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Hydrostatic pressure effects on the free and self-trapped exciton states in CsI

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The s-like (Γ_8^-,Γ_6^+) and d-like (Γ_8^-, Γ_8^+) free exciton (FE) states and the corresponding self-trapped exciton (STE) states in CsI have been studied under hydrostatic pressure up to 1.3 GPa. As the pressure is increased, the lowest-energy FE state is changed from the s-like (Γ_8^-,Γ_6^+) state to the d-like (Γ_8^-,Γ_8^+) state, and consequently the lowest-energy STE state is changed from the s-like state to the d-like state: The latter is evidenced by the replacement of the s-like STE luminescence (3.7-eV band) by the d-like STE luminescence (4.7-eV band). At high pressure the s-like and d-like STE's fall into a quasithermal equilibrium distribution. Based on the results, we discuss the pressure-induced changes of the adiabatic potential energy surfaces of the STE states in CsI. [S0163-1829(96)08347-6]

I. INTRODUCTION

In CsI the d-like (Γ_8^-,Γ_8^+) free exciton (FE) state is located just above (0.2 eV) the s-like (Γ_8^-,Γ_6^+) FE state,[1,2] and the self-trapped exciton (STE) states corresponding to the respective FE states are both assumed to be stable.[3] The model of STE in CsI has been considered to be a cluster composed of two nearest-neighbor I^- ions and 12 neighboring Cs^+ ions with the D_{4h} point symmetry (upper left in Fig. 1).[3,4] Two luminescence bands peaking at 4.3 and 3.7 eV are attributed to the STE's in CsI.[3–11] Iida *et al.*[3,7,8] have assigned the 4.3-eV band to the d-like ${}^3\Gamma_5^-$ STE state composed of the Γ_3^+ ($5d$) electron and the Γ_2^- ($5p$) hole, and the 3.7-eV band to the s-like ${}^3\Gamma_5^-$ STE state composed of the Γ_1^+ ($6s$) electron and the Γ_2^- ($5p$) hole. These spin-triplet ${}^3\Gamma_5^-$ STE states are partially allowed because of mixing with the singlet ${}^1\Gamma_5^-$ STE state composed of the Γ_1^+ ($6s$) electron and the Γ_5^- ($5p$) hole by the spin-orbit interaction.

Tsujimoto *et al.*[9] have studied the effect of hydrostatic pressure on the 4.3- and 3.7-eV bands and on the s-like (Γ_8^-,Γ_6^+) and d-like (Γ_8^-, Γ_8^+) FE states, and concluded that the 4.3-eV band does not arise from the d-like STE state, but arises from the s-like STE state in the on-center configuration with the D_{4h} point symmetry, and the 3.7-eV band arises from the same s-like STE state but in the off-center configuration with the C_{4v} point symmetry (upper right in Fig. 1). Nishimura *et al.*[10,11] have obtained the similiar conclusion (${}^1\Gamma_2^-$ and ${}^3\Gamma_5^-$ states for the 4.3-eV band, and ${}^1\Gamma_1$ and ${}^3\Gamma_5$ states for the 3.7-eV band) from the time-resolved spectra of the 4.3- and 3.7-eV bands. They found the 4.3-eV band to have a fast decaying component (2 ns), which should be assigned to a singlet transition. This result is inconsistent with the assignment (d-like ${}^3\Gamma_5^-$ STE state) proposed by Iida *et al.*,[3] because the singlet transition in the d-like STE (${}^1\Gamma_4^-$ state), to which the 2-ns component should be assigned, is symmetry forbidden. The assignments proposed by Nishimura *et al.*[10,11] are summarized in Fig. 1.

In the present study, we have carried out a hydrostatic pressure experiment on the FE and STE states in CsI at 77 K, and observed that the 3.7-eV band disappears above 0.9 GPa and a third band appears at 4.7 eV. We conclude that the 4.7-eV band arises from the d-like ${}^3\Gamma_5^-$ STE state to which Iida *et al.* assigned the 4.3-eV band.

