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Author(s)	Iwanaga, M; Shirai, M; Tanaka, K; Hayashi, T
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Self-trapped states and related luminescence in PbCl₂ 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 Pb²⁺ ions and form self-trapping hole centers of Pb³⁺. The holes transfer to other trapping centers above 70 K. On the other hand, electrons localize on two Pb²⁺ ions at higher than 50 K and form self-trapping electron centers of Pb₂³⁺. 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.¹ The structure of ST states has been extensively examined with the electron-spin-resonance (ESR) technique in ionic crystals.^{2,3} 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 PbCl₂ 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”⁵ 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.”⁵ Though some trials were performed,^{4–6} the localized state responsible for the A signal has been disputed⁷ and the origins of the B and C signals have not yet been identified. The next advance was reported by Nistor *et al.*⁸ and Hirota *et al.*⁹ in 1993; self-trapped electrons (STEL’s) induced by x-ray⁸ and γ -ray⁹ irradiation at 80 K were observed and found to be dimer-molecular Pb₂³⁺ centers. The ESR spectrum of Pb₂³⁺ is also presented in Fig. 1.

Localized states in cubic PbF₂ (Ref. 10) and PbBr₂ (Ref. 11) have been revealed with the ESR technique. In PbF₂, only holes get self-trapped and form Pb³⁺ centers.¹⁰ On the other hand, both electrons and holes get self-trapped in PbBr₂, and form electron centers of Pb₂³⁺ and hole centers of Br₂⁻, respectively.¹¹ The configurations of self-trapped holes

(STH’s) are different between PbF₂ and PbBr₂. The difference is qualitatively explained by the components at the top of the valence bands; the 6*s* states of Pb²⁺ are the main component in PbF₂, while the 4*p* states of Br⁻ mainly constitute the valence band in PbBr₂ (Ref. 12). According to the cluster calculation¹² for PbCl₂, the top of the valence band is composed of about half Pb²⁺ (6*s*) and half Cl⁻ (3*p*) ions. Therefore, the structure of localized hole centers in PbCl₂ is significant to clarify the relation of hole-relaxation dynamics with the electronic-band structure in PbCl₂ and to understand the relation in lead halides comprehensively.

Luminescence in PbCl₂ 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

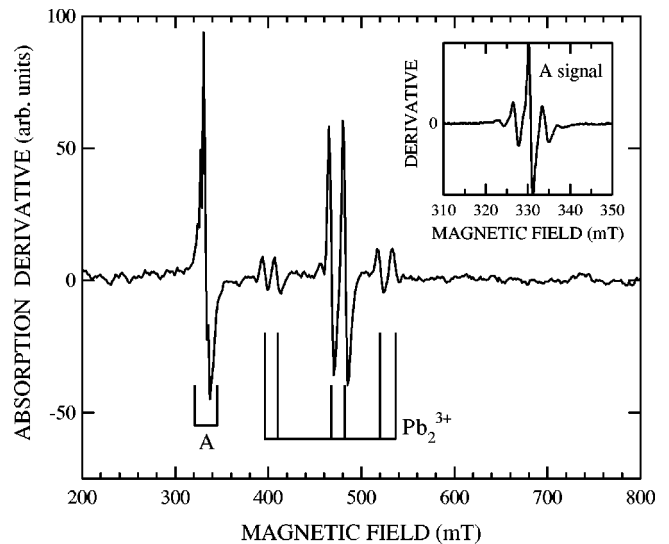


FIG. 1. Typical ESR spectrum measured at 9 K after photoirradiation at 80 K; the light source is described in Sec. II. The inset enlarges the A signal around 330 mT. The microwave frequency was 9.400 GHz. The magnetic field vector **B** was in the *bc* plane; the angle between the **B** and the *b* axis was 10°.

eV, the blue PL band at 2.8 eV, and the blue-green (BG) PL band at 2.5 eV.^{5,13,14} 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.¹⁵ 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 (STE's) with the configuration of ($\text{Pb}^+ + \text{hole}$) were proposed, and the origin of the BG PL band was attributed to the STE's of ($\text{Pb}_2^{3+} + \text{hole}$).¹⁶⁻¹⁸ 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;¹⁹ it declares that the uv and blue PL bands come from the STE's of ($\text{Pb}_2^{3+} + \text{hole}$) and the BG PL band originates from the tunneling recombination of the pairs of a STEL of Pb_2^{3+} and a STH of Cl_2^- . On the other hand, another PL study²⁰ 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 $I_{\text{uv}} \propto I^{0.6}$ 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 the blue PL bands. Thus, the origins of PL bands are still under dispute.

