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Magnetic field effects on the triplet excitons in β-ZnP$_2$: Possibility of optical dipole relaxation in the exciton system

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Magnetic field effects on the excitation spectra of the 1s triplet exciton luminescence in monoclinic β-ZnP$_2$ are observed at 2 K. Under a magnetic field of 1 T, the luminescence splits into two components with a separation of about 0.2 meV. The excitation spectrum for each of Zeeman-split luminescence components is measured. The spectrum for one component is definitely different from that for the other. Excitation into some of the excitation peaks produces only one component of the luminescence. It is concluded that the triplet excitons relax through a selective path. Relaxation processes through the multiple phonon scatterings are discussed, and possible processes through optical dipole transitions in the triplet exciton system of β-ZnP$_2$ are also proposed.

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I. INTRODUCTION

A monoclinic zinc diphosphide β-ZnP$_2$ crystal is characterized by a clear and well-separated exciton series of both singlet and triplet systems. An allowed hydrogenic s exciton series is observed in the reflection spectrum for electric polarization parallel to the c axis ($E\|c$). On the other hand, a forbidden triplet exciton series is observed for $E\|b$ up to $n=7$ in the absorption spectrum of a single crystal.[1–3] In the triplet exciton absorption series, lines with $n\geqslant 3$ show a doublet structure. The doublet results from the mixing of a d-type exciton envelope function into an s-type function due to the nonspherical potential in the crystal, as observed in the two-photon absorption spectrum in Cu$_2$O.[4]

In the luminescence spectrum of the singlet exciton, besides the 1s exciton luminescence, very weak luminescence peaks of higher members of the series $n\geqslant 2$ have been confirmed.[5,6] The luminescence spectrum of the 1s exciton at 2 K under the interband excitation is shown in Fig. 1(a), which was observed without a polarizer. Symbols E_T and E_L, indicated by the vertical bars, stand for the transverse and longitudinal singlet exciton energies, respectively. Dispersion curves of lower and upper polariton branches of singlet exciton (LP and UP), those of transverse and longitudinal excitons (TE and LE), and that of the triplet exciton are shown in Fig. 1(b) for the help of understanding. Components C_{L1} and C_{L2} are singlet exciton polariton luminescence allowed for $E\|c$. Component C_U around E_L comes from the bottom region of the UP. By about 2 meV below the C_{L1} component, a very sharp triplet exciton luminescence is observed for $E\|b$ which is denoted by B in the figure.[5,7,8] The high energy component C_{L2} comes from the polaritons relaxed from the higher energy states and then populated in the bottleneck region of the LP. The low energy component C_{L1} results mainly from the anti-Stokes phonon scatterings of the lowest triplet excitons into the low energy photonlike part of the LP.[9,10]

It is emphasized that most of the lowest triplet excitons are easily scattered back into singlet states through multiple acoustic phonon scatterings.[10] This process explains well the short decay time of the triplet exciton luminescence 2 ns.[9,11] Information on acoustic phonons in the dispersion direction perpendicular to the bc-plane was obtained by Brillouin scattering experiments.[12] Many aspects of the exciton luminescence of β-ZnP$_2$ at low temperatures have been explained in terms of the interplay between the singlet and triplet excitons through phonon scatterings.[10]

From the excitation spectrum for the triplet exciton luminescence B, singlet excitons are found to be converted into triplet excitons at a nearly constant rate over a wide energy range in the course of relaxation.[8] Contrary to the case of the singlet excitons, a conversion of triplet excitons in excited states into singlet excitons hardly ever occurs[8] except in the lowest triplet state described above.[10]

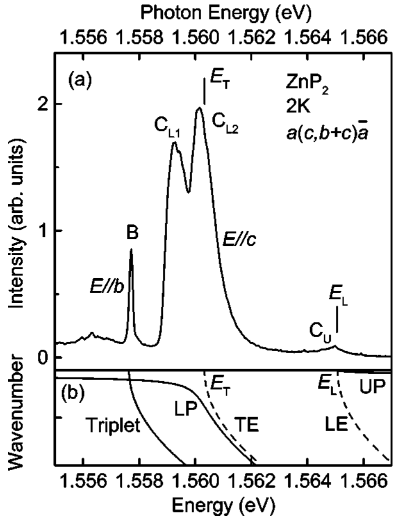

FIG. 1. (a) Exciton luminescence spectrum of β-ZnP$_2$ at 2 K under the interband excitation. E_T and E_L stand for transverse and longitudinal singlet exciton energies, respectively. (b) Dispersion curves of lower and upper polariton branches of singlet exciton (LP and UP), those of transverse and longitudinal excitons (TE and LE), and that of a triplet exciton. Component C_U comes from the upper polariton branch UP, C_{L1} and C_{L2} from the lower branch LP, and B from the triplet exciton.

