

## Magneto-optical study of paraexcitons in NaI

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Effects of an external magnetic field on the free-exciton luminescence (FEL) and the paraexciton resonance have been studied for NaI. The Zeeman splitting of the paraexciton is observed with use of the technique of magnetic-electric dipole two-photon absorption, from which the effective  $g$  value is derived to be 1.15. It is also found that the field-induced redshift of the zero-phonon luminescence line from free excitons follows exactly the Zeeman shift of the lowest level of the paraexciton. This fact provides clear evidence that the FEL of NaI originates from the radiative annihilation of paraexcitons, and not of orthoexcitons, which were proposed in previous works. [S0163-1829(96)01020-X]

### I. INTRODUCTION

Excitons in alkali halides have been the subject of many studies of solid-state spectroscopy. Not only electronic structures of excitons, including the dispersion relation of exciton polaritons, but also several properties of the self-trapped state which is caused by the strong exciton-phonon interaction have been studied in the past three decades.<sup>1-4</sup> From these extensive experimental and theoretical studies of excitons in alkali halides, it is now well established that the free state of excitons forms a metastable state separated by an energy barrier from the most stable self-trapped states. This coexistence of the two distinct excitonic states is one of the most attractive phenomena in these materials.<sup>5</sup>

The coexistence of the two excitonic states manifests itself in the luminescence spectra, particularly in alkali iodides, excited with ultraviolet (UV) photons of an energy equal to or exceeding the lowest excitonic absorption. The free excitons generate a sharp resonance luminescence line and its phonon sidebands near the band edge, whereas the self-trapped excitons (STE's) emit Stokes-shifted broad luminescence. In contrast with almost comprehensive understanding of the luminescent properties of STE's achieved in recent years,<sup>4</sup> the luminescent process of free excitons is still controversial.

According to the polariton picture,<sup>6</sup> excitons, first created optically on the polariton-dispersion curve at points having finite values of translational wave vector, relax along the dispersion curve through successive scattering by phonons and are then accumulated around the bottleneck region, at which conversion to photons takes place, giving rise to a sharp luminescence line. This picture certainly explains excitonic luminescence in some semiconductors well. However, free-exciton luminescence (FEL) in other crystals involves rather complicated processes; the complexity comes from the presence of the paraexciton states which lie just below the orthoexciton states. The roles of paraexcitons have been revealed to be crucial in FEL in semiconducting material such as  $\text{Cu}_2\text{O}$ .<sup>7</sup>

The initial state of FEL in alkali iodides has been studied

by several authors. In an earlier stage of the study, Nishimura<sup>8</sup> argued that optically created spin-singlet orthoexcitons relax to the band bottom while keeping their spin memory. Consequently he attributed the FEL in all alkali iodides to a radiative recombination of the orthoexcitons populated on the band bottom. Later, Itoh<sup>9</sup> proposed that the FEL could be assigned to the spin-triplet paraexciton state which lies a few tens of meV below the orthoexciton state. This conclusion was based on optical studies of thin KI and RbI crystals. Recently, the triplet nature of the initial state of the FEL in KI and RbI has been confirmed unambiguously by magneto-luminescence studies;<sup>10,11</sup> it has been shown that the field-induced shift of the peak energy of the zero-phonon line (ZPL) follows the Zeeman splitting of the lowest triplet level of the paraexciton.

On the other hand, the singlet nature of the FEL in NaI has been claimed by O'Connell-Bronin<sup>12</sup> in the investigation of the temperature dependence of the luminescence spectra. Nishimura<sup>13</sup> has ascribed the ZPL of FEL in NaI to a radiative decay of orthoexcitons, based on the results of spectral changes under uniaxial stress and also on the results of Raman enhancement effects. Furthermore, the same conclusion has been reached by Tsujibayashi-Kishigami,<sup>14</sup> who has done the experiments on FEL in iodide crystals with use of a narrow-band UV laser. Thus the FEL in NaI has been interpreted by many authors as arising from the orthoexcitons.

