

## Absorption Band Shape and Urbach's Rule of Localized Excitons\*

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(Received 29 July 1963)

An empirical description of the shape of optical absorption bands due to localized excitons in ionic crystals is proposed. The new formula links a nearly Gaussian description of the band near its maximum with an exponential description of the band on the low-energy tail (Urbach's rule). The applicability of the proposed shape formula over a range of  $4\frac{1}{2}$  orders of magnitude of absorption constants is demonstrated for localized excitons in KCl. The theoretical background which led to the proposed formula suggests that the existence of an exponential tail (Urbach's rule) is indicative of a predominantly quadratic interaction of certain lattice modes with the exciton formation.

### INTRODUCTION

IN ionic crystals, electronic transitions which are strongly coupled<sup>1</sup> to the lattice give rise to very broad absorption bands of half-width 0.1 to 1 eV in the range of photon energy of 1 to 10 eV. Especially in alkali halide crystals a large variety of these bands has been investigated. For the  $F$  centers in alkali halides<sup>2</sup> and the Tl ion in<sup>3</sup> KCl the shape and the half-width of the absorption or emission bands were studied at various temperatures. It was observed that in these cases a *Gaussian curve* fits the data rather well. The temperature variation of the half-width can be fit by a law:  $H^2(T) = H^2(0) \coth(\hbar\omega/2kT)$ , to the degree of accuracy and availability of data points in each case. These experimental results agree with the predictions of a simple model, the Franck-Condon model,<sup>4</sup> if one assumes in addition that thermal vibrations of the lattice surrounding the absorption center can be represented by an effective harmonic oscillator of frequency  $\omega_{\text{eff}}$ .<sup>4</sup> Assuming a strong *linear* coupling of the electronic transition to lattice displacements, the Franck-Condon model predicts—already in its simplest semiclassical version—the shape and temperature variation of the half-width which was found experimentally. So theory and experiment are in agreement if one limits, as is usual in these experiments, the determination of the band shape to values larger than 1% of the absorption maximum.

In contrast, measurements have been carried out far into the low-energy tail of the first exciton band of pure alkali halides. In<sup>5</sup> KI, an *exponential dependence* of the absorption constant on the photon energy (Urbach's rule) was observed over a range of seven orders of mag-

nitude of the absorption constant:  $K(h\nu) = K_0 \times \exp[-\sigma_0(h\nu_0 - h\nu)/kT]$  with three constants  $K_0$ ,  $\sigma_0$ , and  $h\nu_0$ . Similar results were obtained with<sup>6</sup> KCl and<sup>7</sup> KBr crystals and it was found that  $\sigma_0 = 0.80 \pm 0.02$  in all three cases. Assuming a strong *quadratic* coupling of the electronic transition to certain lattice displacements Toyozawa<sup>8</sup> derived theoretically Urbach's rule for these exciton bands.

A recent study of the optical characteristics of localized excitons in KCl single crystals<sup>9</sup> closed the gap between these two different experimental results. For an appropriately small concentration of iodine ions in KCl, a low-energy absorption band, due to the iodine ions, could be studied in great detail over a range of  $4\frac{1}{2}$  orders of magnitude in absorption constant, including the region of maximum absorption as well as an appreciable part of the low-energy tail. As reported previously,<sup>9</sup> the experimental results can be described by a Gaussian curve from the band maximum to about 3% of the maximum absorption. For smaller absorption constants on the low-energy tail the results can be fit well by Urbach's rule—that is, an exponential dependence of the absorption constant on photon energy.

This paper proposes a *single formula* covering both the range of absorption constants where a Gaussian shape has been found as well as the region of absorption constants where Urbach's rule has been verified. For the absorption of the  $I^-$  ion in KCl, a close fit of the data points by the proposed new shape function could be achieved over the total measured range of  $4\frac{1}{2}$  orders of magnitude of the absorption constant. In the following section, the shape formula will be presented and compared with the experimental results. The third section contains the theoretical background leading to the formulation of this general shape function.

### EMPIRICAL SHAPE CURVE

The proposed new shape curve is given by

$$K(h\nu) = K_0 \exp[-\sigma(h\nu_0 - h\nu)] \int_{\alpha}^{+\infty} \exp(-x^2) dx \quad (1)$$

\* Work supported by the U. S. Office of Naval Research and the Advanced Research Projects Agency.