Magnetic field effects on the triplet exciton absorption spectra up to 40 T were investigated in detail by Goto *et al.* in a series of works, and the electronic structure of the exciton system was characterized by assuming the crystal is in a quasiorthorhombic phase.[3] Magnetic field effects on the triplet exciton luminescence and its excitation spectra have been measured with high resolution. A definite difference in the Zeeman splitting pattern of the triplet luminescence between the monoclinic and its twin polymorph was confirmed.[13,14] On the other hand, Fröhlich *et al.* observed anisotropic p exciton series in β-ZnP$_2$ by the two-photon absorption technique,[15] and also determined many exciton parameters by the magnetoabsorption of the p excitons.[16]

In this work, excitation spectra for the $1s$ triplet exciton luminescence under a magnetic field up to 1 T are measured in detail at 2 K in order to investigate the fine structure of the excitons and also the relaxation processes in the triplet exciton system. Preliminary results were presented in the International Conference DPC'01.[17] An interpretation of the result will be discussed.

II. EXPERIMENT

Starting materials of zinc diphosphide were metallic zinc (99.999 %) and red phosphorus (99.9999 %), both from Furuuchi Chemicals. Single crystals of β-ZnP$_2$ were grown from the vapor phase, as described in Ref. 6. The size of the specimen used for the optical measurement was typically 6 $\times 2 \times 1$ mm $(c\times b\times a)$. The surface obtained in an as-grown crystal is the bc face.

For luminescence measurements, a cw Ti:sapphire laser (Spectra Physics 3900S), pumped by an Ar ion laser (Spectra Physics 2017), was used as an exciting light source. For measuring excitation spectra, the birefringent filter in the laser cavity was driven via a set of gear wheels with a synchronous motor to change the excitation energy continuously over the exciton region $n \geqslant 2$ with $E\|b$. Using this device, we can obtain excitation spectra with a high resolution limited by the linewidth of the Ti:sapphire laser. A magnetic field B up to 1 T was applied parallel to c and b axes of the crystal immersed in superfluid helium in a glass cryostat placed between pole pieces of small electromagnet. The crystal was rotated by 90° when the direction of the magnetic field was changed. The emitted luminescence was focused on the end of an optical fiber, and led to a double monochromator (Spex 1401) detected by a cooled photomultiplier (Hamamatsu R943-02). Slit widths of the double monochromator were adjusted to observe the excitation spectra for either narrow or wide energy ranges of the Zeeman-split luminescence bands. Signals were detected with the lock-in or photon-counting method. All measurements were performed in the Voigt configuration.

III. RESULTS

Figure 2 shows luminescence spectra of the $1s$ triplet exciton under a magnetic field (a) for $B\|c$ and (b) for $B\|b$ up to 1 T. They show clear Zeeman splittings into two components W and X for the $B\|b$ configuration and also Y and Z for the $B\|c$ configuration, both with $g = \sim 4$. The crystal used in measuring (a) was also used in (b) by rotating it by 90° on the crystal holder. The irradiated spot was not the same as the one in (a), which leads to the slight difference between the spectra in (a) and those in (b). The Zeeman splitting is about 0.2 meV at 1 T. In the monoclinic phase, however, the line should split into three components under the field $B\|c$, reflecting the low symmetry.[14] The above result suggests that the specimen used crystallizes into a quasiorthorhombic twin phase.[3,14]

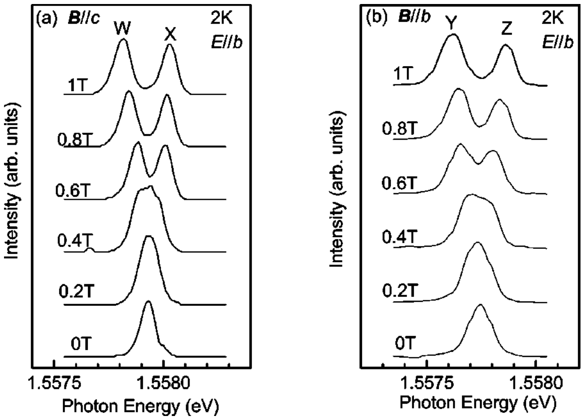

FIG. 2. Zeeman splitting of $1s$ triplet luminescence spectrum of β-ZnP$_2$ at 2 K under a magnetic field up to 1 T (a) for $B\|c$ and (b) for $B\|b$. Excitation is made into the band-to-band region. The spectra in (b) are obtained by irradiation into different sites of the crystal from the one for those in (a).

