PHYSICAL REVIEW B VOLUME 5, NUMBER 2 15 JANUARY 1972

Toward a Unified Theory of Urbach's Rule and Exponential Absorption Edges

John D. Dow*
Joseph Henry Laboratories, Princeton University, Princeton, New Jersey 08540
and RCA Laboratories, Princeton, New Jersey 08540

and

David Redfield
RCA Laboratories, Princeton, New Jersey 08540

(Received 21 April 1971)

Exponential absorption edges $\alpha = Ae^{g(\hbar\omega - \hbar\omega_0)}$ have been observed in both ionic (Urbach's rule: $g = \sigma/k_B T^*$) and covalent materials. Arguments are given to show that a unified theory of exponential absorption edges must (i) rely on electric microfields as the cause, (ii) include exciton effects and the final-state interaction between the electron and the hole, and (iii) ascribe Urbach's rule to the relative, internal motion of the exciton. An approximate calculation has been made in which the nonuniform microfields are replaced by a statistical distribution of uniform microfields; this calculation is a generalization to physically relevant intermediate-strength fields of previous strong- and weak-field theories of Redfield and Dexter. In contrast with the other microfield models, which obtain the exponential spectral shape by averaging over microfield distributions, the present theory obtains a quantitatively exponential edge as an inherent feature. The temperature dependences of the edges in various materials follow qualitatively from the nature of the microfield sources. The specific temperature dependence of Urbach's rule in ionic crystals is obtained from this model, with supplementary arguments to account for nonuniformity of the fields.

I. INTRODUCTION

The empirical characterization of the fundamental optical-absorption edge known as Urbach's rule was first enunciated in 1953 to describe the observations in AgBr.[1] As reported then, the absorption coefficient α varied with temperature T and photon energy $\hbar\omega$ (in the spectral range of the edge) as

$$\alpha = A \exp[\sigma(\hbar\omega - \hbar\omega_0)/k_B T] , \qquad (1)$$

where k_B is Boltzmann's constant; $\hbar$ is Planck's constant divided by 2π; and A, ω_0, and σ are fitting parameters.[2] Subsequent measurements have led many others to a slightly modified version of this rule in absorption edges of an extensive number of ionic materials for photon energies as much as 1 eV below the first absorption peak.[3] The chief modification which has occurred has been the replacement of the temperature T by an effective temperature T^* such that, in ionic crystals,[4]

$$T^* = (\hbar\Omega_0/2k_B)\coth(\hbar\Omega_0/2k_B T) , \qquad (2)$$

where $\hbar\Omega_0$ is the energy of an optical phonon. We note that T^* and T differ significantly only at low temperatures. Aside from this, the only other alteration to the use of Eq. (1) for ionic crystals has been an occasional indication that σ, A, and ω_0 may be temperature dependent.

In semiconductors (both crystalline and amorphous), exponential absorption edges have often been observed, but the effective Urbach "temperature" is not given by Eq. (2). The exponential behavior as a function of photon energy might be termed a "spectral Urbach's rule," since

$$\alpha = A\, e^{g(\hbar\omega - \hbar\omega_0)} , \qquad (3)$$

with g, A, and ω_0 being fitting parameters whose temperature dependences may vary even from sample to sample of the same material. While the logarithmic slope $\sigma(k_B T^*)^{-1}$ of the absorption edge in ionic crystals has been correlated with the optical-phonon frequency Ω_0 (through T^*) and the electron–optical-phonon coupling constant (through σ),[5] the slope g in covalent semiconductors has been shown to be dependent on the concentration[6] and state of electrical charge of impurities.[7,8] Also, in contrast with the 0.1–1-eV-wide Urbach tails in ionic crystals, the impurity-induced exponential edges of semiconductors extend over spectral ranges of only tens of meV.[9–11]

In addition to the exponential edges observed in alkali halides,[12] II-IV compounds,[13] III-V semiconductors,[14] organics,[15] and amorphous systems,[16] extrinsic absorption bands in ionic materials sometimes exhibit exponential tails.[4] The spectral Urbach rule is so universally obeyed that we believe a single physical mechanism *must* be the cause of all the exponential absorption edges.[17,18]

Most previous theories of exponential edges do not pretend to explain the data in a unified manner. For example, theories of Urbach's rule in alkali halides have been based primarily on configuration coordinate models[5,19–24] [in which the configuration coordinates generally have some specific (e.g., parabolic) shape]. Various phonon-sideband and polaron models have been used to explain the phonon-induced edge shapes in II-VI and some III-V semiconductors.[25–32] In contrast, the impurity-related tails in covalent semiconductors have traditionally been described in terms of densities of states for random potentials[33] or Franz-Keldysh effects.[34] Of the many previous theories, only four seem to offer a potentially unifying mechanism: Dexter's original deformation-potential theory,[35] Redfield's internal Franz-Keldysh model,[34] Dexter's Stark-shifted exciton mechanism,[36] and the one-electron density-of-states theories.[33] The first of these[35] led to a nonexponential edge shape and has been abandoned by Dexter in favor of his more recent Stark-shift model.[36]

As we shall see in Sec. II, none of the previous theories is capable of explaining the essential physics of exponential edges in a quantitatively accurate and unified manner. Nevertheless, the primary conclusion of the present work is that there exists at least one unified mechanism for causing exponential edges (a preliminary report of this work has appeared[37]). The physical model is the electric field ionization of the exciton (i.e., the electron tunnels through the Coulomb barrier away from the hole). This unified mechanism, which builds upon the electric field theories of Redfield[34] and Dexter,[36] is general, but the sources of electric fields[38] may be optical phonons, impurities, or other imperfections.

In Sec. II, we establish criteria for a unified theory and discuss the relationship of previous theories to these criteria; Sec. III discusses the qualitative physics of the present field-ionization model (which satisfies the criteria of Sec. II). To illustrate the model, calculations of quantitatively exponential edges are presented in Sec. IV, using a uniform-microfield approximation (we are unable to solve the general problem of nonuniform microfields accurately). Section V is devoted to a discussion of the consequences of the theory and an analysis of the difficulties of the uniform-microfield approximation; the work is summarized in Sec. VI. Short reviews of the relevant experiments and theories may be found in Appendices A and B; Appendix C contains a derivation of the electric field distribution for LO phonons.

II. CRITERIA FOR UNIFIED THEORY

A. Role of Microfields

The first challenge of any unified theory of exponential absorption edges is to resolve the apparent conflict in the evidence that the Urbach edge is caused by optical phonons in most ionic solids[3–5,11] but by impurities in covalent semiconductors.[6–8] The mere existence of impurity-related exponential tails indicates that a unified theory cannot depend exclusively on the kinetic energy of the phonons and the lattice *dynamics*.[39] Therefore, those existing theories which ascribe Urbach's rule to polaron and phonon-sideband effects,[25–32] or configuration coordinates[5,19–24] cannot be general as they stand. These arguments do not mean that we reject phonons as the dominant agent in shaping the absorption edges of ionic solids—the evidence for the dominance of phonons is overwhelming. Rather, they emphasize the need for a mechanism by which the phonons participate in ionic materials and which is consistent with the results in semiconductors.