Excitons in PbBr_2 crystals, which belong to the same crystallographic group²¹ with PbCl_2 and have similar electronic-band structures,^{12,22-24} undergo uncommon relaxation;²⁵ they spontaneously dissociate and relax into spatially separated STEL's and STH's. The recent ESR study¹¹ supports the relaxed state of excitons structurally. A similar relaxation in PbCl_2 has been pointed out,²⁰ 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 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}^{16} (Ref. 21) was cut in the size of $3 \times 3 \times 3$ mm³ along the right-angled crystallographic a , b , and c axes.

The sample was photoirradiated with the second harmon-

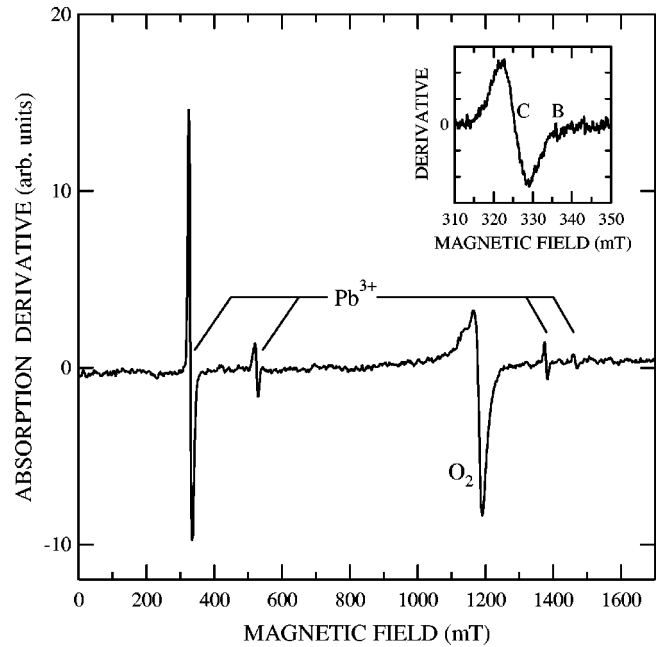


FIG. 2. Typical ESR spectrum measured at 7 K after photoirradiation at 6 K. The inset enlarges the signals around 330 mT. The microwave frequency was 9.400 GHz. The magnetic field vector \mathbf{B} was in the bc plane; the angle between the \mathbf{B} and the b axis was 40° . Descriptions for Pb^{3+} , O_2 , B, and C are given in Sec. III A.

ics (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/cm² 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 ± 0.004 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 ($\hbar\omega \geq 4.8$ 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,

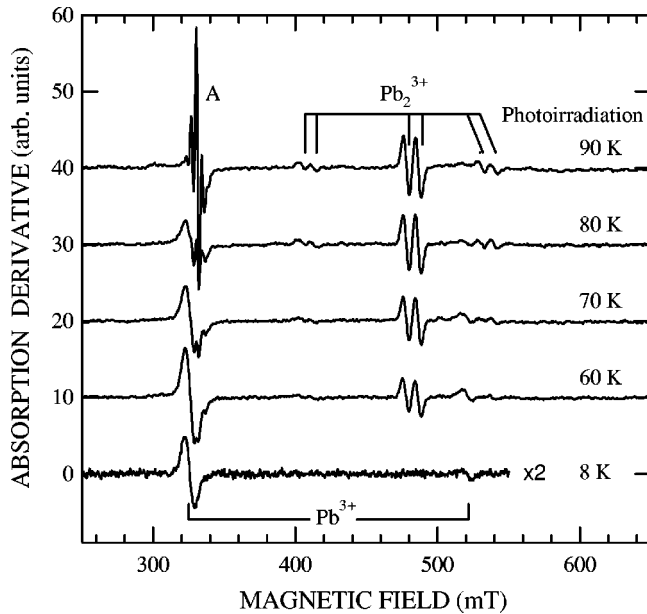


FIG. 3. ESR spectra measured at 9 K after photoirradiation at various temperatures. They are displayed with a vertical offset. The ESR spectrum at 8 K is doubly enlarged. The microwave frequency was 9.400 GHz. The magnetic field vector \mathbf{B} was in the bc plane; the angle between the \mathbf{B} and the b axis was 10° .