II. EXPERIMENTAL PROCEDURES

Hydrostatic pressure experiments at 77 K were carried out by using a sapphire-anvil cell immersed in liquid nitrogen. A sample of pure CsI with a typical dimension of $0.3 \times 0.3 \times 0.3\ \mathrm{mm}^3$ was placed with a ruby chip in a pinhole (0.6 mm diameter) made in a gasket with a thickness of 1 mm. The crystal was provided from Hershaw Chemical Co. We used liquid nitrogen as a pressure-transmitting material. The pressure was controlled by a piston moved by high-pressure he-

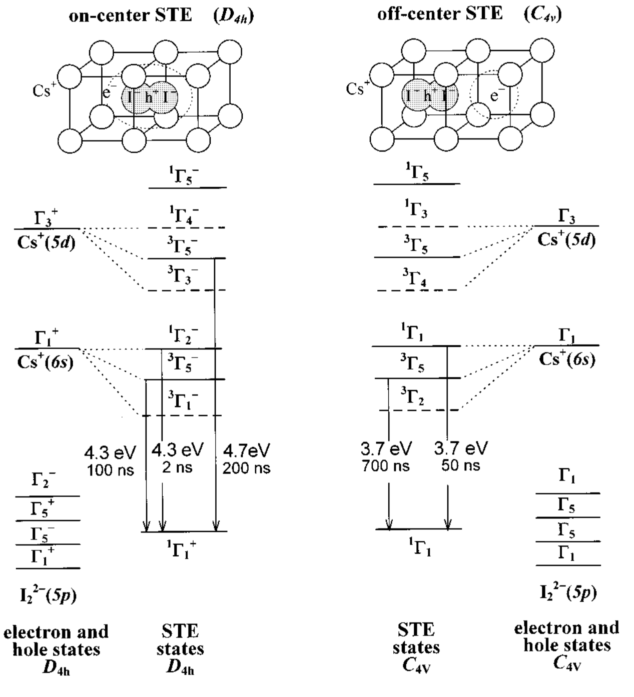

FIG. 1. Lattice configurations and electronic states of the on-center and off-center STE states in CsI: Spin-orbit interactions are considered for the STE states. Broken lines indicate forbidden states.

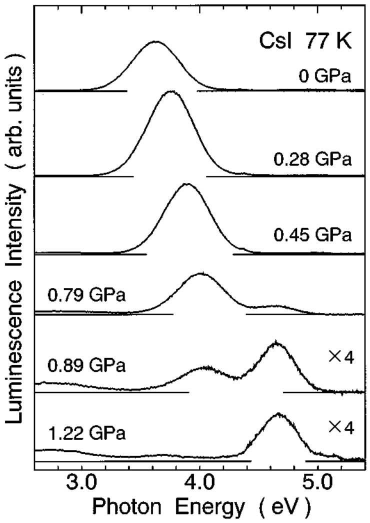

FIG. 2. Pressure-induced spectral changes observed at 77 K. The luminescence is excited in the exciton band.

lium gas and monitored by the energy shift of the ruby R_1 line.

A deuterium lamp (Original Hanau D-200) combined with a grating monochromator (Hitachi 139) was used for the luminescence excitation. Luminescence spectra were measured with a photomultiplier tube (Hamamatsu R-955) and a prism monochromator (Carl Zeiss M4QIII). The resolution for the luminescence spectra was 0.075 eV at 400 nm, and that for the excitation spectra was 0.02 eV. The luminescence spectra were corrected for the sensitivity of the detecting system. To measure the luminescence decay times, we used the fourth harmonic (206-nm light) of a Ti-sapphire laser (CF-131M) pumped by a Nd-YAG laser (Solar LF-114). The decay curves were observed by a 500-MHz digitizing oscilloscope (Tektronix TDS-520). These experiments were carried out in the forward scattering geometry.

