

## Infrared transient absorption and electronic state of localized self-trapped excitons in KCl:I

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The infrared transient absorption and electronic state of the on-center-type self-trapped exciton (STE) localized at an iodine dimer in KCl:I were investigated. The polarization properties and vibronic structure of the absorption band indicate that the electronic state of the on-center-type STE is rather extended so that the splitting of the  $2p$ -like sublevels is very small.

### I. INTRODUCTION

The existence of self-trapped excitons (STE's) in alkali-halide crystals is one typical feature accompanying a strong electron-phonon coupling in solid states. Since the STE is known as a precursor state of the succeeding formation process of lattice defects induced by electron excitation, the study of the electronic structure as well as the geometric configuration of the STE is very important to understand the primary process of light-induced defect formation.

Recently, it has become clear that several configurations of the STE may appear in relation to the crystal characteristics.<sup>1</sup> The traditional model of the STE is referred to as the "on-center" type,<sup>2</sup> consisting of a hole-trapping center ( $X_2^-$ ) occupying two adjacent halogen sites together with a trapped electron. Another model of the STE is termed the "off-center" type,<sup>3</sup> consisting of an  $X_2^-$  occupied in one halogen site and an electron trapped by the nascent halogen vacancy. Several experimental results have provided the evidence of the existence of the off-center-type STE. These include electron-nuclear double resonance,<sup>4</sup> transient absorption,<sup>5</sup> and resonant Raman scattering<sup>6</sup> experiments. However, little experimental evidence for the existence of the on-center-type STE has been reported thus far, and its electronic states are still unclear. Theoretically, it has been predicted that the electronic state of the on-center-type STE is strongly anisotropic, reflecting its site symmetry ( $D_{2h}$ ); the energy difference between the ground state of the STE ( $a_g$ ) and one of the  $2p$ -like excited states ( $b_{3u}$ ) is approximately 1 eV or less, and the oscillator strength of the absorption concentrates on the transition between these states.<sup>7</sup> As a consequence, intense and polarized optical absorption, due to the electronic transition ( $a_g \rightarrow b_{3u}$ ), is expected in the infrared region. The authors discovered infrared transient absorption due to the STE localized at iodine dimers<sup>8,9</sup> and those of NaBr and NaI.<sup>10</sup> These results indicate that the configuration of these STE's is

the on-center type. However, an important problem was left unsolved, the polarization property of the absorption band. If the theoretical prediction is correct, the absorption band should be strongly polarized, provided that the direction of the STE is aligned using some technique. STE's localized at iodine dimers in a host crystal such as KCl:I are useful for checking this prediction, because they can be easily aligned by excitation with linearly polarized light.<sup>11</sup> In this paper, we report the polarization properties and the vibronic structure of the infrared transient absorption band characteristic of the STE localized at an iodine dimer in KCl:I, and discuss the electronic state of the on-center-type STE.

### II. EXPERIMENTAL PROCEDURE

A single crystal of KCl:I doped with 1 mol% iodine was produced using the Czochralski method in an argon atmosphere. The sample was cleaved into approximately a  $10 \times 10 \times 3$  mm piece and attached onto the cold finger of a cryostat. The basic setup of the experiment was nearly identical to that described in our previous report.<sup>9</sup> The sample was excited using an ArF excimer laser (Lambda Physik, EMG101MSG), the wavelength of which falls into the excitation band of the luminescence, due to the iodine dimer in KCl:I.<sup>12-14</sup> The pulse duration of the excimer laser was 17 ns. A transmission-type polarizer consisting of ten quartz glass plates situated at the Brewster angle was used to polarize the excitation light. A Xenon flash lamp with a MgF<sub>2</sub> window (Hamamatsu Photonics, special model) was used as a probe light source. The pulse duration of the probe light was approximately 10  $\mu$ s. A wire-grid-type polarizer was used as a polarization analyzer of the probe light. The probe light passed through a grating monochromator and was detected by an InSb or HgCdTe photodetector. The signal was accumulated by a boxcar integrator synchronized with the excitation laser.

