Magneto-optical study of the free-exciton luminescence in RbI

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Free-exciton luminescence (FEL) in RbI has been shown to exhibit a low-energy shift of the peak energy under an external magnetic field. The shift is in accord with the Zeeman shift of the lowest triplet-exciton level, providing evidence that the initial state of FEL in RbI is the triplet-exciton state.

Excitons in alkali halides have been a subject of extensive studies of solid-state spectroscopy. The studies have been devoted, on the one hand, to clarifying the electronic structure of these solids as typical direct-band-gap insulators, having high (O_h point-group) symmetry.[1-3] On the other hand, extensive studies have been carried out to clarify the properties of the self-trapped excitons (STE's) formed in alkali halides due to strong exciton-phonon interaction.[4-6] Formation of the STE and its coexistence with the free-exciton state[7-9] are unique features of excitons in this material, which have attracted much attention in view of the relaxation of the fundamental excitation in solids.

The relation between the two excitonic states, free and self-trapped, and the dynamics of the relaxation from free to self-trapped states have been studied experimentally by measuring the excitation spectrum of the luminescence due to radiative decay of STE's.[9-12] An important feature is that the STE luminescence due to the singlet STE's, the σ luminescence, is not emitted when the lowest ($n=1$) exciton is generated, while the luminescence due to the triplet STE's, the π luminescence, is emitted. It has also been shown that both emissions are produced efficiently when excitation is made to higher ($n \geq 2$) exciton bands lying near the band gap.

The relaxation of excitons includes two processes: the relaxation within the band (intraband relaxation) and the lattice relaxation. Although it is rather widely believed that the two processes are consecutive, it has been pointed out that they compete with each other in some cases.[13-16] In any case, the intraband relaxation of excitons plays an important role in the process of the relaxation of the singlet free-exciton state generated optically. The intraband relaxation of excitons has been studied extensively by Nishimura and colleagues.[9] They concluded that the optically generated excitons in the $n=1$ singlet state relax to the band bottom through phonon scattering while keeping their singlet spin state, and then they are subjected to self-trapping and radiative recombination. According to them, the free-exciton luminescence (FEL) due to radiative decay of free excitons is emitted from the singlet free excitons. On the other hand, Itoh[17] has shown that the peak of FEL in thin crystals of KI and RbI agrees with the peak of the triplet-exciton absorption, which is allowed by the internal stress included in the thin crystals.[18] Based on the results, he examined the relation between the crystal thickness and the peak energy of FEL, and suggested that the initial state of FEL in the bulk sample is emitted from the triplet state of the free exciton. Thus the identification of the initial state of FEL is still controversial, and the intraband relaxation of excitons in alkali halides is far from being well understood.

The electronic structure of the excitons in alkali halides has been studied thoroughly theoretically.[1,19,20] Recent three-photon spectroscopic studies have provided the detailed spectroscopic property of the excitonic states,[2,3] which is a fundamental basis for studies of the relaxation processes. In this Brief Report, we present experimental results of the external magnetic-field effects on the FEL in RbI at 1.2 K. The shift of the peak of FEL by applying a magnetic field is clearly observed, and found to follow exactly the Zeeman shift of the lowest level of the triplet exciton obtained by Beerwerth *et al.*[3] The results have revealed that the initial state for FEL in RbI is the triplet exciton.

Specimens with a size of $5\times10\times1$ mm^3, cleaved from a crystal block purchased from the University of Utah, were set inside of the sample chamber of a magneto-optical cryostat (Oxford, SM-4) capable of applying a magnetic field (B), of which the strength at the sample position was up to 6 T. The sample chamber was filled with liquid helium, and the temperature of the sample, which was controlled by evacuating the chamber, was measured by a Pt resistor. A $\langle 100 \rangle$ crystal axis of the specimen was oriented nearly (2° off) along the magnetic-field direction, and the specimen was excited by a monochromatic uv light propagating parallel to the magnetic-field direction. Luminescence was measured, under the Voigt configuration, by a grating monochromator (Jobin/Yvon, HR-320) and a multichannel detector (Prinston, IRY1024). A grating with 4960 grooves/mm was mainly used to achieve high spectral resolution. Wavelength correction of the detection system was made carefully by measuring several lines of a Hg lamp placed at the sample position.