However, the above experimental results supporting the singlet nature of the FEL in NaI are not definite; they are still circumstantial, and some of them are even ambiguous. For example, coincidence of the energy of the ZPL to the energy of the transverse exciton ( $E_T=5.620$  eV), which was determined from the Kramers-Kronig analysis of the reflection spectrum,<sup>13</sup> has been regarded as evidence favorable for this interpretation. However, as Fröhlich *et al.* pointed out,<sup>15</sup> it is difficult to determine  $E_T$  precisely from one-photon spectra because of the rather broad exciton band. In fact, a more reliable value of  $E_T$  was determined to be 5.626 eV by three-photon spectroscopy,<sup>15</sup> which is higher than the one-photon data. In addition, it is not very easy to determine experimentally the energy in the UV region with high accuracy, since

the refractive index of air in this region is highly sensitive to the wavelength and to the ambient conditions, together with general difficulties in calibrating the wavelength of the spectroscopic system used. In fact, the peak energies of the ZPL in NaI reported in previous studies<sup>12–14,16</sup> are ranged from 5.55 to 5.618 eV, showing significant uncertainty of the energy value. It is also pointed out that the line shapes and spectroscopic features of the FEL in NaI are strongly sensitive to the purity of specimens and to the surface conditions. Therefore further studies using a more sophisticated method are highly desired to identify the initial state of the FEL in NaI definitely.

It should be stressed here that the clarification of the initial state of the FEL in NaI is not simply a new finding for a specific crystal. It is more than that; it provides essential information to obtain general understanding of the process of exciton relaxation in alkali halides. As pointed out by several authors,<sup>10,17–19</sup> there exists a strong correlation between the internal states of free excitons and the relaxed configurations of STE's. If the FEL in NaI is due to the orthoexcitons as interpreted by several authors, then the feature of the intraband relaxation of excitons in NaI turns out to be essentially different from those in KI and RbI, in which optically generated orthoexcitons are converted efficiently into paraexcitons during the intraband relaxation. The difference, if it is the case, should then be related to different features of STE's formed in these crystals.

In the present paper, we study the effects of external magnetic fields on the paraexcitons and the FEL in NaI. Based on the same strategy as the previous studies in KI and RbI,<sup>10,11</sup> we measure the field-induced changes of the FEL spectra, and compare them with the Zeeman shift of the paraexcitons in NaI. This comparison is a very good way to identify the origin of the FEL, because the Zeeman splitting of the paraexcitons is more than two times greater than that of the orthoexcitons.<sup>15</sup> In order to clarify the precise structures of the paraexcitons, we use the technique of magnetic-electric dipole two-photon absorption (MED-TPA) that has recently been introduced by Fröhlich, Itoh, and Pahlke-Lerch.<sup>20</sup> Applying this high-resolution technique to specimens under an external magnetic field, we observe the Zeeman splitting of the paraexciton resonance, and therefore get the effective  $g$  value that is an important quantity characterizing the paraexciton structure. The results obtained have shown that the field-induced shift of the ZPL of FEL follows exactly the Zeeman shift of the lowest level of the paraexciton. This provides strong evidence that the FEL in NaI arises indeed from the radiative decay of paraexcitons.

## II. EXCITONS IN ALKALI HALIDES AND MED-TPA

Excitonic structures of alkali halides have been discussed in detail in the literature.<sup>1–3,15</sup> The uppermost valence band is derived from a  $p_{3/2}$  state of halogen ions, which transforms like  $\Gamma_8^-$  in the cubic point group  $O_h$ . On the other hand, a lowest conduction band is derived from an  $s_{1/2}$  state of alkali metal ions, with  $\Gamma_6^+$  symmetry. From the direct product  $\Gamma_8^- \otimes \Gamma_6^+$ , we get the lowest  $S$  excitons of  $\Gamma_3^-$ ,  $\Gamma_4^-$ , and  $\Gamma_5^-$  symmetry. The  $\Gamma_4^-$  state is a singlet-triplet mixed state (orthoexciton), which has the total angular momentum  $J=1$  and is dipole active. The  $\Gamma_3^-$  and  $\Gamma_5^-$  states are pure triplet

states (paraexcitons) with  $J=2$ , and thus strictly spin forbidden for electric-dipole transitions. The orthoexciton and paraexciton states are split by the analytic exchange interaction as discussed by Onodera and Toyozawa.<sup>2</sup> The paraexciton states of  $\Gamma_3^-$  and  $\Gamma_5^-$  symmetry are further split by the anisotropic exchange interaction.<sup>21</sup> Taking spherical quantum number into account, the former state consists of two components,  $\Gamma_{31}^-$  ( $M=0$ ) and  $\Gamma_{32}^-$  ( $M=\pm 2$ ), while the latter state consists of three components,  $\Gamma_{50}^-$  ( $M=\pm 2$ ),  $\Gamma_{5+}^-$  ( $M=-1$ ), and  $\Gamma_{5-}^-$  ( $M=+1$ ).