Excitation spectra for the triplet luminescence under a magnetic field up to 1 T for (a) $B\|c$ and (b) $B\|b$ are shown in Fig. 3. These spectra were measured for $E\|b$ with a wide slit width ($\sim$1 meV) of the analyzing monochromator to receive both Zeeman-split luminescence components shown in Fig. 2. Excitation spectrum without a magnetic field is very similar to the absorption spectrum for $E\|b$.[8,13] They are very sharp and well resolved. Two spectra for the zero field in (a) and (b) are slightly different due to the difference in

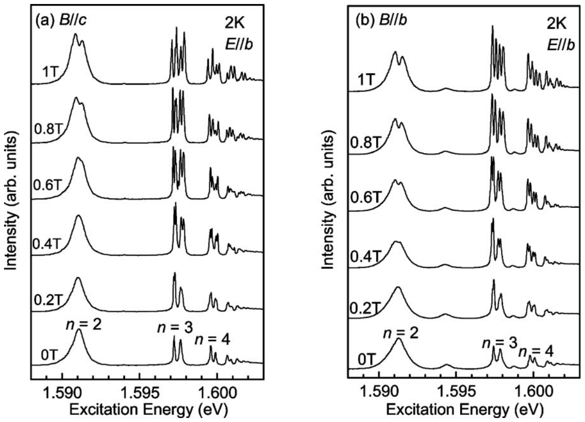

FIG. 3. Excitation spectra of the $1s$ triplet exciton luminescence under a magnetic field up to 1 T for (a) $B\|c$ and (b) $B\|b$. A wide slit width of about 1 meV is employed for an analyzing monochromator to receive all the Zeeman-split components of the luminescence.

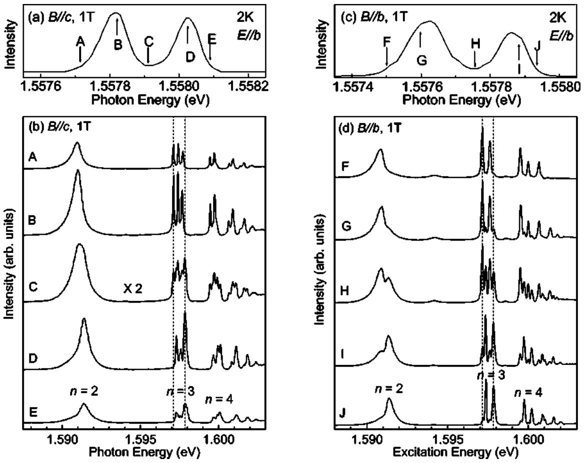

FIG. 4. (a) Zeeman-split 1s triplet exciton luminescence at 1 T for $B\|c$. Arrows *A*, *B*, *C*, *D*, and *E* indicate energy positions observing the excitation spectra. (b) Change of the excitation spectra with the change of monitoring energies in the $n=1$ triplet exciton luminescence bands at 1 T for $B\|c$. The symbol indicating the energy in (a) is put on the left end of each curve. (c) Zeeman-split 1s triplet exciton luminescence at 1 T for $B\|b$. (d) Change of the excitation spectra with the change of the monitoring energies on the $n=1$ triplet exciton luminescence at 1 T for $B\|b$. Two vertical broken lines indicate the positions of the lowest and highest excitation peaks of $n=3$ multiplets, respectively. The slit width of the analyzing monochromator is 0.18 meV.

irradiated sites as mentioned above. Under the magnetic field, the line $n=2$ splits into two components above 0.6 T. Note here that the halfwidth of the $n=2$ line is considerably wide in contrast to the other lines and, therefore, splitting appears at a rather high field. The g value of the $n=2$ line is seemingly very large (~ 8). The reason for this is not clear at present. For $B\|c$, each sharp line for $n=3$ begins to split into two at 0.2 T, and shows more complex splittings and changes of the relative intensities for higher fields above 0.6 T. For lines with $n \geqslant 4$, the splitting becomes complex owing to the configuration interaction between higher n's, because they have almost the same symmetries, and energy separations among them are small. On the other hand, each of the peaks splits simply into two for $B\|b$. The observed excitation peaks are very sharp and clearly resolved under a magnetic field. These results reproduce the previous results well.[13,14] By making use of sharp and well resolved exciton absorption lines and fine scanning of a Ti:sapphire laser, excitation spectra for each Zeeman-split component of the 1s triplet exciton luminescence were measured at 2 K under a magnetic field at 1 T to study the relaxation processes in the triplet exciton system.

Figure 4(a) shows the Zeeman-split 1s triplet exciton luminencence for $B\|c$ at 1 T on an expanded scale. We measured excitation spectra for five monitoring points from *A* to *E* chosen on tails and peaks of the luminescence bands. In Fig. 4(b) excitation spectra taken for the five points from *A* to *E* indicated in Fig. 4(a) are shown. The slit width of the monochromator was 0.18 meV to receive only one component of the doublet. Curves *A* and *B* show the same features except for the intensity. These are both for the low energy luminescence component. The peak of $n=2$ is simple and broad. The doublet peaks of $n=3$ in Fig. 3(a) at 0 T change into triplet peaks with similar intensities, as shown in curve *B*. Curves *D* and *E* are for the high energy luminescence component. In curve *D*, the energy of the peak $n=2$ is a little higher than that in curve *B*, and $n=3$ peaks are considerably different from those in *B*.

