Relaxation of Excitons Perturbed by Self-Trapped Excitons in RbI: Evidence for Exciton Fusion in Inorganic Solids with Strong Electron-Phonon Coupling

Katsumi Tanimura and Noriaki Itoh

Department of Physics, Faculty of Science, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-01, Japan
(Received 31 July 1989)

We have measured the luminescence and optical-absorption change induced by optical excitation at the exciton band perturbed by a triplet self-trapped exciton (STE) in RbI. We have identified two channels of deexcitation of the exciton complexes thus generated, comprising an exciton and a STE: the transformation to an F-H pair with a yield of 0.04 and the transition to the singlet luminescent state of a STE with a yield of 0.38. These results are interpreted in terms of exciton fusion, either accompanied with specific lattice relaxation or due to Auger transitions.

PACS numbers: 71.35.+z, 78.55.Fv

Phenomena under dense electronic excitation in non-metals have been extensively investigated during recent years.[1-4] It has been shown that dense electronic excitation of nonmetals with weak electron-phonon coupling results in formation of an biexcitons and/or electron-hole plasma.[1-3,5] For solids with strong electron-phonon coupling in which excitons are self-trapped, dense electronic excitation results in effects specific to these solids, including a decrease of the self-trapped–exciton luminescence yield[6,7] and a superlinear increase of the defect production yield as the density of excitation is increased.[8-10] Since these observations have been made mainly by high-energy ion irradiation, the primary processes which results in these high-density effects remain unclear. Recently, the present authors have found that two-photon excitation of RbI at high density at liquid-helium temperatures produces F-H pairs (pairs comprising an F center and an H center) and a new luminescence band at 2.5 eV, and that the concentration of the F-H pairs and the intensity of the luminescence are in proportion to the square of the density of excitation.[11] These results suggest a mechanism involving interaction of two excitons in producing luminescence and F-H pairs.

Since the time required for self-trapping is short in solids with strong electron-phonon coupling,[12] pairing of free excitons (biexcitons) is not favored; instead collisions between free excitons (FE's) and self-trapped excitons (STE's) is considered to be the most probable channel of exciton interaction.[11,13] The microscopic mechanism of the FE-STE interaction, however, is not yet clear: whether a FE is relaxed near a STE to form a paired STE, or a FE approaches neighboring sites of a STE to form an exciton complex comprising an unrelaxed exciton and a STE. The optical-absorption band for formation of an exciton perturbed by a STE in alkali iodides has been found by Williams and Kalber,[14] indicating that the binding energy between a FE and a STE is 0.12 eV in RbI. Studies of the relaxation of the exciton complexes and the comparison of their results with the relaxation of densely generated excitons will give fur-

ther insight into exciton interaction processes.

Here we report an experimental study of the relaxation followed by optical excitation of the exciton band perturbed by a STE in RbI. We chose RbI as a model system, since the perturbed exciton band occurs at 5.61 eV, to which the 222-nm line of a KrCl-excimer laser falls almost exactly in resonance. We found two relaxation channels: formation of STE's in the singlet luminescent state with a quantum yield of 0.38 and generation of stable F-H pairs with a quantum yield of 0.04. The latter yield is higher by 10^3 than that of the F-H pair formation from an exciton. The results of the present investigation provide the first experimental observation of exciton fusion in solids with strong electron-phonon coupling, and can be a clue for understanding the effects of dense electronic excitation.

The specimens used in this study were obtained from a crystal block of pure RbI purchased from the University of Utah. A specimen with a size of $5 \times 8 \times 1$ mm^3 was attached to a cold finger of a cryostat and was placed in the optical path of an apparatus for measurements of optical absorption and of luminescence changes induced by irradiation with an electron pulse and a subsequent light pulse. Pulsed electron beams from a Febetron (HP43710A) were incident on an area of 1×3 mm^2 on a 5×8-mm^2 surface of the specimen for generation of STE's. For further excitation to generate a second exciton in the proximity of a STE, a light pulse from a KrCl-excimer laser (Lamda Physik EMG201MSC) was delivered to the opposite surface within the STE lifetime. Its fluence was less than 12.5 mJ/cm^2, below which luminescence and defect formation due to two-photon absorption were negligible. Time-resolved measurements were made of the resulting change in luminescence and optical absorption by use of detection systems consisting of mirrors, lenses, grating monochromators, and either photomultipliers or a multichannel detector with gates. The light source for optical-absorption measurements is a Xe flash lamp which generates a white light pulse having a duration of 0.9 μs at a given delay after an electron pulse. Details of the detection system have been de-

scribed elsewhere.[15] All measurements were carried out at 5 K.