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 ,²⁷ 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 8, 60, 70, 80, and 90 K. A sequence of the spectra was measured by carrying out the photoirradiation and the ESR data taking alternately. The ESR spectra after

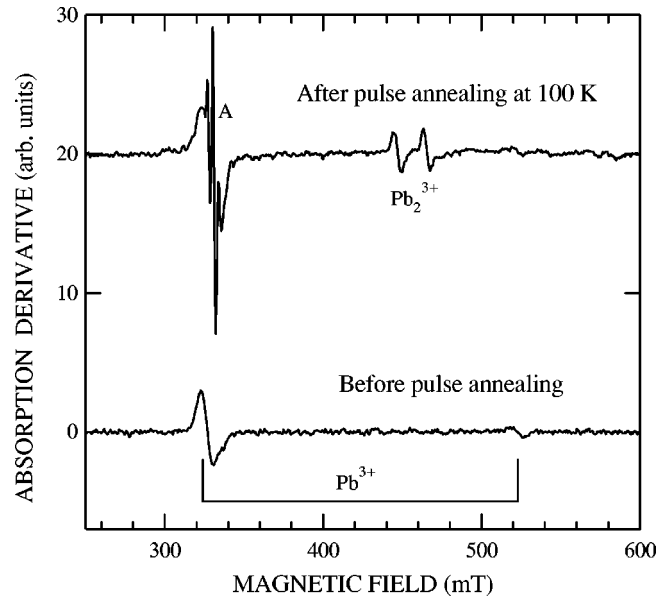


FIG. 4. Photoinduced ESR signals before and after pulse annealing at 100 K. Both spectra were measured at 12 K. The microwave frequency was 9.400 GHz. The magnetic field vector \mathbf{B} was in the bc plane; the angle between the \mathbf{B} and the b axis was 40° .

irradiation at 8–50 K are essentially the same in shape. At 60 K, Pb_2^{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.

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_2^{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,¹⁶ 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

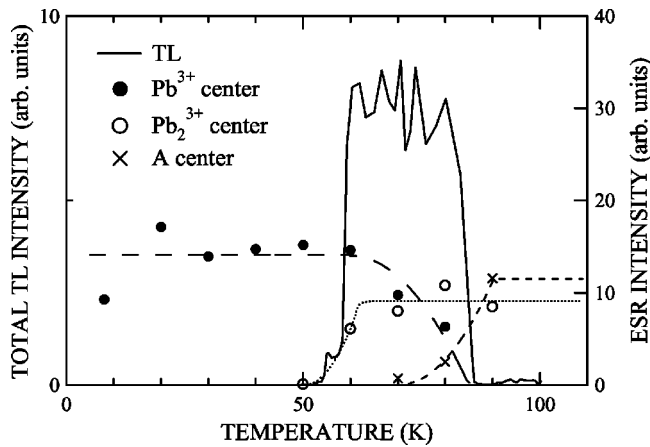


FIG. 5. TL-growth curve (solid line) measured with raising temperature at 0.5 K/s. ESR intensity in Fig. 3 is shown for comparison; Pb^{3+} (closed circle), Pb_2^{3+} (open circle), and A centers (cross). Dashed, dotted, and broken lines are drawn for guides to the eye.

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 ($\hbar\omega \geq 4.8$ 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 $I(t) = (K/t) \times [1 - \exp(-t/\tau)]$, where K is a proportionality constant and $\tau = 100 \mu\text{s}$.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 μs .