Such a unifying mechanism is available in the electric microfield[40] model originally proposed by Redfield[34] and subsequently developed by Dexter.[36] The importance of the electric microfields is strongly supported by the experiments of Dixon and Ellis[6] on InAs and of Redfield and Afromowitz[7,8] on GaAs, which show that the exponential edges in nearly covalent semiconductors are related to the concentrations and electrical charges of impurities.[41,42] (The root-mean-square electric fields in the materials showing impurity-caused Urbach tails are typically 10^4–10^5 V/cm.) In ionic crystals, the slopes of the spectral Urbach rule have been correlated with the strength of the polaron coupling, indicating that the LO phonons are responsible for the great breadth of those absorption edges.[5] The enormous electric fields associated with the longitudinal optical phonons in strong-coupling materials (~ 10^7 V/cm near room temperature, see Table I)[43] are consistent with the notion that electric fields[44] are primarily responsible for Urbach's rule.

In addition to the impurity fields in III-V and IV semiconductors and the LO-phonon fields in alkali halides and II-VI compounds, there are electric fields in elemental materials such as Se and Te because of the presence of more than two atoms per unit cell,[45] in amorphous systems because of impurities and disorder,[16,46] and in acoustoelectric experiments because of piezoelectric interactions.[47] If a unified mechanism of exponential absorption edges exists, it must be due to the electrostatic interactions between the excited-state electron-hole pair and these various (nonuniform) electric fields.

For the ionic solids, this treatment of the lattice vibrations in terms of their microfields must be recognized as a classical picutre of lattice dynamics. This is justified by noting that any theoretical description of a phonon-induced *exponential* edge demands an infinite number of phonons participating.[10] Every many-phonon con-

TABLE I. Static (ϵ_0), optical (ϵ_∞), and effective polaron [$\epsilon^* = (\epsilon_\infty^{-1} - \epsilon_0^{-1})^{-1}$] dielectric constants; conduction-band effective masses m^*; 1*s* exciton radii ($a = \hbar^2\epsilon_0/m^*e^2$) and energies ($R = e^2/2\epsilon_0 a$); longitudinal ($\hbar\Omega_{\text{LO}}$) and transverse ($\hbar\Omega_{\text{TO}}$) optical-phonon energies; polaron lengths [$l = 4\pi\epsilon^* a/\epsilon_0$ and $L = (\hbar/2m^*\Omega_{\text{LO}})^{1/2}$]; polaron coupling constants α; root-mean-square electric field strength F_{rms} and potential energy V_{rms} due to LO phonons at 300 K; and $f \equiv |e|F_{\text{rms}}a/R$ for various ionic materials. The polaron cutoff is taken to be $\pi/2a$. The Lyddane-Sachs-Teller relationship $\epsilon_0/\epsilon_\infty = (\Omega_{\text{LO}}/\Omega_{\text{TO}})^2$ is assumed to hold. Data for this table were taken from Ref. 51 and references therein.

Substance	ϵ_0	ϵ_∞	ϵ^*	m^* (m_0)	a (Å)	R (meV)	$\hbar\Omega_{\text{TO}}$ (meV)	$\hbar\Omega_{\text{LO}}$ (meV)	l (Å)	L (Å)	α	F_{rms} (kV/cm)	V_{rms} (meV)	$\bar{f}$
InSb	18	16	187	0.015	620	0.67	23	25	10^5	100	0.015	0.27	1.8	2.5
GaAs	12	11	88	0.067	94	6.1	34	37	8320	39	0.060	6.9	6.7	1.1
GaP	10	8.5	51	0.34	16	44	33	50	340	8.7	0.32	703	37	0.29
CdS	8.9	5.1	12	0.20	23	35	29	38	390	22	0.71	158	37	1.0
ZnO	7.9	4.0	8.1	0.24	17	53	51	72	255	15	0.83	336	51	1.1
ZnS	8.3	5.1	13	0.28	16	55	38	48	310	17	0.68	278	43	0.79
ZnTe	9.7	7.1	26	0.15	35	20	22	26	1200	32	0.33	54	20	0.89
PbS	170	19	21	0.16	575	0.072	16	50	890	22	0.31	1.0	5.5	79
Cu_2O	10	4.0	6.5	0.80	6.9	100	33	53	54	9.4	2.2	1380	91	0.96
AgCl	9.5	4.0	7.0	0.35	14	52	13	20	134	24	2.2	390	60	1.1
AgBr	11	4.6	8.0	0.24	23	29	9.9	15	226	32	1.8	175	43	2.1
TlCl	38	5.1	5.9	0.32	62	3.1	7.8	21	123	24	2.4	48	32	9.6
TlBr	31	5.4	6.6	(1)	16	15	5.9	14	44	16	4.7	348	60	3.6
MgO	9.8	3.0	4.2	(1)	5.2	140	81	148	28	5.1	2.3	3870	130	1.4
LiF	9.0	2.0	2.5	(1)	4.8	160	38	82	17	6.8	5.1	4360	176	1.3
NaCl	5.9	2.3	3.9	(1)	3.1	390	20	32	26	11	5.3	5400	175	0.43
KCl	4.5	2.1	4.0	0.50	4.8	330	18	26	54	17	4.0	2730	138	0.44
RbCl	4.6	2.2	4.3	0.52	4.7	330	15	21	56	19	4.2	2680	136	0.38
CsCl	7.2	2.6	4.1	(1)	3.8	260	12	20	27	14	6.3	3760	154	0.55
KI	5.1	2.6	5.4	0.40	6.8	208	13	18	90	23	3.3	1380	100	0.45

figuration is equivalent to a classical state which can be adequately represented—for LO phonons—by its classical electric field pattern.[48] The emphasis on the microfield representation, however, is primarily to show the unifying feature common to all of the materials concerned.

B. Exciton Effects

Once it has been recognized that the microfields must be generally responsible for exponential edges, it is necessary to determine how they affect the absorption edge shape—do they perturb primarily the motion of the electron, the hole, or both? And to what extent are the final-state Coulomb interaction and the correlations in the positions of the electron and the hole important? Recent calculations of optical absorption in a uniform electric field show that the Coulomb scattering between the electron and the hole enhances the optical absorption in the tail, relative to the one-electron Franz-Keldysh[49,50] absorption, *by several orders of magnitude.*[50] Therefore, the role of the Coulomb interaction between the electron and the hole cannot be overlooked in any quantitative treatment of Urbach's rule. So Redfield's theory,[34] which acknowledged the qualitative importance of the final-state electron-hole interaction, is incomplete because it neglects exciton effects.[51]

Other results of these uniform-field calculations[50,52] are that, for strong fields F (i.e., strong enough to shift the exciton energy by an amount equal to the binding energy) (i) perturbation theory diverges badly, (ii) the Stark shift is no longer quadratic, and (iii) the Stark broadening is much larger than the Stark shift. Thus Dexter's Stark-shift theory[36]—which relies on perturbation theory, neglects Stark broadening and relies on the quadratic nature of the Stark shift even for strong fields—must also be improved upon.

