Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Dephasing and Relaxation Processes on the Stacking Fault Exciton in BiI_3 Under High Density Excitation

M. Ichiad [a b], T. Kawai [a b], T. Karasawa [a b] & T. Komatsu [a b]

[a] Department of Physics, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka, 558, Japan

[b] Department of Natural Science, Osaka Women's University, Daisen-cho, Sakai, 590, Japan

Version of record first published: 04 Oct 2006.

To cite this article: M. Ichiad , T. Kawai , T. Karasawa & T. Komatsu (1992): Dephasing and Relaxation Processes on the Stacking Fault Exciton in BiI_3 Under High Density Excitation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 218:1, 31-36

To link to this article: http://dx.doi.org/10.1080/10587259208047011

Mol. Cryst. Liq. Cryst. 1992, Vol. 218, pp. 31–36
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

DEPHASING AND RELAXATION PROCESSES ON THE STACKING FAULT EXCITON IN BiI_3 UNDER HIGH DENSITY EXCITATION

M.ICHIDA, T.KAWAI†, T.KARASAWA and T.KOMATSU
Department of Physics, Faculty of Science, Osaka City University,
Sumiyoshi-ku, Osaka 558, Japan
†Department of Natural Science, Osaka Women's University,
Daisen-cho, Sakai 590, Japan

Abstract An exciton confined at a two-dimensional stacking fault in BiI_3 crystal reveals large optical nonlinearity and ultra fast response for high density excitation. It shows three resonant luminescences whose decay-time constants are 20ps, 40ps and 900ps from the higher energy states reflecting cascade-type relaxation processes. By the degenerate four-wave mixing (DFWM) measurements, the dephasing times of three exciton states were obtained as 8.6ps, 15ps and 34ps. The dephasing at the lowest state is governed mainly by the LA-phonon intra-band scattering. While, at the higher states, it is governed by the cascade relaxation to the lower states in addition to the phonon scattering. It is found that the dephasing is also influenced by the exciton-exciton scattering under the high density excitation. A nonlinear transition involving a multi-photon process is observed in the excitation response of the DFWM signal. This result suggests the existance of the excitonic molecule.

INTRODUCTION

One of the recent attractive themes in molecular systems is to investigate nonlinear optical effects. Many specimens of organic and inorganic materials have been examined to reveal optical nonlinearity through the phenomena such as SHG, hole burning and photon echo. Using these effects, the elementary relaxation processes governing the efficiencies of the phenomena can be obtained.[1]

In this report, we provide the optical spectra including the nonlinear effects, which reflects the dephasing and relaxation processes in a characteristic molecular system at a quasi two-dimensional space in BiI_3. In this crystal, three sharp absorption lines named R, S and T from the higher energy side appear in the transparent energy region. The origin of these lines have been ascribed to the

localized excitons at a stacking fault plane produced during crystal growth.[2] We call them stacking fault excitons (SFE's). The SFE's have large oscillator strength reflecting the intra-molecular transition (Frenkel type exciton) and the localization to the low dimension. Resonance luminescences of SFE's show no stokes shifts, and their intensities become larger in order of R, S and T. The luminescence excitation indicates the efficient cascade type relaxation from R to S and from S to T.[3] For the high density excitation, the SFE spectra are seriously influenced due to the exciton-exciton interaction.[4]

EXPERIMENTAL PROCEDURE

Figure 1 shows the experimental set-up for the measurements of (a) the time behavior of luminescence and (b) the degenerate four-wave mixing (DFWM) signal. For the exciting laser, a dye laser (Rhodamine 6G ; Spectra-Physics:Model375B) pumped by a mode-locked Nd:YAG laser (Spectra-Physics:Model3800) was used. The pulse duration and the spectral width of the laser light were $\sim$ 3psec and $\sim$ 4meV in FWHM, respectively. A Streak Camera system (HAMAMATSU:C2909) with a CCD analyzer for the luminescence has the time resolution of $\sim$5ps by using deconvolution method. For the DFWM measurements, the exciting laser pulse which frequency was tuned into the excitonic resonance was divided to the two pulses, and focused on the sample. The self-diffraction signal $\vec{k}_3$ induced by the

