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Shape of the π -luminescence band in NaCl: adiabatic potential surface at the lowest state of the self-trapped exciton

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Abstract. The shape of the π -luminescence band due to the self-trapped excitons in NaCl has been measured in a temperature range between 4.2 and 80 K. It is found that the band shape deviates from a Gaussian shape, that the deviation is enhanced with increasing temperature and that the peak of the band shows a blue shift. The experimental results including the Stokes shift are analysed and explained satisfactorily using two-dimensional configuration coordinate potential surfaces having a first-order coupling with a hard mode and first- and second-order couplings with a soft mode. It is suggested that the soft mode is the translational mode of the halogen molecular ion, and hence the configuration of the lowest-triplet self-trapped exciton is of an off-centre type.

1. Introduction

Frenkel pairs or vacancy–interstitial pairs are generated as the result of electronic excitation [1–3] in a certain type of insulator, such as alkali halides, alkaline-earth fluorides and amorphous silicon dioxide. In such processes of defect formation, the self-trapping of the excitons is considered to play an essential role, localising the widely spread wavefunction of an exciton and triggering the displacement of an atom to an interstitial position. In spite of many experiments on the atomic structures of the self-trapped excitons and on the dynamics of defect formation in alkali halides, the mechanism of the conversion from a self-trapped exciton to a vacancy–interstitial pair is still controversial [4, 5].

It has been established that a self-trapped exciton in alkali halides consists of an electron and a self-trapped hole or (halogen)₂⁻ molecular ion. Two luminescence bands are emitted from the self-trapped exciton in NaCl: π - and σ -luminescence. The π -luminescence is known to be emitted from the lowest state of a self-trapped exciton with the electron in the 1s orbital, while the σ -luminescence is emitted from a higher excited state with the electron in the 2s orbital. From the photon energy of 3.3 eV for the π -luminescence and the energy of 7.96 eV for the first exciton peak, the S-factor (the Huang–Rhys factor) was evaluated to be about 50.

ENDOR studies in [6] have shown that the halogen molecular ion of the self-trapped excitons in KCl is off-centre at the lowest excited state. Recent theoretical calculations

in [7–9] show that the minimum of the total energy of the lowest state of a self-trapped exciton in KCl occurs at an off-centre position, possibly at the configuration of the closest pair of an F centre (an electron at the vacancy) and an H centre (a halogen molecular ion occupying a halogen site). Thus the defect pair, a distant pair of an F centre and an H centre, generated from a self-trapped exciton, is on the same adiabatic potential surface as the self-trapped exciton. In fact, anti-correlation has been observed between the yields of the π -luminescence for the F centre for several alkali halides [10–12], including NaCl. From the temperature dependence of the rate of the conversion from the self-trapped excitons to the F centres, it is pointed out that a potential barrier of about a few tens of millielectronvolts exists between the self-trapped exciton and the distant F–H pair [13].

In [7–9] it was also shown that the adiabatic potential surface against the translational motion near the off-centre potential minimum is remarkably soft compared with the characteristic lattice frequency. Such a peculiar character of the adiabatic potential surface should manifest itself in the following features of the luminescence spectra: the temperature dependences of the band shape, of the peak energy and of the half-width. No detailed measurement of these properties of the π -luminescence has yet been carried out.

The purpose of this paper is to report the detailed studies of the temperature dependence of the band shape of π -luminescence, including the band tail. By comparisons of the decay times and the changes induced by excitation of the self-trapped excitons with a laser pulse, we showed that the non-Gaussian tail is indeed due to the radiative recombination of the self-trapped excitons. We found a blue shift of the band peak and enhancement of the deviation from a Gaussian shape of the π -luminescence band with increasing temperature. The results were analysed in terms of the transition between two-dimensional adiabatic potential surfaces, which include a soft phonon mode with first-order and second-order couplings.

2. Experimental technique

A specimen of size 10 mm \times 5 mm \times 1 mm was cleaved from a single-crystal block of NaCl, obtained from Harshaw Chemical Co. The specimen was attached to a sample holder of a variable-temperature cryostat which had quartz windows. The temperature of the specimen was measured using a (Au–Fe)–chromel thermocouple attached to the sample holder.