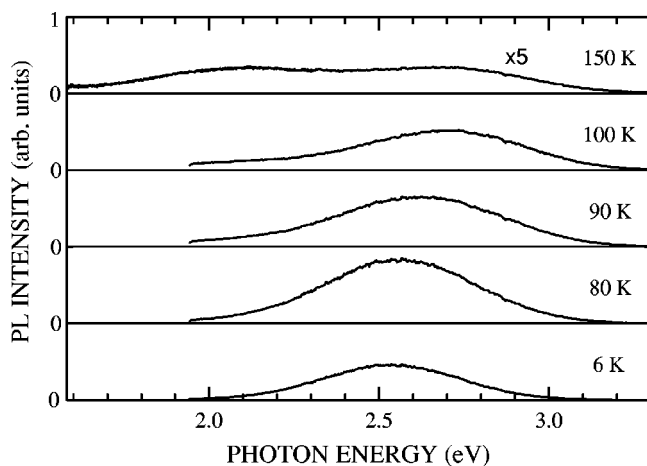


FIG. 6. PL spectra at 6, 80, 90, 100, and 150 K under exciton-resonant two-photon excitation at 4.66 eV. The PL spectrum at 150 K is enlarged five times.

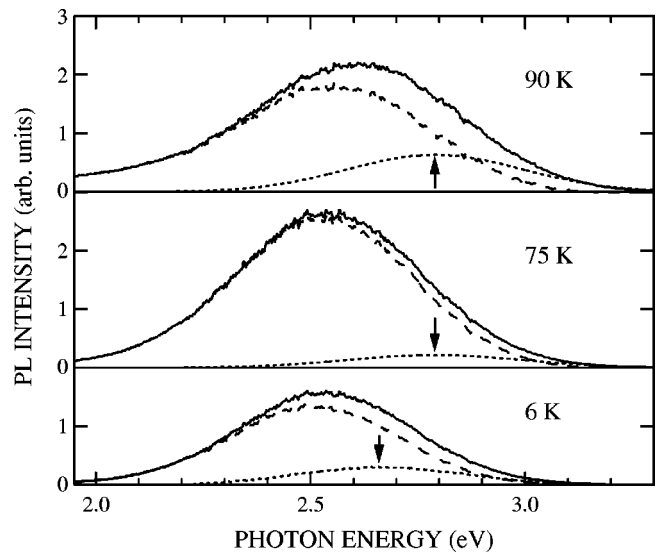


FIG. 7. PL (solid lines) and time-resolved PL (dashed and dotted lines) spectra at 6, 75, and 90 K under two-photon excitation at 4.66 eV. PL in μs range corresponds to blue PL (dotted line) and the rest of PL to the phosphorescent blue-green PL band (dashed line). Arrows indicate the blue PL peaks and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

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 μs 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

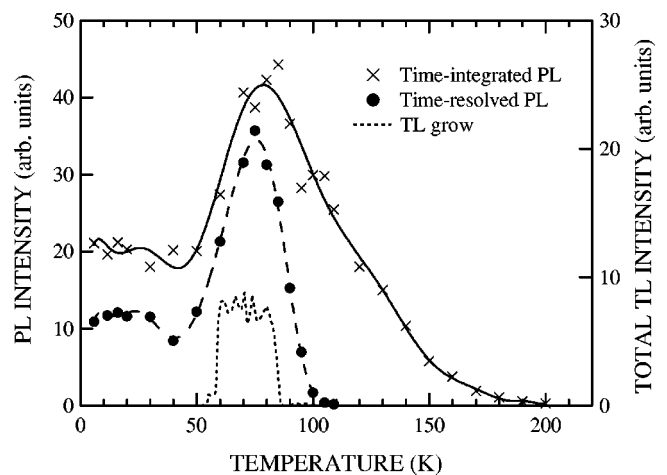


FIG. 8. PL intensity integrated over 2.0–3.2 eV vs temperature; cross denotes time-integrated PL intensity over 0–99 ms and closed circle stands for time-resolved PL intensity over 1–99 ms. Solid and dashed lines are drawn with polynomial functions for guides to the eye. TL-growth curve (dotted line) is also presented for comparison.

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

$$\mathcal{H} = \mu_B \mathbf{B} \cdot \underline{g} \cdot \mathbf{S} + \mathbf{S} \cdot \underline{A} \cdot \mathbf{I} - \mu_n \mathbf{B} \cdot \underline{g}_N \cdot \mathbf{I}, \quad (1)$$

where μ_B denotes the Bohr magneton, \mathbf{B} the magnetic field vector, \underline{g} the Zeeman tensor, \mathbf{S} the hole spin, \underline{A} the hyperfine tensor, μ_n the nuclear magneton of ^{207}Pb ($\mu_n = 0.5892\mu_N$, where μ_N is the nuclear magneton), \mathbf{I} the nuclear spin, and \underline{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^{2+} 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)]. The parameters of Pb^{3+} centers in other host crystals are cited for comparison. The A values are represented in GHz.

