

Luminescence of the self-trapped exciton in KI under pressure

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(Received 15 April 1994)

This work reports the behavior of the luminescence bands of the self-trapped exciton (STE) in KI under hydrostatic pressure. The STE was created by populating the upper branches of the transverse exciton-polaritons using multiphoton excitation. The polariton can then scatter to the lower branches and relax to a “bottleneck” from which it will eventually become self-trapped. The σ and π bands of the STE experience different blue shifts under pressure and show significant changes in their intensity and bandwidth. A qualitative interpretation of the phenomena is given in terms of the nearest-neighbor F - H pair representation of the off-center STE configuration and how they are affected by the lattice compression.

I. INTRODUCTION

Perhaps in part due to the geometric appeal of the self-trapped exciton's (STE's) spatial structure, the luminescence in alkali halides has been a subject of ongoing discussion. For a thorough recent review of this subject, see the book by Song and Williams.¹ The process of self-trapping starts when the hole of an exciton strongly attracts the nearest-neighbor halogen ion to form a singly ionized molecule I_2^- embedded in the lattice. The excited electron can then be trapped by the Coulomb potential arising from the hole I_2^- and the surrounding cations. The luminescence of the STE is emitted when the electron and hole recombine.

In our experiment, we excite the $2p$ and $1s$ upper polariton branch with two- and three-photon absorption processes, respectively (the selection rules allow $1s$ and $2s$ excitation using one- and three-photon absorption and $2p$ excitation using two-photon absorption). Once an exciton-polariton is created, it will travel through the crystal until it is scattered by phonons to the lower polariton branch, trapped at impurities, or becomes directly self-trapped. Among these three possible decaying channels, the decay to the lower polariton branch through emission of phonons is believed to be the dominant process. On the lowest polariton branch, the polariton will continue to lose its kinetic energy through successive emission of phonons, until it reaches the so-called “bottleneck”² region. Further relaxation becomes increasingly difficult because of the much smaller density of final states. At this region, the polariton is more photon like and it can leave the crystal by becoming a photon. The luminescence emitted in this process is called the free-exciton (FE) luminescence and has an energy fairly close to the exciton energy. However, due to the relatively strong exciton-phonon coupling in alkali halides, the probability of free exciton emission is negligible compared to the possibility of the exciton getting trapped in a potential well of the self-induced local lattice distortion [the quantum efficiency of the FE luminescence in KI is estimated to be 0.0002 (Ref. 3)].

It has been believed for a long time^{4,5} that the STE is a V_k center (i.e., a self-trapped hole localized on two adjacent halide ions along the $[110]$ axis) plus an excited electron, where both are thought to remain on the same lattice site keeping D_{2h} symmetry (like a homonuclear diatomic molecule). This is the so-called “on-center” ($V_k + e$) model. Based on this model, two STE luminescence bands observed in most of the alkali halides were classified as σ and π luminescence, where σ and π luminescence were thought to be emitted from $2s$ singlet and $1s$ triplet orbitals, respectively. Many experimental data seemed to be explained successfully by this model.^{6,7} However, more recent experimental and theoretical results⁸⁻¹¹ indicate that the STE may not be represented by this simple on-center model. Leung, Brunet, and Song¹² have found that in the lowest state of the STE (π band), the “on-center” configuration is unstable against axial displacement of the V_k core, and in equilibrium, the STE occupies an off-center position, in between the two halide ions, of C_{2v} symmetry. The current understanding is summarized in Ref. 13 for RbI which has not two but three intrinsic STE luminescence bands. The authors of Ref. 13 propose that all luminescence bands σ , Ex , and π , originate from local minima on the same adiabatic potential surface (APS) depending on a single configuration coordinate along the $[110]$ direction (there are actually a pair of singlet and triplet surfaces about 10 meV apart and nearly parallel). According to the off-center model, the σ , Ex , and π bands are identified with on-center, somewhat off-center, and off-center configurations of STE, respectively. Kan'no, Tanaka, and Hayashi¹⁴ proposed a new classification of these luminescence bands as I, II, and III, in the order of increasing Stokes shift of the bands relative to the lowest exciton excitation energy.