<sup>1</sup> For a definition of the coupling parameter see, for example, R. H. Silsbee, Phys. Rev. **128**, 1726 (1962).

<sup>2</sup> G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956); R. V. Hesketh and E. E. Schneider, Phys. Rev. **95**, 837 (1954); R. W. Pohl, Proc. Roy. Soc. (London) **49** (extra part) 3 (1937); J. D. Konitzer and J. J. Markham, J. Chem. Phys. **32**, 843 (1960); F. Lüty and W. Gebhardt, Z. Physik **169**, 475 (1962).

<sup>3</sup> P. D. Johnson and F. J. Studer, Phys. Rev. **82**, 976 (1951); D. A. Patterson and C. C. Klick, Phys. Rev. **105**, 401 (1957).

<sup>4</sup> For a review see: C. C. Klick and J. H. Schulman in *Solid State Physics* edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5; D. L. Dexter, *ibid.*, Vol. 6; J. J. Markham, Rev. Mod. Phys. **31**, 956 (1959); D. L. Dexter, Suppl. Nuovo Cimento **7** (1958); M. Wagner, Z. Naturforsch. **15a**, 889 (1960); Z. Naturforsch. **16a**, 302 (1961).

<sup>5</sup> U. Haupt, Z. Physik **157**, 232 (1959).

<sup>6</sup> K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan **16**, 1417 (1961).

<sup>7</sup> W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).

<sup>8</sup> Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **22**, 455 (1959); **20**, 53 (1958); Suppl. **12**, 111 (1959).

<sup>9</sup> H. Mahr, Phys. Rev. **125**, 1510 (1962).

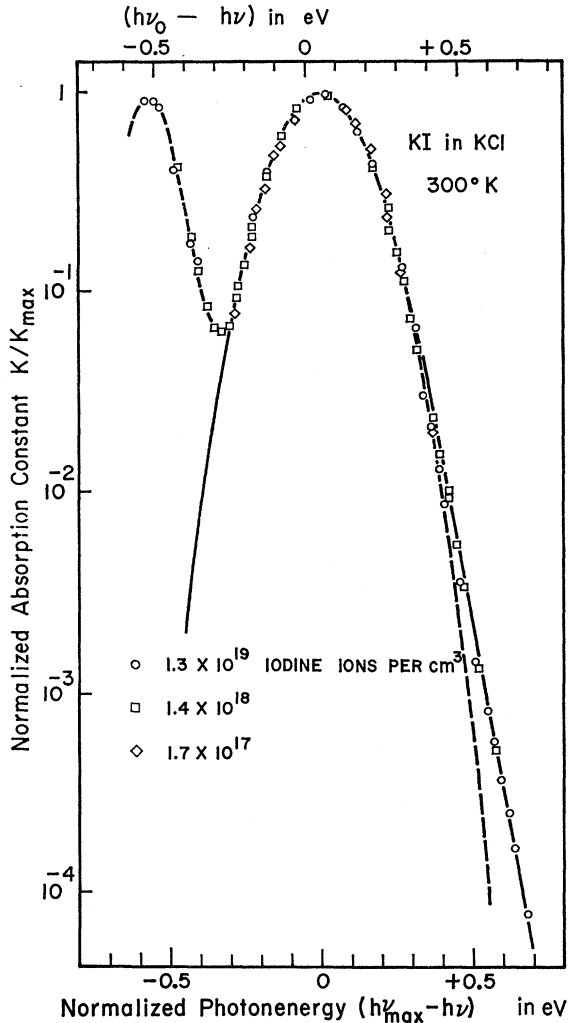


FIG. 1. Comparison of the results of absorption measurements obtained with localized excitons in KCl at 300°K with a proposed empirical shape curve (solid line) calculated from Eq. (1). The data, obtained from a variety of KCl crystals doped with different amounts of iodine ions, are plotted on a logarithmic scale of the relative absorption constant versus the normalized photon energy. The dashed curve represents an attempt to fit the data points by a Gaussian-shaped function [formula (3)].

with  $\alpha = -\{\tau(h\nu_0 - h\nu) - (\sigma/2\tau)\}$  and  $\sigma$  and  $\tau$  two constants which depend on the temperature. It will be shown first that Eq. (1) has a simple asymptotic behavior.