Host of Pb^{3+}	g values			A values (GHz)
	g_x	g_y	g_z	
PbCl_2^a	2.044 ± 0.001	2.062 ± 0.001	2.044 ± 0.001	26.7 ± 0.4
KCl:Pb^b		2.034 ± 0.001		33.0 ± 0.1
$\text{ThO}_2:\text{Pb}^c$		1.967 ± 0.001		36.8 ± 0.2
ZeSe:Pb^d		2.072 ± 0.001		20.7 ± 0.1
ZeTe:Pb^e		2.167		15.7

^aThis work.

^bReference 27; g tensor is assumed to be isotropic.

^cReferences 29 and 30.

^dReference 31.

^eReference 32; the accuracy of g and A values is not reported.

resonances are described by the electron Zeeman and isotropic hyperfine terms to a fairly good approximation. Pb^{3+} centers in other host crystals^{27,29–32} were analyzed within this approximation. However, to estimate g_N values, we choose to include the effective value in the energy eigenvalues. The obtained equations of the eigenvalues are the same as the Breit-Rabi formula,³³ which was applied to Pb^{3+} centers in other hosts.^{27,29–32} Figure 9 depicts the energy diagram of Eq. (1) for $\mathbf{B} \parallel a$; broken lines denote energy levels for $I=0$, and solid lines for $I=1/2$. Arrows in Fig. 9 represent the ESR transitions observed in the measurement. Numerical estimation on g_N gives the values between 0.1 and 6 for various directions of \mathbf{B} . The anisotropy of the g_N tensor is responsible for the rotation-angle dependence of the ESR signals around 1400 mT; moreover, the rotation-angle dependence indicates the deviation of principal g_N axes from the a , b , and c axes. In the unit cell of PbCl_2 crystal, there exist two equivalent Pb-ion sites that reflect the crystallographic symmetry. The twofold splits around 1400 mT in Fig. 2 are explained by the two possible configurations of Pb^{3+} centers in the unit cell and by the anisotropy of the g_N tensor.

The evaluated g and A values are listed in Table I together

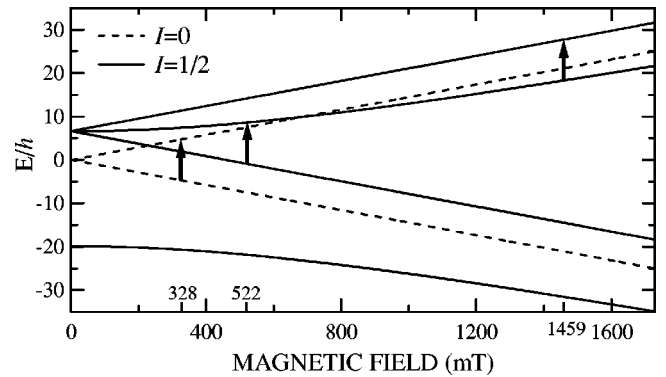


FIG. 9. Energy diagram of the spin Hamiltonian [Eq. (1)] for $\mathbf{B} \parallel a$. Broken lines: energy levels for $I=0$, describing electron Zeeman levels. Solid lines: energy levels for $I=1/2$. Arrows stand for observed ESR transitions at 9.404 GHz. The ordinate is represented in GHz.

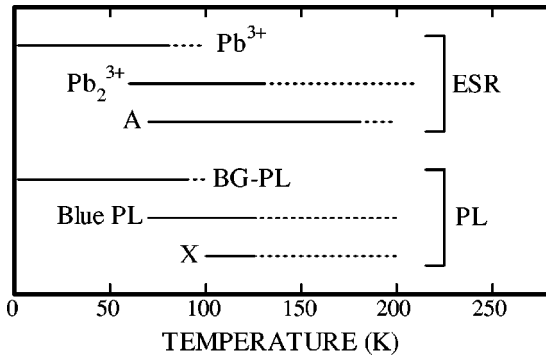


FIG. 10. Schematic diagram for thermal stability of the photo-induced ESR signals and PL bands. Solid line: the stable range of the signals. Dotted line: the unstable but still detectable range. Blue PL denotes the blue PL band at 2.79 eV in Fig. 7. X stands for the broad PL band around 2.1 eV in Fig. 6.