It is emphasized that the peak energies in curve *B* are definitely different from those in curve *D*. Two vertical broken lines indicate the positions of the lowest and highest excitation peaks of $n=3$ as a guide for eyes. Curve *C* is a superposition of curves *B* and *D*. Both luminescence components were equally received at point *C*, with a slit width of 0.18 meV.

Figures 4(c) and 4(d) are for $B\|b$ at 1 T. Figure 4(d) shows the changes of excitation spectra. Curves *F*–*J* correspond to arrows in (c). In curve *G*, a single peak is observed for $n=2$ with a shoulder on the high energy tail, and doublet peaks are observed for $n \geqslant 3$ with a small satellite peak on the high energy side of each peak. In curve *I*, doublet peaks are observed for $n \geqslant 3$. Every peak, including $n=2$, has a small satellite peak on the low energy side. These satellite peaks have the same energies as the main peaks in curve *G*. Curve *H* is a weighted superposition of curves *G* and *I*. The halfwidth of the luminescence is ~ 0.1 meV. These satellite peaks are due to the mixing of the other luminescence component. The employed slit width of the monochromator 0.18 meV is, therefore, somewhat wider to receive only one component of the Zeeman-split luminescence.

It is concluded that two excitation peaks are associated with $n \geqslant 3$ for each luminescence component. Two verical broken lines indicate the positions of the lowest and highest excitation peaks of $n=3$ as a guide for eyes. Energies of main peaks in curve *G* are definitely different from those in curve *I*.

Figure 5(a) shows the excitation spectrum in Fig. 3(a) for $B\|c$ at 1 T around $n=3$ on an expanded scale. Symbols from *A* to *I* represent excitation energies for the 1s triplet exciton luminescence. The luminescence spectra excited at the points in (a) are shown in Fig. 5(b). The symbol is on the right edge of each curve. The slit width of the analyzing monochromator is ~ 0.1 meV. The low energy luminescence component is mainly observed when excited at *B*, and the high energy component is mainly excited at *H*. This result is complementary to those in Figs. 4(a) and 4(b).

Similarly, Fig. 5(c) shows a part of the excitation spectrum in Fig. 3(b) for $B\|b$ at 1 T around $n=3$. Changes of luminescence spectra by changing the exciting energies from *J* to *R* indicated in Fig. 5(c) are shown in Fig. 5(d). Only the low energy luminescence component is observed when excited at *K* and *O*, while the high energy luminescence component is excited at *M* and *Q*. This result should be compared with that in Figs. 4(c) and 4(d).

In order to make the difference clear, in Fig. 6 we show the results summarizing those in Figs. 4 and 5. The triplet exciton luminescence under the magnetic field 1 T for $B\|c$ is shown in Fig. 6(a). The luminescence line splits into two components *W* and *X* as shown in Fig. 2(a). Their excitation spectra are shown in Fig. 6(b). Two curves for the compo-

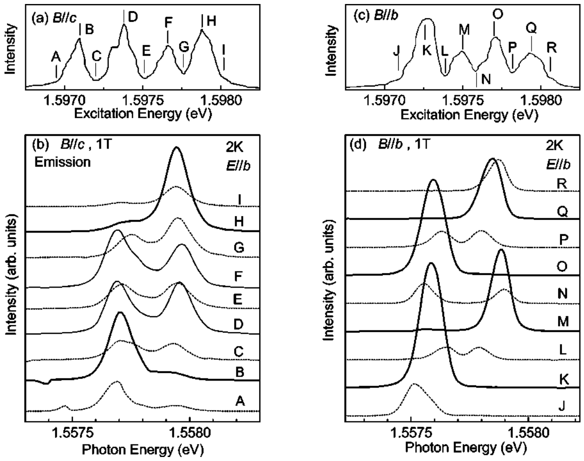

FIG. 5. (a) Excitation spectrum around $n=3$ for the $1s$ triplet exciton luminescence obtained with a wide slit width of ~ 1 meV under a magnetic field at 1 T for $B\|c$. (b) Change of the luminescence spectra with the change of the exciting energies on the $n=3$ excitation spectra at 1 T for $B\|c$. The symbol indicating the energy in (a) is shown on the right end of each curve. (c) Excitation spectrum around $n=3$ for the $1s$ triplet exciton luminescence obtained with a wide slit width of ~ 1 meV under a magnetic field at 1 T for $B\|b$. (d) Change of the luminescence spectra with the change of the exciting energies on the $n=3$ excitation spectra at 1 T for $B\|b$. The slit width of the analyzing monochromator is ~ 0.1 meV.

nents W (solid curve) and X (dotted curve) are clearly different. Such a difference in the excitation spectra for small energy separation (~ 0.2 meV) is found for the first time, to our knowledge.

