

**A Proposed Model for the  
Explanation of the  
Urbach Rule**

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The role of electron-lattice interaction in the fundamental optical absorption in insulator has been discussed by many authors. In the case of band-to-band transition, it causes a temperature dependent shift of the absorption edge<sup>1)</sup>. The line shape of the exciton absorption band in the central portion was discussed using the method of generating function.<sup>2)</sup> In both cases, the electron-lattice interaction also causes indirect transition by making the electron system violate the momentum selection rule.<sup>3)</sup> Most of the experimental results on the fundamental absorption of insulators can be explained qualitatively by means of these theories, with one very remarkable exception.

That is the so-called Urbach rule<sup>4)</sup>, according to which the absorption coefficient  $A$  in the long wave-length part of the fundamental absorption decays exponentially with the decrease of photon energy  $h\nu$ :

$$A(\nu) \propto \exp\{-\sigma(h\nu_0 - h\nu)/\kappa T\}, \quad (1)$$

where  $T$  is the absolute temperature and  $\sigma$  is a dimensionless constant of the order of unity. This rule is valid for many ionic crystals (silver-halides<sup>4),5)</sup>, alkali halides<sup>6)</sup>, cadmium-sulfides<sup>7)</sup>, thalliumchloride<sup>8)</sup>, etc.) for the range of  $A$  as wide as several decades, and for moderate and higher temperatures.

Dexter<sup>9)</sup> proposed an explanation by making use of the deformation potential. His idea consists in that the energy of the excited states changes by  $\delta E = -E_1 \Delta$ , while the probability distribution of the local dilation  $\Delta$  is given by  $\exp(-\Delta^2/C\kappa T)$  with an appropriate elastic constant  $C$ . As the result  $A$  is given by  $f(\nu, T)\exp\{-(h\nu_0 - h\nu)^2/E_1^2 C\kappa T\}$  where  $f(\nu)$  is a factor originating from the energy band width. By a suitable choice of parameters, he obtained a curve which resembles to (1) in a certain range of  $A$ . However, it seems difficult to fit it to (1) through the whole range especially in cases of KI and KBr where (1) is valid while  $A$  varies as large as  $10^{5-6}$  times.

By an extension of Dexter's idea, we obtained a satisfactory explanation for the whole range. As we are concerned with the tail part of the absorption band, the important contribution comes from those parts of the crystal which deforms markedly, so that it is necessary to add a quadratic term to the energy change:

$$\delta E = E_1 \Delta + E_2 \Delta^2. \quad (2)$$

A similar term was taken by Koshino<sup>10)</sup> in discussing the temperature dependence of mobilities in semiconductors. If we take into account only the second term

( $E_2$ , being assumed negative), and follow Dexter's procedure, we obtain the absorption constant

$$\exp\{- (\hbar\nu_0 - \hbar\nu) / |E_2| \kappa T\}$$

multiplied by a factor with slow  $\nu$ -dependence, and the values of  $|E_2|$  determined by comparison with experimental data are several eV, which seem to be reasonable values.

However, we encounter a new difficulty. The width of the central part of the excitation absorption band is due to the linear term  $E_1 \mathcal{A}$ , and  $|E_1|$  can be estimated to be several eV from the observed widths.<sup>2)</sup> Then the linear term is not negligible to the quadratic even for the tail part where  $-\delta E = \hbar(\nu_0 - \nu) \sim 0.5$  eV ( $\nu_0$ : the absorption peak).

Consequently, it is necessary to assume that the mode of lattice vibration responsible for the tail part is different from that mode which contributes to the width of the central portion, the latter being probably the longitudinal acoustical mode as was discussed in (I). Then we have two possibilities for the former modes. The first is the transverse acoustical mode which is expected to have usually rather small linear term of the exciton-lattice interaction. In fact it vanishes exactly in the continuum approximation for cubic crystals. Moreover, there is some reason to believe that the quadratic term is rather large in case of alkali- and silver-halides, because in these crystals a positive hole has strong tendency of forming a molecular binding between a pair of neighbouring halide ions, and lattice deformation makes pairs of halide ions with certain relative direction to draw nearer

to each other.

The second possibility is the longitudinal optical mode, which is expected to have relatively small linear terms of exciton-lattice interaction if the effective masses of an electron and a hole are not very different, because the exciton is electrically neutral. As was noted in (I), however, this interaction has large matrix elements between different exciton energy bands. In other words, the polarization wave  $\mathbf{P}(\mathbf{r})$  of ionic lattice causes electric field  $\mathbf{F}(\mathbf{r})$ , which in turn polarizes the exciton, the energy change of the latter being given by  $\delta E = -\alpha \mathbf{F}^2 / 2 \propto -P^2$ . Assuming that the exciton is in the hydrogen-like  $1s$  state, and making use of the fact that polarizability of the hydrogen atom is given by  $\alpha_H = (9/2) \cdot a_H^3$ , we get the quadratic exciton-lattice interaction:

$$\begin{aligned} H_{el} = \delta E = & -\frac{9}{4} \left( \frac{m}{\mu} \kappa_0 a_H \right)^3 \\ & \times \frac{2\pi \hbar \omega}{V} \left( \frac{1}{\kappa_0} - \frac{1}{\kappa} \right) \\ & \times \left\{ \sum_w (b_w e^{iwr} + b_w^* e^{-iwr}) \right\}^2. \quad (3) \end{aligned}$$