III. EXPERIMENTAL RESULTS

Figure 2 shows the changes of the luminescence spectra in CsI at 77 K under hydrostatic pressure. At 77 K the 4.3-eV band is well known to be very weak, and only the 3.7-eV band appears strongly. As the pressure is increased, the 3.7-eV band shifts to higher energy with a coefficient of +0.47 eV/GPa. The intensity of the 3.7-eV band decreases above 0.8 GPa, and a third band appears at 4.7 eV. The peak energy of the 4.7-eV band is almost independent of the pressure. We note that the 4.7-eV band has originally been reported by Laisaar, Shcherbakov, and Kuznetsov,[12] although the origin has been left unclear.

Figure 3 shows the excitation spectra of the 3.7-eV band observed at 0 and 0.13 GPa. The dips denoted by s_s, d_s, and d_t correspond, respectively, to the reflection peak due to the singlet s-like (Γ_8^-,Γ_6^+) FE transition, and those due to the singlet and triplet d-like (Γ_8^-,Γ_8^+) FE transitions. It is seen that the s-like (Γ_8^-,Γ_6^+) FE state shifts to higher energy and the d-like (Γ_8^-,Γ_8^+) FE states shift to lower energy as the pressure is increased from 0 to 0.13 GPa.

Figure 4 shows the excitation spectrum of the 4.7-eV band observed at 1.22 GPa. The 4.7-eV band is excited only in the fundamental absorption region, suggesting that the band is intrinsic. Figure 5 shows the excitation spectra of the 3.7- and 4.7-eV bands detected by using a band-pass filter (UV-D25) instead of the analyzing monochromator: The resolution for the excitation spectra is 0.006 eV. In the measurements, we detected some impurity luminescence in addition to the 3.7- and 4.7-eV bands, so that a structure appears in the lower-energy side of the lowest-energy FE state: The structure is remarkable in the spectrum at the highest pressure.

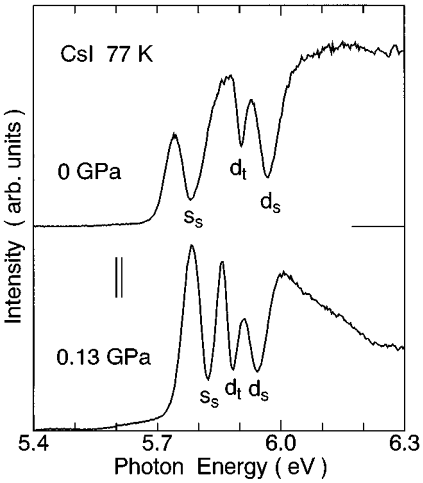

FIG. 3. Excitation spectra of the 3.7-eV band observed at 0 and 0.13 GPa (77 K). The dips denoted by s_s, d_s, and d_t correspond to the reflection peaks due to the singlet s-like (Γ_8^-,Γ_6^+) FE transition, and those due to the singlet and triplet d-like (Γ_8^-,Γ_8^+) FE transitions, respectively.

We obtained the pressure-induced shifts of the s-like (Γ_8^-,Γ_6^+) and d-like (Γ_8^-,Γ_8^+) FE states from the dips in the excitation spectra shown in Fig. 5, and summarized the FE energies in Fig. 6(a). As the pressure is increased, the s-like FE state shifts to higher energy with a coefficient of +0.18 eV/GPa, and the d-like FE states shift to lower energy with a coefficient of −0.11 eV/GPa. Figure 6(a) shows that the s-like FE state crosses over the triplet d-like FE state at 0.4 GPa, and over the singlet d-like FE state at 0.6 GPa. We note that anticrossings of the s-like FE state and the d-like FE state are clearly observed at the crossover points. A simi-

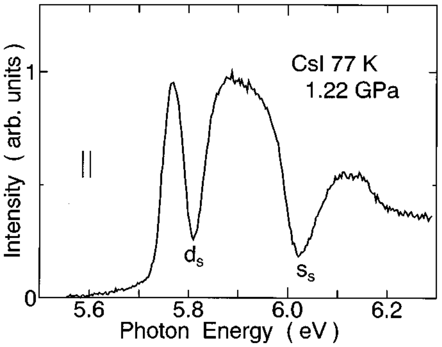

FIG. 4. Excitation spectrum of the 4.7-eV band observed at 1.22 GPa (77 K).

