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Numerical Experiments on the Absorption Lineshape of the Exciton under Lattice Vibrations. III.
The Urbach Rule

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We analyze the low-energy tail of the exciton absorption spectra calculated numerically on the standard model of exciton-phonon interaction. The empirical Urbach rule is established in its exponential decay for several orders of magnitude with a decay constant proportional to inverse temperature T^{-1} in two and three dimesnions and to $T^{-2/3}$ in one dimension. A posteriori, the exponential tail is unambiguously ascribed to the "momentarily localized" excitons by considering the behaviour of the average oscillator strength per state. We introduce the steepness index s which relates the steepness coefficient σ and the exciton-phonon coupling constant g through $\sigma=s/g$. Our calculated values of 1.24 for square and 1.50 for simple cubic lattices enable us to correlate experimental observations on Urbach behaviour and self-trapping consistently.

§1. Introduction

After the discovery of Urbach[1] the optical experiments of a variety of insulators[2,3] have established that the low-energy tail of the exciton absorption spectra depends exponentially on the energy, with a decay constant proportional to the reciprocal temperature at high temperatures:

$$F(E)=A\exp\left(-\sigma\frac{E_0'-E}{k_BT}\right). \tag{1.1}$$

The converging point, E_0', of the semi-logarithmic plots of the absorption spectra at various temperatures is usually situated near the absorption peak at the lowest temperature. The dimensionless "steepness coefficient" σ is a material constant of the order of unity.[3,4]

The universality and simplicity of this empirical rule—now called the Urbach rule—have evoked a number of theoretical[4–14,3] and experimental[15–25,3] studies to explain it on a microscopic basis. A comprehensive survey of these studies will be made elsewhere. In this paper we neglect the internal degrees of freedom of the exciton and demonstrate that the Urbach tail can be explained as an effect of the phonon field on the translational motion of the exciton.

This situation was already investigated in parts I and II of the present series of papers,[26] which will be referred to as I and II hereafter. With respect to the low-energy side of the absorption peak, it was already mentioned in II that the renormalized perturbation expansion starting from free exciton states converges extremely slowly and yields a sharp cut-off of the exciton absorption spectra at any tractable stage of approximation. It therefore seemed to be an extremely roundabout picture in describing the exponential tail. This led one of the authors (Y. T.) to assume that the low-energy tail originates from momentarily localized exciton states formed below the free exciton states in the random potential of lattice vibrations.[4]

This notion of coexistent itinerant and localized states was formulated by Cho and Toyozawa,[27] with particular attention to existence or non-existence of the low-energy tail at absolute zero of temperature which was correlated with the existence or non-existence of self-trapped states. Sumi and Toyozawa[10] improved the formulation of the problem within the adiabatic approximation by incorporating the localized states into the self-energy. This average-t-matrix approximation (ATA) was further improved by Sumi[28] with the use

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of the coherent potential approximation (CPA). Klafter and Jortner extended these studies so as to include the effect of lattice disorder.[29]

These investigations for finite temperatures reproduced the empirical rule (eq. (1.1)) fairly well, except that log F-versus-E curves were somewhat concave (positive curvature) bending upwards just below the absorption peak especially at low temperatures, and that the steepness coefficient σ slowly decreased towards low temperature. The former discrepancy was ascribed to the use of the one-site approximation; this was supposed to underestimate the number of shallow localized states with giant oscillator strengths, especially those states which originate from coherent multi-site shallow attractive potentials. An improvement of ATA or CPA towards a multi-site approximation, though possible in principle, would lead to complicated equations, which are prohibitively difficult to solve.

Recapitulating, although several authors showed the possibility of assigning the Urbach rule to momentarily localized (ML) excitonic states, the severe approximations neccessary for the analytical treatment made these works not ultimately convincing in favour of the ML-model.