Figure 1 shows the dependence of the luminescence intensities on time (t), measured at (a) 540 nm and (b) 305 nm, induced by sequential irradiation with an electron pulse at t_e and a 222-nm light pulse at t_l. The 540-nm luminescence monitors the π-luminescence intensity and hence the concentration of the STE's in the lowest triplet state. It is clear from the figure that the lowest triplet STE is partially destroyed upon photoexcitation at 222 nm. Since the optical absorption near 222 nm after irradiation with an electron pulse is exclusively due to the transition to create excitons perturbed by STE's,[14] we conclude that the reduction is due to generation of exciton complexes and subsequent nonradiative recombination. Thus the decrease ΔI_T of the π-luminescence intensity can be a measure of the concentration of the exciton complexes which are converted to states other than the lowest state of the STE.[16]

As seen in Fig. 1(b), luminescence is observed at 305 nm upon photoexcitation. The time response of the luminescence at 305 nm follows almost exactly the exciting light pulse; thus the lifetime of the luminescent state can be no more than a few nanoseconds. A study of the emission spectrum revealed that the band shape of the photogenerated luminescence is identical to that of the σ luminescence, which has been ascribed to the recombination luminescence from an excited singlet STE. We also found that the increase ΔI_S in the luminescence intensity at 305 nm induced by photoexcitation is proportional to

$-\Delta I_T$ and hence to the concentration of the exciton complexes, consistent with the interpretation that the excited singlet STE is a result of their relaxation. The results indicate that two excitons, an unrelaxed exciton and a STE, merge into an exciton. This is the first observation of exciton fusion in a strong electron-phonon coupling system, although exciton fusion is well known for weak-coupling organic crystals.[17]

We evaluated the quantum yield, i.e., the ratio of the number ΔN_S of the STE's in the singlet luminescent states relative to the number N of the exciton complexes, transformed to the states other than the lowest triplet state. The method is similar to that used previously[18] in evaluating the yield for excitation of the electron of a STE. The $\Delta N_S/N$ value obtained is 0.38.

We also measured the optical-absorption change induced by sequential irradiation, in order to examine possible conversion from the exciton complexes to F-H pairs. The results are shown in Fig. 2. In the figure, curve a shows the optical-absorption spectrum measured 5 μs after an electron pulse. This spectrum of absorption decays uniformly throughout with a time constant of 13 μs, which is identical to the lifetime of the lowest triplet STE; hence we identified it as the lowest triplet STE. Curve b in Fig. 2 is the spectrum measured after seventeen shots of electron pulses alone, while curve c is the spectrum measured after seventeen cycles of sequential irradiation of an electron pulse and a 222-nm light pulse delayed by 6 μs. In these measurements, each electron pulse (for b) or each pair of an electron and laser pulse (for c) was followed by a light pulse for optical-
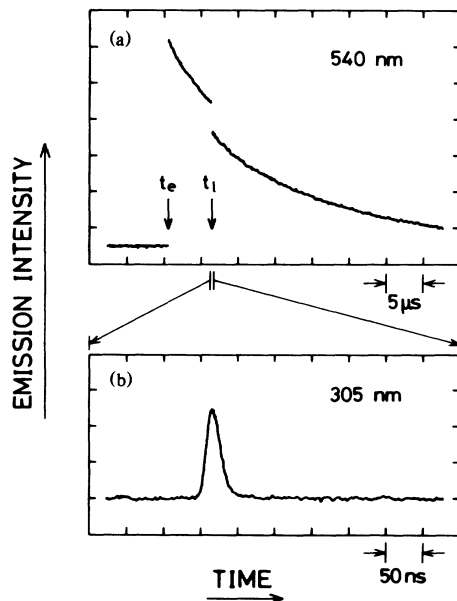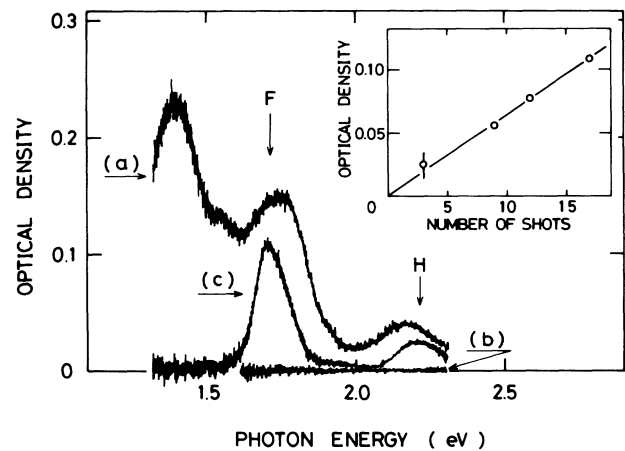

FIG. 1. The dependence of the luminescence intensities on time t, measured at (a) 540 nm and (b) 305 nm, induced by sequential irradiation at 5 K with an electron pulse at t_e and a 222-nm light pulse at t_l. Note that the abscissa in (b) is expanded.