For the member $n=2$, the lower (higher) Zeeman-split excitation component with solid (dotted) curve relaxes to the lower (higher) component of the $n=1$ triplet exciton luminescence W (X). Four or more excitation peaks for $n=3$ observed in Fig. 3(a) are classified into two groups, each of which has nearly equidistant three peaks. The lower (higher) group corresponds to component W (X). The excitation into the lowest peak of $n=3$ produces luminescence component W and the highest peak produces component X.

Similar results were obtained for the field $B\|b$ as shown in Figs. 6(c) and 6(d). Every excitation peak without a field splits into two components under the field. In the measurement the slit width was kept narrow enough to receive only one component of the luminescence, which reduces the satellite peaks appeared in Fig. 4(d). The lower (higher) Zeeman-split excitation component relaxes to the lower (higher) component of the $n=1$ triplet exciton luminescence Y (Z). The main difference from the case of $B\|c$ is that each group has two excitation peaks.

Relaxation processes from $n=3$ levels in the triplet exciton system into the $1s$ triplet sublevels under the magnetic field are schematically summarized in Fig. 7. Without a magnetic field, the excitons relax into the single luminescence peak of the $1s$ triplet exciton from any of the doublet states of $n=3$. Under a field 1 T with (a) a $B\|c$ configuration, excitation peaks are grouped into two sets, each of which consists of three peaks (triplets). The lower triplet peaks (solid curve) produce a lower Zeeman-split component W of the $1s$ triplet exciton luminescence, and the higher triplets (broken curve) produce a higher luminescence component X. Decay paths into components W and X are indicated by solid and broken arrows, respectively.

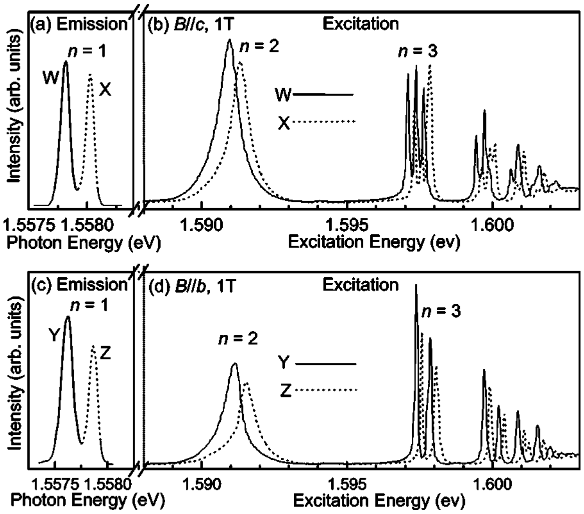

FIG. 6. (a) Luminescence spectrum of a Zeeman-split $1s$ triplet exciton under the interband excitation. The applied magnetic field is 1 T and $B\|c$. The splitting of the luminescence is about 0.2 meV. (b) Excitation spectra of the Zeeman-split components of the $1s$ triplet exciton luminescences W (solid curve) and X (dotted curve) at 2 K under the magnetic field $B\|c$. Note that the energy scales in (a) and (b) are different. (c) The luminescence spectrum of a Zeeman-split $1s$ triplet exciton under interband excitation. The applied magnetic field is 1 T, and $B\|b$. (d) Excitation spectra of the Zeeman-split components of the $1s$ triplet exciton luminescences Y (solid curve) and Z (dotted curve) at 2 K under the magnetic field $B\|b$. The slit width is kept narrow to receive only one component of the luminescence.

In Fig. 7(b), the case for the field $B\|b$ is shown. Each peak of $n=3$ in a zero field splits into two under the field.

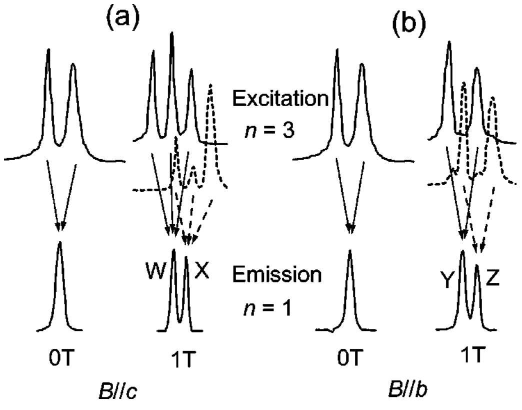

FIG. 7. Relaxation processes of an exciton from $n=3$ to 1 in the triplet exciton system without (left side) and with (right side) magnetic field (a) for $B\|c$ and (b) for $B\|b$. On the right side of each figure, solid (broken) arrows represent selective relaxation paths into the low (high) energy component of Zeeman-split $1s$ luminescence under the magnetic field 1 T.