It should also be noted that neither of the previous microfield theories obtains an accurately exponential spectral shape as an inherent feature. They achieve the exponential shape by suitable averaging techniques.

Finally the one-electron density-of-states models are eliminated from consideration because they neglect not only the exciton effects but also the important field-induced correlations in the positions of the electron and the hole.[42]

C. Relative Motion

Since the electron-hole interactions are important for uniform fields, any general theory of exponential edges caused by nonuniform microfields should also be formulated in an exciton framework. To treat the electron-hole interaction, it is appropriate to consider the center-of-mass and the relative motions of the exciton rather than the separate motions of the electron and the hole. The question of whether the microfields cause an Urbach tail by perturbing the center-of-mass or the relative motion appears to have been decided by Schnatterly's experiments in KI. Those measurements[53] of circular dichroism lead to the conclusion that either the hole-phonon interaction is not responsible for the Urbach tail or else the lattice distortions of noncubic symmetry contribute less than 7% to the Urbach tail. We consider the latter alternative to be highly improbable. Therefore, since the center of mass of the exciton in KI is very nearly at the position of the hole, we infer that the *relative motion* of electron and hole—and not the center-of-mass motion—is responsible for Urbach's rule. This last conclusion has far-reaching consequences because it imposes severe limitations on many of the well-accepted theories.

III. FIELD-IONIZATION MODEL: PHYSICS

In Sec. II, we argued that none of the previous theories provided a quantitative unified explanation of exponential absorption edges. In this section we shall present a unified theory of exponential absorption edges which is consistent with the criteria of Sec. II and capable of explaining both Urbach's rule in alkali halides and the impurity-related edges in semiconductors. The treatment of the absorption edge will be given in terms of the Elliott theory of optical absorption by Wannier excitons.[54] The Elliott theory assumes the validity of the effective-mass approximation[55] and expresses the optical absorption coefficient in terms of the wave function $U(\vec{r})$ of the internal (relative) motion of the hydrogenic exciton; here $\vec{r}$ is the position vector of the electron relative to the hole. The absorption coefficient is proportional to the probability that the electron and the hole are in the same unit cell $|U(0)|^2$ times the density of relative-motion states per unit energy

$$\alpha(E) \propto \textstyle\sum_\nu |U_\nu(0)|^2 \delta(E - E_\nu). \tag{4}$$

Here $E = (\hbar\omega - E_{\text{gap}})$, where ω and E_{gap} are the photon angular frequency and the energy gap, respectively.

In the presence of a nonuniform electrostatic potential $V_e(\vec{r}; \vec{R}_{\text{c.m.}})$, the exciton wave function $U(\vec{r})$ solves the effective-mass equation

$$\left(-\frac{\hbar^2}{2\mu}\nabla^2 - \frac{e^2}{\epsilon_0 r} + V_e(\vec{r};\vec{R}_{\text{c.m.}})\right) U_\nu(\vec{r}) = E U_\nu(\vec{r}) \ . \tag{5}$$

Here μ is the reduced effective mass of electron and hole (assumed scalar) and ϵ_0 is the static dielectric constant. $V_e(\vec{r}; \vec{R}_{\text{c.m.}})$ is the potential energy associated with the microfields in the crystal[56]; the "$\vec{R}_{c.m.}$" is included to remind us that, in general, V_e depends parametrically on the coordinate of the center of mass of the exciton. But general theoretical arguments,[57] as well as Schnatterly's data[53] cited in Sec. II C, indicate that the center-of-mass motion primarily affects the shift of the absorption edge and is not an essential feature of Urbach's rule. Taking the center-of-mass wave function to be a plane wave, we henceforth suppress the "$\vec{R}_{c.m.}$" as the argument of the electrostatic potential V_e. The potential $V_e(\vec{r})$ is responsible for the Urbach edge by its tendency to ionize the exciton.

The physical reason for the exponential shape is demonstrated in Fig. 1(a), where the wave function and the potential energy for internal exciton motion are sketched, assuming a typical electrostatic potential distribution in the vicinity of the exciton. The essential feature is that an electron initially localized in a quasibound state near the hole can eventually tunnel out to the potential trough created by the potential fluctuations. In addition, the nonuniform potential creates new states at lower energies than in the field-free case. If V were constant, there would be no states below the 1s exciton; but in the presence of a quasistatic electric field[58,59] the final-state electron can be in a low-energy state with part of its wave function free (i.e., in the potential trough outside of the Coulomb well) and part of its wave function localized near the hole. If the outer potential trough is sufficiently wide and deep, the stationary-state wave function[60] will have almost all of its amplitude in the trough, and will have *exponentially* small amplitude near the hole (i.e., $\ln|U(0)| \propto E$). (We may also view this as a nonstationary-state problem in which an electron initially localized in the trough tries to tunnel into the hole with exponentially small tunneling probability.) This exponentially small amplitude for $U(0)$ is what leads, via the Elliott formula (4), to the exponential absorption edge of Urbach's rule.

It should be emphasized that the exponential shape is a *general* consequence of the field-ionization model and is independent of the details of the source of the microfield.

IV. UNIFORM MICROFIELD APPROXIMATION

A feature of this model is that the problem of understanding absorption edges is separated into two parts: (i) the evaluation of the optical absorption by excitons in a prescribed (nonuniform) electric field, and (ii) the (statistical) determination of the microfield distribution.[38] The optical absorption in an electric field is the component of the problem which is universal; the sources of the microfields are not universal and may be LO phonons, impurities, defects, or other phonons with accompanying electric fields. In order to calculate absorption tails and Urbach's rule, we need to (i) solve the Schrödinger equation (5) for a given disorder potential V_e, (ii) calculate the absorption according to the Elliott theory [Eq. (4)], and (iii) perform an average of the calculated absorption coefficient over the ensemble of all possible electrostatic potential distributions $V_e(\vec{r})$.