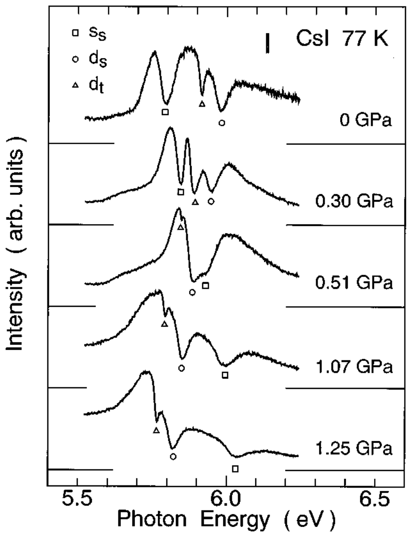

FIG. 5. Excitation spectra of total intensities of the 3.7- and 4.7-eV bands measured by using a band-pass filter (UV-D25).

lar result obtained from the reflection spectra has been reported by Kuznetsov *et al.*,[13] although their pressure coefficients are different from our results. In Fig. 6(b), the pressure-induced shifts of the 3.7- and 4.7-eV bands are shown, together with the result of the 4.3-eV band reported previously.[9] The results of Figs. 6(a) and 6(b) show clearly that the 4.7-eV band appears, after the d-like (Γ_8^-,Γ_8^+) FE state becomes the lowest-energy state.

We observed the decay curves of the 3.7- and 4.7-eV bands under hydrostatic pressure. The decay curve of the 4.7-eV band observed at 1.17 GPa is shown in Fig. 7. The decay time is 200 ns, and no fast decaying component, which should be assigned to a singlet transition, is observed. In Fig. 8, the decay times of the 3.7- and 4.7-eV bands are shown as a function of pressure. The decay time of the 3.7-eV band decreases gradually as the pressure is increased. At 0.9 GPa, at which the intensities of the 3.7- and 4.7-eV bands are equal to each other, the decay time of the 3.7-eV band falls suddenly to 0.5 μs, and that of the 4.7-eV band grows to 0.5 μs, which suggests that the 4.7-eV band is attributed to a kind of STE, and that the STE's are in quasi-thermal equilibrium with the STE's responsible for the 3.7-eV band at 0.9 GPa.

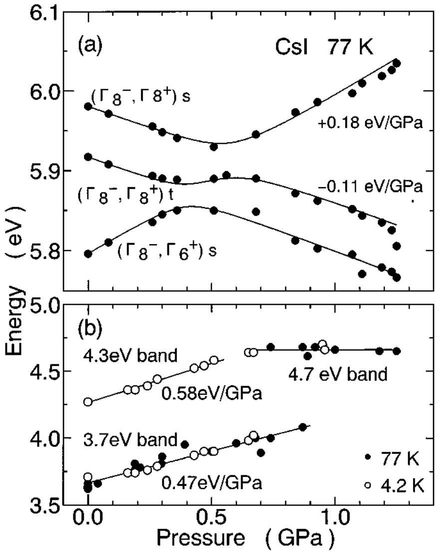

FIG. 6. Pressure-induced shifts of the s-like (Γ_8^-,Γ_6^+) and d-like (Γ_8^-,Γ_8^+) FE energies and those of the peak energies of the 3.7-, 4.3-, and 4.7-eV bands. The open and solid circles represent the data obtained at 4.2 and 77 K, respectively.

