°.

Figure 4 presents ESR spectrum (lower) after photoirradiation at 10 K, namely, before pulse annealing and ESR spectrum (upper) after pulse annealing at 100 K. Both spectra were measured at 12 K. The ESR spectrum before pulse annealing has the two prominent signals at 326 and 522 mT, which come from Pb\(^{3+}\) centers. In the spectrum after pulse annealing, the signals from STEL centers of Pb\(^{3+}\) appear around 460 mT, the A signal is observed around 330 mT, and the residual signal from Pb\(^{3+}\) centers is still detected in the low-magnetic-field side of the A signal.

Figure 5 shows TL-growth curve (solid line) and the intensity of ESR signals in Fig. 3 (open and closed circles and cross). TL is observed strongly at 60–85 K under the condition of raising temperature at 0.5 K/s. The TL spectrum in the temperature range is in agreement with the BG PL spectrum.

In a previous TL experiment, the TL-growth curve measured with increasing temperature at 0.1 K/s shows two discrete peaks at 51 and 74 K. The difference probably results from the temperature-rising rate; the rising rate in the previous report is slower than that in our measurement. The discrete peaks suggest the two different thermal activation in 50–80 K. The two thermal transfers were assigned to hole activation in Ref. 16. We discuss the activated carriers in Sec. IV B.

B. Photoluminescence

Figure 6 presents PL spectra under exciton-resonant two-photon excitation at 4.66 eV. The PL spectra at 6–70 K are irradiation at 8–50 K are essentially the same in shape. At 60 K, Pb\(^{3+}\) signals become prominent, and the signals around 330 mT are composed of Pb\(^{3+}\) signals and other split signals at 60–80 K. The Pb\(^{3+}\) signals are eventually replaced by the A signal at 90 K.
peaked at 2.52 eV and almost invariant in shape. Above 70 K, the PL spectrum begins to move toward high-energy side, and the peak reaches 2.7 eV at 100 K. In the range above 100 K, low-energy PL around 2 eV relatively increases with raising temperature, and finally the PL spectrum consists of broad PL bands at 150 K. The thermal behavior of PL induced under one-photon excitation into the fundamental absorption region ($h\omega \approx 4.8$ eV) is the same as that in Fig. 6.

Figure 7 shows PL spectra (solid lines) and time-resolved PL (TRPL) spectra (dashed and dotted lines) under two-photon excitation at 4.66 eV, measured at 6, 75, and 90 K. The dashed line at 6 K represents the BG PL band at 2.50 eV; the spectrum is obtained by measuring the PL over 1–99 ms, that is, by gating the CCD camera with a 1-ms delay and 98-ms width. The BG PL band decays phosphorescently; the intensity $I(t)$ is well described by $I(t) = (K/t^\tau) \times [1 - \exp(-t/\tau)]$, where $K$ is a proportionality constant and $\tau = 100 \mu$s.\textsuperscript{20} The rest of the PL at 6 K is the PL band at 2.66 eV (arrow) and decays single-exponentially in 5.0 $\mu$s.

This blue PL band is different from the blue PL band at 2.88 eV mentioned in Sec. I; the blue PL band at 2.88 eV is not induced under the present excitation. The PL spectra at 75 and 90 K are spectrally resolved with the TRPL spectra peaked at 2.79 eV (arrow). The blue PL band at 2.79 eV decays single-exponentially in 2.6 $\mu$s at 75 K. Thus, the relative increase of the blue PL band results in the apparent high-energy shift of the PL spectrum in Fig. 6.

The PL intensity integrated over 2.0–3.2 eV at 6–200 K is plotted against temperature in Fig. 8; time-integrated PL intensity over 0–99 ms is represented with crosses, and TRPL intensity over 1–99 ms with closed circles. The PL intensity.