Since types I, II, and III are associated with increasingly large off-center relaxation, the application of pressure should have an effect on the Stokes shifts of the luminescence bands as well as on the relative stability of the on- and off-center STE configurations. The recent work by Itoh, Hashimoto, and Ohno¹⁵ on NaBr and NaI has shown that lattice dilation favors the off-center relaxa-

tion. In this work we will present the effects of lattice compression on the STE luminescence and implications about relative stabilities of the relaxed structures.

II. EXPERIMENTAL ASPECTS

A serious weakness of one-photon absorption or excitation spectra seems to be that it is hard to correct for reflection losses. These are especially significant in the absorption region where the reflectivity is strongly dependent upon the excitation energy, i.e., most of the incoming light is reflected at the surface when near a resonance, instead of entering the crystal. Reflection losses are quite often neglected¹⁶⁻¹⁸ and can generate significant spectral shifts. However, this problem can be solved by the use of multiphoton excitation spectroscopy,¹⁹ where the reflection losses are small and essentially constant over the relevant range of excitation energies. This is because the individual photons forming a multiphoton excitation are far from resonant energies. Furthermore, in multiphoton excitation experiments, the relaxation process towards the STE luminescence is more clearly defined since only an exciton-polariton of specific k is initially populated. Also, the undesirable strain effects in thin crystals which must be used in the one-photon absorption measurements are avoided.

The experimental setup has been previously described in more detail.²⁰ The measurements were made on crystals from two different labs of Utah and Harshaw. A freshly cleaved crystal of size $4 \times 1.2 \times 1.2$ mm was mounted in a sapphire ball cell²¹ and connected to a two-stage pressure generator and mounted in a closed-cycle cryogenic refrigerator. Helium was used as the pressure medium because it ensured hydrostatic conditions for the sample. Our pressure range extended up to 8 kbar. The temperature throughout this work was 10 K. To obtain the three-photon excited luminescence spectra, the luminescence light was focused onto the entrance slit of a small computer-controlled double monochromator with a bandpass of 8 nm. The light was then collected by a photomultiplier tube. The stray light rejection ratio of the monochromator (about 10^{-9}) was not sufficient to suppress the pumplight completely. Therefore, color filters had to be inserted into the path of the luminescence light. The pump light was fixed at $\frac{1}{3}$ of the energy of the maximum of the exciton polariton resonance. The energy was kept constant at $20 \mu\text{J}$ for all scans with an estimated intensity of $1 \text{ GW}/\text{cm}^2$. At higher pressures, the pumplight wavelength was varied in accordance with the pressure-dependent excitation energy of the transverse polariton.

The two-photon excited luminescence measurements of the σ band were obtained near atmospheric pressure at 12 K. The technique is described in more detail in Ref. 22. The pumplight was fixed at the $\frac{1}{2}$ of the energy of the $2p$ polariton (6.192 eV) during the scan. Typical pulse energies were about $10 \mu\text{J}$ with an estimated intensity of $10 \text{ MW}/\text{cm}^2$. The π and Ex bands could not be measured using two-photon absorption because the pumplight energies were near the luminescence energies.

III. RESULTS

During the measurement the following signal intensity S is detected:

$$S(\lambda) = \int_{-\infty}^{+\infty} g(\lambda - \lambda') f(\lambda') I(\lambda') d\lambda' \quad (1)$$

with $g(\lambda - \lambda')$ representing the spectrometer response function, $I(\lambda')$ the intensity of the luminescence emitted by the sample, and $f(\lambda')$ the transmission of the filter. The spectral response curve of the photomultiplier tube (R212UH, Hamamatsu) is already neglected because it is quite flat in the region of interest. However, for a thorough investigation the measured spectra would have to be deconvoluted which does not seem to be done in the literature when dealing with the luminescence bands of alkali halides. Therefore, we only corrected for the transmission of the filters and then combined the spectra for the different wavelength ranges (250–375 nm for the measurements with the UG5 filter and 330–480 nm for the measurements with the BG12 filter) together. This was done in a way that the overlapping parts of the luminescence bands were made equal to each other by multiplying the longer-wavelength part with a constant factor so that the signal intensity for the common wavelength range was equal.