As a simple approximation to this procedure,[34,36] we (i) replace the electrostatic potential $V_e(\vec{r})$ by an ensemble of uniform-field potentials,[61] $-e\vec{F}\cdot\vec{r}$; (ii) use existing procedures to calculate the optical absorption by excitons in a uniform electric field; and then (iii) multiply the uniform-field absorption coefficient by the probability $P(F)$ that there is a field of magnitude F in the solid—and sum over all fields[62]:

$$\langle \alpha(E) \rangle = \int_0^\infty P(F)\alpha(E;F)dF \quad . \tag{6}$$

This uniform-microfield approximation is the same as the approximations used by Redfield[34] and Dexter[36]; the calculations are different from theirs only in that we use the *exact* result[51] [Eqs. (4) and (5)] for the uniform-field absorption coefficient $\alpha(E,F)$, while they use approximations valid only in the strong- and weak-field limits, respectively. It turns out (see Table I) that the microfields occurring in ionic solids or heavily doped covalent semiconductors are generally of intermediate strength.

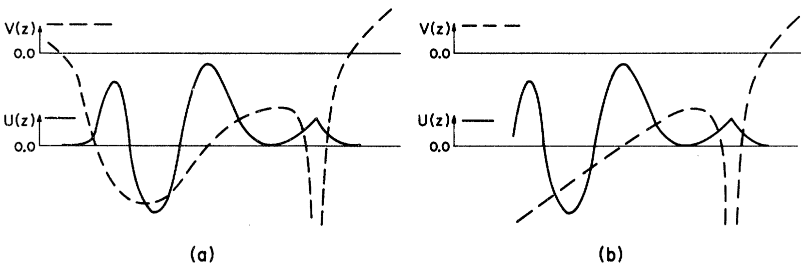

FIG. 1. Sketch of potential energy $V(z)$ (dashed line) and wave function $U(z)$ (solid line) as a function of position z along a typical direction. Here we have $V(z) = -e^2/\epsilon_0|z| + V_e(z)$, (a) for a typical electrostatic potential distribution $V_e(z)$; (b) for the uniform-field approximation $V_e(z) = -eFz$. Note that the model reproduces all the important qualitative aspects of the wave function including the excitonic exponential enhancement in the Coulomb well.

The probability $P(F)$ depends on the details of the source of the microfields. For an alkali halide, $P(F)$ depends primarily on the electron–optical-phonon coupling constant and the temperature; in a covalent semiconductor it depends primarily on the number and spatial distribution of ionized impurities. If the distribution of fields is Gaussian, then we have

$$P(F)=(\tfrac{2}{3}\pi\langle F^2\rangle)^{-3/2}4\pi F^2 e^{-3F^2/2\langle F^2\rangle}, \tag{7}$$

where $\langle F^2\rangle = F_{\text{rms}}{}^2$ is the mean-square field in the solid. This is essentially the case for compensated semiconductors[63] and for LO phonons in ionic solids.[36,64] In the latter materials we have (see Appendix C)

$$\langle F^2\rangle = \frac{\hbar\Omega_0 q_c^3}{3\pi\epsilon^*}\coth\left(\frac{\hbar\Omega_0}{2k_BT}\right) = \frac{2q_c^3 k_B T^*(\epsilon_0-\epsilon_\infty)}{3\pi\epsilon_0\epsilon_\infty}\ . \tag{8}$$

Here q_c is the polaron cutoff, normally of order π/a_L, where a_L is the lattice constant, T^* is the effective temperature [see Eq. (2)], k_B is Boltzmann's constant, and ϵ_0 and ϵ_∞ are the static and optical dielectric constants, respectively.

The replacement of the actual potential V_e [Fig. 1(a)] by a uniform field [Fig. 1(b)] is, of course, the most drastic simplification of the calculation and will be discussed below. It amounts to creating an infinitely deep and wide trough into which the electron can tunnel, and allows for a continuum of states throughout the previously forbidden region of the spectrum below the 1s exciton. Thus we should anticipate that those predictions of the uniform-microfield approximation which depend critically on the polaron cutoff wave vector q_c may be incorrect. Still the approximation contains the essential features of the real problem—namely, it accounts for the tunneling of the electron away from the hole (i.e., field ionization of the exciton) and introduces a continuum of states below the perfect-solid absorption threshold. In addition, the uniform-microfield approximation acknowledges a fact overlooked by density-of-states models: The electron and the hole are created in the same electrostatic environment and, as a consequence, their motions are highly correlated.

The optical absorption by excitons in a uniform field has been shown to have an edge with the exponential spectral dependence of Urbach's rule:

$$\alpha \propto e^{C(\hbar\omega-\hbar\omega_0)/F}\ , \tag{9}$$

where C is a constant.[51] There remains only the question of whether an exponential edge remains after field averaging via Eq. (6). In fact, the spectral Urbach rule does survive the averaging process as shown in Fig. 2, at least over the experimentally relevant[65] region of the spectrum. The fact that the exponential form Eq. (9) persists after averaging is an important feature of the present theory since it indicates that the exponential shape is insensitive to the details of the microfield distribution. Thus the tunneling model presented here can explain the spectral portion of Urbach's rule in alkali halides, as well as the impurity-induced exponential edges in covalent materials.

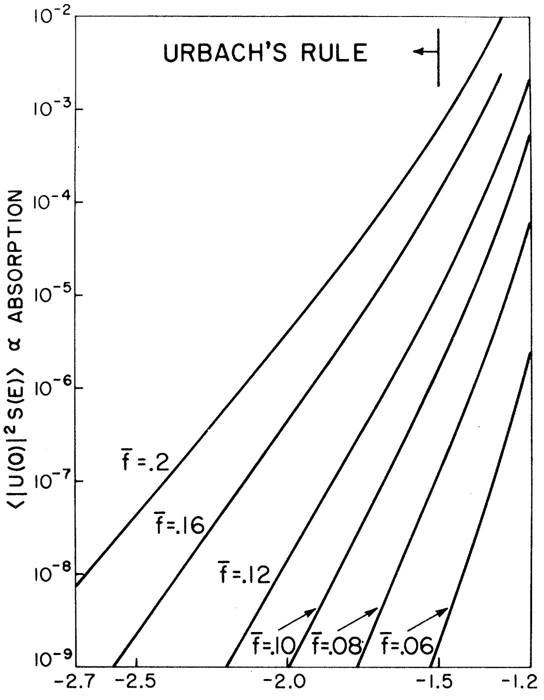

FIG. 2. Semilogarithmic plot of averaged theoretical optical absorption $\langle|U(0)|^2S(E)\rangle$ as a function of $E=(\hbar\omega-E_{\text{gap}})/R$ for various values of (reduced) root-mean-square field strength $\bar{f}=|e|F_{\text{rms}}a/R$ and for energies somewhat below the zero-field exciton ($E=-1.0$). Units are $a=1=R$ where a and R are the radius and the binding energy of the unperturbed 1s exciton, respectively. In alkali halides, the center of the exciton line is normally broadened by acoustic phonons, so that the exponential edge is seen only for $E<-1.5$. Note that the lines are straight over several decades of absorption and therefore exhibit Urbach behavior.