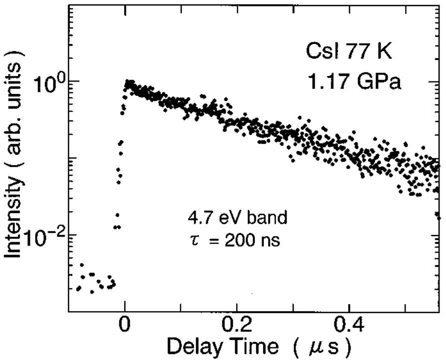

FIG. 7. Decay curve of the 4.7-eV band observed at 1.17 GPa (77 K).

IV. DISCUSSION

A. Origin of the 4.7-eV band

As described in Sec. I, the STE's in CsI are considered to be of two types of clusters with the D_{4h} and C_{4v} point symmetries: The former is called on-center STE and the latter off-center STE. The lattice configurations and the electronic states of the STE's are shown in Fig. 1. Tsujimoto *et al.*[9] and Nishimura *et al.*[10,11] have proposed that the 4.3-eV band appearing strongly below 10 K is ascribed to the s-like ${}^1\Gamma_2^-$ and ${}^3\Gamma_5^-$ STE states in the on-center configuration, and the 3.7-eV band to the same s-like ${}^1\Gamma_1$ and ${}^3\Gamma_5$ STE states but in the off-center configuration.

For the 4.7-eV band, we conclude the band to be intrinsic and assigned to the on-center d-like ${}^3\Gamma_5^-$ STE state, based on the results mentioned in Sec. III: (1) The band is excited only in the fundamental absorption region (Fig. 4), (2) the band

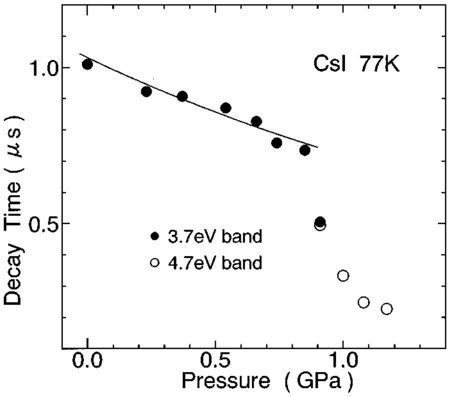

FIG. 8. Decay times of the 3.7- and 4.7-eV bands as a function of pressure (77 K).

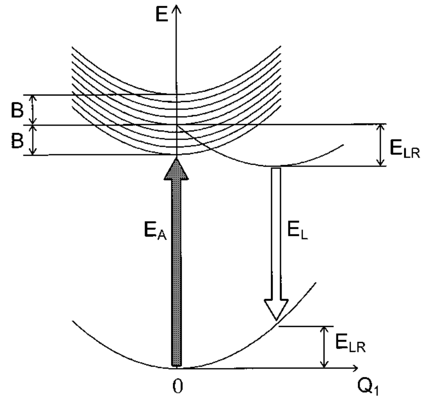

FIG. 9. Typical diagram of an APES for an on-center STE state. E_A and E_L represent the absorption and luminescence energies.

has a long decay time (200 ns) and appears when the d-like (Γ_8^-,Γ_8^+) FE state becomes the lowest-energy state under high pressure (Fig. 6), and (3) the Stokes-shift energy of the band is the smallest (1.1 eV) of the corresponding energies of all luminescence bands arising from the on-center STE's in alkali halides; 1.4 eV for the 4.2-eV band in NaI and 1.5 eV for the 4.3-eV band in CsI, which are the smallest Stokes-shift energies except for the 4.7-eV band in CsI. The assignment of the 4.7-eV band to the on-center d-like ${}^3\Gamma_5^-$ STE state is confirmed by the absence of a fast decaying component (Fig. 7), because the singlet ${}^1\Gamma_4^- \rightarrow {}^1\Gamma_1^+$ transition in the d-like STE is forbidden owing to the symmetry.