Figure 1 shows the luminescence spectra obtained in

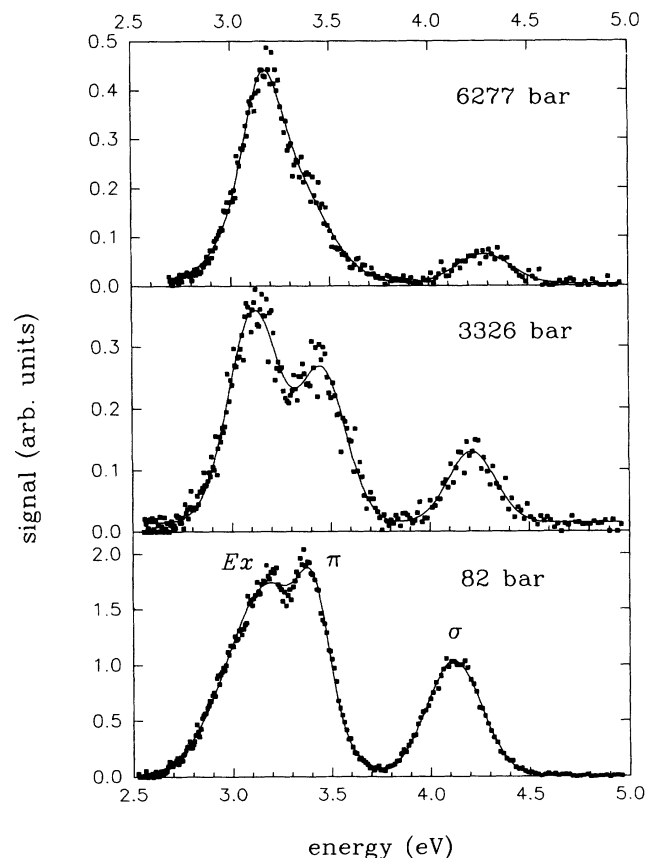


FIG. 1. Ex , π , and σ bands in KI (in order of increasing energy) for different pressures at 10 K. The solid line represents the nonlinear least-squares fit (sum of two Gaussians for the π and Ex bands).

this way for several different pressures at a temperature of 10 K. The highest-energy band is the singlet σ band (type I) and it has the smallest Stokes shift with respect to the $1s$ exciton excitation energy. The next two bands in the decreasing order of energy are the triplet π band (type II) and the Ex band. The Ex band of KI is generally regarded to be due to an extrinsic impurity that is emitted only when KI is excited with the energy close to the excitation energy of the $1s$ exciton.^{23,24} The sum of two Gaussians plus a constant background was fitted against the observed π and Ex bands and a single Gaussian was fitted against the σ band.

Figure 2 shows the pressure dependence of the peak position of all luminescence bands. The value for the pressure-dependent blue shift of the type-II π band is smaller than that of the type-I σ band as has also been found for the case of RbI.²⁵ The σ -band pressure shift of 28 meV/kbar is higher than the pressure blue shift of the first transverse exciton of KI which is 16.0 meV/kbar (Ref. 20) indicating a reduction of the very large Stokes shift which accompanies the STE formation and hinting at pressure-induced destabilization of the σ -STE. Figure 3 shows the bandwidth (FWHM) dependence on pressure. The σ bandwidth does not change significantly with pressure whereas the linewidth of the π band increases strongly with pressure (from about 0.17 eV at 80 bar to 0.28 eV near 8 kbar). The bandwidth of the Ex band decreases from 0.45 down to 0.21 eV in our full pressure range.