In the present paper, instead of invoking ad hoc the ML model we present a numerical calculation into which none of the mentioned approximations enter. We employ the Hamiltonian which was introduced in I for the standard situation specified by harmonic lattice vibrations, linear on-site exciton-phonon interaction ($-cq_n$) with the neglected intersite correlation, and adiabatic treatment. It can be written in the site representation as

$$\hat{H}=H_e+H_{eL}=\sum_n\sum_m |n\rangle V\langle m|-\sum_n |n\rangle cq_n\langle n|, \tag{1.2}$$

with the nearest neighbour exciton transfer V, where the interaction modes q_n follow the thermal distribution

$$P(q_n)=\exp\left(-\frac{1}{2}q_n^2/k_BT\right), \tag{1.3}$$

since the lattice potential energy is given by

$$U_L=\sum_n \frac{1}{2}q_n^2. \tag{1.4}$$

We will show in the following chapter that the low-energy side of the absorption-lineshape function for the direct exciton edge

$$F(E)=\frac{1}{N}\langle\sum_i \delta(E-E_i)(\sum_n e_{in})^2\rangle, \tag{1.5}$$

calculated from the eigenvalues E_i and corresponding eigenvectors $e_i=(e_{i1},\cdots,e_{iN})$ of this Hamiltonian (eq. (1.2)) and averaged over all possible configurations $\{q_1,\cdots,q_N\}$ according to the Gaussian distribution (eq. (1.3)), in fact decays exponentially for any dimensionality studied, with the temperature dependence as described by eq. (1.1) except in one dimension.

With regard to the steepness coefficient σ, it was argued[4,10] throughout the theories based on the ML-model that σ should be proportional to the reciprocal of the exciton-phonon coupling constant g:

$$\sigma=s/g. \tag{1.6}$$

g is defined[30,31] as the ratio of the lattice relaxation energy E_{LR}, which after creation of an exciton the lattice would gain for vanishing transfer by relaxing to the new position of minimum energy (given by eqs. (1.2) and (1.4)), to the band halfwidth B which means the maximum energy gain due to the transfer (given by eq. (1.2))

$$g=\frac{E_{LR}}{B}=\frac{c^2/2}{\nu|V|}. \tag{1.7}$$

The relation (1.6) can also be deduced from the following scaling argument: A transformation to the dimensionless energies $\tilde{E}\equiv(E-E_0')/2B$ and $\tilde{\varepsilon}_n\equiv\varepsilon_n/2B=-cq_n/2B$ shows (cp. eqs. (1.2) and (1.3)) that the lineshape function (normalized in the new scale)

$$\tilde{F}(\tilde{E})=2B\cdot F(E), \tag{1.8}$$

is uniquely determined by the parameter

$$\lambda^2=\frac{gk_BT}{2B}, \tag{1.9}$$

which means that g, T and B are not independent parameters for the lineshape problem as discussed already in I. In order to obtain the exponential energy dependence of the Urbach rule, one has to put

$$F(E)=\frac{1}{2B}A(\lambda)\exp\left(-\frac{2B\cdot(-\tilde{E})}{2B\cdot\theta(\lambda)}\right), \tag{1.10}$$

where $A(\lambda)$ and $\theta(\lambda)$ are arbitrary functions yet to be determined. To achieve the temperature dependence of the Urbach rule, one has to choose $\theta(\lambda)\propto\lambda^2$ (see eq. (1.3)), which in turn leads to eq. (1.6). The existence of the convergence point E_0' requires that $A(\lambda)$ is constant. This argumentation shows that the proportionality factor s depends only on the lattice structure as far as transfer energies beyond nearest neighbours can be neglected. The factor s will hereafter be called steepness index.

The size of the coupling constant g governs the self-trapping of excitonic states, the threshold being given by $g_c\approx 1-(2\nu)^{-1}$ [30] except in the one-dimensional case where $g_c\to 0$.[32] An exact determination of s would therefore be important in order to correlate the steepness coefficient σ with the self-trapping. We shall determine values of s from the exact numerical solution of the standard model and compare them with the experimental information about self-trapping in chapt. 3.