At the *low-energy absorption tail*, i.e., for  $h\nu < h\nu_0$ , Eq. (1) predicts an *exponential* dependence of the absorption constant on photon energy (Urbach's rule). In this case,  $(h\nu_0 - h\nu)$  is large and positive and, thus,  $\alpha$  large and negative. The error function integral  $\int_{-\text{large}}^{+\infty} e^{-x^2} dx$  is then a constant and Eq. (1) reduces to a purely exponential function of the photon energy. This property of Eq. (1) is asymptotic, that is, the smaller  $h\nu$ , the better it holds.

At the *high-energy side* and in the vicinity of the *band maximum*, Eq. (1) predicts an approximately *Gaussian*

shaped function. In this case,  $h\nu$  is larger than  $h\nu_0$  ( $h\nu_0$  is only approximately the position of the band maximum) and, therefore,  $\alpha$  large and positive. The integral of formula (1) can be approximated by:

$$\int_{+\alpha \text{ large}}^{+\infty} e^{-x^2} dx = \frac{e^{-\alpha^2}}{2\alpha} \left( 1 - \frac{1}{2\alpha^2} \pm \dots \right) \approx \frac{e^{-\alpha^2}}{2\alpha},$$

with increasing accuracy for increasing  $+\alpha$ . With  $-\alpha^2 = -\tau^2(h\nu_0 - h\nu)^2 + \sigma(h\nu_0 - h\nu) + \text{const}$ , we get approximately:  $K(h\nu) \sim \exp\{-\tau^2(h\nu_0 - h\nu)^2\}$ , a Gaussian-shaped function.

Equation (1) will now be compared with the experimental data of Ref. 9. Figure 1 reproduces the results of absorption measurements obtained at room temperature with localized excitons formed at iodine ions in KCl single crystals. The data points shown are taken from the results obtained with crystals of three different concentrations. Each single run consists of many measurements done with a great variety of sample thicknesses. All the data points were normalized and plotted versus the normalized photon energy  $(h\nu_{\text{max}} - h\nu)$  in Fig. 1. Low-photon energies are to the right. The dashed curve is an attempt to fit the results with a Gaussian curve:  $K(h\nu) = K_0 \exp\{-\tau^2(h\nu_0 - h\nu)^2\}$  of parameter  $\tau^2 = 29.7 \text{ eV}^{-1}$  over its entire range of  $4\frac{1}{2}$  orders of magnitude. Although this curve fits the measurements rather well in the vicinity of the band maximum, at low-absorption constants the agreement becomes increasingly poor. The solid curve is the best fit of the proposed new shape formula, Eq. (1), with  $\tau^2 = 32.6 \text{ eV}^{-1}$  and  $\sigma = 21$  for these room temperature data. The agreement is very close over the total range of measurements. The calculated solid line shows well both features of Eq. (1): A Gaussian shape around the band maximum and an exponential dependence of  $K$  on  $h\nu$  for low-photon energies.

The iodine absorption (Ref. 9) in KCl was also measured over a wide temperature range—from helium temperature to 700°K. *In all cases* it was found that the absorption constant was described well by an exponential dependence of the absorption constant on photon energy at the low-photon energy tail:  $K(h\nu) = K' \times \exp\{-\sigma(h\nu_0 - h\nu)\}$  (Urbach's rule) and by a Gaussian shaped curve:  $K(h\nu) = K_0 \exp\{-\tau^2(h\nu_0 - h\nu)^2\}$  in the vicinity of the band maximum. The characteristic parameters for these two regions,  $\sigma$  and  $\tau$ , were determined at all these temperatures and are given by (Ref. 9):

$$\tau^2 = (\tau_0^2/kT)F(\omega_1) \quad \text{and} \quad \sigma = (\sigma_0/kT)F(\omega_2)$$

where

$$F(\omega) = (2kT/\hbar\omega) \tanh(\hbar\omega/2kT). \quad (2)$$

We will now use the temperature dependence of  $\tau$  and  $\sigma$  of Eqs. (2) together with the proposed shape formula (1) and hold that this combination will fit the

