

Exciton absorption tails in one-dimensional systems

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Exciton absorption tails in direct- and indirect-gap materials are investigated using Toyozawa's exciton self-trapping model as well as Halperin's solution of the random impurity-potential problem. In contrast to the Urbach rule obeyed in two- and three-dimensional systems, the logarithm of the absorption coefficient of a one-dimensional chain is shown to depend on the energy as $E^{3/2}$, as well as on the inverse temperature T^{-1} , in accordance with the respective dependences of the density of states in one dimension derived by Halperin.

The exponential dependence of the low-energy tail of the fundamental exciton absorption line with respect to energy and inverse temperature—the Urbach rule¹—

$$F(E) = F_0 \exp\left(-\sigma \frac{E_0 - E}{k_B T}\right) \quad (1)$$

has long been experimentally established for a wide variety of insulators and semiconductors² and has provoked several theoretical attempts at explanation.² In a series of papers,³⁻⁷ Toyozawa and the present author have demonstrated, by numerical simulation, that the Urbach rule can be reproduced⁵⁻⁷ by the exciton self-trapping model.³ A deviation from Eq. (1), however, was derived for the temperature dependence of the exponent in one-dimensional (1D) systems ($T^{-2/3}$ rather than T^{-1}) for direct⁵ as well as indirect⁶ absorption edges. Moreover, the exact solution to the 1D impurity problem in the continuum limit gives a density of states⁸

$$\rho(\tilde{E}) \propto \exp(|\tilde{E}|^{3/2}),$$

\tilde{E} being measured from the band edge of the ideal crystal. Applying scaling arguments to this result has led to the conclusion⁹ that the slope of the Urbach tail in 1D crystals should follow $\tilde{E}^{3/2}$ as well as $T^{-2/3}$, in contrast to the conclusions of Ref. 5. It is the purpose of this report to clarify this open point by theoretical considerations, as well as an analysis of more extensive numerical experiments.

Our former investigation attributed the Urbach tail to the existence of excitonic states trapped momentarily at energies below the band edge of the ideal crystal due to thermal lattice vibrations.^{5,6} In its simplest form the model Hamiltonian in the site representation

$$H = \sum_n |n\rangle \varepsilon_n \langle n| + \sum_{n,m}^{\text{NN}} |n\rangle V \langle m| \quad (3)$$

contains the transfer between nearest neighbors (NN) only and a fluctuating site energy due to a linear on-site exciton-phonon interaction; for harmonic lattice vibrations the fluctuation of the site energies ε_n is governed by a Gaussian distribution with variance proportional to the temperature.³

This Hamiltonian has been studied widely in a different context, namely for the analysis of the localization behavior of disordered systems.¹⁰ Assuming that the exci-

ton is localized in a d -dimensional well of size λ^d , the treatment of Halperin and Lax¹¹ yields the density of states

$$\log(\rho/\rho_0) = \sigma' \frac{|\tilde{E}|^y}{W^2}, \quad y = 2 - d/2, \quad (4)$$

where W^2 is the variance of the random potential ($k_B T$ in our case). In Eq. (4) a dependence on \tilde{E}^2/W^2 arises from the Gaussian distribution; the additional energy dependence $|\tilde{E}|^{-d/2}$ is due to the spatial confinement of the wave function resulting in a kinetic energy $\tilde{E} \propto \lambda^{-2}$. However, a variety of experiments on amorphous 3D systems has established an Urbach-like behavior of the density of states, i.e., Eq. (4) with $y=1$. In a recent Letter¹² it has been shown that this dependence does indeed follow from the approach of Halperin and Lax (where localization arises due to long-wavelength fluctuations), if one employs the correct scaling between energy and size of the localized states known from localization studies, i.e., if one takes into account the effect of small-scale fluctuations of the potential on the energy of localization. For 1D and 2D random systems Eq. (4) is not changed by that argument.¹² In particular, the disorder always enters as W^{-2} .

In a different approach,¹³ the 1D result of Halperin and Lax ($y = \frac{3}{2}$) has been established as a universal behavior (i.e., independent of the employed probability distribution for the disorder) for the near-tail density of states within the coherent-potential approximation. In that derivation the (natural) unit of energy contains $W^{4/3}$, so that $y = \frac{3}{2}$ yields a universal dependence of the exponent on W^{-2} , i.e., on inverse temperature.

Thus the Urbach-like dependence of the tail of the density of states holds for all dimensions with respect to temperature, and for 2D and 3D with respect to energy. The 1D dependence on energy remains $y = \frac{3}{2}$. In all cases, this behavior sets in only somewhat below the band edge defined in the absence of disorder, and it will turn into Gaussian dependence for extreme energies.^{5,12} The exponential tailing in between covers two or three orders of magnitude.