The temperature dependences of the exponential edges in various materials also follows simply and generally from the nature of the microfield sources. Thus the present theory is consistent with the experimental fact[7] that the impurity-related edge shapes in GaAs remain exponential but their logarithmic slopes vary as the microfield intensities change with temperature (viz., as the impurities become more or less ionized).

The temperature dependence in Urbach's rule for ionic crystals can be deduced from Eq. (8) which notes the proportionality

$$F^2_{\text{rms}} = \langle F^2\rangle \propto k_BT^*(q_ca)^3(\epsilon_0-\epsilon_\infty)/\epsilon_\infty\ . \tag{10}$$

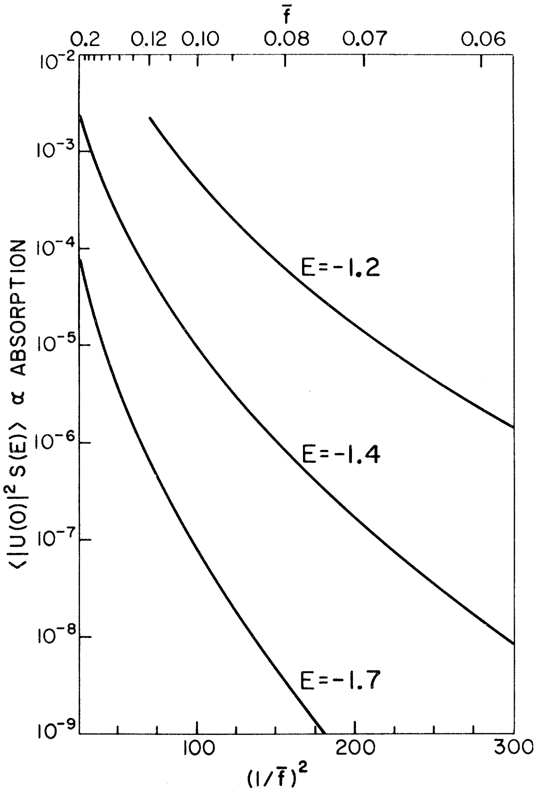

FIG. 3. Semilogarithmic plot of averaged theoretical optical absorption below the edge as a function of $(\bar{f})^{-2}$ for various values of E. If q_c^3 is independent of T^* [see Eq. (10)], then these lines must be straight for the temperature dependence of Urbach's rule in alkali halides to be adequately described by the present theory.

The ratio $(\epsilon_0-\epsilon_\infty)/\epsilon_\infty$ gives just the (weak) dependence of the Urbach exponent on the polaron coupling constant as noted by Toyozowa.[5] Since q_c is the polaron cutoff and a is the 1s exciton radius, it is appropriate to choose $(q_c a)$ to be less than or equal to unity. This choice automatically excludes electric fields due to LO phonons of wavelength shorter than an exciton radius; i.e., it ensures that only nearly uniform fields are included. The calculated temperature dependence of the absorption edge shape is also contained in Eq. (10) since the averaged absorption [Eq. (6)] will depend on $F_{\rm rms}$. If the polaron cutoff is taken to be independent of T^* (a choice which we believe to be physically incorrect), then the model would predict an absorption which is not proportional to $\exp[C(\hbar\omega-\hbar\omega_0)/F^2_{\rm rms}]$, the form necessary to obtain Urbach's temperature dependence $\exp[C(\hbar\omega-\hbar\omega_0)k_B T^*]$. That is, a semilogarithmic plot of absorption vs $F^{-2}_{\rm rms}$ should yield straight lines, but as we see in Fig. 3 the lines are not quite straight. It follows that either (i) the polaron cutoff is not independent of $F_{\rm rms}$ and T^*; or (ii) the logarithmic slopes of the measured spectral Urbach edges should not be strictly proportional to $(T^*)^{-1}$, but should show slight deviations from the predicted Urbach behavior[66]; or (iii) the tunneling model of Urbach's rule is incorrect, and no theory of exponential absorption edges is universal. We believe that the source of the difficulty lies with the uniform-field model and the choice of polaron cutoff. As we see in Fig. 4, the calculated absorption varies nearly as

$$\alpha \propto e^{C(\hbar\omega-\hbar\omega_0)/F_{\rm rms}}\,, \tag{11}$$

in consequence of the constant-cutoff approximation rather than as $e^{C(\hbar\omega-\hbar\omega_0)/F^2_{\rm rms}}$. Hence the constant-cutoff theory demands a logarithmic Urbach slope which varies at $(T^*)^{-1/2}$ instead of the experimentally determined $(T^*)^{-1}$ dependence.

Basically, the reason for the failure of the constant-cutoff model to obtain an Urbach temperature dependence is ascribable to the arbitrary choice of the cutoff $q_c \sim a^{-1}$. In fact, this choice can be improved upon. First, the field should be quasiuniform over a tunneling distance, not just

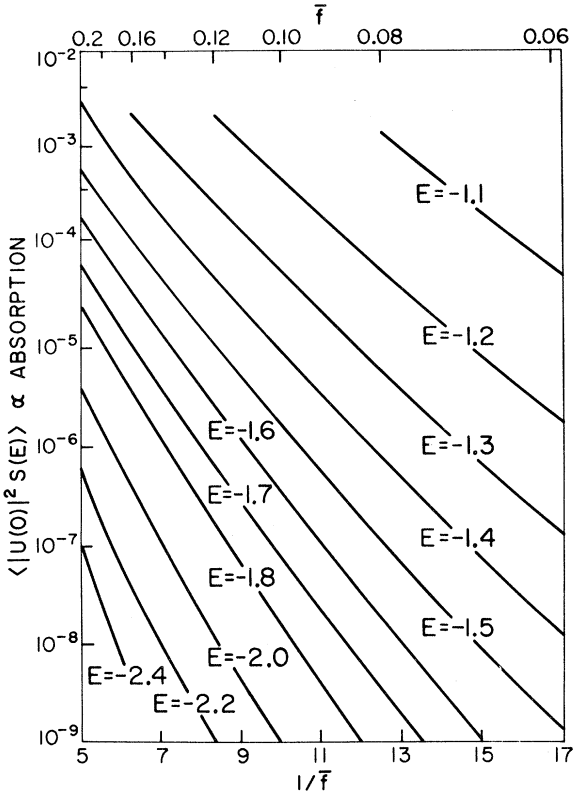

FIG. 4. Semilogarithmic plot of averaged theoretical optical absorption below the edge as a function of $\bar{f}^{-1}$ for various values of E. The straightness of these lines indicates that the present theory with q_c^3 proportional to T^* is able to describe the temperature dependence of Urbach's rule in alkali halides.

over an exciton radius (i.e., field ionization must be possible); and second, the potential trough [see Fig. 1(a)] must be deep enough and wide enough for a bound state to exist in it. Both of these requirements have the qualitative effect of giving a temperature dependence which is more nearly the Urbach dependence. Note that both the field strength and the depth of the trough in Fig. 1(a) will be proportional to $(T^*)^{1/2}$; the uniform-field constant-cutoff approximation omits the second factor of $(T^*)^{1/2}$ and therefore obtains an incorrect Urbach temperature dependence. We have not tried to formulate a quantitative theory of the cutoff, because a uniform-field theory which depends in detail on the short-wavelength cutoff of the fields is not a very satisfactory theory in the first place. Still, we believe that we understand the qualitative physics of the Urbach temperature dependence: As the temperature is increased, the shorter-wavelength optical phonons become more important.