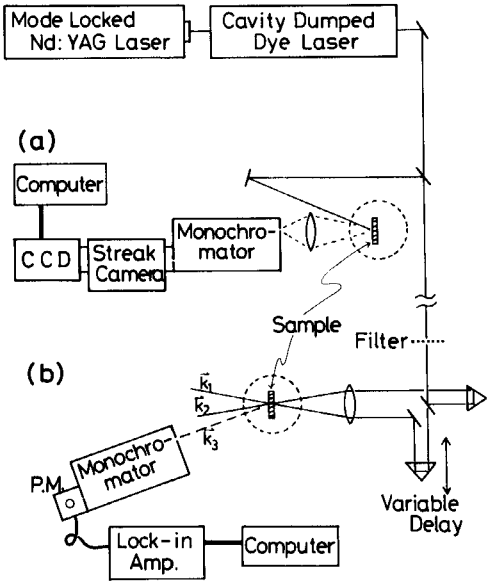

FIGURE 1 Experimental set-up (a) for the time-resolved luminescence measurements, and (b) for the degenerate-four-wave-mixing measurements in a forward configuration.

two exciting pulses $\vec{k_1}$ and $\vec{k_2}$, gives the dephasing time of the system concerned as a function of the relative delay τ between the two pulses.[5]

RESULTS and DISCUSSION

Time Resolved Luminescence

Figure 2 shows the streak image of the temporal behavior of SFE luminescence for the excitation with very weak intensity at 2.013eV above the R line. The integrated luminescence intensities becomes larger from R to S and S to T in order; the intensity ratios are R:S:T=1:30:1000. The luminescence decay-time constant becomes much longer in the same order of R, S and T with characteristic delayed rise. The phonon side band T_C appears at the lower energy side by 14meV from the T resonance with weak intensity reflecting weak exciton-phonon coupling.

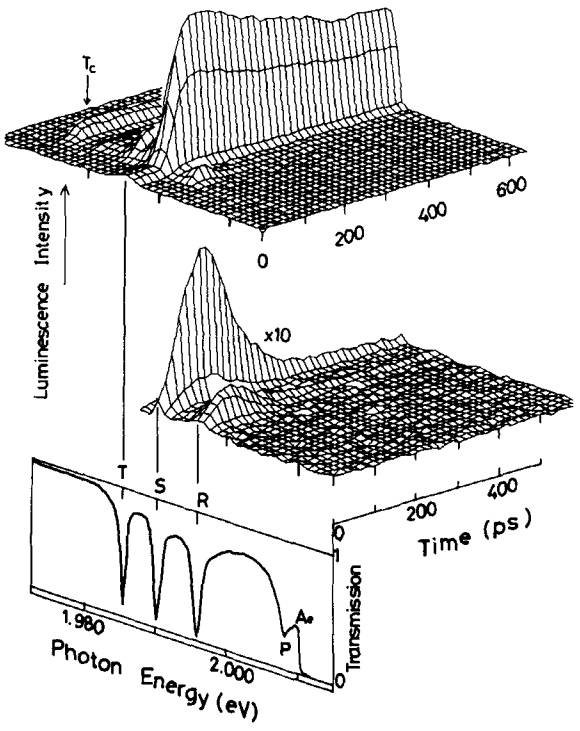

FIGURE 2 Time-resolved luminescence spectra of BiI_3 at 4.2K. The lowest one shows the transmittance spectrum of the SFE's.