MED-TPA was introduced as a spectroscopic technique for the study of paraexcitons in semiconductors and insulators.<sup>20</sup> In MED-TPA, one of the incident photons induces a magnetic-dipole transition and the other an electric-dipole transition. In the cubic group  $O_h$ , the magnetic-dipole operator transforms like an axial vector (irreducible representation  $\Gamma_4^+$ ), while the electric-dipole operator transforms like a polar vector ( $\Gamma_4^-$ ). From a  $\Gamma_1^+$  ground state, transitions to odd-parity states of  $\Gamma_1^-$ ,  $\Gamma_3^-$ ,  $\Gamma_4^-$ , and  $\Gamma_5^-$  symmetry are thus allowed for MED-TPA (direct product  $\Gamma_4^+ \otimes \Gamma_4^-$ ). The situation of MED-TPA is in sharp contrast to classical two-photon absorption where only spin-allowed even-parity states can be excited.

In MED-TPA, the dipole-allowed  $S$  excitons (orthoexcitons) serve as intermediate states for a magnetic-dipole transition to the final states (paraexcitons). Applying the polarization selection rules of MED-TPA to the orthoexcitons and paraexcitons in alkali halides,<sup>20</sup> the  $\Gamma_{50}^-$  and  $\Gamma_{32}^-$  states can be excited by [100]- and [110]-polarized light, respectively. These two states have quantum numbers  $M=\pm 2$ . In magnetic fields, therefore, we get a complete mixture of them;  $|M=\pm 2\rangle = (1/\sqrt{2})(|\Gamma_{32}^- \pm |\Gamma_{50}^- \rangle)$ . The field-induced splitting of the paraexciton states has been studied in detail by Beerwerth *et al.*<sup>15</sup> According to them, the field dependence of the  $M=\pm 2$  components is given by

$$E(M=\pm 2) = E_p + \varepsilon_{\text{ex}}/2 \pm [(2g_p \mu_B B)^2 + (\varepsilon_{\text{ex}}/2)^2]^{1/2}, \quad (1)$$

where  $E_p$  and  $g_p$  are the resonance energy and effective  $g$  value of the paraexciton, respectively.  $\varepsilon_{\text{ex}}$  is the anisotropic exchange splitting between the  $\Gamma_3^-$  and  $\Gamma_5^-$  states, and  $\mu_B$  stands for the Bohr magneton. It is worth noting here that magneto-optical experiments of MED-TPA can be easily performed, since the paraexcitons are now two-photon allowed. This technique is therefore very well suited for the detailed study of paraexciton states.

## III. EXPERIMENT

Nominally pure crystal of NaI was obtained from Harshaw Chemical Co. A specimen with a size of  $5 \times 10 \times 1$  mm<sup>3</sup> was cleaved and handled in an extremely dry nitrogen atmosphere, because NaI is very hygroscopic. The sample was mounted on the copper holder of a magneto-optical cryostat (Oxford, SM-4) capable of applying a magnetic field  $B$  up to 6 T, and it was then immersed in liquid helium.

For experiments of MED-TPA, an excimer-laser-pumped dye laser (Lambda Physics EMG-201 MSC and FL3002) was used as a light source. The spectral resolution of the system was better than 20  $\mu\text{eV}$ , having the maximum pulse energy of about 10 mJ. The laser beam was incident along the magnetic-field direction on a (100) surface of the sample.