The low (high) energy component at 0 T shows that the group is represented by a solid (broken) curve. The lower doublet peaks (solid curve) produce lower Zeeman-split component *Y* of the 1*s* triplet exciton luminescence, and the higher doublets (broken curve) produce higher luminescence component *Z*. Decay paths into components *Y* and *Z* are indicated by solid and broken arrows, respectively.

The splitting scheme in the $n=3$ levels under the magnetic field is qualitatively explained in terms of mixing of *d*-type envelope functions into an *s* envelope. Without a magnetic field, the mixing of *d*-type envelope function simply makes $n\geqslant 3$ level split into two. Under the field, however, the symmetry of the system is lowered and many *s-d* mixed states having the same representation contribute to optical transitions. The symmetry of the system under the field $B\|c$ (C_i) is lower than that for $B\|b$ (C_{2h}). Hence, for $n\geqslant 3$, we have more Zeeman-split components for $B\|c$ than for $B\|b$.

IV. DISCUSSION

As described above, the triplet excitons created in the excited states under the magnetic field relax through a definite path into one of the lowest exciton states, producing a Zeeman-split 1*s* triplet exciton luminescence component. Generally, the electron-phonon interaction is believed to be dominant in condensed matter. First we assume, therefore, that the relaxation path consists of multiple phonon scatterings. Resonant Raman scattering has not been observed in the triplet exciton system, partly due to the very small oscillator strengths of triplet excitons. Contributions of optical phonons are, therefore, not yet confirmed in the triplet exciton system.

The binding energy of the 1*s* triplet exciton is ~45 meV. Let ΔE_j be the energy difference from the *j*th excited level of the triplet exciton to $n=1$. Then the energy difference ΔE_2 from $n=2$ to 1, for example, is about 33 meV, and ΔE_3 from $n=3$ to 1 is about 40 meV. If the phonons participating in the relaxation processes are all acoustic ones, the number of related phonons will be significantly large.

In the process, of course, momentum and energy conservation laws should be obeyed. When the relaxation proceeds from the *j*th level and *m* phonons particitate in the process, conservation laws are

$$\sum_i^m \mathbf{k}_i = \sim 0, \tag{1}$$

$$\sum_i^m \hbar\omega_i = \Delta E_j, \tag{2}$$

where $\mathbf{k}_i$ and $\hbar\omega_i$ represent the wave vector and the energy of the *i*th phonon, respectively, and number *i* runs over all possible combinations of phonons in the Brillouin zone. Combinations depend on the electron-phonon coupling strengths. For one energy difference, the number *m* is not unique.

We have observed that the lowest triplet excitons are easily and efficiently converted into singlet excitons through multiple anti-Stokes scatterings with acoustic phonons.[10] In addition, the excitation spectrum for the triplet exciton luminescence *B* in Fig. 8(a) shows that singlet excitons are found to be converted into triplet excitons easily at a nearly constant rate over a wide energy range in the course of relaxation process.[8] Contrary to singlet excitons, triplet excitons are hardly converted into singlet as shown in Fig. 8(b).[8,10]

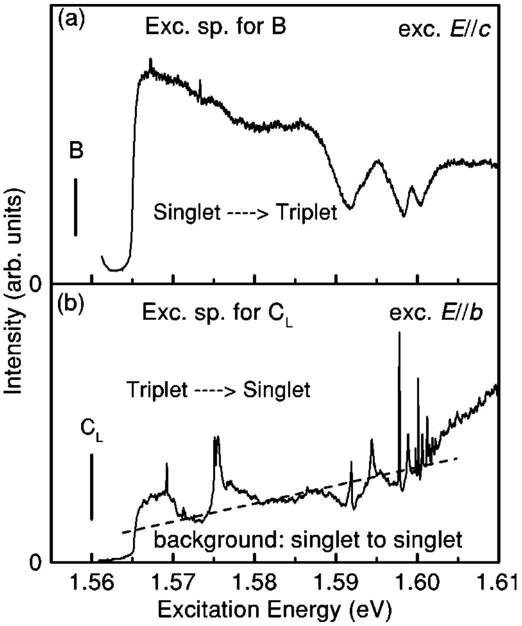

FIG. 8. Intersystem conversion between singlet and triplet excitons. (a) Excitation spectrum for 1*s* triplet exciton luminescence *B* excited with $E\|c$. Singlet excitons are easily converted into triplets on average over the wide energy range. (b) Excitation spectrum for 1*s* singlet exciton luminescence C_{L1} excited with $E\|b$. Triplet excitons are hardly converted into singlet excitons. The spectrum below the energy gap (~1.603 eV), roughly indicated by the dotted line, is mainly the background representing singlet-to-singlet conversion produced by the small strain in crystal (Ref. 8.)