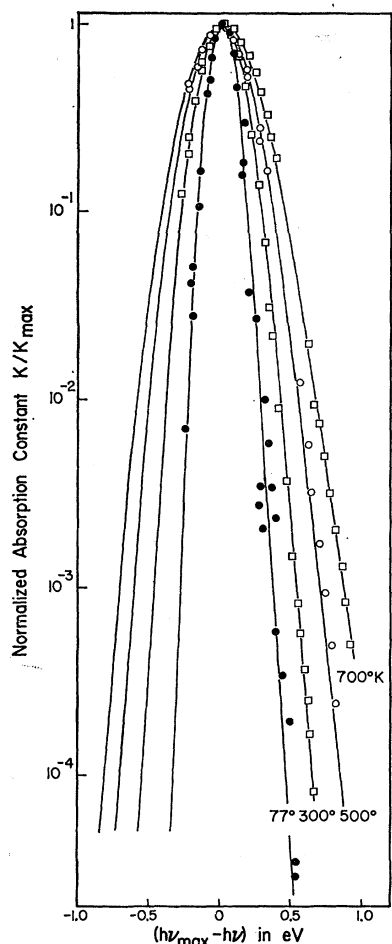


FIG. 2. Comparison of the whole set of normalized data obtained from absorption measurements of a localized exciton band in KCl over the temperature range from 77 to 700°K with the set of calculated shape curves obtained from Eqs. (1) and (2). The solid lines were calculated using the parameters  $\tau_0^2 = 0.87 \text{ eV}^{-1}$ ;  $\sigma_0 = 0.77$ ;  $\hbar\omega_1 = 16 \times 10^{-3} \text{ eV}$ ;  $\hbar\omega_2 = 60 \times 10^{-3} \text{ eV}$ .

experimental results of Ref. 9 over the entire range of measurements. Figure 2 shows the normalized experimental data for several temperatures. The solid lines are computed from Eq. (1), using Eqs. (2) with  $\tau_0^2 = 0.87 \text{ eV}^{-1}$ ;  $\sigma_0 = 0.77$ ;  $\hbar\omega_1 = 16 \times 10^{-3} \text{ eV}$ ;  $\hbar\omega_2 = 60 \times 10^{-3} \text{ eV}$ . The agreement is fair considering the fact that the whole set of calculations has been carried out by using a best fit to the room temperature data only (Fig. 1). From the two values of  $\sigma(300^\circ\text{K})$  and  $\tau^2(300^\circ\text{K})$  and the experimentally determined values of  $\hbar\omega_1$  and  $\hbar\omega_2$  (Ref. 9), the curves of Fig. 2 were thus calculated with no further adjustment.

Experimental determinations of the shape of broad optical absorption bands are mostly restricted to the region of the band maximum down to 1% of the maximum absorption. A conclusive test of the proposed shape formula in cases other than localized excitons in alkali halides would require experimental results taken far out into the tail of absorption bands. As mentioned earlier, such measurements have been performed with the low-energy exciton bands of several pure alkali halides. Two difficulties, theoretical and experimental in nature, are encountered. A mathematical expression for the absorption constant as a function of photon

energy  $h\nu$  is derived under the assumption that  $n$ , the index of refraction, is wavelength independent over the region of the absorption band.<sup>3</sup> This theoretical treatment is true for impurity absorption bands but certainly needs correction in the case of intrinsic exciton absorption bands, especially near the absorption peak.<sup>10</sup>

Experimental determinations of the band shape are difficult because of the very high intrinsic absorption. Various measurements have been reported,<sup>11</sup> using either thin films for transmission measurements or single crystals for reflectivity measurements. In neither case has an analysis of the measured shape of the band in terms of relevant mathematical expressions been attempted by the authors. Nevertheless, Urbach's rule has been demonstrated so impressively in the tail of exciton bands of pure KBr,<sup>7</sup> KCl,<sup>6</sup> and KI<sup>5</sup> over as much as seven orders of magnitude of the absorption constant, that we have been led to attempt to apply Eqs. (1) and (2) to Haupt's results<sup>5</sup> with excitons of pure KI. Lacking more precise knowledge, it was assumed that near the band maximum a Gaussian shaped curve would describe the experimental results best, and that a value of  $\tau_0^2 = 1.7 \text{ eV}^{-1}$  in Eqs. (2) would approximately agree with the measured half-width of the KI exciton band<sup>5,12</sup> in the temperature range of 200 to 900°K. In this temperature range  $F(\omega) = 1$ . The only parameter reliably known from the experiments is  $\sigma_0 = 0.82$ .