FIG. 5. TL-growth curve (solid line) measured with raising temperature at 0.5 K/s. ESR intensity in Fig. 3 is shown for comparison; $\text{Pb}^{3+}$ (closed circle), $\text{Pb}_2^{3+}$ (open circle), and A centers (cross). Dashed, dotted, and broken lines are drawn for guides to the eye.

FIG. 6. PL spectra at 6, 80, 90, 100, and 150 K under exciton-resonant two-photon excitation at 4.66 eV. The PL spectrum at 150 K is enlarged five times.

FIG. 7. PL (solid lines) and time-resolved PL (dashed and dotted lines) spectra at 6, 75, and 90 K under two-photon excitation at 4.66 eV. PL in $\mu$s range corresponds to blue PL (dotted line) and the rest of PL to the phosphorescent blue-green PL band (dashed line). Arrows indicate the blue PL peaks and are located at 2.66 eV for 6 K and at 2.79 eV for 75 and 90 K.

FIG. 8. PL intensity integrated over 2.0–3.2 eV vs temperature; cross denotes time-integrated PL intensity over 0–99 ms and closed circle stands for time-resolved PL intensity over 1–99 ms with closed circles. The PL intensity.

FIG. 7. PL (solid lines) and time-resolved PL (dashed and dotted lines) spectra at 6, 75, and 90 K under two-photon excitation at 4.66 eV. PL in $\mu$s range corresponds to blue PL (dotted line) and the rest of PL to the phosphorescent blue-green PL band (dashed line). Arrows indicate the blue PL peaks and are located at 2.66 eV for 6 K and at 2.79 eV for 75 and 90 K.
intensity remains almost constant below 50 K and increases at 50–70 K. The increase is coincident with TL growth (dotted line), and the peaks of PL and TRPL intensity are located at about 80 K. Because the TRPL intensity corresponds to the phosphorescent component of PL, the increase of the PL intensity is ascribed to that of the phosphorescent BG PL. Indeed, PL at 75 K decays proportional to \( t^{-1} \) for \( t \geq 1 \) ms. The TRPL intensity decreases at 80–100 K and is hardly observed above 100 K. The TRPL quenching is also coincident with the high-energy shift due to the relative increase of the blue PL band at 2.79 eV as shown in Fig. 7. Thus, the phosphorescent BG PL band is induced below 100 K. Above 100 K, the blue PL band and other PL band around 2 eV are dominantly induced and are finally quenched around 200 K.

### IV. DISCUSSION

#### A. Spin-Hamiltonian analysis of self-trapping hole centers

The ESR signals at 326, 522, and about 1400 mT in Fig. 2 show the same temperature profile and the intensity ratio (326 mT):(522 mT+1400 mT)=8:2. The ratio is consistent with the isotope ratio of Pb ions; they have two isotope series such as \( I = 0 \) and 1/2, and the natural ratio is about 8:2. If the intense signal at 326 mT corresponds to Zeeman transition, the \( g \) value is estimated to be 2.06; the value larger than the free-electron \( g \) value of 2.0023 implies that the center is a hole center.\(^{28}\) Indeed, from comparison with Pb\(^{3\+}\) in KCl:Pb,\(^{27}\) the ESR signals are ascribed to hole centers of Pb\(^{3\+}\). The spin Hamiltonian \( \mathcal{H} \) of the hole center is given by

\[
\mathcal{H} = \mu_B \mathbf{B} \cdot g \cdot \mathbf{S} + S \cdot A \cdot I - \mu_n \mathbf{B} \cdot g_N \cdot I,
\]

where \( \mu_B \) denotes the Bohr magneton, \( \mathbf{B} \) the magnetic field vector, \( g \) the Zeeman tensor, \( \mathbf{S} \) the hole spin, \( A \) the hyperfine tensor, \( \mu_n \) the nuclear magneton of \( ^{207} \text{Pb} \) (\( \mu_n = 0.5892 \mu_N \), where \( \mu_N \) is the nuclear magneton), \( I \) the nuclear spin, and \( g_N \) the nuclear Zeeman tensor. We note that the first-order hyperfine interaction of the hole with surrounding Cl nuclei is not included in the Hamiltonian because our experimental results give no evidence of the superhyperfine (SHF) effect that the interaction splits each resonance at 326, 522, and 1400 mT in Fig. 2 into tens of fine resonances as observed in PbF\(_2\) (Ref. 10). Equation (1) describes the center over which a hole strongly localizes on a Pb\(^{3\+}\) ion, namely, the self-trapping hole center of Pb\(^{3\+}\).