The intersystem conversion from singlet to triplet excitons, or vice versa, is considered to occur through the magnitude of mixing of singlet state into triplet by spin-orbit interaction in the course of phonon scatterings. The results obtained in this work indicate that selective relaxation paths are definitely present in the excited states of the triplet exciton system, i.e., triplet excitons in excited states keep their spin states rather firmly during the relaxation process.

It is not easy to believe that triplet excitons in excited states relax efficiently to the lowest triplet state through multiple phonon scatterings, keeping their spin states and always satisfying the conservation laws [Eqs. (1) and (2)] written above. Under the field, furthermore, the number of relaxation paths increases considerably due to complex Zeeman splittings of exciton levels, and thereby every path, with a delicate energy change, should satisfy laws (1) and (2). Halfwidths of the excitation peaks in $n\geqslant 3$ are, in addition, very narrow, though excitons populated there are subject to scatterings by many phonons.

Here we propose another possibility of relaxation processes, i.e., relaxation through optical dipole transitions. These transitions proceed following the dipole selection rules, and thereby ambiguity associated with multiple phonon scatterings is avoided. In a hydrogenic system of exciton states, this type of transition should be, more or less, possible even in the solid state.

Naka and Nagasawa, in their two-photon excitation experiment for photoluminescence in Cu_2O, observed that the linewidth of the *s* exciton series in Cu_2O decreases with the increase of *n*.[18] They suggested that the lifetime of the excited *s* exciton states is mainly governed by the radiative damping.

Nikitine calculated the optical transition probabilities among exciton levels in Cu_2O by using an atomic model without phonon interactions, and predicted the possibility to observe some transitions.[19] He argued that some of the transitions, e.g., $(n,l \rightarrow n',l \pm 1,$ where *l* is the azimuthal quantum number) have rather large oscillator strengths. Recently, Göppert *et al.* reported infrared absorption spectra due to the excitonic transition from $1s$ to $2p$ exciton levels in Cu_2O by a pump-probe experiment.[20] It is considered that this absorption in Cu_2O can be observed owing to the long lifetime of the $1s$ paraexciton of 0.3 ms. Taking account of the phonon scatterings of excitons in the excited states, however, the result does not necessarily mean that the reverse process (emission) occurs with a perceptible intensity.

The present system is characterized by a very weak electron-phonon interaction. Furthermore, the spin-orbit interaction is also very weak. For the relaxation of *s*-type excitons by optical dipole transitions, the participation of *p*-type "triplet" excitons is indispensable as intermediate states. Information on the *p*-type triplet exciton, however, is not available at present. The singlet *p* series was confirmed by two-photon absorption,[15] as mentioned above. Figure 9 shows the optical dipole relaxation scheme in the triplet exciton system. Only a part of the energy levels of the triplet exciton system is schematically depicted. Only one level of the singlet *p* series is indicated for reference. The triplet *p* level will be present below the singlet level by the exchange energy. The symbol Δ in the figure represents the exchange energy in the multiplet. The arrows represent some of the optical dipole transitions, and these transitions produce "Lyman," "Balmer," etc. emission series in the infrared (IR) and far-IR regions. Thus created excitons in n'^3s's are, first, transferred to n^3p's and finally by transitions from n^3p's to the 1^3s level, which can produce triplet luminescence *B*.

The halfwidth of $n=2$ is extrordinarily wide compared with those of $n \geqslant 3$. Here the energy difference between the 2^3s and 2^3p states is not so large. In this connection, the peak energy of the $n=2$ triplet absorption and that of $n=2$ singlet luminescence are almost the same.[6] Hence the oscillator strength of the transition between them will be small, because the oscillator strength is proportional to the energy difference. Transitions between them are possible through the phonon scatterings, for example, by two phonon Raman processes or further higher processes. Many phonons and their combinations participate in the processes. This may explain the wide halfwidth of the $2s$ absorption band.

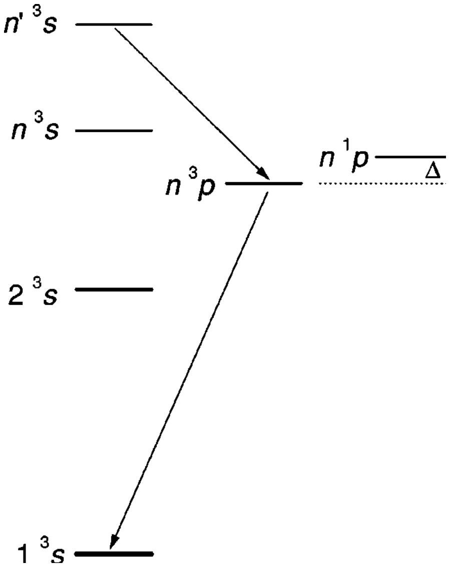

FIG. 9. A part of energy levels of the triplet exciton system is schematically depicted. The singlet *p* series was confirmed by two-photon absorption (Ref. 15). The symbol Δ represents the exchange energy in the np multiplet. Arrows represent some optical transitions.