The specimen was populated with self-trapped excitons by irradiation with an electron pulse generated with a Febetron accelerator. The luminescence spectrum induced by irradiation with an electron pulse was determined at several temperatures between 10 and 100 K either by using a multi-channel spectrum analyser or by measuring the decay curves at several wavelengths (point-to-point method). The spectrum response functions of the optical system were determined using a standard lamp (Eppley Laboratory EPI-1761) with an accuracy of 2%. The spectra obtained using the multi-channel analyser and the point-to-point method were the same within 2%. The effects of excitation of the self-trapped excitons on the π -luminescence was also measured. In this case the specimen in which the self-trapped excitons were generated using an electron pulse was bombarded further with a 308 nm excimer laser pulse within the lifetime of the self-trapped excitons, and the induced luminescence charge was measured.

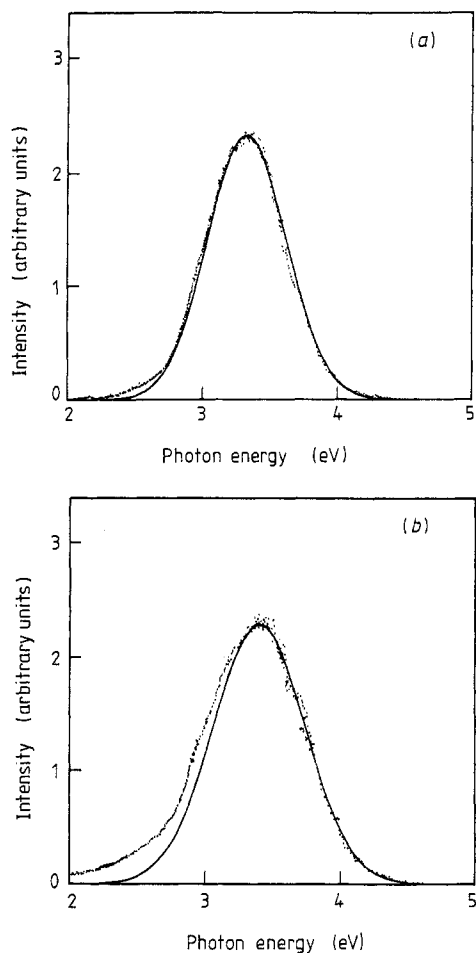


Figure 1. The luminescence spectra induced by irradiation with an electron pulse at (a) 10 K and (b) 80 K: ●, experimental results; —, Gaussian fits to the high-energy side of the experimental data.

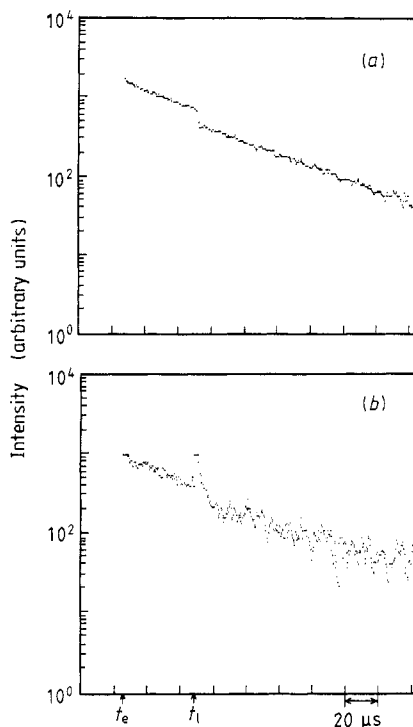


Figure 2. The time change of the luminescence at 80 K for (a) 3.26 eV and (b) 2.06 eV, induced by an electron pulse at t_e and by a subsequent laser pulse at t_l .

3. Experimental results

The luminescence spectra induced by irradiation of NaCl with an electron pulse and obtained at 10 K and 80 K are shown in figures 1(a) and 1(b), respectively. In the figure the full circles are the experimental results and the full curve is a Gaussian fit to the high-energy side of the experimental data. A deviation from a Gaussian shape is observed in the low-energy side of the spectra, more pronounced for the 80 K spectrum.