FIG. 2. Optical-absorption spectra of RbI: curve a, induced by an electron pulse, measured 5 μs after irradiation; curve b, induced by seventeen shots of electron pulses; and curve c, seventeen cycles of sequential irradiation with an electron pulse and a 222-nm light pulse. The arrows show the peak energies of the F and H bands. Inset: The relation between the peak height or optical absorption at 726 nm (the F-band maximum) and the number of cycles of the sequential irradiation. Measurements were made at 5 K.

absorption measurements from a flash lamp with 10-s delay, and these combinations were repeated with an interval of 1 min. It is clear that no absorption band is produced by the irradiation with electron pulses only, when measured at 10 s after incidence of the electron pulses. Furthermore, no absorption band was detected after more than twenty shots of laser pulses alone. We found that only the sequential irradiation produces the F and H bands, whose peaks are shown by arrows. The inset of Fig. 2 shows the relation between the height of the F absorption band and the number of cycles of the sequential irradiation. The results show that stable Frenkel pairs are produced from exciton complexes in RbI at low temperatures, in which almost no stable F-H pair is produced by the single-exciton mechanism.[19]

By using Smakula's equation, we evaluated the conversion ratio $\Delta N_F/N$ to stable F centers to be 4.1×10^{-2}. The value is substantially larger than the absolute quantum yield 10^{-5}-10^{-6} of F-H pairs per electron-hole pair in RbI at liquid-helium temperature.[19,20] Since it has been shown that a transient F center is generated by excitation of the electron and hole of a STE in some alkali halides,[21] we measured carefully the time response of the optical-absorption change at the F-band maximum (726 nm), with a time resolution of a few ns, induced by a light pulse that follows an electron pulse within the STE lifetime. The change was only a stepwise decrease due to annihilation of STE's, and no transient increase of the optical absorption was detected in this time range.

By measuring changes in luminescence and in optical absorption arising by excitation of the exciton band perturbed by a STE, we found two relaxation channels of the exciton complexes comprising an unrelaxed exciton and a STE: one leading to generation of STE in the singlet excited state and the other to formation of stable F-H pairs. Since the fractions of the branching into these channels have been obtained to be 0.38 and 0.04, respectively, more than half of the complexes are annihilated by the third channel. Although the nature of the third channel has not been specified, we presume that it involves a nonradiative transition to the crystal ground state.

The relaxation of an exciton perturbed by a STE, which involves essentially two excitons, may involve fusion of two excitons or consecutive self-trapping of the unrelaxed exciton, resulting in a paired STE. Two types of fusion are plausible: One is the Auger transition, excitation of the STE by virtue of the exciton recombination or the Auger recombination of the STE,[22] and the other is deexcitation accompanying lattice relaxation, forming a new type of relaxed state.

It has been shown that electron-hole pairs or excited STE's in RbI are subjected to deexcitation predominantly to the σ-luminescent state and to the lowest triplet state of the STE, but not to the F-H pairs.[19,20,23] Thus we suggest that the deexcitation of an exciton perturbed by an STE to the initial state of the σ luminescence should arise from the fusion by Auger transitions. The absolute yields for branching to each of the channels from an electron-hole pair is known only approximately, 0.1 to the lowest triplet STE and 0.03 to the σ-luminescent state.[23] Thus the major fraction of the deexcitation channel of an electron-hole pair is the nonradiative decay directly to the crystal ground state. Therefore the transition of the exciton complexes to the ground state is considered to occur also after the fusion.

The exciton fusion accompanying lattice relaxation implies formation of relaxed configurations which are not formed from a single excitation event. The channel can occur if the electronic energy of the exciton is transferred not to the Auger process but to lattice deformation. Since the yield of F-H pairs from electron-hole pairs is extremely low, the relaxation of the exciton complex to a stable F-H pair falls in this category.

We considered that paired STE's emit luminescence in the same wavelength range as that for isolated STE's. The 2.5-eV luminescence has been observed previously[11] under dense electronic excitation by two-photon absorption of 308-nm laser light. We assign the luminescence band to the recombination of paired STE's. This luminescence band was not observed by excitation of the exciton band perturbed by a STE. We suggest that paired STE's are generated only by diffusion-limited collisions between STE and FE but not from an exciton perturbed by an STE, which can be regarded as a strongly interacting pair of a FE and a STE. We note the relatively high Auger transition yield of an exciton perturbed by a STE. Furthermore, the relaxation of the second exciton appears to involve the STE, resulting in the formation of an F-H pair rather than of a paired STE. On the other hand, when an FE approaches a STE, it appears that the FE feels a weak perturbation of another STE several lattice distances away and self-trapped. Formation of exciton-STE complexes by the diffusion-limited interaction is also likely to occur, in view of the results that dense electronic excitation by two-photon absorption leads to the formation of F-H pairs.[11]