The increasing importance of the short-wavelength phonons with temperature can be seen by the following three qualitative arguments. First, consider an electron of energy E well below the 1s exciton level in Fig. 1. Furthermore, suppose that the electrostatic potential in that figure is approximated by a single Fourier component of the potential plus the electron-hole interaction. If this component has a long wavelength ($q \approx 0$), the trough in Fig. 1(a) will be deep ($V_q \propto q^{-1}$) and wide—permitting the electron to tunnel into it easily. In contrast, a short-wavelength potential will create a narrow trough which may not be deep enough to permit the tunneling. Now as the temperature is increased, the potential trough will get deeper as $T^{*1/2}$; thus as T^* increases, the short-wavelength phonons will eventually give rise to a sufficiently deep potential to induce tunneling.

Second, a semiquantitative understanding of this effect follows from this dimensional analysis of q_c as a function of temperature. Consider the limitations the uncertainty principle puts on the choice of q_c. To fit into a trough of wavelength q_c^{-1}, the electron must have

$$q_c \sim \Delta p_x/\hbar \sim [(2m^*/\hbar^2)(E-V)]^{1/2} \quad . \tag{12}$$

Noting that the amplitude of the fluctuations in the electrostatic potential V [see Eq. (16) in Appendix C] is proportional[67] to $(T^* q_c)^{1/2}$, we find [ignoring E in Eq. (12)] that we have

$$(q_c a)^3 \sim k_B T^* \, 4\epsilon_0/\pi R \epsilon^*, \tag{13}$$

where R is the binding energy of the 1s exciton. If this argument were quantitatively, and not just qualitatively, correct F_{rms} would be proportional to T^* [see Eq. (10)] and we would predict the correct Urbach rule relationship [Eq. (11)]

$$\alpha \propto e^{\sigma(E-E_0)/k_B T^*} \quad . \tag{14}$$

A third, more quantitative, way to look at this same problem of the requirement that the potential valley be capable of supporting a quantum-mechanical bound state is to consider the following model of a typical nonuniform-field fluctuation

$$V = \begin{cases} -eF_{\mathrm{rms}} z, & \text{if } |x| < q_c^{-1}, \quad |y| < q_c^{-1}, \\ & \text{and } |z| < q_c^{-1} \\ \infty \;, & \text{otherwise.} \end{cases} \tag{15}$$

The lowest-energy bound state of this potential occurs for q_c such that

$$q_c^{-3} + \frac{a_1}{2\bar{f}^{\,1/3}} + \frac{E}{2R\bar{f}} q_c^{-2} - \frac{\pi^2}{\bar{f}} = 0 \quad . \tag{16}$$

Here $\bar{f} = |e| F_{\mathrm{rms}} a/R$, and a_1 is the first zero of the Airy function. Dimensionally (neglect the second term) we see that[68]

$$q_c^3 \propto F_{\mathrm{rms}} \; . \tag{17}$$

Since q_c^3 is proportional to the root-mean-square field strength, we find from Eq. (10) that $F_{\mathrm{rms}} \propto k_B T^*$, giving the exact Urbach rule relationship. Thus three different qualitative arguments lead us to the result for Urbach's rule

$$\alpha(\omega) = A\, e^{\sigma(\hbar\omega - \hbar\omega_0)/k_B T^*} \quad ,$$

with σ a constant which may depend on ϵ^*.[69]

In summary, the tunneling theory quantitatively predicts the spectral dependence of Urbach's rule, but, in the uniform-microfield approximation, the model can predict the proper temperature dependence only qualitatively, because the detailed temperature variation is somewhat sensitive to the shorter-wavelength phonons and the details of the polaron cutoff.

V. CONSEQUENCES AND DIFFICULTIES

In this section we indicate the problems with the present theory and sketch general lines along which experimenters might try to test this and other theories.

One of the real difficulties with this model is its inability to cope quantitatively with phonons of very short wavelength. Since each phonon gives rise to an electric field of the same magnitude, and the number of phonon states is highest near the Brillouin-zone boundary, we must be prepared to argue for the omission of phonons with q such that $q_c < q < q_{\mathrm{Debye}}$. In fact, we shall argue that if the short-wavelength phonons do contribute significantly to Urbach's rule, then they do so in a manner similar to that of the long-wavelength phonons. Thus the uniform-field model presents a qualitatively correct picture of exponential absorption edges; however, a more quantitative treatment will require generalization of the model to include the effects of the nonuniform fields associated with short-wavelength potential fluctuations. First, we note that the electron-phonon interaction is proportional to q^{-1} (see Appendix C), thus weakening the influence of all short-wavelength modes. Second, note that in alkali halides the exciton radius is nearly equal to a lattice constant. Therefore q_c and q_{Debye} are of the same order of magnitude, and a significant fraction of the phonons have wave vectors less than q_c. Third, short-wave phonons by their very nature, tend to average to zero over the distances of interest. Fourth, even though a particular short-wavelength potential hump may tend to reduce the rate of tunneling in a given direction (by increasing the size of the potential mountain), it does not change the qualitative picture of tunneling which is mostly determined by the longer-wavelength components of the field.[70] Furthermore, the short-wavelength potential valleys will tend to increase the tunneling rate exponentially, more than compensating for the effects of the short-wavelength humps. Finally, in tunneling through the potential mountain from the hole, the electron will (statistically) go through the mountain at its narrowest point, and then travel through valleys of the potential around subsequent mountains (see Fig. 5). Note that the hole can always minimize its energy by residing in a region of the crystal where the electrostatic potential repels the electron, and the electron, by virtue of its lighter mass, finds it easier to tunnel through the potential mountain. Even if the closest valley into which the electron tunnels does not have enough action $(\Delta z \Delta p_z)$ in the tunneling (z) direction, the electron can still tunnel if the potential valley can provide enough additional phase space in the other directions $(\Delta x \Delta y \Delta p_x \Delta p_y)$ to support a bound state $(\Delta x \Delta y \Delta z \Delta p_x \Delta p_y \Delta p_z \gtrsim h^3)$. Therefore, what is probably important is "How far must the electron tunnel to the nearest valley?"—and this distance will be generally shortened by the high-q phonons. Hence, the short-wavelength phonons, if they have an effect, will not qualitatively change the results of the model calculation presented here. These arguments do make it clear, however, that a complete understanding of the Urbach tunneling will come only after an understanding of three-dimensional potential fluctuations and random potential problems.