Figure 3 shows the temporal behavior at each peak energy of the SFE luminescence. The rate equations including the cascade relaxation are written as

$$\frac{dn_i}{dt} = f_i(t) - \frac{1}{\tau^i} n_i, \qquad i = \text{R,S and T}, \tag{1}$$

where n_i is the population of i-th SFE state, $f_i(t)$ the source term, τ^i the total decay time of ith-state. Each source term and the decay time of SFE state can be written as,

$$
\begin{aligned}
f_R &: \text{laser profile} \\
f_S &= \xi^{RS} n_R \\
f_T &= \xi^{ST} n_S \\
1/\tau^R &= 1/\tau_r^R + \xi^{RS} \\
1/\tau^S &= 1/\tau_r^S + \xi^{ST} \\
1/\tau^T &= 1/\tau_r^T
\end{aligned}
$$

where ξ^{RS} and ξ^{ST} are the cascade relaxation rates from R to S and from S to T, and τ_r^i the radiative decay time. Open circles in the figure are the calculation from Eq.(1). The best fitting of the calculation yields decay time constants τ^i of 20ps, 40ps and 900ps for R, S and T, respectively. Because of the same oscillator strength of each SFE state, each radiative decay should have the same value as $\tau_r^R \sim \tau_r^S \sim \tau_r^T \sim$900ps, and then the cascade rate can be estimated as $1/\xi^{RS} \sim$20ps, $1/\xi^{ST} \sim$40ps.

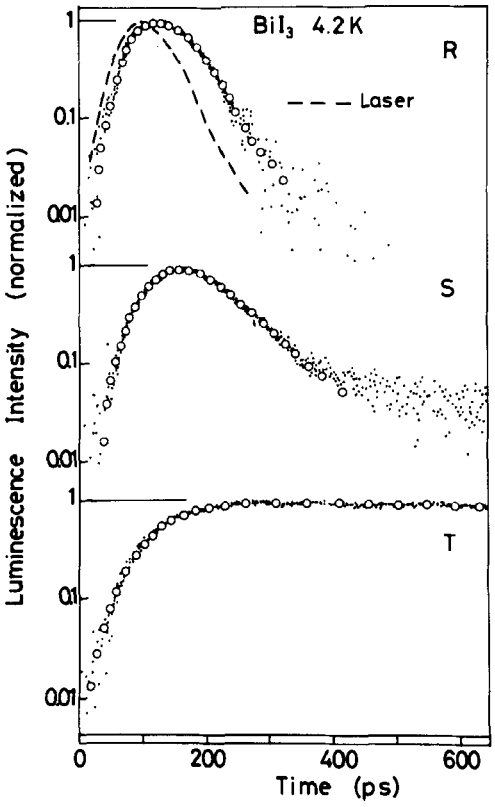

FIGURE 3 Decays of the SFE luminescences of the R, S and T lines at 4.2K in the normalized intensity. Open circles represent a fit to the data by Eq.(1). Broken line indicates the exciting laser.

Dephasing Time Measurements

Figure 4 shows the DFWM signal of SFE's as a function of delay time τ at 2K. The dephasing time T_2 is estimated by the relation $T_2 = 2\tau_d$ in the homogeneously broadened system, where τ_d is the signal decay time constant. From the observed value of τ_d , the dephasing times T_2 are estimated as 8.6ps, 13ps and

34ps for the R, S and T states, respectively, under the lower excitation intensity of I_0 /32; I_0 is the maximum excitation intensity, $\sim 10^5 W/cm^2$. The T_2 value of the T state is much shorter than the radiative decay constant τ_r^T , because the homogeneous width coming from the dephasing of the T line is governed by the LA-phonon intra-band scattering.[4] In the higher energy states, there appear additional dephasing components ξ^{RS} and ξ^{ST} corresponding to the cascade relaxation processes. Thus, the value of T_2 on each SFE can be understood qualitatively, although the quantitative discrepancy among the T_2 and the total decay time τ^i (i=R,S) exists. The dephasing T_2 of T drastically changes depending on the exciting laser intensity as shown in the figure; T_2 is 34ps for I_0 /32 and becomes 11ps for I_0 . This results can be explained that the dephasing is also influenced by the exciton-exciton scattering for the high density excitation. Then, the high density excitation effect is one of the origins of the time-constant discrepancy between T_2 and τ^i .