One of the characteristic features of our observations is the presence of the σ band at low pressures which is either not seen in one-photon excitation spectra until one reaches an excitation energy of 6.18 eV (Refs. 18 and 26) or seen only as a very weak band.¹⁶ (The strong increase in σ -luminescence intensity reported in Ref. 16 starts at

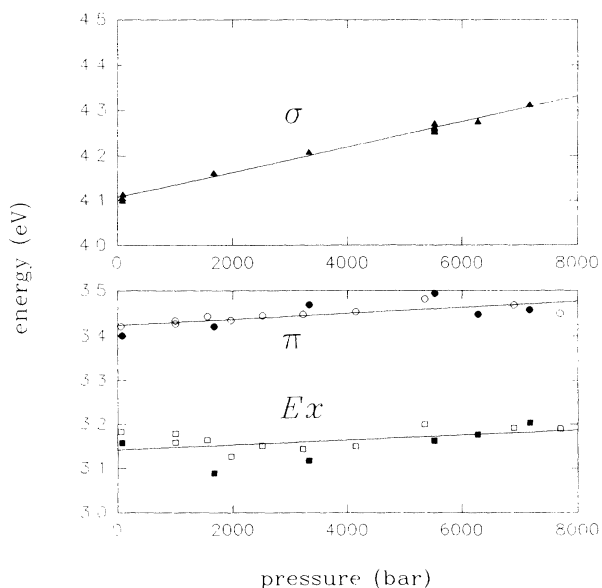


FIG. 2. Pressure shift of STE bands in KI at 10 K: triangles, σ band; circles, π band; squares, Ex band; solid symbols, Harshaw crystal; open symbols, Utah crystal.

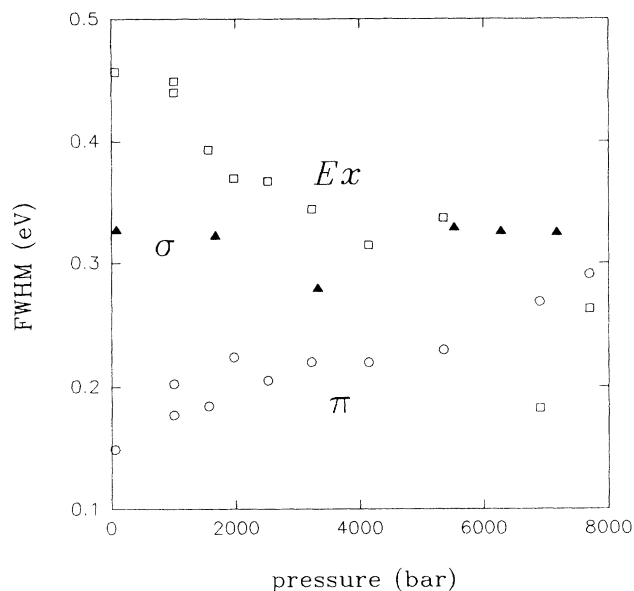


FIG. 3. Pressure-dependent bandwidth (FWHM) of STE bands in KI at 10 K: triangles, σ band; circles, π band; squares, Ex band; solid symbols, Harshaw crystal; open symbols, Utah crystal.

about the same excitation energy of 6.18 eV.) However, our three-photon excitation energy at 6.04 eV for the zero-pressure spectra is accompanied by a strong σ luminescence. The difference of photon momentum between one- and three-photon excitation must play a role. Also, the difference between near-surface and bulk excitation may be significant in populating the σ band.

Both σ - and π -band intensity are observed to decrease with increasing pressure. The luminescence intensity above 6 kbar was quite weak. The disappearance of the intrinsic bands at high pressures were observed for both Utah and Harshaw crystals. The only difference observed in the behavior of the two crystals was the intensity ratio between the intrinsic bands and the extrinsic band.

Table I contains the relations of energy and bandwidth with pressure. The Stokes shift values correspond to the energy difference between the $1s$ transverse exciton energy of 5.846 eV (Ref. 27) and the STE luminescence energy. We obtained the same energy and bandwidth for the σ -band from exciting the $2p$ polariton using two-photon absorption.