To analyze the polarization property of the absorption

band, we used the procedure described below. The  $2p$ -like electron-excited state of the on-center-type STE consists of three sublevels ( $b_{1u}$ ,  $b_{2u}$ , and  $b_{3u}$ ), each of which represents the irreducible representation of  $D_{2h}$  symmetry. Thus, if the splitting between these sublevels is large enough, polarization dichroism is expected in the optical absorption band corresponding to transitions from the ground state ( $a_g$ ) to each of these sublevels. To detect the dichroism experimentally, one should align the directions of the STE's in the sample. Polarization-selective bleaching<sup>15</sup> is one method, which has proven successful to this end, for STE's in pure crystals. However, there is a simpler way to align STE's localized at halogen-impurity dimers in a host crystal such as KCl:I. A linearly polarized ArF laser produces polarization-selective excitation of the STE's localized at iodine dimers.<sup>11</sup> In this case, the number ( $n_q$ ) of created STE's localized at iodine dimers associated with an orientation  $q$  is given by

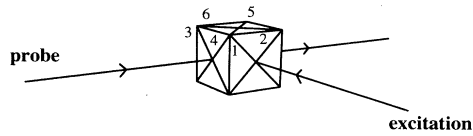
$$n_q \propto \cos^2 \theta_q, \quad (1)$$

where  $\theta_q$  is the angle between the electric vector of the excitation light and the molecular axes of the STE's.

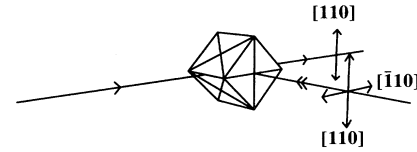
Figure 1 shows the three optical configurations used in our measurement. Hereafter, these will be referred to as the (a) unpolarized, (b)  $\langle 110 \rangle$ -polarized, and (c)  $\langle 100 \rangle$ -polarized configurations. The diagonal lines on the samples, which are expressed by cubes, represent the  $\langle 110 \rangle$  axes of the crystal, i.e., the molecular axes of the STE's. There are six equivalent orientations of the STE's. The probe light propagates in a direction perpendicular to the excitation beam. The absorption coefficient  $\alpha$  for the probe light is given by<sup>15</sup>

$$\alpha(E) = \sum_q \sum_i^3 n_q \sigma_i(E) \cos^2 \phi_{iq}, \quad (2)$$

(a) Unpolarized



(b)  $\langle 110 \rangle$



(c)  $\langle 100 \rangle$

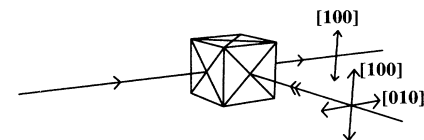


FIG. 1. Schematic diagrams of (a) unpolarized, (b)  $\langle 110 \rangle$ -polarized, and (c)  $\langle 100 \rangle$ -polarized optical configurations. Samples are represented by cubes, and the diagonals on the cubes indicate the  $\langle 110 \rangle$  axis of the host crystal.

where  $E$  is the photon energy of the probe light,  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$  are the cross sections corresponding to the transitions  $a_g \rightarrow b_{2u}$ ,  $a_g \rightarrow b_{1u}$ , and  $a_g \rightarrow b_{3u}$ , respectively, and  $\phi_{iq}$  is the angle between the electric vector of the probe light and the transition dipole vector. Thus the optical density  $\mathcal{O}_0$  measured with an unpolarized configuration becomes

$$\mathcal{O}_0 \propto \frac{5}{8}(\sigma_1 + \sigma_3) + \frac{3}{4}\sigma_2. \quad (3)$$

In the  $\langle 110 \rangle$ -polarized configuration, the polarization of the probe light is oriented in the  $[110]$  direction, and the difference ( $\Delta\mathcal{O}_{\langle 110 \rangle}$ ) between the optical densities for  $[110]$  and  $[\bar{1}10]$ -polarized excitations is given by

$$\Delta\mathcal{O}_{\langle 110 \rangle} \propto -\sigma_1 + \sigma_3. \quad (4)$$

Similarly, in the  $\langle 100 \rangle$ -polarized configuration, the difference ( $\Delta\mathcal{O}_{\langle 100 \rangle}$ ) between the optical densities for  $[100]$ - and  $[010]$ -polarized excitations is given by

$$\Delta\mathcal{O}_{\langle 100 \rangle} \propto \frac{1}{2}(\sigma_1 + \sigma_3) - \sigma_2. \quad (5)$$

Thus, using Eqs. (3), (4), and (5), one can derive the spectra of the cross sections  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_3$  from the observed spectra of  $\mathcal{O}_0$ ,  $\Delta\mathcal{O}_{\langle 110 \rangle}$ , and  $\Delta\mathcal{O}_{\langle 100 \rangle}$ .