B. Energy shifts of the s-like and d-like STE states

Based on the considerations above, we discuss the pressure-induced shifts of the s-like and d-like STE states. The pressure coefficients of the 4.3- and 3.7-eV bands arising from the s-like on-center and s-like off-center STE states are $+0.58$ and $+0.47$ eV/GPa, respectively. A part of the high-energy shift is caused by the energy shift of the corresponding s-like (Γ_8^-,Γ_6^+) FE state, and the rest is caused by the decreasing relaxation energies E_{LR} of the respective STE states under hydrostatic pressure.

In Fig. 9 we show a typical adiabatic potential energy surface (APES) expected for an on-center STE state. The APES is cut along the Q_1 axis in the on-center type lattice relaxation. The value of E_{LR} can be estimated by a simple relation; $E_{\mathrm{LR}}=(B+E_{\mathrm{Stokes}})/2$, where B represents half of the exciton bandwidth, and E_{Stokes} is the Stokes-shift energy $(=E_A-E_L)$. For the value of B, we use half of the valence-band width (0.6 eV) measured by DiStefano and Spicer,[14] for the reason that the exciton mass in CsI has not been measured, and that the hole mass is much larger than the electron mass in alkali halides. The hydrostatic pressure of 1 GPa reduces the lattice constant a_0 of CsI by 2%. Considering a simple relation $B\propto a_0^{-2}$ based on a parabolic exciton band, we estimate 4% expansion of the exciton bandwidth $2B$.

Using above relation, we estimate the pressure-induced change of the value of E_{LR} for the s-like on-center STE state responsible for the 4.3-eV band as follows: The value of E_{LR} decreases from 1.1 eV at 0 GPa to 0.93 eV at 0.8 GPa, leading to a pressure coefficient of -0.21 eV/GPa. Similar large decrease (-0.15 eV/GPa) of E_{LR} for the s-like off-center STE state responsible for the 3.7-eV band is obtained from the large peak-energy shift ($+0.47$ eV/GPa) of the band.

For the 4.7-eV band arising from the d-like on-center STE state, the pressure coefficient is very small (~ 0 eV/GPa). This small coefficient suggests that the decrease of E_{LR} is canceled by the low-energy shift of the d-like (Γ_8^-,Γ_8^+) FE state (-0.11 eV/GPa). We then estimate the pressure coefficient of E_{LR} to be -0.005 eV/GPa for the 4.7-eV band. This value is much smaller than the value (-0.21 eV/GPa) of the 4.3-eV band, reasonable for the d-like and s-like STE states.

C. Decay times of the 3.7- and 4.7-eV bands

Next we discuss the pressure-induced changes of the decay times of the 3.7- and 4.7-eV bands shown in Fig. 8. The decay time of the 3.7-eV band, which is attributed to the s-like off-center STE state, decreases with increasing pressure. Song and Chen[15] have pointed out that the decay time τ of off-center STE luminescence is sensitive to the separation d_{FH} between the electron wave function (F center) and hole wave function (H center), and is given by

$$\tau^{-1}=A(h\nu)^3|\langle ex|\mathbf{r}|gr\rangle|^2=B(h\nu)^3 d_{FH}^2\exp(-2\alpha d_{FH}), \tag{1}$$

where A and B are constants, $\langle ex|\mathbf{r}|gr\rangle$ is the transition matrix element, $h\nu$ is the luminescence energy, and α is a parameter of the spatial extension of the electron wave function; $\exp(-\alpha r)$. Song and Chen assumed $d_{FH}=Q_2+a_0/\sqrt{2}$ for the NaCl structure, where Q_2 is the coordinate of the off-center relaxation. This formula can be transformed into $d_{FH}=Q_2+a_0/2$ for the CsCl structure.