One aspect of the absorption edge which does not lend itself to treatment by the classical field approach is the low-temperature behavior of the edge. It is noteworthy that, contrary to the prevailing opinion, the exponential spectral variation does *not* continue at low temperatures in any ionic materials except possibly for the alkali halides. That is, Eqs. (1) and (2) do not apply in that temperature range. This has been shown clearly in II-VI compounds by the work of Thomas *et al.*[25] and by Marple.[27] It is true for the silver halides,[71] SrTiO$_3$,[72] and SnO$_2$.[73] In all of these materials, the absorption edge at low temperatures develops structure that is clearly related to phonons, even though some have direct energy gaps. It should be emphasized that this low-temperature structure is related to the dynamics of the lattice and is a quantum effect.

A theory for such behavior in the II-VI com-

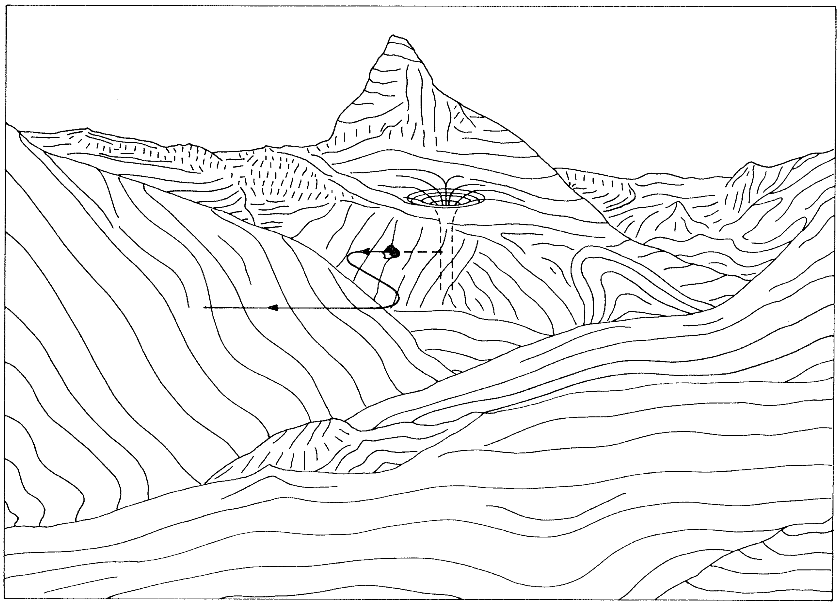

FIG. 5. Plot of the potential energy of the electron as a function of position in two dimensions. Note that the electron's wave function is large in the attractive Coulomb well of the hole and then tunnels out of the mountain, distorting on the valleys so that it finds enough phase space to permit the existence of a quantum state at that energy.

pounds[74] was advanced initially by Thomas, Hopfield, and Power[25] and developed subsequently by Segall.[26] These theories invoke phonon absorption sidebands on the direct exciton transitions and Segall believes that increasing temperature causes such sidebands to broaden in such a way that their envelope forms the exponential edge of Urbach's rule. Segall's mechanism seems to differ from the one proposed here in two important respects: (i) It specifically requires the quantum dynamics of the lattice vibrations and therefore seems incapable of explaining impurity-related exponential edges in other materials, and (ii) it seems to obtain the exponential edge by having the phonons perturb the energy of the exciton center of mass. If Segall's interpretation of Marple's measurements on the Urbach edge of CdTe is correct, and if the conclusions drawn here from the experiments of Schnatterly on KI and of Redfield and Afromowitz on GaAs are likewise valid, then it is likely that there is no universal mechanism underlying Urbach's rule in alkali halides, II-VI, and III-V compounds. It is important to emphasize the difference between Segall's interpretation of Marple's absorption edge[27] in CdTe and ours: For Segall, the (broadened) phonon sidebands at low temperature become increasingly broad as temperature increases, forming the Urbach tail. For us the phonon sidebands and Urbach's edge coexist at low temperatures, with the exponential edge almost completely frozen out and the phonon sidebands (ideally) almost without width. As temperature is increased the exponential edge becomes relatively more important, causing the sidebands to broaden and eventually disappear. For Segall, the sidebands become the Urbach tail when broadened at high temperatures; for us the "broadening" is the Urbach rule and the low-temperature phonon-sideband behavior is a separate quantum-dynamical effect.

The present model assumes that the microfields perturb only the internal, relative motion of the exciton. Although this assumption seems to be amply justified by Schnatterly's experiment in KI, its validity has not been demonstrated in any other system. Therefore, it is possible that in some nonconducting solid the exponential absorption edges may be due to the electric field perturbed motion of the exciton center of mass.[75] Since the exciton has zero total charge, the center-of-mass motion does not couple to a uniform electrostatic field but does interact with the higher multipoles of the field distribution associated with short-wavelength potential fluctuations. (Contrast this with the relative motion which interacts strongly with a uniform field and the long-wavelength potential fluctuations.) This interaction between the center of mass and the short-wavelength microfields may serve to (statistically) shrink the average effective band gap. Therefore, a general theory of Urbach's rule based on the interaction of (primarily) short-wavelength electrostatic potential fluctuations is possible, although such a theory would have several features in common with the original Dexter deformation-potential theory.[35] However, such a theory probably would give a Gaussian edge rather than the observed exponential edge of Urbach's rule.

In spite of the abilities of the present theory to explain a broad range of experimental data, the claim that it can describe all exponential edges must be justified or disproved by experiments. In addition to testing the hypotheses in Sec. II and determining their validity in ionic and covalent materials, experimental studies of exponential edges should determine the relative importance of long- and short-wavelength potential fluctuations and of center of mass and internal exciton motions.

For example, the importance of long- vs short-wavelength phonons in ionic materials might be determined by overpopulating the phonons of a given wavelength and observing the changes in the edge shape. A nonequilibrium distribution of polar optical phonons of long wavelength can be obtained by first creating large numbers of free-electron–hole pairs (by the absorption of laser light) and then letting the free electrons and holes decay via multiple-phonon emission. Thus the electron-phonon interaction, which varies as q^{-1}, will favor the $q \approx 0$ long-wavelength phonons.[76]

The question of center-of-mass vs internal exciton motion being responsible for exponential edges should be amenable to an experimental answer. For example, some probes such as uniform electric fields couple only to the internal relative motion of the exciton, while others (e.g., stresses and deformations) interact primarily with the center of mass. Therefore, modulation spectroscopic studies[77] of absorption edges should yield valuable information about Urbach's rule: If the exponential edge is due to electric field ionization of the exciton, an additional electric field should further broaden the edge without appreciably shifting the peak; if the Urbach tail is a center-of-mass effect, a pure center-of-mass probe should shift the edge and the peak rigidly to lower energy.[78]