In order to prove that the tail extending to the low-energy side arises also from the radiative recombination of the self-trapped excitons, we measured the decay of the luminescence and its change induced by irradiation with a 308 nm laser pulse at several wavelengths. Typical results for the luminescence at 380 nm (the peak of the π -luminescence) and at 600 nm obtained at 80 K are shown in figure 2. In the figure an electron pulse is incident at t_e and a laser pulse at t_l . It is clear that the decay time constants of the

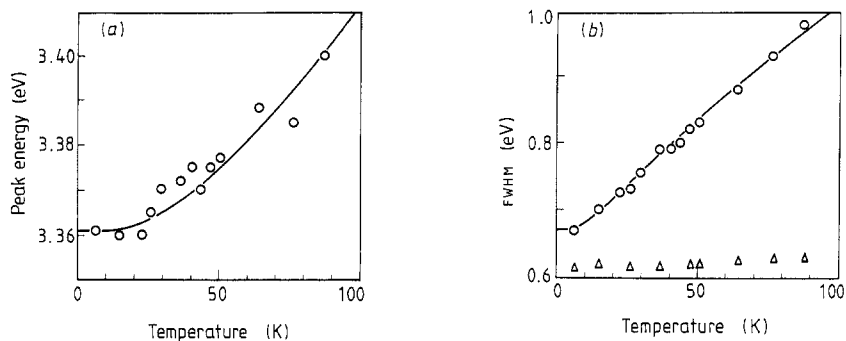


Figure 3. Temperature dependence of (a) the peak energy and (b) the FWHM of the π -luminescence (\circ). In (b) the FWHM of the σ -luminescence (\triangle) band is also shown. The results of the analysis (—) are also given.

luminescence measured at the two wavelengths are the same. Furthermore, the laser pulse reduces the luminescence intensity measured at the two wavelengths by the same fraction. Therefore it is clear that the tail is also due to the radiative recombination of the self-trapped excitons.

The results of the measurements of the luminescence spectra at several temperatures indicate that the deviation from a Gaussian shape is more pronounced; the width becomes broader and the peak shifts to higher energy as the temperature increases. Figures 3(a) and 3(b) show the temperature dependence of the peak energy and the full width at half-maximum (FWHM) of the π -luminescence band. In figure 3(b) triangles show the FWHM of the σ -luminescence band, for reference. We note in particular that the blue shift and the broadening of the π -luminescence band occur even at low temperatures. These results are in contrast with the constant FWHM of the σ -luminescence band, for which the peak energy was also found to be almost constant. The full curves in the figure are the results of the analysis described later.

4. Discussion

4.1. Analysis

From the experimental results described above, we give first several key points to establish a model for the analysis:

- (i) the persistence of the temperature dependence of the FWHM to very low temperatures which suggests a coupling with soft-phonon modes;
- (ii) the deviation of the π -luminescence band from a Gaussian shape, which suggests a second-order electron–lattice coupling;†
- (iii) a large Stokes shift of several electronvolts, which suggests first-order coupling with a hard mode.

The blue shift of the peak which takes place at low temperatures is also one of the key issues to be explained. From the arguments above, in order to explain experimental

† The deviation from a Gaussian shape may occur within the regime of first-order coupling if S does not exceed 10 but approaches a Gaussian shape if S is much larger [14]. Because of the large value of S , we consider that second-order coupling should be invoked.

results, we should assume that the lowest excited state of the self-trapped excitons in NaCl couples with at least two phonon modes: a soft mode and a hard mode. We assume further that a hard mode have a lattice characteristic frequency and interacts with lattice through the ordinal first-order electron–lattice coupling. This assumption is not crucial to the shape of the luminescence bands at low temperatures. Consequently we assumed that the second-order electron–lattice coupling takes place only with the soft mode, leaving the magnitudes of the first- and the second-order coupling with the soft mode and its phonon frequency as fitting parameters.