$\mu$  and  $m$  are the exciton reduced mass and the true electron mass, respectively,  $\kappa$  and  $\kappa_0$  are static and optical dielectric constants,  $\hbar\omega$  the phonon energy and  $V$  the total volume.

We now make use of the general formula presented in (I) and note that the generating function for small values of  $t$  is important in determining the absorption coefficient at the tail part. In this limit, with  $H_{el}$  given by (3), each term  $U_n$  of the expansion (I, 3.15) can be calculated by collecting all possible graphs, with the result:

$$\sum_{n=0}^{\infty} U_n(t) = \left(1 - \frac{it}{\hbar} B\right)^{-1/2}, \quad (4)$$

$$A(\nu) d\nu = \left(\frac{h\nu_0 - h\nu}{B(T)}\right)^{-1/2} \times \exp\left(-\frac{h\nu_0 - h\nu}{B(T)}\right) \frac{d(h\nu)}{\sqrt{\pi B}}. \quad (5)$$

(5) is normalized to unity, and  $B$  is given by

$$B(T) = 18\pi \left(\frac{1}{\kappa_0} - \frac{1}{\kappa}\right) \times \left(\frac{m}{\mu} \kappa_0 a_{\text{H}}\right)^3 / v_0 \cdot \frac{\hbar\omega}{2} \coth\left(\frac{\hbar\omega}{2\kappa T}\right), \quad (6)$$

and is proportional to  $T$  at high temperatures. (5) practically fits the experimental formula (1) in the whole range of  $\nu$  in which (1) was ascertained by experiments, because the first factor of (5) has a much slower  $\nu$ -dependence. In order to get the values  $\sigma=0.79$  (determined by Martienssen<sup>6)</sup> from his data) both for KBr and KI, from Eq. (6) with known values of  $\kappa_0$ ,  $\kappa$ ,  $\omega$  and  $v_0$  (the volume of a unit cell), we have to take  $\mu/m=0.64$  and  $0.63$ , respectively, which are reasonable values. However, Martienssen's data on KBr at the lowest temperature ( $T=20^\circ\text{K}$ ) shows that (1) is valid with  $T$  replaced by  $T_0 \sim 60^\circ\text{K}$ , while according to our theory  $T_0=120^\circ\text{K}$  for longitudinal optical mode (see (6)) and  $T_0 \sim 50^\circ\text{K}$  for transverse acoustic modes (averaged over propagation direction). It seems that in alkali halides, the linear interaction between an exciton and optical phonons is appreciable due to the large difference in effective masses, preventing quadratic term from contributing to the tail part, and transverse acoustic mode plays the

main rôle.

Although there still remains some difficulty in the general derivation of the rule, especially concerning the effect of width of the exciton energy band (or of the electron and hole bands, in the case of band-to-band transition), it seems to be rather well established that the quadratic interaction of the exciton (or, the electron and the hole) with those modes of lattice vibrations which do not make appreciable contributions to the main part of the exciton (or band-to-band) absorption plays an essential rôle in causing the tail part described by Urbach's rule. The detail of this work will soon be reported in this journal.

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- 1) T. Muto and S. Oyama, *Prog. Theor. Phys.* **5** (1950), 833; **6** (1951), 81.  
H. Y. Fan, *Phys. Rev.* **82** (1951), 900.
- 2) Y. Toyozawa, *Prog. Theor. Phys.* **20** (1958), 53 (referred to as (I) in this letter).
- 3) L. H. Hall, J. Bardeen and F. J. Blatt, *Phys. Rev.* **95** (1954), 557.  
R. J. Elliot, *Phys. Rev.* **108** (1957), 1384.
- 4) F. Urbach, *Phys. Rev.* **92** (1953), 1324.
- 5) F. Moser and F. Urbach, *Phys. Rev.* **105** (1957), 406.
- 6) W. Martienssen, *J. Phys. Chem. Solids* **2** (1957), 257. *ibid.* **8** (1959), 294.
- 7) D. Dutton, *Phys. Rev.* **112** (1958), 785.
- 8) H. Zinggrebe, *Zeits. f. Phys.* **154** (1959), 495.
- 9) D. L. Dexter, *Nuovo Cimento* **7** (1958), Supplement.
- 10) S. Koshino, *Prog. Theor. Phys.* **18** (1957), 23.
- 11) W. Känzig and T. O. Woodruff, *Phys. Rev.* **109** (1958), 220.