§2. Results and Discussion

We have calculated the exciton absorption spectra for the direct exciton edge of one-, two-, and three-dimensional crystals choosing, respectively, a linear chain of 30 sites, a square lattice with 13·12 sites, and a simple cubic lattice with 10·9·8 sites. The details of the computation of the lineshape function (eq. (1.5)) and related spectra like the density of states and the average oscillator strength per state (AOSPS) have already been commented upon in I and II with particular emphasis in II on the problematic statistics for the low-energy side. For the analysis of the absorption tail on this side we present the semilogarithmic plots of the lineshape functions in Figs. 1 through 3 for the energy range of and below the absorption peak, which would coincide with $E=-B=-0.5$ eV for the rigid lattice. (Note that in view of eq. (1.9) we have chosen $2B=1$ eV and $g=1$ arbitrarily as in I and II.) For all three dimensionalities we find a linear relationship of the logarithm of the absorption versus energy over a range of three to five decades in intensity for various temperatures. This agrees with the energy dependence of the Urbach rule (eq. (1.1)).

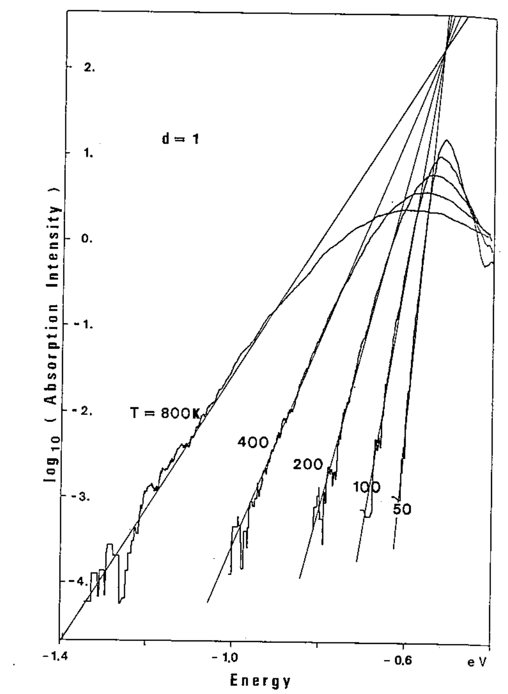

Fig. 1. Urbach tails for a one dimensional lattice (linear chain).

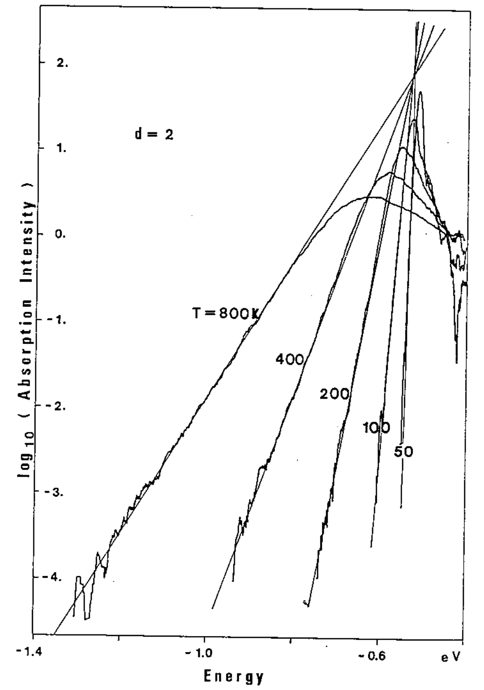

Fig. 2. Urbach tails for a two dimensional lattice (square).