We analysed the experimental results in the following way. Consider the two-dimensional configuration coordinate space, Q_1 and Q_2 . We denote the adiabatic potential surfaces of the lowest triplet state and the ground state by W_e and W_g , respectively. W_e and W_g are given by

$$W_e = \omega_1^2(Q_1 - \Delta_1)^2/2 + \omega_{e2}^2(Q_2 - \Delta_2)^2/2 + E_0 \quad (1)$$

$$W_g = \omega_1^2 Q_1^2/2 + \omega_{g2}^2 Q_2^2/2 \quad (2)$$

where ω_1 and Δ_1 are the frequency and the displacement due to excitation, respectively, of the Q_1 mode, ω_{e2} and ω_{g2} are the frequencies at the lowest triplet state and at the ground state, respectively, of the Q_2 mode, and Δ_2 is the displacement by excitation of the Q_2 mode. We introduced the second-order electron–lattice coupling to the Q_2 mode by putting $\omega_{e2} \neq \omega_{g2}$. Using the Franck–Condon principle, the luminescence spectrum $I(E, T)$ for a photon energy E and at a temperature T is given by

$$I(E, T) = \iint dQ_1 dQ_2 P(Q_1, Q_2) \delta(W_e - W_g - E) \quad (3)$$

where $P(Q_1, Q_2)$ is the distribution function at the adiabatic potential surface of the lowest triplet state and is given by

$$P(Q_1, Q_2) = \sqrt{\alpha_1/\pi} \exp[-\alpha_1(Q_1 - \Delta_1)^2] \sqrt{\alpha_2/\pi} \exp[-\alpha_2(Q_2 - \Delta_2)^2]. \quad (4)$$

In equation (4),

$$\alpha_1 = (\omega_1/\hbar) \tanh(\hbar\omega_1/2kT) \quad (5)$$

$$\alpha_2 = (\omega_{e2}/\hbar) \tanh(\hbar\omega_{e2}/2kT).$$

Assuming that $\omega_{e2} \approx \omega_{g2}$, after a perturbation expansion of the integrand in equation (3) with a small parameter $1 - \omega_{e2}^2/\omega_{g2}^2$ and neglecting the higher-order terms, we obtained a Gaussian band

$$I(E, T) = (1/\sqrt{2\pi}D) \exp[-(E - E_p)^2/2D^2] \quad (6)$$

where E_p is the peak energy and is given by

$$E_p = E_0 - \omega_1^2 \Delta_1^2/2 - \omega_{g2}^2 \Delta_2^2/2 + (\omega_{g2}^2 - \omega_{e2}^2)[2(\omega_{g2}^2 \Delta_2)^2/\alpha_2 - (\omega_1^2 \Delta_1)^2/\alpha_1]/8\alpha_2 D^2. \quad (7)$$

In equation (7), D is the width of the band and is given by

$$2D^2 = (\omega_1^2 \Delta_1)^2/\alpha_1 + (\omega_{g2}^2 \Delta_2)^2/\alpha_2. \quad (8)$$

Using approximations (6), (7) and (8) as a guide, we obtained the best-fit parameters of the experimental luminescence spectra to equation (3) as follows:

$$\hbar\omega_{e2} = 2.2 \text{ meV} \quad \hbar\omega_{g2} = 7.9 \text{ meV} \quad \Delta_2 = 8.42/\sqrt{M}$$