This type of dipole relaxation is a competing process against the phonon scatterings. If the phonon scattering probability could be assumed to be far smaller than that of the dipole relaxation, the obtained results could be explained simply by the optical dipole model. The above assumption is fundamental for the processes being realized.

The observation of the infrared absorption from the $1s$ triplet exciton state into the levels $n \geqslant 2$ under laser irradiation into the $1s$ triplet absorption band seems to be effective. The lifetime of the $1s$ triplet exciton in β-ZnP_2 is, however, very short $(\sim 2$ ns$)$. Moreover, one of the LO phonons 32.2 meV (Ref. 5) near the energy ΔE_2 may cause a disturbance. A pump-probe method by short pulses might detect the absorption.

To our knowledge, nobody has ever found the luminescence associated with the optical dipole relaxation described above. However, direct observations of the IR "Lyman," "Balmer," or other series luminescence will be confirmatory evidence of this interpretation.

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[1] A. B. Pevtsov, S. A. Permogorov, A. V. Sel'kin, N. N. Syrbu, and A. G. Umanets, Fiz. Tekh. Poluprovodn. 16, 1399 (1982) [Sov. Phys. Semicond. **16**, 897 (1982)].

[2] N. N. Syrbu and V. M. Mamaev, Fiz. Tekh. Poluprovodn. **17**, 694 (1983) [Sov. Phys. Semicond. **17**, 433 (1983)].

[3] T. Goto, S. Taguchi, K. Cho, Y. Nagamune, S. Takeyama, and N. Miura, J. Phys. Soc. Jpn. **59**, 773 (1990), and references therein.

[4] D. Fröhlich, R. Kenklies, Ch. Uihlein, and C. Schwab, Phys. Rev. Lett. **43**, 1260 (1979).

[5] O. Arimoto, M. Sugisaki, K. Nakamura, K. Tanaka, and T. Suemoto, J. Phys. Soc. Jpn. **63**, 4249 (1994).

[6] M. Sugisaki, O. Arimoto, K. Nakamura, K. Tanaka, and T. Suemoto, J. Phys. Soc. Jpn. **65**, 3506 (1995).

[7] O. Arimoto, S. Okamoto, and K. Nakamura, J. Phys. Soc. Jpn. **59**, 3490 (1990).

[8] M. Sugisaki, O. Arimoto, and K. Nakamura, J. Phys. Soc. Jpn. **65**, 23 (1996).

[9] K. Nakamura, M. Shigoku, K. Kondo, and O. Arimoto, J. Phys. Soc. Jpn. **67**, 1890 (1998).

[10] K. Nakamura, M. Shigoku, K. Kondo, H. Nagasaki, and O. Arimoto, J. Phys. Soc. Jpn. **70**, 3001 (2001).

[11] O. Arimoto, D. Miki, K. Nakamura, M. Ashida, and K. Kan'no, J. Phys. Soc. Jpn. **68**, 2139 (1999).

[12] M. Sugisaki, O. Arimoto, and K. Nakamura, J. Phys. Soc. Jpn. **70**, 3134 (2001).

[13] M. Sugisaki, O. Arimoto, and K. Nakamura, Prog. Cryst. Growth Charact. **33**, 81 (1996).

[14] M. Sugisaki, O. Arimoto, and K. Nakamura, J. Lumin. **72-74**, 85 (1997).

[15] D. Fröhlich, M. Schlierkamp, J. Schubert, S. Spitzer, O. Arimoto, and K. Nakamura, Phys. Rev. B **49**, 10 337 (1994).

[16] J. Engbring, D. Fröhlich, R. Schepe, S. Spitzer, O. Arimoto, and K. Nakamura, Phys. Status Solidi B **196**, 461 (1996).

[17] K. Nakamura, K. Ohya, and O. Arimoto, J. Lumin. **94-95**, 393 (2001).

[18] N. Naka and N. Nagasawa, Solid State Commun. **116**, 417 (2000).

[19] S. Nikitine, J. Phys. Chem. Solids **45**, 949 (1984).

[20] M. Göppert, R. Becker, C. Maier, M. Jörger, A. Jolk, and C. Klingshirn, in *Proceedings of 2000 International Conference on Excitonic Processes in Condensed Matter, Osaka 2000*, edited by K. Cho and A. Matsui (World Scientific, Singapore, 2001), p. 47.