The comparison of the calculation with Fig. 6 of Ref. 5 was made in the following way. Normalized absorption curves of Eq. (1) were calculated for various temperatures, using Eqs. (2) with  $\tau_0^2 = 1.7 \text{ eV}^{-1}$  and  $\sigma_0 = 0.82$ . An attempt was then made to copy the temperature shift of position and height of the experimental results of Fig. 6, Ref. 5 [reproduced as Fig. 3(a) in this text]. The result is given by Fig. 3(b). Agreement could not be achieved around the band maximum; especially at low temperatures the calculated band maximum lies to higher photon energies.

#### RELATION TO THEORETICAL MODELS

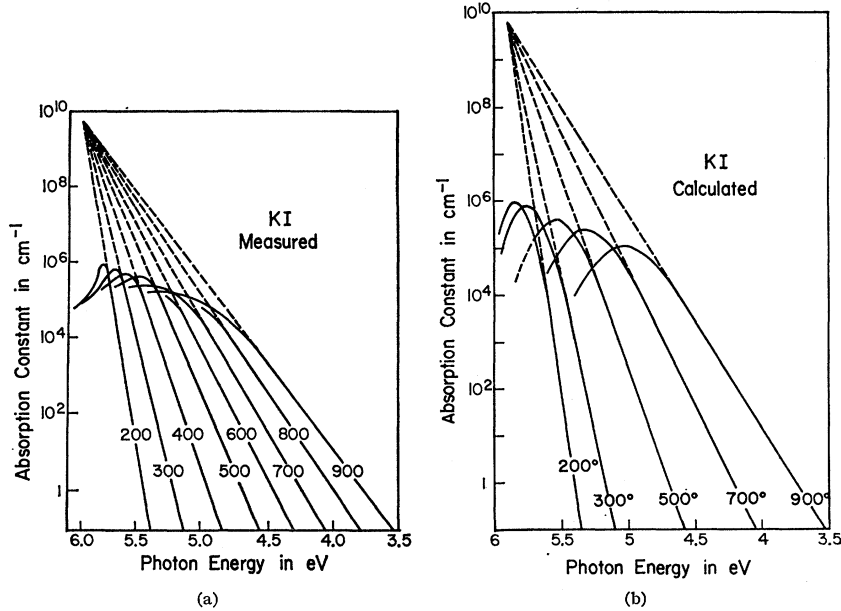
Various theoretical models<sup>4,8,10</sup> have been proposed to calculate the shape of broad absorption bands for an electronic dipole transition between ground and excited state at an absorption center in a real, vibrating ionic lattice. In all models proposed for ionic crystals, the energy difference  $\Delta E$  between ground and excited state is assumed to be strongly dependent on the instantaneous position of the ions surrounding the absorption center and is therefore critically affected by lattice vibrations and displacements of ions.

<sup>10</sup> For a discussion see: J. J. Hopfield, *Phys. Rev.* **112**, 1555 (1958); D. L. Dexter, *Phys. Rev.* **101**, 52 (1956); S. I. Pekar, *J. Phys. Chem. Solids* **5**, 11 (1958).

<sup>11</sup> For a review see James H. Schulman and W. Dale Compton in *International Series of Monographs on Solid State Physics*, edited by R. Smoluchowski and N. Kurti (The Macmillan Company, New York, 1962), Vol. 2.

<sup>12</sup> W. Martienssen, *J. Phys. Chem. Solids* **2**, 257 (1957).

FIG. 3. Comparison of the results obtained with the low-energy exciton band of pure KI with calculated shape curves using the proposed empirical formula (1). Figure 3(a) reproduces the experimental results of Fig. 6 of Ref. 5. The solid lines of Fig. 3(b) are calculated from Eqs. (1) and (2) using  $\tau_0^2=1.7$  eV<sup>-1</sup> and  $\sigma_0=0.82$ . Position and height of the calculated curves have been adjusted to give a best fit to the measured tail portions (Urbach's rule) of the KI exciton band.