Equation (1) for \( I = 0 \) is reduced to the electron Zeeman term. The intense signal at 326 mT in Fig. 2 slightly depends on rotation angles. The spin-Hamiltonian analysis for the Zeeman transition provides principal \( g \) values as shown in Table I; we set \( x = c, y = b, \) and \( z = a \) in this analysis.

In analyzing the spin Hamiltonian for \( I = 1/2 \), we can assume that the \( A \) tensor is isotropic because the resonance at 522 mT is independent of rotation angles. Furthermore, we replace, for simplicity, the contribution of the nuclear Zeeman term to the energy eigenvalues with the effective nuclear \( g_N \) value along the corresponding magnetic field. The simplification is justified because the contribution of the nuclear Zeeman term to Eq. (1) is quite small; indeed, the

#### Table I. Principal \( g \) and \( A \) values of the spin Hamiltonian [Eq. (1)].

<table>
<thead>
<tr>
<th>Host of Pb(^{3+})</th>
<th>( g ) values</th>
<th>( A ) values (GHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbCl(_2)(^a)</td>
<td>( g_x ) = 2.044 ± 0.001</td>
<td>( g_y ) = 2.062 ± 0.001</td>
</tr>
<tr>
<td>KCl:Pb(^b)</td>
<td>( g_x ) = 2.034 ± 0.001</td>
<td>( g_y ) = 33.0 ± 0.1</td>
</tr>
<tr>
<td>ThO(_2):Pb(^c)</td>
<td>( g_x ) = 1.967 ± 0.001</td>
<td>( g_y ) = 36.8 ± 0.2</td>
</tr>
<tr>
<td>ZeSe:Pb(^d)</td>
<td>( g_x ) = 2.072 ± 0.001</td>
<td>( g_y ) = 20.7 ± 0.1</td>
</tr>
<tr>
<td>ZnSe:Pb(^e)</td>
<td>( g_x ) = 2.167</td>
<td>( g_y ) = 15.7</td>
</tr>
</tbody>
</table>

| \( a\) This work. |
| \( b\) Reference 27; \( g \) tensor is assumed to be isotropic. |
| \( c\) References 29 and 30. |
| \( d\) Reference 31. |
| \( e\) Reference 32; the accuracy of \( g \) and \( A \) values is not reported. |
with the \(g\) and \(A\) values of Pb\(^{3+}\) centers in other hosts. The \(g\) values are about 2 in all hosts, while the \(A\) values vary from 16 to 37 GHz. The \(A\) values imply that the spatial spread of the hole is quite different in each host.

### B. Thermal stability of ESR signals and PL bands

Below 70 K holes localize on Pb\(^{2+}\) ions and form self-trapping hole centers of Pb\(^{3+}\), and, on the other hand, electron centers are not detected at 0–1700 mT below 50 K. As STEL centers with a simple configuration, monomer Pb\(^{+}\) and dimer Pb\(^{2+}\) centers are possible in PbCl\(_2\). Indeed, Pb\(^{3+}\) centers are observed above 60 K. Pb\(^{+}\) centers usually have a \(g\) value of 1.0–1.6 in Pb-doped alkali chloride;\(^{34}\) in our measurement, the ESR signal would appear at 400–700 mT if it exists. However, the STEL centers of Pb\(^{+}\) have not been detected. Thus, it is improbable that the Pb\(^{+}\) centers are induced in PbCl\(_2\).