The present experimental results are the first direct observation of the relaxation processes of an exciton complex comprising an unrelaxed exciton and a STE and present evidence for exciton fusion (to a F-H pair) involving relaxation and Auger transitions. Even though the mean free length of excitons differs from material to material, excitons perturbed by STE's may be formed above a certain excitation density in any insulators in which STE's are formed. Furthermore, the binary electron-hole diffusion[24,25] to a STE can be the cause of the formation of an exciton complex. Thus exciton interaction as described in the present paper is common in many solids: in heavy-ion tracks, where the density of excitation is extremely high and the exciton complexes may be generated without diffusion processes. As sug-

gested recently[26] the registration of energetic heavy-ion tracks in insulators may originate from the STE interactions or the STE-exciton interaction.

[1]C. Klingshirn and H. Haug, Phys. Rep. 70, 315 (1981).

[2]V. B. Timofeev, in *Excitons,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), Chap. 9, p. 349.

[3]J. B. Grun, B. Honerlage, and R. Levy, in *Excitons,* edited by E. I. Rashba and M. D. Sturge (North-Holland, Amsterdam, 1982), Chap. 11, p. 459.

[4]N. Itoh and T. Nakayama, Nucl. Instrum. Methods Phys. Res., Sect. B 13, 550 (1986).

[5]Y. Mitsushima, T. Kinoshita, K. Morita, and N. Itoh, Phys. Lett. 67A, 305 (1978).

[6]N. Matsunami, T. Ohwaki, N. Itoh, and Y. Horino, Nucl. Instrum. Methods Phys. Res. 194, 39 (1982).

[7]K. Kimura and M. Imamura, Phys. Lett. 67A, 159 (1978).

[8]M. Lung, P. E. Thompson, R. B. Murray, and D. J. Whittle, Radiat. Eff. 31, 89 (1977).

[9]D. L. Griscom, Proc. SPIE Int. Soc. Opt. Eng. 541, 38 (1985); M. R. Pacucci, J. J. Jutchinson, and L. W. Hobbs, Radiat. Eff. 74, 219 (1983).

[10]K. Tanimura and N. Itoh, Nucl. Instrum. Methods Phys. Res., Sect. B 32, 211 (1988); 33, 815 (1988).

[11]K. Tanimura and N. Itoh, Phys. Rev. Lett. 60, 2753 (1988).

[12]M. Ueta, H. Kanzaki, K. Kobayashi, Y. Toyozawa, and E. Hanamura, *Excitonic Processes in Solids* (Springer-Verlag, Berlin, 1986), Chap. 4.

[13]K. Tanimura, T. Eshita, and N. Itoh, J. Phys. Soc. Jpn. 53, 2145 (1984).

[14]R. T. Williams and M. N. Kabler, Solid State Commun. 10, 49 (1972).

[15]K. Tanimura, T. Katoh, and N. Itoh, Phys. Rev. B 40, 1282 (1989).

[16]An exciton perturbed by a STE may be deexcited to the lowest triplet state of a STE, although this fraction cannot be detected in the present experimental technique. If it occurs, the decay time should also be shorter than the width of a laser pulse.

[17]C. E. Swenberg and N. E. Geacintov, in *Organic Molecular Photophysics,* edited by J. B. Birks (Wiley, New York, 1973), p. 489.

[18]T. Yoshinari, H. Iwano, and M. Hirai, J. Phys. Soc. Jpn. 45, 1926 (1978).

[19]A. E. Hughes, D. Pooley, H. V. Rahman, and W. A. Runciman, Atomic Energy Research Establishment Report No. R5604, 1967 (unpublished).

[20]M. Ikezawa, K. Shirahata, and T. Kojima, Sci. Rep. Tohoku Univ. Ser. 1, L11, 45 (1969).

[21]R. T. Williams, Phys. Rev. Lett. 36, 529 (1976); see also N. Itoh, Adv. Phys. 31, 491 (1982).

[22]Two kinds of Auger transitions are plausible: (i) a recombination of STE and an excitation of FE and (ii) the recombination of FE and excitation of STE. The consequence of the relaxation for both cases may be similar to each other.

[23]D. Pooley and W. A. Runciman, J. Phys. C 3, 1815 (1970).

[24]H. B. Dietrich, A. E. Purdy, R. B. Murray, and R. T. Williams, Phys. Rev. B 8, 5894 (1973).

[25]E. D. Aluker, R. G. Deich, F. V. Pirogov, and S. A. Cherrov, Fiz. Tverd. Tela (Leningrad) 22, 3689 (1980) [Sov. Phys. Solid State 22, 2159 (1980)].

[26]N. Itoh, Radiat. Eff. Defects Solids 110, 19 (1989).