Toyozawa<sup>8</sup> has recently analyzed the problem of Urbach's rule in connection with published experimental results of the shape of the first excitation band in pure alkali halides.<sup>5-7</sup> He assumed that the different mathematical description of the absorption curve around the band maximum and in the tail part of the first excitation band can be explained by an interaction of the electronic transition with two different types of lattice modes. Contributions to the absorption constant around the band maximum arise from those lattice modes  $Q_i$  which generate a *linear* dependence of the energy difference  $\Delta E$  on the ionic displacements of this mode:  $\Delta E=C_1Q_i$ . Toyozawa assumes that longitudinal acoustic modes are of this type. As a consequence, the shape of the absorption constant around the band maximum is described by a Gaussian function:

$$K(h\nu) \sim \exp\{-\tau^2(h\nu_0-h\nu)^2\} \quad (3)$$

with

$$\tau^2 = (\tau_0^2/kT)F(\omega_1)$$

and

$$F(\omega_1) = (2kT/\hbar\omega) \tanh(\hbar\omega/2kT).$$

On the other hand, Toyozawa assumes that the absorption constant at the low-energy tail of the exciton band is due to the interaction with other lattice modes  $Q_i$ , which give rise to an energy difference  $\Delta E$  *quadratic* in the ionic displacements of this mode:  $\Delta E=C_2Q_i^2$ . Toyozawa believes that longitudinal optical modes and transverse acoustical modes have this property. Using a Hamiltonian given by Frölich, Toyozawa then calculates the shape curve due to sole interaction with optical longitudinal modes. He gets essentially an exponential behavior of the absorption constant on the low-energy

tail (Urbach's rule):

$$K(h\nu) \sim [1/(h\nu_0-h\nu)]^{\frac{1}{2}} \exp\{-\sigma(h\nu_0-h\nu)\} \quad \text{for } h\nu_0 > h\nu \quad (4)$$

where

$$\sigma = \frac{\sigma_0}{kT} F(\omega_2), \quad \sigma_0 = \frac{V_0}{18\pi [1/\kappa - 1/\kappa_0] [(m/\mu)\kappa_0\alpha_H]^{\frac{1}{3}}}$$

and

$$F(\omega_2) = (2kT/\hbar\omega_2) \tanh(\hbar\omega_2/2kT).$$

$V_0$  is the volume of the unit cell,  $\hbar\omega_2$  the phonon energy of the optical phonons (assumed to be all of the same frequency),  $\kappa$  and  $\kappa_0$  are the static and optical dielectric constants,  $\mu$  the reduced mass of the formed exciton or excitation and  $m$  the mass of the electron. Assuming  $\mu=0.65m$ , the measured values of  $\sigma_0$  in KI, KBr, and KCl can be explained.

Toyozawa's approach will now be employed to calculate the shape of an absorption band over its entire range. It is assumed that *both* types of modes  $Q_i$  ("linear") and  $Q_l$  ("quadratic") interact with the electronic transition. For the normalized probability  $P_i$  that absorption occurs only because of an interaction with mode  $Q_i$ , formula (3) will be used. Formula (4) will be employed to describe the normalized probability  $P_l$  that the absorption is influenced by mode  $Q_l$  alone.

The probability  $P$  that a photon  $h\nu$  is absorbed under the *combined* action of modes  $Q_i$  and  $Q_l$  is given by a summation over all products  $P_iP_l$  with the condition that the energy difference between ground and excited state is  $h\nu = \text{constant} = h\nu_0 - h\nu_i - h\nu_l$ . In a normalized energy scale, counting from  $(h\nu_0 - h\nu)$  as reference, both  $h\nu_i$  and  $h\nu_l$  represent effective total phonon energies of the corresponding modes  $Q_i$  and  $Q_l$ .