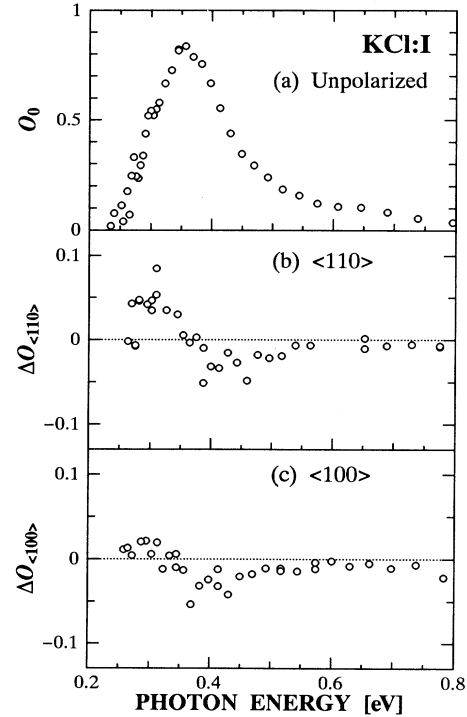


FIG. 2. (a) Transient absorption spectra, due to the localized STE in KCl:I measured with an unpolarized configuration. (b) Difference spectra ( $\Delta\mathcal{O}_{\langle 110 \rangle}$ ) between the optical densities with  $[110]$ - and  $[\bar{1}10]$ -polarized excitations, using the  $\langle 110 \rangle$ -polarized configuration. (c) Difference spectra ( $\Delta\mathcal{O}_{\langle 100 \rangle}$ ) between the optical densities with  $[100]$ - and  $[010]$ -polarized excitations, using the  $\langle 100 \rangle$ -polarized configurations.

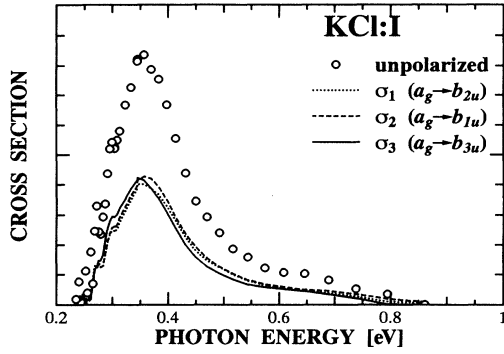


FIG. 3. Decomposition of the transient absorption band ( $\circ$ ) into the three components ( $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$ ), corresponding to the electron transitions from  $a_g$  to the  $b_{2u}$ ,  $b_{1u}$ , and  $b_{3u}$  states, respectively.

### III. RESULTS

Figure 2(a) shows the transient absorption spectrum measured with the unpolarized configuration ( $\mathcal{O}_0$ ), due to the STE's localized at iodine dimers in KCl:I at 80 K. Figures 2(b) and (c) display the difference spectra of  $\Delta\mathcal{O}_{\langle 110 \rangle}$  and  $\Delta\mathcal{O}_{\langle 100 \rangle}$ , respectively. A noteworthy feature of these spectra is that the absolute amounts of  $\Delta\mathcal{O}_{\langle 110 \rangle}$  and  $\Delta\mathcal{O}_{\langle 100 \rangle}$  are very small, contrary to the theoretical prediction mentioned earlier. This fact indicates that the absorption band consists of all three components ( $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$ ), whose energies may split from each other. In fact, the spectra of  $\Delta\mathcal{O}_{\langle 110 \rangle}$  and  $\Delta\mathcal{O}_{\langle 100 \rangle}$  look like differential spectra of  $\mathcal{O}_0$ , indicating a slight splitting among the spectra of  $\sigma_1$ ,  $\sigma_2$  and  $\sigma_3$ . The spectrum of each component ( $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$ ), derived from the observed spectra using Eqs. (3), (4), and (5), is shown in Fig. 3. One can clearly see that the three components are closely positioned and that their intensities are nearly the same. This result indicates that the  $2p$ -like excited states are nearly degenerate and that the oscillator strengths of the transitions from the  $1s$  ground state to all the  $2p$ -like states are nearly identical. Strictly speaking, the  $b_{3u}$  state has the lowest energy, although the splitting between  $b_{3u}$  and the other states is 10 meV or less.

