Two-photon excitation spectra of exciton luminescence in CaF$_2$ obtained by using synchrotron radiation and laser

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Abstract

Excitonic states in CaF$_2$ are studied with luminescence-detected two-photon spectroscopy using synchrotron radiation and laser. The two-photon excitation spectrum for the luminescence due to self-trapped excitons (STEs) exhibits a clear peak on the high-energy side of the 1S exciton band. The peak is assigned to the 2P exciton state. The two-photon excitation spectrum for perturbed-STE luminescence is different from that for the STE luminescence, suggesting that localized excitons generated by SR are re-excited by the laser irradiation. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Two-photon spectroscopy (TPS) is an important technique in optical measurements for investigation of electronic structures in condensed matter because of the difference in the parity-selection rules between one- and two-photon absorption transitions. Since the transition probability of two-photon absorption is much lower than that of one-photon absorption, intense light from high-power lasers has been widely used for TPS. The restriction of laser wavelengths prevents TPS from being applied to wide-gap materials.

Synchrotron radiation (SR) is one of the most promising light sources since it provides continuous distribution of photons in a wide energy range from X-ray to infrared. The combination of the wide spectral range of SR and the high power of lasers must give us fruitful information on the electronic structures of many materials. We have measured the excitonic states of BaF$_2$ by using a time-gated photon counting method [1–3]. In the present study, we have extended SR-laser combined TPS to CaF$_2$, which has a band gap of about 12 eV.

2. Experiment

The single crystal of CaF$_2$ used here was grown at Oxford University. The SR light from UVSOR storage ring at the Institute for Molecular Science, Okazaki, was dispersed through a 1-m Seya-Namioka-type monochromator. The pulse duration of the SR light was about 1.6 ns. The second harmonic light of a Nd : YAG laser ($h\nu_{\text{laser}} = 2.33$ eV) was introduced in the direction opposite to that of the SR light. Its averaged power and duration were about 10 W and 800 ns, respectively.
luminescence arising from self-trapped excitons (STEs) or perturbed-STEs was monitored as TPS signal with a micro-channel plate photomultiplier tube (MCP-PM). The signal from the MCP-PM was fed to a three-channel time-gated photon counter [3]. The photon signals just before and after the incidence of the laser pulses were counted at channels 1 and 2, respectively. Channel 1 (CH1) counts the signal \( n_{\text{CH1}} \) induced only by the SR light, while CH2 counts the signal \( n_{\text{CH2}} \) due to the simultaneous irradiation with SR and laser. The difference \( n_{\text{CH2}} - n_{\text{CH1}} \) thus represents TPS signal. CH3 counts the signal \( n_{\text{CH3}} \) all the time for reference, so that the spectrum of \( n_{\text{CH3}} \) has the same shape as the one-photon excitation spectrum.

### 3. Results and discussion

Fig. 1 shows luminescence spectra measured at 15 K under the excitation with photons at 11.3 eV (solid line) and at 9.5 eV (broken line). The STE luminescence is observed at 4.4 eV. Another luminescence band appears at 3.8 eV under the excitation in the region below the 1S exciton band at 11.2 eV [5]. This band is attributed to STEs perturbed by some residual impurities or defects in the crystal. TPS spectra using SR and laser were measured through a monochromator at fixed wavelengths with narrow-band filters for eliminating scattered light from the laser. Two arrows in Fig. 1 indicate wavelengths at which the STE and perturbed-STE luminescence were monitored.

The solid line in Fig. 2 shows the TPS spectrum monitored through the STE luminescence at 15 K. The one-photon excitation spectrum for the STE luminescence is also drawn by a broken line for comparison. The energy of the 1S exciton peak is indicated by the arrow marked with \( E_{1S} \) [5]. Note that the abscess of the figure represents the photon energy of SR. The TPS spectrum shows a peak at 9.5 eV with a rise at around 8.3 eV. The one-photon excitation spectrum has negligible intensity in this energy region. We attribute the 9.5-eV peak to the two-photon absorption due to the 2P state of the \( \Gamma \) exciton because of a parity-selection rule. The 2P exciton energy (\( E_{2P} \)) is determined to be 11.8 eV (= 9.5 eV + \( \hbar \omega_{\text{lasem}} \)). A peak at 10.5 eV may be ascribed to some conduction-band state, the transition to which is forbidden in one-photon absorption but allowed in two-photon absorption. The TPS spectrum shows a rapid increase above \( E_{1S} \). This is likely due to photo-stimulated recombination of an electron with a self-trapped hole [6].

Assuming the simple hydrogen-like model, the exciton binding energy is expressed by \( \frac{4}{3}(E_{2P} - E_{1S}) \). We estimate the binding energy of the \( \Gamma \) exciton in CaF\(_2\) at 0.8 eV. This value is about 0.2 eV smaller than that obtained by Tomiki and Miyata [4]. The value was derived from the band-gap energy determined by an analysis of reflection spectra. On the other hand, the present result is based on the direct observation of the 2P exciton peak, which makes our value more reliable than the previous one.

In the 8–10 eV region, where the 2P exciton band was observed in the TPS spectrum, the perturbed-STE luminescence is dominantly excited as shown by the broken line in Fig. 1. The one-photon excitation spectrum for the perturbed-STE luminescence is drawn by a broken line in Fig. 3. This spectrum has a peak at 7.9 eV and a hump around 9.3 eV. The solid line in Fig. 3 shows the TPS spectrum monitored through the perturbed-STE luminescence. This spectrum has a broad band peaking at 9.3 eV, and rises rapidly above \( E_{1S} \) in the same manner as the TPS spectrum monitored through the STE luminescence.

The broad band at 9.3 eV in the TPS spectrum in Fig. 3 may possibly be attributed to the two-photon absorption associated with localized excitons, which will lead to the perturbed-STE luminescence. However, its spectral width is much larger than that of the 2P peak found in the TPS spectrum monitored through the STE.  

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**Fig. 1.** Luminescence spectra of CaF\(_2\) measured at 15 K under the excitation at 11.3 eV (solid line) and at 9.5 eV (broken line). No correction for the sensitivity of the detection system has been made.

**Fig. 2.** Two-photon excitation (solid line) and one-photon excitation (broken line) spectra of CaF\(_2\) monitored through the STE luminescence at 15 K. The low-energy part is magnified by 5.
luminescence. The existence of the hump at 9.3 eV in the one-photon excitation spectrum for the perturbed-STE luminescence suggests another possibility that this broad band is related to the localized excitons generated by SR, which are subsequently re-excited by the laser irradiation.

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