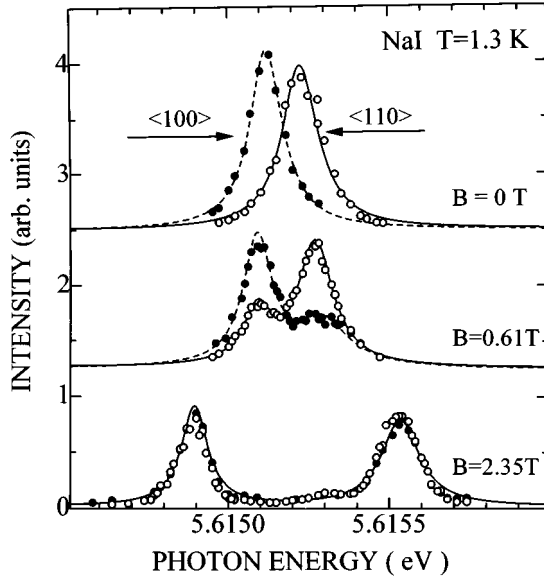


FIG. 1. Magnetic-electric dipole two-photon absorption (MED-TPA) of the paraexciton of NaI in external magnetic fields ( $B=0, 0.61, \text{ and } 2.35 \text{ T}$ ) at 1.3 K. Open and closed circles correspond to the polarization  $E\parallel[110]$  and  $E\parallel[100]$ , respectively.

For selective excitation of the  $M=\pm 2$  components of the paraexcitons, we used a linearly polarized laser beam ( $E\parallel[100]$  and  $E\parallel[110]$ ), the direction of which was adjusted by a half-wave plate. Two-photon signals were monitored via the STE luminescence at 298 nm through a suitable filter and a grating monochromator, and they were detected by a gated multichannel detector (Princeton, D/SIDA 700).

As the experimental setup for luminescence measurements was almost the same as that reported in Ref. 11, only the main points are briefly described here. The UV light from a 150-W  $D_2$  lamp was dispersed through a grating monochromator with a band pass of 1 nm, and was incident on a (100) surface of the sample in Faraday configuration ( $k\parallel B$ ). Luminescence emitted along the direction perpendicular to the magnetic-field direction was analyzed by means of a Jobin Yvon HR-320 monochromator equipped with a 4960-groove/mm grating. The signal was detected with a multichannel detector (Princeton, IRY1024). The accuracy of the wavelength obtained by our system was within an error of  $\pm 0.1 \text{ \AA}$ , which corresponds to  $\pm 0.3 \text{ meV}$  in the energy range concerned.

#### IV. RESULTS

Experimental results of MED-TPA are shown in Fig. 1, where open and closed circles correspond to the polarization  $E\parallel[110]$  and  $E\parallel[100]$ , respectively. From the spectra at  $B=0$ , we get the paraexciton energy  $E_p(\Gamma_{50}^-)=5.6151\pm 0.0001 \text{ eV}$  and the anisotropic exchange splitting  $\varepsilon_{\text{ex}}=100\pm 20 \text{ \mu eV}$ . These values are in fairly good agreement with the data in Ref. 20. When a magnetic field is applied, the  $\Gamma_{32}^-$  and  $\Gamma_{50}^-$  states become mixed with each other and their separation increases slightly, as can be seen already at  $B=0.61 \text{ T}$ . At higher field  $B=2.35 \text{ T}$ , one gets a complete mixture of them, with the separation of  $650 \text{ \mu eV}$ .

The magnetic-field dependence of the  $M=\pm 2$  components of the  $J=2$  paraexciton is depicted by open circles in

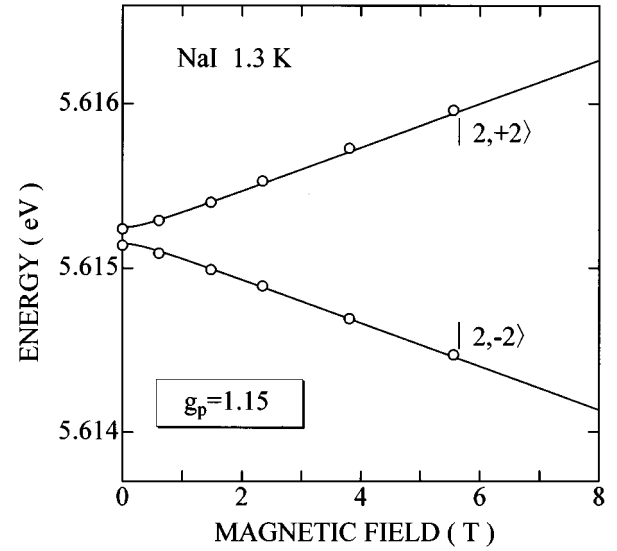


FIG. 2. Field-dependent splitting of the  $M=\pm 2$  components of the paraexciton ( $J=2$ ) in NaI. Solid curves represent a best fit of Eq. (1) to the data, with the effective  $g$  value  $g_p=1.15$ .