where M represents the mass of Q_2 mode in atomic mass units. The full curves in

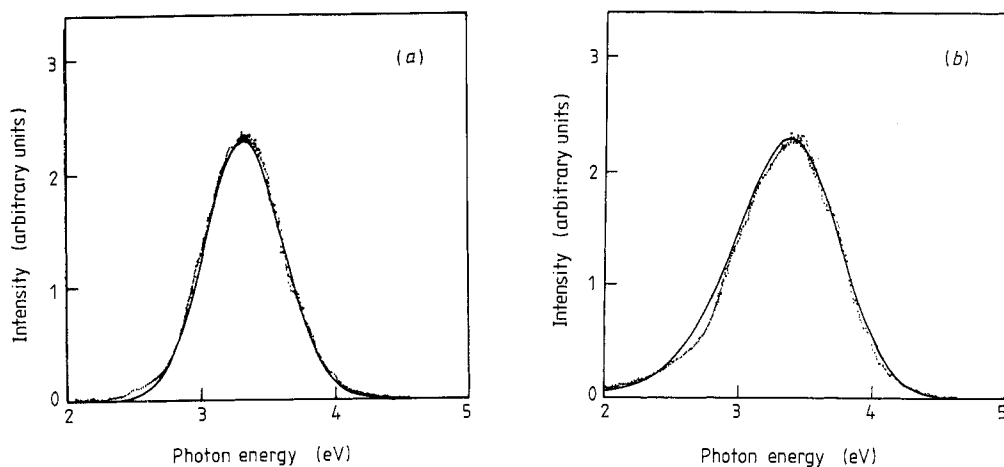


Figure 4. Comparisons of the experimental luminescence spectra (●), shown in figure 1, with the results of numerical calculation (—) for (a) 10 K and (b) 80 K.

figure 3 are the results of calculations with these parameters. Figure 4 compares the experimental results with the numerically calculated band shape (full curve). The deviation from a Gaussian shape is explained well.

4.2. Discussion on the configuration of the self-trapped exciton

In the analysis, we used two phonon modes: the Q_1 mode of the lattice characteristic frequency and the Q_2 mode of a low frequency and with second-order coupling. The stretching mode of the Cl_2^- molecular ion is known to make a large contribution to the Stokes shift and hence we assign the Q_1 mode to the stretching vibration. According to the calculation [15] of the local mode of the V_k centres in alkali halides, a few soft local modes are known to be associated with a V_k centre, including the translational motion (b_{3u}) and the rotational motion (b_{1g}) of the halogen molecular ion. It is more likely that the Q_2 mode having first and second-order couplings is the b_{3u} mode for the following reasons. In the first place, the first-order coupling should be accompanied by a mixing of the wavefunctions of higher electronic states. Since the p-like state (b_{3u}), which should mix for first-order coupling with the translational motion, is lower in energy than the d-like state (b_{3g}), which should mix for coupling with the rotational motion, linear coupling with translational motion is more likely to be induced. Secondly, even though the off-centring of the halogen molecular ion is known experimentally only for KCl, it has been shown theoretically that similar off-centring occurs in NaCl. Thus it is most likely that the Q_2 mode employed in the analysis represents the translational motion of the halogen molecular ion. Assuming that the mass of the Q_2 mode is twice the mass of a Cl atom, we obtained the off-centre distance to be 1.0 Å.

The present experimental results have shown unambiguously that the adiabatic potential surface of the lowest triplet self-trapped excitons show peculiar features. These features include coupling with a soft mode which induces not only a shift of the equilibrium position but also a difference in the phonon frequency in the ground and excited states. The self-trapped excitons in alkali halides are characterised by the formation of a molecular bond, leaving more open space for translational motion. It has

been suggested that the inherent instability of the on-centre self-trapped exciton arises from Coulomb repulsion [16] between the halogen molecular ion and the electron and from pseudo-Jahn–Teller interaction [7, 17]. This instability of the self-trapped exciton is considered to be responsible for the peculiar features of the adiabatic potential surface.

For σ -luminescence, no change in the width of the band was observed at low temperatures, indicating that there is no coupling with a soft mode. The σ -luminescence has been ascribed to the radiative recombination of the electron in the 2s orbital. No theoretical calculation has yet been made for the pseudo-Jahn–Teller coupling for the 2s orbital. We consider that the pseudo-Jahn–Teller interaction for the 2s orbital is weaker because of the larger radial spread of the wavefunction. It is also likely that the interaction with the low-lying $2p\sigma_u$ orbital tends to make the on-centre configuration stable.

The features of the adiabatic potential surface described above may be related to the defect formation from the self-trapped excitons. The small potential barrier to form a distant F–H pair from a self-trapped exciton is understood if the soft Q_2 mode represents the translational motion of the halogen molecular ion. Further studies on other alkali halides are in progress.

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