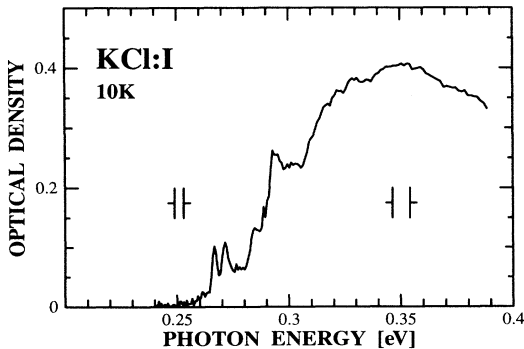


FIG. 4. Vibrational sidebands observed in the transient absorption, due to the localized STE in KCl:I. The pairs of vertical lines indicate the experimental resolution at each photon energy.

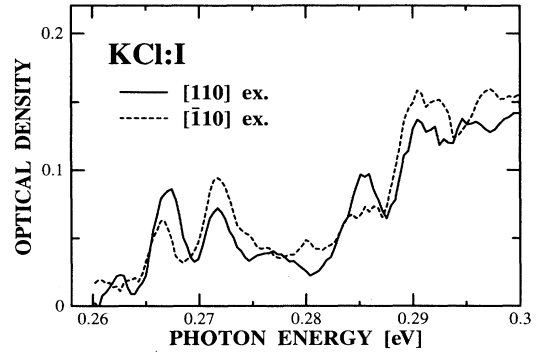


FIG. 5. Polarized spectra around the vibrational sidebands of the transient absorption, due to the localized STE in KCl:I.

The absorption band has an asymmetric shape with a tail on the high energy side. The prediction due to the theory of vibronic transitions<sup>16</sup> with a moderate amount of the Huang-Rhys parameter ( $S \sim 3.5$ ) fits the data reasonably well. Thus, one can expect that some vibrational sidebands will appear at low temperature. Figure 4 shows the high-resolution spectrum of the low energy side of the absorption band measured at 10 K. The most distinct structures are the doublet peaks around 0.27 eV. Considering the previously mentioned finding that the sublevels of the  $2p$ -like excited states are only slightly split, it is not unreasonable to conjecture that the doublet peaks correspond to the zero-phonon lines belonging to different electronic transitions. The amount of the splitting (5 meV) is also consistent with the splitting of the absorption bands ( $\leq 10$  meV) described earlier. Figure 5 shows the absorption spectra under the  $\langle 110 \rangle$ -polarized configuration. One can see that the polarization dependence is different for the two peaks of the doublet. Applying Eqs. (3) and (4), it is concluded that the upper and lower-lying peaks correspond to the  $a_g \rightarrow b_{2u}$  and  $a_g \rightarrow b_{3u}$  transitions, respectively.<sup>17</sup> The peaks at 0.267 eV and 0.286 eV have similar polarization dependence, as do those at 0.272 eV and 0.290 eV. The energy separation between these peaks ( $\sim 19$  meV) represents the phonon energy associated with the transition.