Moreover, the extensions of the straight lines for different temperatures approximately lead to a converging point with an energy E_0' near the absorption peak $E_0=-B$ at vanishing temperature. The existence of such converging point was also experimentally established for

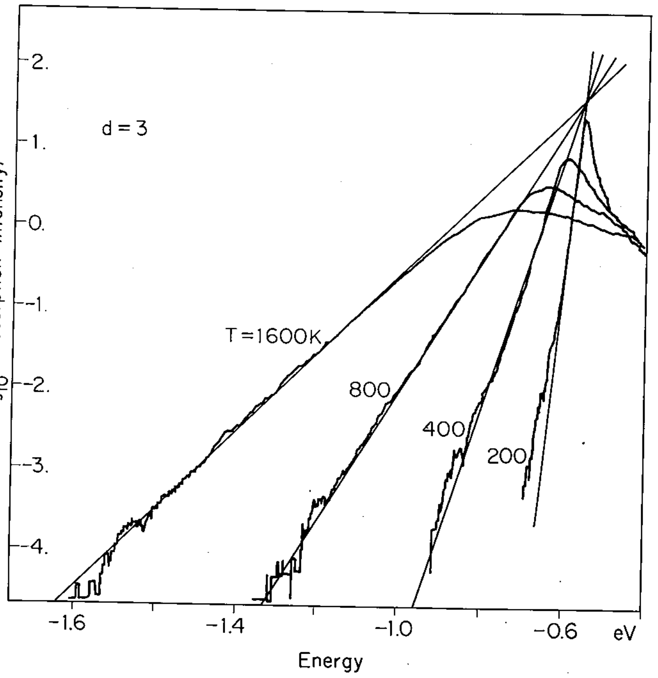

Fig. 3. Urbach tails for a three dimensional lattice (simple cubic).

the Urbach rule,[2,3] although the absorption intensity at the observed converging point is usually a few orders of magnitude larger than that of the observed absorption peak, in contrast to Figs. 1 through 3. This effect is probably caused by the red shift of the exciton line due to the thermal expansion of the lattice. In addition to the dynamical effects considered in this paper, the red shift would spread the "bundle" of straight lines and thus raise the absolute value of the absorption at which these lines intersect.

It has recently been shown that the Urbach rule in band-to-band absorption of amorphous semiconductors is essentially caused by the exponential tailing of the density of states (DOS).[33] Turning to the semi-logarithmic plots of our DOSs which are shown in Fig. 4, we indeed observe such an exponential tailing, i.e. Urbach-like dependence on the energy. The range of the respective straight lines in Fig. 4 is, however, rather limited and no converging energy E_0' can be found.

The DOS $\rho(E)$ and the lineshape $F(E)$ are related by the average oscillator strength per state $f(E)$ as studied in II: $F(E)\cdot\rho(E)$. We conclude from the above discussion that this factor $f(E)$ with its rather strong energy dependence plays an important role for the validity of the Urbach rule over several orders of magnitude in absorption intensity and with the well-defined convergence point as described phenomenologically by eq. (1.1).

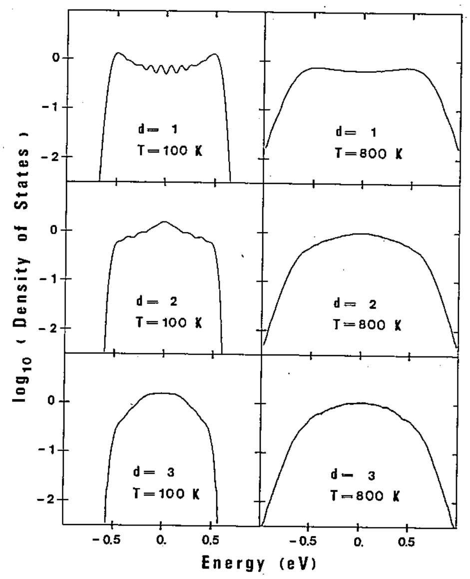

Fig. 4. Density of states for different dimensions d and temperatures T.

For three dimensional samples, however, we observe a deviation from the Urbach rule in the far tail (i.e. for lowest energies), concave for low temperatures and tending towards convex behaviour for high temperatures. We ascribe this deviation to the finite number of lattice sites which are used in the calculation; in the three-dimensional samples this effect should be most prominent as the linear size is smallest. This assumption was born out for one temperature (T=400 K) by computing the absorption tail for samples with nearly doubled linear size (i.e. eightfold volume), namely $18\cdot 17\cdot 16=4896$ sites. In the semi-logarithmic plot the resulting tail showed the same Urbach-like straight line but it extended somewhat further towards lower energies.