The summation gives

$$\begin{aligned}
 P(h\nu_0 - h\nu) \sim & \int_{-\infty}^{+\infty} \int_0^{+\infty} P_i(h\nu_i) P_l(h\nu_l) \delta[(h\nu_0 - h\nu) - h\nu_i - h\nu_l] \\
 & \times dh\nu_i dh\nu_l \sim \\
 & \int_{-\infty}^{(h\nu_0 - h\nu)} \exp\{-\tau^2(h\nu_i)^2\} \\
 & \times \exp\{-\sigma[(h\nu_0 - h\nu) - h\nu_i]\} dh\nu_i \sim \\
 & e^{-\sigma(h\nu_0 - h\nu)} \int_{\alpha}^{+\infty} e^{-x^2} dx; \quad \alpha = -\left\{ \tau(h\nu_0 - h\nu) - \frac{\sigma}{2\tau} \right\}.
 \end{aligned}$$

The result is formula (1). Using the special temperature dependence of  $\tau^2$  and  $\sigma$  of formulas (3) and (4), postulated and verified singly in previous cases, we arrive at Eqs. (2).

#### DISCUSSION

(a) The experimental verification of formula (1) for localized excitons in KCl seems to suggest that the exciton formation is simultaneously affected by lattice vibrations having a strong *linear* coupling and by other lattice vibrations having a predominantly *quadratic* coupling to the electronic transition. In particular the observation of an appreciable exponential tail of the exciton band (Urbach's rule) seems to be coupled with the existence of certain modes around the "point defect" which are quadratically coupled to the electronic transition. Toyozawa argued qualitatively in the case of excitons of pure alkali halides that longitudinal, optical, or transverse acoustical modes are of the  $Q_l$  type. For localized excitons this type of mode has not been considered previously. Further experimental work with localized excitons in other alkali halides and a theoretical study of localized or quasilocated modes around a point-defect in the NaCl-type lattice would certainly contribute to a deeper understanding of the nature of these various types of modes.

(b) The assumption that two different types of lattice modes  $Q_i$  and  $Q_l$  interact with localized excitons has consequences for the interpretation of the half-width and the temperature shift of the absorption band peak position. The position of the band maximum,  $h\nu_{\max}$ , is different from  $h\nu_0$  of formula (1) (see the abscissas of Fig. 1). The differences are given in Table I for the range of calculations. The temperature shift of the position of the band maximum which was found experimentally is, therefore, different from the corresponding shift of  $h\nu_0$ .

The half-widths, as determined from formula (1), are

TABLE I. Differences ( $h\nu_0 - h\nu_{\max}$ ) calculated from Eq. (1) using the experimental parameters of localized excitons in KCl (Ref. 9).

Temperature $T$ in °K	$(h\nu_0 - h\nu_{\max})$ in eV	Temperature $T$ in °K	$(h\nu_0 - h\nu_{\max})$ in eV
4	0.03	300	0.04
20	0.03	400	0.05
77	0.03	500	0.06
150	0.03	600	0.07
200	0.04	700	0.07

also a sum of the contributions of the "linear" and the "quadratic" mode. Only the "Gaussian" half-width due to the linear interaction is related to parameters of a simple configurational coordinate model (Frank-Condon model). Therefore, in the presence of an appreciable exponential tail in the absorption band shape (as in the case of localized excitons), one must be careful in the interpretation of the results obtained from measurements of the half-width and the maximum position of the absorption band.

(c) Urbach's rule has been found experimentally in a number of materials<sup>5-7,9,12</sup>; various theoretical papers<sup>4,8,13,14</sup> have appeared on the subject. Several different physical mechanisms seem to lead to exponential tail parts of impurity absorption bands, exciton bands or band to band transitions. For strongly coupled allowed electronic transitions in ionic crystals, quadratic interactions due to certain lattice modes seem to be important.

(d) The Frank-Condon model has been very successful in demonstrating graphically the particular influence of "linear" modes on the shape of absorption bands. A calculation of the absorption constant with a Frank-Condon model, assuming "quadratic" interactions with  $Q_l$  modes, yields results which are not in agreement with the experiment. It remains to be seen if and how the result of Toyozawa's abstract calculations can be graphically demonstrated in Frank-Condon plots.

#### ACKNOWLEDGMENT

The author would like to thank Professor J. A. Krumhansl, Professor R. H. Silsbee, Dr. M. Wagner, and T. Watanabe for helpful suggestions and discussions. The help of E. Logothetis with the numerical calculation is appreciated.

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