TABLE I. Three-photon excited STE luminescence energy and bandwidth versus pressure in KI. All uncertainties are threefold standard deviation as obtained by the fitting procedure.

Luminescence band	E (eV)	dE/dP (meV/kbar)	Stokes shift with respect to $E_T(1s)$ (eV)	FWHM (eV)
σ	4.11 ± 0.02	28 ± 3	1.74 ± 0.02	0.32 ± 0.06
π	3.42 ± 0.04	6 ± 3	2.43 ± 0.04	0.17 ± 0.05
Ex	3.14 ± 0.06	4 ± 6	2.71 ± 0.06	0.45 ± 0.1

IV. DISCUSSION

Kan'no, Tanaka, and Hayashi¹⁴ have shown empirically that the normalized Stokes shifts of the luminescence bands in different alkali halides decrease with the reduction of the lattice constant as one goes from one alkali halide to another. Their diagram of the normalized Stokes shift (with respect to the $1s$ exciton energy) versus the Rabin-Klick ratio S/D for 15 identified luminescence bands among the fcc alkali halides is redrawn in Fig. 4. The Stokes shift values are obtained from Ref. 1, and the ionic radii and the lattice spacings are obtained from Ref. 28, the atomic radii obtained from Ref. 29. S is the separation distance between two adjacent halide ions along the $[110]$ direction minus the halide-ion diameter (i.e., the "excess space" measured between hard spheres placed at the ion positions at ground-state equilibrium). D is the diameter of the halogen atom.

The theoretical analysis of the STE by Song and Chen³⁰ shows that the triplet STE (π band) has an equilibrium position shifted off center along the molecular axis of the V_k center. According to their description, a singly ionized tightly bound halogen molecule, I^0I^- , shifts away from the symmetric D_{2h} position, eventually creating an H center and a vacancy on the opposite side. The excited electron is then localized on the vacancy forming an F center. The off-center STE is thus equivalent to the nearest neighbor $F-H$ pair. Their re-

sults suggest that the Stokes shift of the π bands increases with increasing distance, d_{F-H} , of the $F-H$ pair. Although they do not obtain the Stokes shift as a function of S/D explicitly, it is expected that an alkali halide with a larger lattice spacing would support a larger d_{F-H} since, according to this model, the excited electron is attracted to the vacancy surrounded by the cations and not to the V_k center. Recently, it has been suspected that even the σ band, which was once thought to be "on center," is slightly off center having the reduced symmetry of C_{2v} .³¹

From this current view of the STE, there are three physical relaxation processes contributing to the Stokes shifts. First, there is a drop in the excited-state energy due to the asymmetric distortion of the cations as the electron moves to one side of the V_k center. Second, there is a further drop in the excited-state energy as the V_k center relaxes toward the off-center equilibrium configuration. Third, since the transition to the ground state from the off-center excited state must obey the Franck-Condon principle, the rising ground-state curvature at the off-center position would be responsible for the additional Stokes shift of the luminescence.

Our data were converted to plot the Stokes shift versus the Rabin-Klick ratio S/D . The lattice constant changes with pressure according to the expression

$$a = a_0 \exp \left[-\frac{P}{3B} \right], \quad (2)$$

where a_0 is the lattice constant at zero pressure, and B is the Bulk modulus. Using the definition, $S = a/\sqrt{2} - d$, the Rabin-Klick ratio is

$$S/D = \frac{1}{D} \left[\frac{a_0}{\sqrt{2}} \exp \left[-\frac{P}{3B} \right] - d \right], \quad (3)$$

where d is the halide ion diameter. Our STE luminescence data are plotted as a function of S/D ratio in Fig. 4. The S/D ratio is reduced from 0.33 to 0.29 corresponding to the pressure increase from 0 to 7.7 kbar (using $B = 130$ kbar, and assuming d and D to be independent of pressure). One can see that KI takes a somewhat special place on the diagram, because NaBr with the smaller S/D value of 0.27 at zero pressure does not support a type-II band, so that the continuous decrease of S/D should make the π band of KI disappear. Exerting hydrostatic pressure brings neighboring halide ions closer together (thus decreasing S/D). One can conclude that the observed gradual decrease of the π -band intensity with compression is caused by the decrease in S/D with pressure. The decrease in the intensity of the σ band might be tied to the fact that an increase in pressure could change the singlet character of the band into a triplet character since this is the case for NaBr and NaI (see also Fig. 4).