Fig. 2. The  $M=+2$  level shifts up, while the  $M=-2$  level shifts down in energy from the zero-field value. The solid curves are a best fit of Eq. (1) to the data. From this fit, the effective  $g$  value of the paraexciton is derived as  $g_p=1.15$ .

The luminescence spectrum due to free excitons in NaI is shown in the top of Fig. 3. The excitation was made at 1.3 K with 5.765-eV photons, the energy of which corresponds to the high-energy side of the lowest exciton absorption band of NaI. For comparison, the FEL spectra of KI and RbI mea-

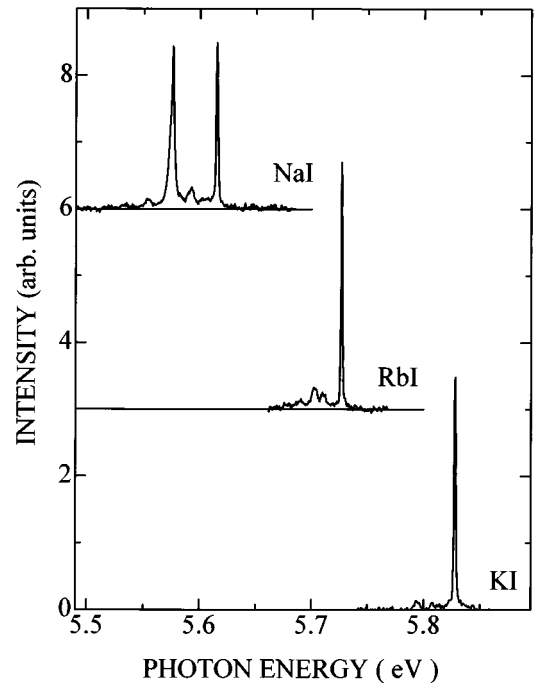


FIG. 3. Luminescence spectra due to free excitons in NaI, RbI, and KI at 1.3 K. The excitation was made with 5.765-eV photons for NaI, 5.990-eV photons for RbI, and 6.140-eV photons for KI. These excitation energies correspond to the high-energy side of the lowest exciton absorption band of the respective iodides.

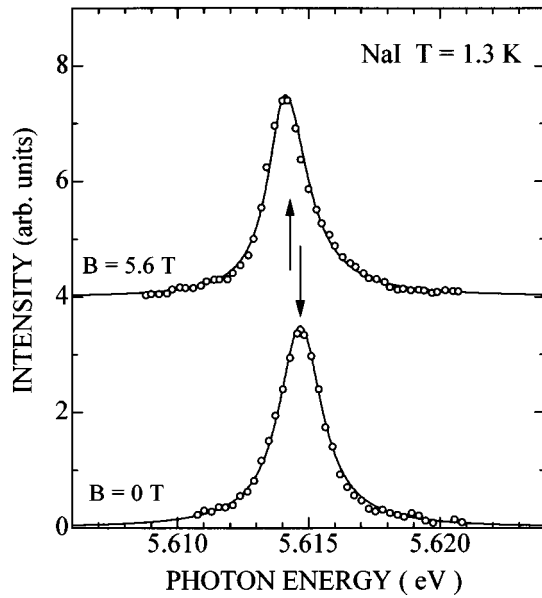


FIG. 4. Spectral change of the zero-phonon line of the free-exciton luminescence in NaI obtained by applying magnetic fields; the lower curve is for  $B=0$  and the upper curve is for  $B=5.6$  T. The excitation was made at 1.3 K with 5.765-eV photons. Arrows indicate the peak positions of the luminescence lines.