The sharp TL growth at 55 K in Fig. 5 indicates thermal activation of trapped carriers. Because the STEL centers of Pb\(^{3+}\) appear at 60 K and the hole centers of Pb\(^{3+}\) are quite stable at 60 K as shown in Fig. 3, the activated carriers at 55 K are ascribed to electrons. However, the trapped state of electrons below 50 K has not been observed at 0–1700 mT if it exists. Moreover, the ESR spectrum, are far different from those of Pb\(^{+}\) in other host crystals.\(^7\)

The A signal was recently assigned to self-trapping hole centers of Cl\(^{2-}\) (\(V_K\) centers).\(^{35}\) The A signal is composed of five resonances as presented in Fig. 1; the intensity ratio at 9 K is estimated to be 1:10:27:10:0.5. However, the ESR spectrum of Cl\(^{2-}\) splits into seven resonances in the first-order hyperfine effect, and the intensity ratio of 1:2:3:4:3:2:1 disagrees with that of the A signal. Moreover, the rotation-angle dependence of the A signal\(^6\) does not show the anisotropy peculiar to the dimer-molecular \(V_K\) centers,\(^5\) but is almost isotropic. Thus, the A signal is unlikely to originate from the \(V_K\)-type hole centers of Cl\(^{2-}\).

Furthermore, the A signal of five resonances does not come from the Pb\(^{3+}\) centers with SHF interaction as observed in PbF\(_2\) (Ref. 10), because (i) the satellite at 522 mT disappears up to 90 K as shown in Fig. 3 and (ii) the SHF structure, which stems from the interaction of the Pb\(^{3+}\) centers with the surrounding Cl\(^{-}\) ions, is composed of tens of fine resonances.\(^{37}\)

As shown in Fig. 4, the A signal appears under pulse annealing at 100 K after photolysis at 10 K. This result indicates that the localized state responsible for the A signal is produced by thermal transfer of the localized states induced at 10 K. In addition, Fig. 3 shows that the STEL centers of Pb\(^{3+}\) are stable over 80–90 K where the Pb\(^{3+}\) signals change into the A signal. Consequently, we declare that the A signal is formed by either of the two following ways: (i) The STEL centers become unstable above 80 K and the holes transfer to other trapped states associated with permanent lattice defects. (ii) Vacancies begin to move thermally around 70 K, affect the STEL centers, and modify the STEL centers or make the STEL center unstable. In any way, the A signal is stand for the stable range, and dotted lines denote the unstable but still detectable range.

**C. Origin of the A signal**

The origin of the A signal has been disputed over the past three decades; it was once attributed to electron centers of Pb\(^{+}\) (Refs. 5 and 6), but the properties of the A signal, the \(g\) value, and the ESR spectrum, are far different from those of Pb\(^{+}\) in other host crystals.\(^7\)

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ascribed to the hole-trapping centers associated with the permanent lattice defects such as vacancies or impurities or both.

D. Relaxation dynamics of electron-hole pairs

We discuss here the relaxation of e-h pairs in PbCl\textsubscript{2} from comparison with relaxation in PbBr\textsubscript{2} (Ref. 25). In PbBr\textsubscript{2}, the spontaneous dissociation of e-h pairs was reported,\textsuperscript{25} and the individual self-trapped states of both electrons and holes have been recently seen with the ESR technique.\textsuperscript{11}

However, the present ESR study on PbCl\textsubscript{2} shows that the relaxed states of e-h pairs are the STH’s and trapped electrons below 50 K, the STH’s and STEL’s at 60–70 K, and the A centers and STEL’s at 80–130 K (Fig. 10). The complicated results probably come from the inevitably dense vacancies in PbCl\textsubscript{2};\textsuperscript{37,38} PbCl\textsubscript{2} crystals are high-ionic conductors and therefore include dense anion vacancies more than 10\textsuperscript{17} cm\textsuperscript{-3}. In the crystals, the anion vacancies or the vacancy-associated defects are electron traps and can be competitors to the STEL centers of Pb\textsuperscript{3+.} Indeed, the thermal production of the STEL’s in Fig. 4 suggests that the competitors are efficient enough to result in the absence of STEL’s below 50 K.