In the above discussion we have shown that the energy dependence of the Urbach tail is well fulfilled by our data. To analyze the temperature dependence, we show the steepness coefficient in Fig. 5, calculated from the straight lines in Figs. 1 through 3 by the Urbach formula (eq. (1.1)). In two and three dimensions it is indeed independent of temperature whereas in one dimension the data can be adequately approximated by $T^{1/3}$ (see Fig. 5), which means that the exponent of the Urbach rule follows a $T^{-2/3}$-law for the one-dimensional lattice. Due to a lack of experimental investigations it was not possible to confirm or contradict this unexpected behaviour.

It is interesting to note, on the other hand, that the "Urbach width" (defined as the energy interval corresponding to the decay of the *tail* to 1/2) and the linewidth (full width at half value as discussed in I) have the same temperature dependence for one ($T^{2/3}$) and two (T^1) dimensions but not for three (T versus $T^{3/2}$) dimension. Why it is so, and whether it has anything to do with the fact that renormalized perturbation theory gives right answer for the temperature dependence of the total width for one and two dimensions but not for three dimension, is not clear at the moment.

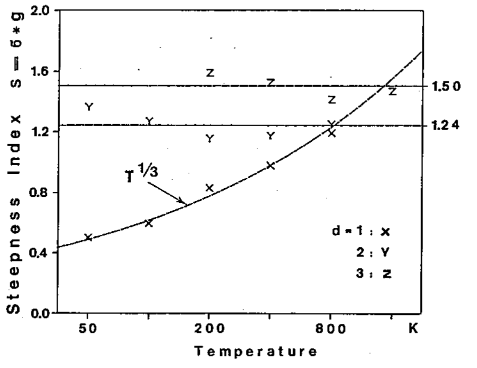

Fig. 5. Steepness coefficients of the Urbach tails in Figs. 1, 2, 3. Broken lines are best fits by a $T^{1/3}$-law for one dimension and by constants for two and three dimensions.

§3. The Steepness Index

In the last chapter we have determined the energy- and temperature-dependence of the low-energy tail of the exciton-absorption lineshape function. We shall now investigate its dependence on the exciton-phonon coupling constant g. The constant behaviour of the steepness coefficient σ on temperature for two and three dimensions (see Fig. 5) readily establishes the relation $\sigma=s/g$ as is seen from the scaling argument in chapter 1 (compare eq. (1.9)). Since g was put equal to unity in our calculation we find immediately from Fig. 5 that the steepness index s equals 1.24 ± 0.06 for the square lattice and 1.50 ± 0.06 for the simple cubic lattice. These values are significantly larger than the previously obtained ones of 2/3[4] or 0.6~1.0[10] for three-dimensional lattices. The knowledge of the steepness index for a given lattice structure allows to determine the exciton-phonon coupling constant g from the experimentally accessible steepness coefficient of the Urbach tail and thus to determine whether the self-trapping of the exciton takes place ($g>g_c=1-(2\nu)^{-1}$) or not.[4,10]

In one of the recent experiments on the Urbach tail of GeS[23] the exciton self-trapping could be established by showing that an Urbach tail exists even at nearly zero temperature.[10,27] The corresponding steepness coefficient $\sigma=1.45$, however, seemed to preclude the self-trapping, as the known values of s predicted a coupling constant well below unity. GeS is a layer-type compound; so we expect its properties to be somewhere between two and three dimensions. The present calculation favours the self-trapping since the estimated coupling constant $g=1.03$ is slightly larger than $g_c\approx 0.92$ according to the three-dimensional model and $g=0.86$ about equal to $g_c\approx 0.87$ according to the two-dimensional model. Thus, the only "intriguing quantitative discrepancy"[23] between this experiment and the momentary-localization model is removed. The similar discrepancy in PbI_2[17] with $\sigma=1.48$ is also removed.