sured by our previous experiment<sup>11</sup> are also shown in this figure. In KI and RbI, sharp luminescence lines are seen at 5.8277 and 5.7266 eV, respectively. These lines are followed by three or more weak LO-phonon sidebands. On the other hand, in NaI, the spectrum mainly consists of two intensive lines at  $5.6148 \pm 0.0003$  and  $5.5753 \pm 0.0003$  eV. These two lines of NaI have been regarded as the ZPL and its 2LO phonon replica.<sup>12,13</sup> Our peak values are slightly different from Nishimura's data (5.618 and 5.577 eV).<sup>13</sup> It is stressed that comparable intensities of the zero- and 2LO-phonon lines testify to a good quality of the crystal investigated, as shown in Ref. 22. Besides the two intense lines, several weak phonon sidebands manifest themselves in the spectrum of NaI.

Figure 4 shows in an expanded scale the spectral change of the ZPL in NaI by applying external magnetic fields at 1.3 K. The lower and upper spectra were taken for  $B=0$  and 5.6 T, respectively. For the spectrum at  $B=0$ , the line shape is symmetric, and is well fitted by a Lorentzian with the full width at half maximum of 1.8 meV. On the other hand, the spectrum at  $B=5.6$  T becomes asymmetric; the width (1 meV) at the high-energy side is wider than that (0.8 meV) at the low-energy side. The solid curves in Fig. 4 are Lorentzian fits to the data points, with the peak positions indicated by arrows. It is clear that the peak energy is redshifted by about 0.6 meV at  $B=5.6$  T.

The shift of the peak energies of the ZPL's from the zero-field value is plotted by open circles as a function of  $B$  in Fig. 5, where the error bars shown on the data points are from determining the peak energies of the broad luminescence lines. The peak position shifts to the lower-energy side progressively with increasing  $B$ . The peak energies of the 5.5753-eV line, assigned to the 2LO-phonon sideband, show a similar redshift. In this figure, the solid curve is a copy of the field dependence of the  $|2, -2\rangle$  level represented in Fig. 2.

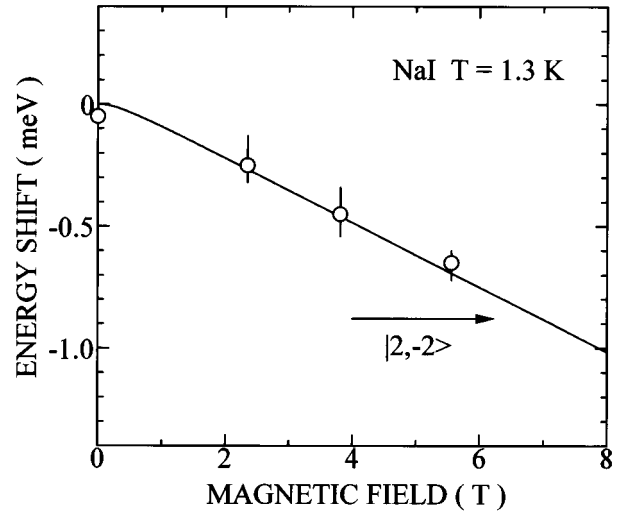


FIG. 5. Energy shift from the zero-field value as a function of external magnetic field at 1.3 K. Open circles are for the zero-phonon line of the free-exciton luminescence. Solid curve is a copy of the field dependence of the lowest  $|2, -2\rangle$  level of the paraexciton represented in Fig. 2.

## V. DISCUSSION

In Fig. 5, it is clearly seen that the amount of redshift of the ZPL induced by applying a magnetic field follows exactly the Zeeman shift of the lowest  $M=-2$  level of the paraexciton. The observed zero-field energy (5.6148 eV) of the ZPL peak is lower by 0.3 meV than the paraexciton energy  $E_p$  determined by MED-TPA. However, this difference lies within the range of the error in determining the absolute magnitude of the wavelength of the luminescence-detection system used. Therefore we cannot say at present whether this difference is due to a real effect or not. In contrast with this ambiguity in determining the absolute wavelength, our multichannel-detection system for the luminescence measurements provides much more reliable values of relative shifts of the peak energies; a shift of 0.1 meV can be determined unambiguously. Therefore, based on the result that the magnetic-field-induced shift of the peak energy of the ZPL is essentially identical to the Zeeman shift of the paraexciton state ( $M=-2$ ), we can conclude definitely that the resonance luminescence in NaI is due to the radiative annihilation of paraexcitons. Consequently, the 5.5753-eV line, which shows a redshift in peak energy similar to that of the ZPL, is confirmed to be the 2LO-phonon sideband of the paraexciton luminescence.