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_2^+ 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_2^{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. The electron center is most likely to have either of the following structures: (i) a center with ESR in the region higher than 1700 mT, or (ii) a center without ESR. We discuss in Sec. IV D the relaxation dynamics of electrons below 50 K, producing the trapped state.

The ESR spectra in Fig. 3 show that Pb^{3+} centers thermally change into the A center above 70 K and are finally replaced at 90 K. In a pulse-annealing experiment³⁵ on Pb-Cl:TI, the A signal is weakened under annealing at 200 K, and the ESR signals coming from hole-trapping centers of Tl^{2+} grow at the temperature. The result implies that the A signal originates from hole-trapping centers. The STEL centers of Pb_2^{3+} appear above 60 K as shown in Figs. 3 and 4, become unstable thermally above 130 K, and are quenched around 210 K.^{8,35}

Figure 10 summarizes and schematically represents the thermal stability of ESR signals and PL bands; solid lines

stand for the stable range, and dotted lines denote the unstable but still detectable range. “Blue PL” in Fig. 10 denotes the blue PL band at 2.79 eV in Fig. 7, and “X” the broad PL band around 2 eV in Fig. 6. Obviously, the BG PL band is thermally coincident with the STH centers of Pb^{3+} . In addition, the thermal activation of electrons at 55 K corresponds to the TL that has the same shape as the BG PL band. Consequently, we ascribe the luminescent state yielding the BG PL band to the STE associated with a Pb^{3+} center; probably, the STE has the configuration of (Pb^{3+} + electron). The disagreement of the BG PL band with Pb_2^{3+} centers in Fig. 10 excludes the model for the BG PL band proposed in Refs. 16–19.³⁶ The blue PL band at 2.79 eV almost corresponds to the STEL centers of Pb_2^{3+} and the A centers. Therefore, this study provides a possibility that the blue PL band comes from the STE’s associated with Pb_2^{3+} centers, but, to identify the origin, further study with optically detected magnetic resonance technique is surely needed.

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

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 signal⁵ does not show the anisotropy peculiar to the dimer-molecular V_K centers,³ 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.²⁷

As shown in Fig. 4, the A signal appears under pulse annealing at 100 K after photoirradiation 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_2^{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 STH centers become unstable around 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 STH centers, and modify the STH centers or make the STH center unstable. In any way, the A signal is

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_2 from comparison with relaxation in PbBr_2 (Ref. 25). In PbBr_2 , the spontaneous dissociation of e - h pairs was reported,²⁵ and the individual self-trapped states of both electrons and holes have been recently seen with the ESR technique.¹¹

However, the present ESR study on PbCl_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_2 ,^{37,38} PbCl_2 crystals are high-ionic conductors and therefore include dense anion vacancies more than 10^{17} cm^{-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_2^{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,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_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_2 is also realized in PbCl_2 .

At the end of discussion, we compare the relaxed states of e - h pairs in PbF_2 , PbCl_2 , and PbBr_2 . Though the crystallo-

graphic structure of β - PbF_2 is cubic and those of PbCl_2 and PbBr_2 are orthorhombic,²¹ STH centers in β - PbF_2 (Ref. 10) and PbCl_2 are monomer Pb^{3+} centers while STH centers in PbBr_2 are dimer Br_2^- centers.¹¹ The relaxed states indicate that holes in β - PbF_2 and PbCl_2 strongly interact with Pb^{2+} ions, while holes in PbBr_2 interact with Br^- ions. The top of the valence band in PbCl_2 is composed of about half Pb^{2+} ($6s$) and half Cl^- ($3p$) ions,¹² but the holes nevertheless localize only on Pb^{2+} ions. On the other hand, though the bottoms of the conduction band in β - PbF_2 , PbCl_2 , and PbBr_2 are composed of the $6p$ states of Pb^{2+} ions,^{12,40} electrons in β - PbF_2 do not get self-trapped while electrons in PbCl_2 and PbBr_2 form STEL centers of Pb_2^{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_2 . As a result, the hole centers below 70 K have been found to be self-trapping centers of Pb^{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_2^{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^{3+} are responsible for STE's yielding the BG PL band at 2.50 eV.

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