Figure 1 compares the emission spectrum of FEL under $B=5.6$ T with that measured without a magnetic field. For the spectrum measured at zero magnetic field, the zero-phonon line (ZPL) is peaked at 5.7266 ± 0.0001 eV, and is associated with several phonon side bands. By applying a magnetic field of 5.6 T, the intensity of ZPL is enhanced by a factor of 2.7, although Fig. 1 compares the normalized spectral shapes. The peak energy of the ZPL

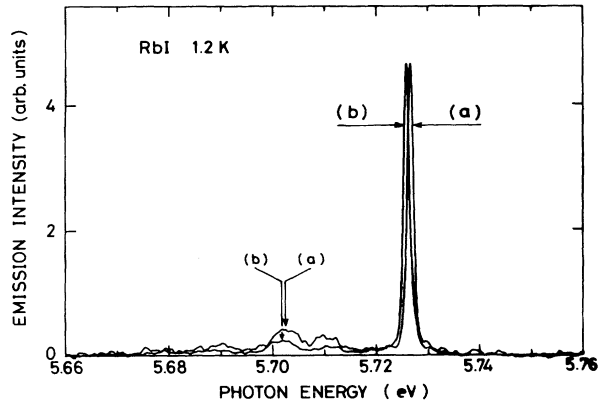

FIG. 1. Luminescence spectra observed in the edge region of the first ($n=1$) exciton absorption band at 1.2 K: curve (a) for without external magnetic field and curve (b) for under $B=5.6$ T. Each spectrum is normalized at the maximum. Excitation was made at 5.987 eV.

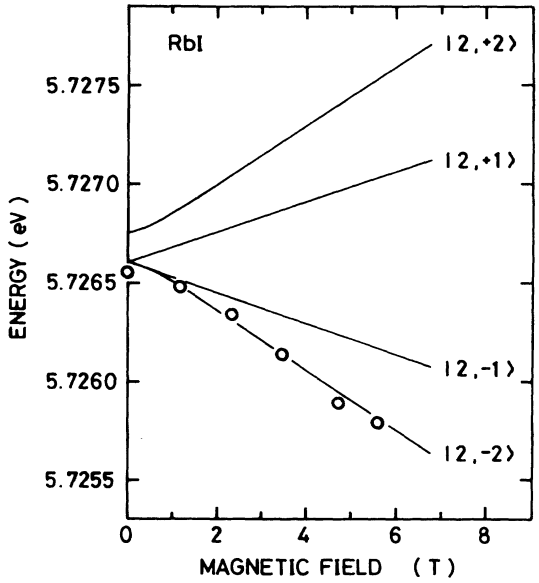

FIG. 2. The peak energy of the zero-phonon line of the free-exciton luminescence as a function of the external magnetic field at 1.2 K. Solid lines represent the Zeeman shifts of the triplet-exciton levels determined by the three-photon absorption study (Ref. 3).

of FEL measured at $B=5.6$ T is 5.7258 eV, showing clearly a low-energy shift. It is also seen that the peaks of the 2 LO-phonon side bands, separated by 22 meV from the ZPL's, also exhibit the low-energy shift by exactly the same amount as the ZPL's. The results substantiate that the energy level of the initial state of the FEL itself is shifted by applying the external magnetic field.

In Fig. 2, we plot the peak energy of the ZPL as a function of B. The solid curves in the figure display the Zeeman shift of the triplet-exciton levels determined by Beerwerth *et al.*[3] It is clear that the shift of the peak energy of the ZPL follows exactly the Zeeman shift of the lowest-energy level, $|2,-2\rangle$, of the triplet exciton. This result has proven that the initial state of FEL in RbI is the lowest-energy level of the triplet free exciton.

The peak energy of the ZPL of FEL obtained in the present study, which agrees well with the lowest triplet-exciton energy determined by three-photon spectroscopy, is a little lower than those reported previously.[8,16] The reason for the difference, besides some difficulties in correcting the wavelength of the detection systems, is found to be related to the difference in the temperature of the specimen. Changing the temperature from 1.2 to 4.2 K, we observed, together with an increase in its intensity, a significant high-energy shift of the ZPL; it moves from 5.7266 to 5.7272 eV, the latter of which is closer to the previously reported values. The temperature-dependent properties of the FEL are closely related to the polariton feature of the exciton as is planned to be discussed in a forthcoming paper.[21]

By excitation with photons of energies below the $n=2$ exciton transition, we could not detect any luminescence lines above the high-energy side other than ZPL. Therefore, the ZPL of FEL is the highest-energy luminescence. This fact, together with the conclusion that the ZPL is due to the radiative decay of the lowest-triplet exciton, indicates that singlet excitons produced by one-photon excitation relax exclusively to the lowest triplet exciton level without emitting any luminescence. Although the mechanism of this efficient spin-flip process is a subject of future studies, the result obtained in this study gives us a clear answer why the yield of the σ luminescence produced by 1*s*-exciton excitation is much lower than the yield of the π luminescence in most alkali halides.

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