From Fig. 3, it is evident that the 2LO-phonon line of the FEL in NaI is more intensive than those in KI and RbI. This feature has been ascribed by O'Connell-Bronin<sup>12</sup> to be due to the strong exciton-LO-phonon interaction in NaI; the intensity of the LO-phonon sideband is proportional to the square of the Fröhlich constant of exciton-phonon interaction. Indeed, it has been shown for orthoexcitons that the Fröhlich constant is larger in NaI than in KI and RbI, from an analysis of the reflection spectra of the iodide crystals.<sup>23</sup> The large Fröhlich constant for excitons near the bottleneck region indicates that the cancellation effects in the phonon scattering process are not effective anymore.<sup>24</sup> This may be caused by the smaller binding energy of the exciton in NaI than in KI

and RbI. This feature of the exciton in NaI, derived from the analysis of the one-photon absorption data, may be evidenced also from the present result of Zeeman shift of the paraexciton.

From the results of MED-TPA, the effective  $g$  value of the paraexciton in NaI has been derived to be  $g_p = 1.15$ . Defining the  $g$  values for conduction electron and valence hole as  $g_c$  and  $g_v$ , respectively, the  $g$  value for the paraexciton is given by  $g_p = (1/4)(3g_v + g_c)$ .<sup>15</sup> In a simple tight-binding model one would expect  $g_c = 2$  and  $g_v = 4/3$  (Landé factor), which leads to  $g_p = 1.5$ . Therefore the value of  $g_p$  in NaI is considerably smaller than that expected for excitons of Frenkel type. As pointed out by Ahrenkiel and Teegarden,<sup>25</sup> the small  $g_p$  can be attributed to an appreciable nearest-neighbor overlap of the hole wave function, which will also lead to the large exciton radius. Although experimental values of  $g_p$ 's in KI (1.35) and RbI (1.33)<sup>15</sup> show some deviation from the value for excitons of purely Frenkel type, the value of NaI shows a much larger deviation. This may indicate that the paraexciton in NaI is characterized by a much larger exciton radius, and hence smaller binding energy, leading to the larger Fröhlich constant.

In Fig. 4, the spectral line shape of the ZPL at  $B = 5.6$  T is fitted by a Lorentzian curve with different half-widths at the low- and high-energy sides. The asymmetry of the line shape, in particular the wider width at the high-energy side, indicates some contributions to the luminescence from high-lying Zeeman-split sublevels of the paraexcitons. This means that the paraexcitons are not in thermal equilibrium among the Zeeman-split sublevels; the thermal energy at 1.3 K (0.112 meV) is substantially smaller than the separation (1.4 meV) of the sublevels at  $B = 5.6$  T. However, the contribution of the high-lying levels to the ZPL intensity under magnetic fields in NaI is much smaller than those in RbI and KI; their contribution is significant in KI.<sup>11</sup> Thermalization will

take place via emission or absorption of a single acoustic phonon within the exciton lifetime. The exciton lifetime is, therefore, an important factor for determining the degree of thermalization and hence the magnitude of the contribution of the high-lying levels to the ZPL intensities. Judging from the spectral line shape in the magnetic field, we may suppose that the lifetime of paraexcitons becomes longer in the order of KI, RbI, and NaI. As argued in Ref. 11, the quantum yield of the FEL may be a good measure of the exciton lifetime; for larger yield, one expects a longer lifetime. In fact, it has been shown that the yield of the FEL is increased in the order described above,<sup>8</sup> which is consistent with our results.

The results obtained in the present study demonstrate clearly that the initial state of the FEL in NaI is the paraexciton, as in the case of KI and RbI.<sup>10,11</sup> In the present experiment, we could not detect any luminescence on the high-energy side of the ZPL in NaI, similarly to the cases in KI and RbI. Therefore it is concluded that the orthoexcitons generated optically are almost exclusively scattered into the paraexciton state during intraband relaxation within the exciton-polariton branch. In alkali halides, self-trapping processes of free excitons have been studied extensively by measuring the excitation spectra for the STE luminescence.<sup>19,26</sup> A striking feature is that the singlet-STE luminescence is hardly excited when the lowest orthoexcitons are generated by one-photon excitation, although the triplet-STE luminescence is predominantly excited. This feature can be understood if the paraexcitons formed exclusively through the intraband relaxation are relaxed into the STE states while keeping the spin-triplet nature.