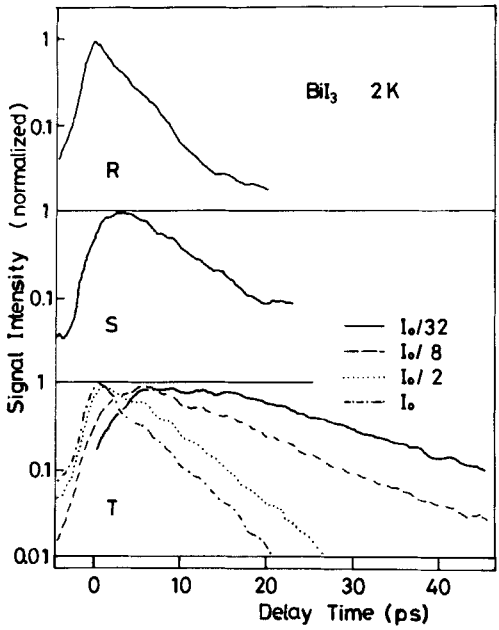

FIGURE 4 The time evolution of the DFWM signal of SFE's at 2K, and it's exciting-laser intensity dependences of T.

Figure 5 shows the spectral profiles of the DFWM signals. The spectrum at the T resonance has a hole due to the reabsorption of the T line. For the excitation below T, a clear response appears with a similar hole (M) at 1.981eV. The transmission in the same sample (upper spectrum) shows no linear transition in this region. The new response appears depending on sample in the same manner as the SFE lines. Then, the nonlinear response at 1.981eV is assigned to be due to the multi-photon process involving the SFE transition. One of the two-photon processes yields a bi-exciton state (excitonic molecule).

The excitonic molecule with the energy E_M has the two photon resonance at $E_M/2$. When we take the M hole as an $E_M/2$ resonance, the binding energy of the molecule $\sim$10meV is obtained on the assumption of the binding of the T excitons. This value is fairly large to make the excitonic molecule stable. The dephasing time of $\sim$6ps on the M state was obtained for the exciting laser intensity giving the T_2 of $\sim$12ps on the T state. This fact might reflect the existence of a stable excitonic molecule.

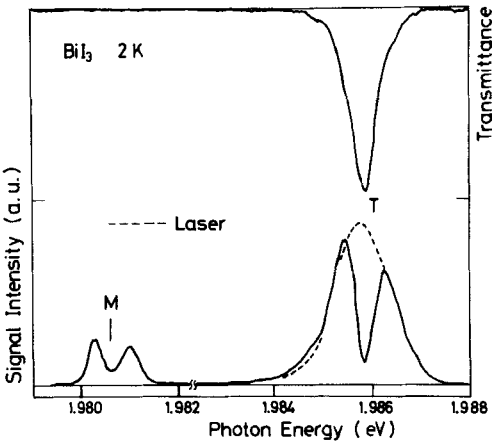

FIGURE 5 Spectra of the diffracted signal (lower) at 2K under the different two exciting laser frequencies of 1.986eV (right) and 1.981eV (left). The upper shows the transmission spectrum.

In summary, we have presented the relaxation mechanism of the quasi two-dimensional exciton system in BiI_3. A characteristic cascade type relaxation governs the temporal behavior of the luminescence and the dephasing in this multi-level system. A multi-photon transition in the DFWM process suggests the existence of an excitonic molecule state in this system.

This work was partially supported by a Grant-in-Aid for General Scientific Research from the Ministry of Education, Science and Culture, Japan.

REFERENCES

1. Y. R. Shen *The Principles of Nonlinear Optics* (Wiley-Interscience Publication, New York, 1984)
2. T. Komatsu, Y. Kaifu, S. Takeyama and N. Miura, Phys. Rev. Lett. **58**, 2259 (1987)
3. I. Akai, T. Karasawa, Y. Kaifu, A. Nakamura, M. Shimura and M. Hirai, J. Lumin. **42**, 357 (1989)
4. K. Watanabe, T. Karasawa, T. Komatsu and Y. Kaifu, J. Phys. Soc. Jpn **55**, 897 (1986)
5. T. Yajima, and Y. Taira, J. Phys. Soc. Jpn. **47**, 1620 (1979)