Both the σ and π bands in Fig. 4 are shown to follow the trend of decreasing normalized Stokes shift with decreasing S/D value which is expected from the off-center STE model. The difference in the rate of Stokes shift with pressure between the σ and π bands is probably due to the curvature of the ground state increasing with pres-

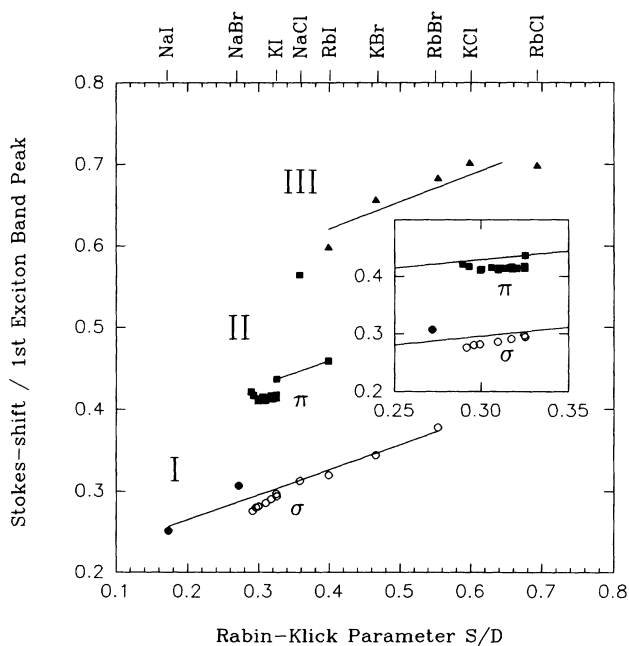


FIG. 4. Difference between the first exciton energy E_1 and the luminescence energy (Stokes shift) normalized with respect to $E_T(1s)$ plotted vs the distance between nearest-neighbor halide ions S scaled with the halogen atom diameter D (the so-called Rabin-Klick parameter). I, II, and III classify the luminescence bands. The solid symbol represents triplet, the open symbol singlet luminescence. In KI, I corresponds to the σ band and II to the π band. The Ex band is an impurity band and is not shown.

sure (i.e., dE/dQ at the transition Q increases with pressure, where Q is the configuration coordinate along the [110] direction), which should also increase the linewidth of the π band. This is consistent with our observation that the bandwidth for the σ band does not change greatly with pressure whereas the width of the π luminescence increases strongly with pressure.

V. CONCLUSION

We were able to use multiphoton spectroscopy to excite the luminescence bands in KI by populating the upper transverse polariton branch of the $1s$ and $2p$ polaritons. When applying hydrostatic pressure we observed a decrease in the intensity of the σ and π intrinsic bands. The reduction of the π -band intensity may be due to the instability of the type-II off-center STE configuration as the Rabin-Klick ratio S/D is reduced, and the reduction of the σ -band intensity may be due to the smaller S/D

favoring a triplet state over a singlet state. The σ band shows a decreasing Stokes shift with pressure while the π and the Ex bands have an increasing Stokes shift with pressure. The linewidth of the σ band is unchanged, while the linewidth of π band was found to increase and that of the Ex band was found to decrease with pressure. These observations, according to the off-center model of the STE, are a direct result of the axial shift of the V_k core along the [110] axis towards the on-center configuration in the excited state and the rising steeper potential surface of the ground state due to the reduction of the lattice spacing at high pressures.

ACKNOWLEDGMENTS

The authors would like to thank Dr. R. T. Williams for many helpful discussions. This work was partially supported by the National Science Foundation through Grant No. DMR 9208517.

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