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<sup>1</sup>R. S. Knox, *Theory of Excitons* (Academic, New York, 1963).

<sup>2</sup>Y. Onodera and Y. Toyozawa, *J. Phys. Soc. Jpn.* **22**, 833 (1967).

<sup>3</sup>F. Beerwerth and D. Fröhlich, *Phys. Rev. Lett.* **55**, 2603 (1985); *Phys. Rev. B* **36**, 6239 (1987).

<sup>4</sup>K. S. Song and R. T. Williams, *Self-Trapped Excitons* (Springer-Verlag, Berlin, 1993).

<sup>5</sup>Ch. B. Lushchik, in *Excitons*, edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), Chap. 12.

<sup>6</sup>Y. Toyozawa, *Prog. Theor. Phys. Suppl.* **12**, 111 (1959).

<sup>7</sup>D. W. Snoke, D. P. Trauernicht, and J. P. Wolfe, *Phys. Rev. B* **41**, 5266 (1990).

<sup>8</sup>H. Nishimura, *J. Phys. Soc. Jpn.* **52**, 3233 (1983).

<sup>9</sup>M. Itoh, *Phys. Rev. B* **35**, 7652 (1987).

<sup>10</sup>K. Tanimura and N. Itoh, *Phys. Rev. B* **45**, 9417 (1992).

<sup>11</sup>M. Itoh, K. Tanimura, and N. Itoh, *Phys. Rev. B* **47**, 10 099 (1993).

<sup>12</sup>A. A. O'Connell-Bronin, *Phys. Status Solidi B* **129**, 675 (1985).

<sup>13</sup>H. Nishimura, *Rev. Solid State Sci.* **4**, 289 (1990).

<sup>14</sup>T. Tsujibayashi-Kishigami, *J. Phys. Soc. Jpn.* **63**, 335 (1994).

<sup>15</sup>F. Beerwerth, D. Fröhlich, P. Köhler, V. Leinweber, and A. Voss, *Phys. Rev. B* **38**, 4250 (1988).

<sup>16</sup>I. L. Kuusmann, P. Kh. Liblik, G. G. Liidya, N. E. Lushchik, Ch. B. Lushchik, and T. A. Soovik, *Fiz. Tverd. Tela (Leningrad)* **17**, 3546 (1975) [*Sov. Phys. Solid State* **17**, 2312 (1975)].

<sup>17</sup>Y. Kayanuma, in *Defect Processes Induced by Electronic Excitation in Insulators*, edited by N. Itoh (World Scientific, Singapore, 1989), p. 13.

<sup>18</sup>M. Itoh, S. Hashimoto, and N. Ohno, *J. Phys. Soc. Jpn.* **60**, 4357 (1991).

<sup>19</sup>T. Matsumoto, M. Shirai, and K. Kan'no, *J. Phys. Soc. Jpn.* **64**, 987 (1995).

<sup>20</sup>D. Fröhlich, M. Itoh, and Ch. Pahlke-Lerch, *Phys. Rev. Lett.* **72**, 1001 (1994).

<sup>21</sup>K. Cho, S. Suga, W. Dreybrodt, and F. Willmann, *Phys. Rev. B* **11**, 1512 (1975).

<sup>22</sup>H. Nishimura and T. Yamano, *J. Phys. Soc. Jpn.* **51**, 2947 (1982).

<sup>23</sup>G. Baldini and B. Bosacchi (unpublished).

<sup>24</sup>M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura, *Excitonic Processes in Solids* (Springer-Verlag, Berlin, 1986), Chap. 4.

<sup>25</sup>R. K. Ahrenkiel and K. J. Teegarden, *Phys. Rev. Lett.* **21**, 1682 (1968).

<sup>26</sup>M. Ikezawa and T. Kojima, *J. Phys. Soc. Jpn.* **27**, 1551 (1969).