As shown in Figs. 2 and 6, the value of $h\nu$ depends strongly on the pressure ($+0.47$ eV/GPa). On the other hand, the value of $|\langle ex|\mathbf{r}|gr\rangle|^2$ seems to be less dependent of the pressure, because the lattice constant a_0 reduces only by 2% at 1 GPa. Thus we suggest that the pressure-dependent decay time of the 3.7-eV band arises mainly from the pressure dependence of $(h\nu)^3$. To confirm this the value of $\tau(p)=\tau(0)\{h\nu(p)/h\nu(0)\}^{-3}$ is shown by a solid curve in Fig. 8: $\tau(0)$ and $h\nu(0)$ are, respectively, the decay time and luminescence energy at 0 GPa. The experimental result is well fitted by the solid curve. We therefore conclude that the pressure-dependent decay time of the 3.7-eV band is well explained by the peak-energy shift $(h\nu)^3$ under pressure. In other words, the value of $|\langle ex|\mathbf{r}|gr\rangle|^2$ in Eq. (1) is less effective on the pressure-induced change of the decay time τ in the case of CsI. This means that the value of Q_2 is hardly changed by hydrostatic pressure below 1 GPa, which is consistent with the small change of the lattice constant a_0 under pressure (-2% at 1 GPa).

The decay time of the 3.7-eV band decreases steeply above 0.85 GPa, and becomes equal to the decay time of the 4.7-eV band at 0.9 GPa. This suggests that the s-like off-center STE's become in quasithermal equilibrium with the d-like on-center STE's as described next.

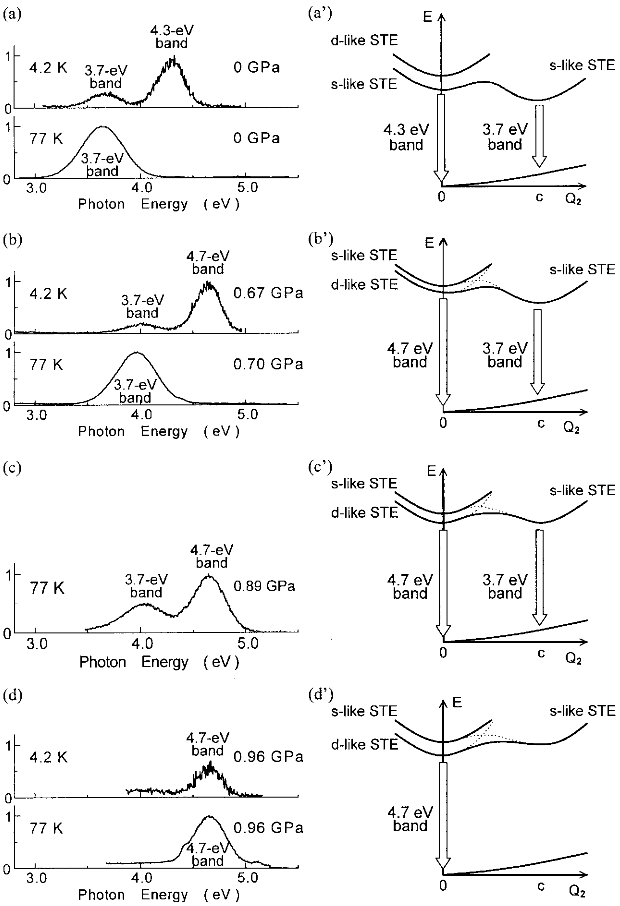

FIG. 10. In the left-hand side, pressure-induced spectra of the 3.7-, 4.3-, and 4.7-eV bands at 4.2 and 77 K are shown, and in the right-hand side, APES's for the *s*-like and *d*-like STE states are shown.