The correlation between σ-value and self-trapping has been shown most clearly in the recent studies on organic crystals by Matsui,[25] who found $\sigma=1.38$ for pyrene and $\sigma=0.93$ and 1.38, respectively, for α- and β-type perylenes. The self-trapping which was directly confirmed for all of these crystals through luminescence study is well consistent with the critical value of the steepness coefficient $\sigma_c \equiv s/g_c$ (1.64 for simple cubic lattice and 1.42 for square lattice) which represents the upper bound of σ for the self-trapping. It is also of interest to note the experimental evidence[25] that the excitons self-trap much more shallowly in pyrene and β-perylene than in α-perylene in accordance with the observed steepness coefficients σ which are much closer to σ_c in the former materials.

The value $s=1.50$ is also consistent with the observations on other well known materials. For example, the observed $\sigma\approx 0.8$ gives $g\approx 1.87$ in alkali halides[2,18] where the exciton is self-trapped while the observed $\sigma\approx 2.2$ yields $g\approx 0.68$ in CdS where the exciton is not self-trapped.[34]

For the Urbach tail of the indirect absorption edge we expect the steepness index to be smaller than for the direct absorption edge because of the absence of the giant-oscillator-strength effect. This expectation agrees well with experimental results on the indirect Urbach tail of $AgCl_xBr_{1-x}$, where a change of σ between 1.0 and 0.8 coincides with a change from self-trapped to free behaviour.[16] These findings suggest an index s of value 0.9 for the indirect edge. This value is also consistent with experiments on the indirect edge of TlCl:[35,36] The observed $\sigma\approx 1.16$ gives $g\approx 0.78$ in accordance with the absence of self-trapping.

Figure 5 shows a constant behaviour of the steepness also for the lowest temperature. In order to reproduce the well known and experimentally established decrease of σ for vanishing temperature, usually obeying a coth-law, one might think of replacing the classical mechanical expression for the variance $\langle q_n^2\rangle = k_B T$ of the distribution of the interaction modes (eq. (1.3)) by the quantal one: $\langle q_n^2\rangle = (\hbar\bar{\omega}/2)\cdot \coth(\hbar\bar{\omega}/2k_B T)$ (see I, Appendix). From the theoretical point of view this procedure is not warranted since the existence of the low-energy tail of finite steepness at $T\to 0$ K is related with the existence of a self-trapped state below the nearly free exciton state[27] rather than with the zero-point vibrations. This point will be discussed elsewhere.

For the one dimensional lattice Fig. 5 gives a temperature-dependent steepness coefficient, so that one cannot define a dimensionless steepness index as in the two- and three-dimensional cases. This behaviour might be related with the vanishing critical coupling constant g_c in one dimension where all states are self-trapped regardless of the coupling strength.

§4. Conclusion

We have shown the validity of the Urbach rule (eq. (1.1)) for two- and three-dimensional lattices (and also for one-dimensional lattice with the above mentioned modification of temperature dependence) by simply solving numerically the standard model of exciton-phonon interaction without the ad hoc picture of momentary localization during the course of computation. However, the analysis of the computed AOSPS spectra and degree of localization in II clearly demonstrates that the exponential tail is due to the momentarily localized states. In fact, the straight sections of $f^{-2/d}$-versus-E curves in Fig. 3 of II exactly correspond to the straight sections of the $\log F$-versus-E curves in Figs. 1, 2, and 3 of the present paper for each temperature. Moreover, our exact calculation reproduces the empirical Urbach rule better than the previous theories which made approximate treatments of the same standard model. Finally we have demonstrated the advantage of the present investigation to derive values of the exciton-phonon coupling constant from experimental steepness coefficients of the Urbach tail and shown that these values allow reliable predictions whether the self-trapping occurs or not. These results altogether lend strong support to the appropriateness of the standard model as well as to the momentary localization picture as the real origin of the Urbach tail.

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