Regarding the absorption intensity, we have to take the average oscillator strength per state into account as an additional factor.⁴ By its energy dependence, it influences the line shape in such a way that the exponential tailing is observed over a considerably wider range (approximately two more orders of magnitude),^{5,6} in agreement with the

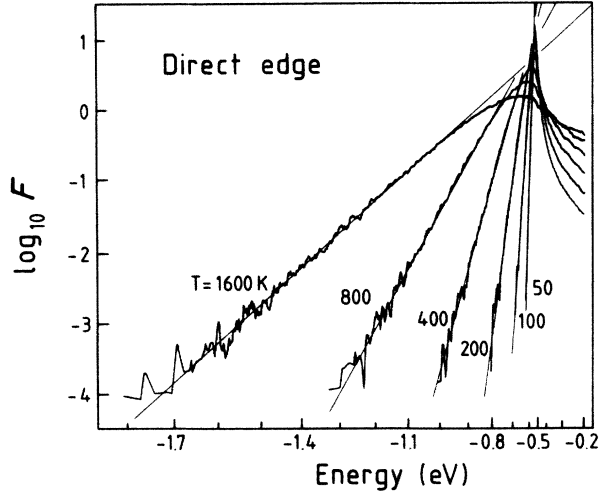


FIG. 1. Exponential tails of the absorption line shape (F is the absorption intensity) of 1D systems with direct edge. The transfer V in Eq. (3) is chosen in such a way that the ideal band would reach from -0.5 to $+0.5$ eV.

fact that absorption experiments on crystals usually show longer Urbach tails than the measurements of the density of states of amorphous systems. The contribution of the oscillator strength does not, however, qualitatively change the tailing behavior,^{5,6,9} so that the above discussion of the energy and temperature dependence holds true for the absorption intensity, too. The Urbach rule remains valid in its original form (1) for 2D and 3D systems, but as a consequence of the behavior of the density of states the absorption tail drops faster in 1D, leading to a modification of the Urbach rule:

$$F(E) = F_0 \exp \left(-\sigma' \frac{|E_0' - E|^{3/2}}{k_B T} \right). \quad (5)$$

It is important to note that the dependence on temperature is not changed.

Finally, we intend to clarify how these 1D results can be reconciled with our previous numerical data.^{5,6} Our attempt to fit the 1D line shape to Eq. (1) emphasizing the energy dependence had led us wrongly to assume $\log(F/F_0) \propto \bar{E}/T^{2/3}$, although due to the bending curves the agreement was somewhat poorer than for the respective 2D and 3D fits. A reevaluation according to Eq. (5) did not turn out to be more convincing either, because the statistics of the absorption curves obtained by a Monte Carlo procedure⁴ were too poor. We have therefore repeated the calculations for direct, as well as indirect absorption edges with a considerably larger system containing 199 instead of 30 atoms and with increased accuracy, diagonalizing up to 40000 different samples of the random Hamiltonian (3) for each temperature. The results are shown in Figs. 1 and 2, employing an energy scale of $\bar{E}^{3/2}$. On this scale, the tails can be convincingly fitted by

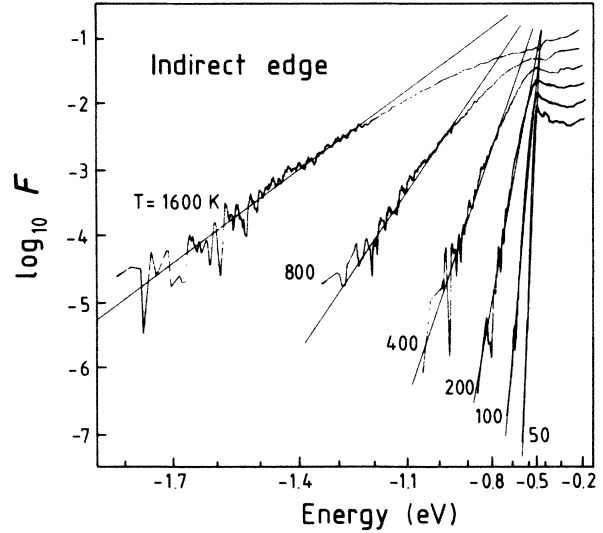


FIG. 2. Exponential tails of the absorption line shape of 1D systems with indirect edge.

straight lines. With respect to the steepness, we have, however, fitted only the curve for the highest temperature. For the other temperatures we have determined the gradient according to Eq. (5), i.e., repeatedly dividing it by 2. The straight lines and the agreement of the determined gradients with the computed absorption tails corroborate the above-derived modified 1D Urbach rule (5). We have ascertained that a tolerable fit of these data by means of Eq. (1) is not possible. It is interesting to realize that our original analysis thus remains valid, in so far that for constant absorption intensity in 1D still $\bar{E} \propto T^{2/3}$ in contrast to the proposal of Ihm and Phillips.¹⁴

In the described way, the knowledge¹¹ of the exact energy dependence of $\rho(E)$ has led to the correct description of the 1D exciton absorption tail, while the Urbach rule of Eq. (1) had been misleading. However, in that region of the tail which corresponds to states localized almost completely on one single site, the above-mentioned universal behavior is no longer correct. In this case, the coherent-potential approximation yields¹³ the usual Urbach result, i.e., Eq. (4) with $y = 1$, for the Gaussian distribution. This region, which is intermediate between the near-tail result of Halperin and Lax and the extreme-tail Gaussian decrease, is barely reached in the numerical results in Figs. 1 and 2, but might complicate comparisons with future experiments aiming at a corroboration of the modified Urbach rule.

In conclusion, the derivation by Soukoulis *et al.* of the exponential band tails in disordered materials applies similarly to the absorption tails in crystals. Thus, an explanation of the puzzling dependence of the slope on $\bar{E}^{3/2}/T$ follows naturally, but a modified Urbach rule for 1D systems is required. Experiments on polyacetylene¹⁵ would rather fit Eq. (5) than Eq. (1), but more extensive experiments on 1D exponential tails are called for.

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