D. Adiabatic potential energy surfaces (APES's) for the *s*-like and *d*-like STE states

In Fig. 10, we show the pressure-induced changes of the 3.7-, 4.3- and 4.7-eV bands observed at 77 and 4.2 K, and also show the corresponding changes of the APES's for the *s*-like and *d*-like STE states. The APES for the *s*-like STE state has been concluded to have two local minima at the on-center site ($Q_2=0$) and off-center site ($Q_2=c$) by Nishimura *et al.*[10,11] On the other hand, the APES for the *d*-like STE state is presumed to have one minimum at the on-center site, because no luminescence band ascribable to the off-center STE state appears. As the pressure is increased, the local minima of the APES for the *s*-like STE state shift to higher energy both at the on-center and off-center sites, while the minimum of the *d*-like STE state hardly shifts as discussed in Sec. IV B, so that the *d*-like STE state becomes the lowest-energy state under high pressure.

We next discuss the pressure-induced changes of the APES's in connection with the pressure-induced spectral changes of the three luminescence bands. The spectra at 0 GPa [Fig. 10(a)] show that the 4.3-eV band appears strongly and the 3.7-eV band appears weakly at 4.2 K, while at 77 K the 3.7-eV band appears strongly. These spectra suggest that at 4.2 K the *s*-like STE's are mainly populated on the on-center site ($Q_2=0$), and a part of the STE's pass through the potential barrier to relax to the lowest-energy off-center site ($Q_2=c$), while at 77 K almost all the STE's relax thermally to the off-center site. The *d*-like STE state at 0 GPa seems to be located in higher energy than the *s*-like STE state, because the 4.7-eV band does not appear. Based on these considerations, we depict the APES's for the *s*-like and *d*-like STE states at 0 GPa in Fig. 10(a').

The spectra at 0.67–0.70 GPa [Fig. 10(b)] show that the 4.3-eV band is replaced by the 4.7-eV band, and the 3.7-eV band remains weakly in the spectrum at 4.2 K, while at 77 K the 3.7-eV band is observed very strongly. These spectra suggest that the lowest energy STE state is still the *s*-like off-center state, and at the on-center site the *d*-like state is lower in energy than the *s*-like state. Thus almost all the *d*-like STE's populated on the on-center site relax thermally to the *s*-like off-center site at 77 K. The APES's in this case are shown in Fig. 10(b').

The spectrum at 0.89 GPa [Fig. 10(c)] shows that the 3.7-eV band coexists with the 4.7-eV band even at 77 K. As is shown in Fig. 8, the decay times of the two bands become equal to each other at 0.9 GPa. These results suggest that the energies of the *s*-like off-center and *d*-like on-center STE states are almost equal to each other as shown in Fig. 10(c'), so that a quasithermal equilibrium distribution between the *s*-like off-center STE's and the *d*-like on-center STE's is established. At 0.96 GPa [Fig. 10(d)] the 3.7-eV band is not seen in the spectra at 4.2 and 77 K, which suggests that the *s*-like STE state is not the lowest-energy state even at the off-center site at this high pressure, but the *d*-like on-center STE state is the lowest-energy state as shown in Fig. 10(d').

We finally refer to the anticrossing of the *s*-like STE state and the *d*-like STE state. Figure 10 shows that the lowest-energy STE state is the *d*-like state at the on-center site and the *s*-like state at the off-center site above 0.67 GPa. In this situation, anticrossings must occur between the local minima. The anticrossing in the *s*-like and *d*-like states corresponds well to the similar anticrossing in the *s*-like and *d*-like FE states, which is shown in Fig. 6(a). This correspondence means that the *s*-like and *d*-like STE states remain well, in the electronic structures, the *s*-like and *d*-like FE states, respectively.

In conclusion, the crossover between the *s*-like and *d*-like FE states in CsI occurs at about 0.4 GPa, and the corresponding crossover between the *s*-like and *d*-like STE states occurs at a little higher pressure (~0.6 GPa). The situation in CsI is very special among alkali halides, and shows a close relation between the FE states and the STE states in electronic structures. The 4.7-eV luminescence, which appears at high pressure (>0.6 GPa), is attributed to the *d*-like $^3\Gamma_5^-$ STE state at the on-center site.

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