### IV. DISCUSSION

#### A. Electronic states of the on-center-type STE

The polarization of the transient absorption band clearly indicates that the  $2p$ -like excited states of the localized STE ( $I_2^{2-}$ ) in KCl:I are nearly degenerate. This result contrasts with the theoretical prediction that the splitting between the  $b_{3u}$  state and the other states should be large ( $\gtrsim 1$  eV) in the on-center-type STE's.<sup>7</sup> The observed small splitting ( $\sim 5$  meV) suggests that the influence of the site symmetry of the  $I_2^-$  core is very small. A possible explanation for this result is that the actual wave function of the excited electron is rather extended, while the theory assumes relatively compact clusters to calculate the electronic states. Assuming hydrogenlike electronic states, the effective Bohr radius of the

1s ground state is estimated to be 7 Å.<sup>9</sup> This value is comparable with those of free excitons in KCl and KI,<sup>18</sup> and the excited 2p-like states must be much more extended. However, the typical cluster used in the theory contains only a halogen molecule ( $X_2^-$ ) and a few neighboring alkali-metal ions. It is noteworthy that the length of the cluster along the molecular axis (110) is chosen to be rather long in order to explain the off-center relaxation along this direction, while only the nearest-neighbor alkali-metal ions are considered along the perpendicular direction. While this cluster size seems appropriate to calculate the electronic states of the off-center-type STE's, in which the electron and the hole are considered as a nearest-neighbor F-H pair, in the case of on-center-type STE's, such as in KCl:I, a larger cluster size may be necessary to improve the accuracy of the calculation.

### B. Vibronic structure

We found a vibronic structure associated with the transient absorption with phonon energy 19 meV. A plausible vibrational mode corresponding to this structure is the stretching mode of the  $X_2^-$ . Although there is no experimental result concerning the stretching mode of  $I_2^-$  in alkali-halide crystals, it has been reported that the stretching mode of  $Br_2^-$  of the STE in NaBr has a phonon energy of 17 meV.<sup>19</sup> Since the mass of an iodine ion is greater than that of a bromine ion, the energy of the  $I_2^-$  stretching mode should be smaller than that of  $Br_2^-$ , provided that the force constant does not change considerably. Thus, the observed energy (19 meV) associated with the STE localized at an iodine dimer in KCl:I seems to be too large to be due to the  $I_2^-$  stretching mode.

Another plausible vibrational mode is the longitudinal optical (LO) phonon of the host crystal (KCl). The energy of the LO phonon at the  $\Gamma$  point is 26.4 meV in KCl.<sup>20</sup> However, since a localized electron couples most strongly with phonons whose wavelengths are comparable with the orbital size of the electron, the appropriate

phonon energy to consider is that corresponding to a wavelength close to this value rather than that at the  $\Gamma$  point. The energy 19 meV corresponds to an LO phonon with  $k=0.6\sim 1.0(2\pi/a)$  along  $\Delta$ , or  $k=0.5\sim 1.0(2\pi/a)$  along  $\Sigma$  in KCl, where  $a$  is the lattice lengths  $1\sim 2a$  ( $6\sim 12$  Å). This range includes the electron orbital radii (about 7 Å for 1s and considerably larger for 2p) of the localized STE in KCl:I. Thus, it is very likely that the observed vibrational mode corresponds to these phonons. Furthermore, since the phonon dispersion is almost flat in this region, a number of phonon modes can couple with the electronic states, and thus produce a localized vibrational mode around the STE.

### V. CONCLUSION

The infrared transient absorption due to the electronic transitions of the on-center-type STE in KCl:I was investigated. The polarization properties indicate that the absorption band consists of three transitions ( $a_g \rightarrow b_{1u}$ ,  $b_{2u}$ , and  $b_{3u}$ ), which are energetically close to each other. The vibrational sideband indicates that the vibrational mode coupled to the electronic state of the STE consists mainly of LO phonons of the host crystal. These results consistently suggest that the electronic state of the STE localized at an iodine dimer in KCl:I is considerably extended compared with those of the off-center-type or F-centers. Since the localized STE in KCl:I is believed to be a prototype of the on-center-type STE's in alkali halide crystals such as NaBr and NaI,<sup>9,10,13</sup> the conclusion can be extended to general on-center-type STE's.

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<sup>17</sup> No distinct line was resolved that corresponds to the  $a_g \rightarrow b_{1u}$  transition. The upper-lying peak of the doublet might involve the  $a_g \rightarrow b_{1u}$  line.  
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