According to the theoretical study by Sumi,\textsuperscript{39} the exciton–acoustic-phonon interaction determines the relaxed state of e-h pairs and classifies the relaxed states by the strength and the sign of the coupling constants. In the theoretical study, the crystallographic field is idealized by omitting lattice defects such as dense vacancies, so that the study is not applicable to PbCl\textsubscript{2} straightforwardly. However, the coexistence of STEL’s and STH’s at 60–70 K shows evidence that both electrons and holes strongly interact with acoustic phonons. Consequently, though the localized states are far more complicated in the real crystal, we believe that e-h relaxation similar to that in PbBr\textsubscript{2} is also realized in PbCl\textsubscript{2}.

At the end of discussion, we compare the relaxed states of e-h pairs in PbF\textsubscript{2}, PbCl\textsubscript{2}, and PbBr\textsubscript{2}. Though the crystallographic structure of β-PbF\textsubscript{2} is cubic and those of PbCl\textsubscript{2} and PbBr\textsubscript{2} are orthorhombic,\textsuperscript{21} STH centers in β-PbF\textsubscript{2} (Ref. 10) and PbCl\textsubscript{2} are monomer Pb\textsuperscript{3+} centers while STH centers in PbBr\textsubscript{2} are dimer Br\textsuperscript{−} centers.\textsuperscript{11} The relaxed states indicate that holes in β-PbF\textsubscript{2} and PbCl\textsubscript{2} strongly interact with Pb\textsuperscript{2+} ions, while holes in PbBr\textsubscript{2} interact with Br\textsuperscript{−} ions. The top of the valence band in PbCl\textsubscript{2} is composed of about half Pb\textsuperscript{2+} (6s) and half Cl\textsuperscript{−} (3p) ions,\textsuperscript{12,13} but the holes nevertheless localize only on Pb\textsuperscript{2+} ions. On the other hand, though the bottoms of the conduction band in β-PbF\textsubscript{2}, PbCl\textsubscript{2}, and PbBr\textsubscript{2} are composed of the 6p states of Pb\textsuperscript{2+} ions,\textsuperscript{12,13} electrons in β-PbF\textsubscript{2} do not get self-trapped while electrons in PbCl\textsubscript{2} and PbBr\textsubscript{2} form STEL centers of Pb\textsuperscript{3+.} From the comparisons here, we note that in lead halides the structure of electronic band does not simply determine the relaxed states of e-h pairs, but the electron-phonon and the hole-phonon interactions play a crucial role in determining the relaxed states.

V. CONCLUSIONS

We have comprehensively investigated photoinduced ESR signals and PL in a wide range of 5–200 K in PbCl\textsubscript{2}. As a result, the hole centers below 70 K have been found to be self-trapping centers of Pb\textsuperscript{3+}. The ESR study in this wide temperature range reveals the thermal change of localized centers; in particular, the growth of the STEL centers of Pb\textsuperscript{3+} and the thermal transfer from the STH centers to the A centers. From the comparison with thermal stability of the localized centers, the origins of PL bands have been discussed; we finally conclude that the STH centers of Pb\textsuperscript{3+} are responsible for STE’s yielding the BG PL band at 2.50 eV.

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From the experimental evidence presented already, we can also discuss the models for the uv and 2.88-eV blue PL bands in Refs. 16–19; the absence of Pb⁺ centers denies the model in Refs. 16–18 and the disagreement of the temperature range of Pb²⁺ centers with those of the uv and blue PL bands excludes the model in Ref. 19.