In addition to these experiments, efforts should be made to test the various theories and to answer more completely a number of fundamental questions. A clear demonstration that there can be no unified theory of exponential edges would certainly upset the present theory. Such a demonstration might show the importance of different mechanisms in different materials or the general importance of center-of-mass effects, quantum phenomena, acoustic phonons, ionic masses, or energy shifts rather than broadenings. Experimenters might try to learn more about the ultimate fate of the electron-hole pair[79] and the relationships among photoconductivity,[80] radiative recombination,[81] and optical absorption. In addition, more should be known about extrinsic edges,[82–84] absorption edges related to deformation potentials and piezoelectric interactions,[47] line shapes in layered (two-dimensional) materials,[85] the effects of large central cell corrections on exponential edges,[83] and surface effects.[86]

VI. SUMMARY

In summary, we find that Urbach's rule and exponential absorption edges can be understood as due to electric-field-induced ionization of the exciton. The source of the ionizing electric field may be LO phonons, impurities, or piezoelectric phonons; the exponential shape of the edge as a function of photon energy is insensitive to the details of the microfield distribution. The proposed mechanism ascribes an exponential spectral dependence to the broadening of the lowest exciton state, which is caused by tunneling of the electron away from the hole. The microfields primarily affect the relative, intermal motion of the exciton.

The formulation in terms of microfields permits a unified theory of exponential absorption edges and allows a separation of the calculation of the edge shape into two parts: (i) the calculation of optical absorption in an electric field and (ii) the determination of the classical microfield distribution appropriate for the particular source of field.

The theory presented here succeeds in obtaining the exponential spectral dependence of Urbach's rule, and it is able to qualitatively predict the temperature dependence of optical-absorption edge shapes in alkali halides. We believe that the correct physics of Urbach's rule is in hand, but a detailed understanding of the temperature dependence in alkali halides awaits a model which includes the effects of nonuniform fields.

Note added in proof. A number of papers on exponential absorption edges have appeared recently. These include work by Robinson and Bosacchi on an exactly solvable polaron model,[87] papers by Toyozawa and co-workers on an acoustic-phonon mechanism for self-trapping the exciton (Ref. 88, which includes comments on the present work, which are considered in Ref. 89), a review of the exponential edge problem,[90] discussions of absorption edge shapes in amorphous semiconductors,[91] and an effective-impurity model calculation of the absorption edge shape as a functional of the densities of band-tail states.[92] This last calculation lends further support to the idea that the internal motion of the electron-hole pair plays a more important role in shaping the edge than the center-of-mass motion.

ACKNOWLEDGMENTS

We gratefully acknowledge stimulating and informative discussions with J. J. Hopfield, D. L. Dexter, S. E. Schnatterly, R. S. Knox, M. H. Reilly, G. Roberts, J. Tauc, and Y. Toyozowa.

APPENDIX A: EXPERIMENTAL OBSERVATIONS OF URBACH'S RULE

The most important, and least recognized, aspect of the many published reports on exponential absorption edges is that observations of the *full* Urbach rule [Eqs. (1) or (2)] are very rare. General usage of this title has often distorted it to refer simply to an exponential *spectral* dependence of α on E, without reference to the temperature dependence. A second type of undifferentiated observation is the quantitatively correct spectral behavior together with only a qualitatively appropriate temperature dependence (i.e., steeper slope at lower temperature) which is not established as exponential in temperature.

Furthermore, careful examination of the literature shows that even the spectral Urbach rule does not apply at low temperatures ($\lesssim 100$ K) for any ionic solids other than the alkali halides. For example, the silver halides, in which this rule was first discovered,[1] are now known to be indirect gap materials and their absorption edges have structure at low temperatures associated with phonon assistance.[71] A similar type of transition from an Urbach-like rule above 200 K to phonon-related structure at low temperatures is also seen in $SrTiO_3$.[72]

The related ferroelectrics $BaTiO_3$ and $KTaO_3$ are examples of the second type of almost-Urbach behavior. Their exponential spectral dependence has been found to be associated with the unusual temperature dependence

$$T^* = T + T_0 \ ,$$

[where this T^* is the same as that in Eq. (2) and T_0 is a constant].[93]

The largest class of materials in which some sort of Urbach rule is observed is the class of II-VI compound semiconductors.[13] In none of these, however, is the Urbach temperature dependence quantitatively shown. Also, the low-temperature spectra have structure in them even though they are generally direct-gap materials.[25–27]

The most detailed studies of Urbach's rule have been in the alkali halides. To our knowledge, the only quantitative demonstration of the Urbach temperature dependence (other than the original crude one) has been in KI by Martienssen and Haupt (working in Martienssen's laboratory).[12] The more detailed measurements and interpretation later by Mahr using KI in KCl suggest that the extent of the fit of the Martienssen-Haupt results to the Urbach formula may have been exaggerated.[4] Mahr's work showed that the exponential spectral dependence does not really set in until α drops about two orders of magnitude below the peak value. Above this, the spectral dependence is Gaussian.

As for the covalent materials, the reported results were still more confused until the dominance of impurities and their electrical charges were demonstrated for the III-V compounds.[7] Se seems to be a special case because the temperature dependence seems intrinsic. As mentioned in the text, however, it has optical phonons with a first-order electrical charge[45]; and we therefore group it with the ionic materials.

Very heavy dopings in Ge (~ 0.2%) have been observed to transform the absorption edge from the phonon-assisted spectrum to an exponential shape.[94] It seems widely believed that the density-of-states band tails caused by doping of semiconductors are solely responsible for the exponential absorption edges.[14] But the spatial separation of the electron and hole causes the transition matrix element to be exponentially small for transitions between band tail states; this matrix element effect is at least as important as the pure density-of-states effect.[8]

Amorphous semiconductors typically show a spectral Urbach rule which is quite broad.[16] Here, too, no well-defined temperature dependence is found and there is still much uncertainty about the relationship of the shape of the edge and the disordered state. Tauc has recently proposed[46] an explanation of such edges based on a viewpoint similar to that used by Redfield and Afromowitz for doped covalent crystalline materials.

APPENDIX B: RELATIONSHIP OF PREVIOUS THEORIES TO PRESENT WORK

The previous theories fall into five general categories: (i) Dexter's deformation-potential theory, (ii) configuration coordinate models,[19–24] (iii) electric microfield theories,[34,36] (iv) polaron and phonon-sideband theories,[25–32] and (v) density-of-states theories.[33]

Dexter's original deformation-potential theory[35] obtains an edge shape which is approximately Gaussian and results from non-electric-field-like antiparallel displacements of valence- and conduction-band edges. In this model, exciton effects are neglected and the Urbach tail arises primarily from perturbations of the center-of-mass energy of the electron-hole pair. Thus the deformation-potential model is in direct opposition to the present model.

The configuration-coordinate theories depend on the dynamics of the lattice, implicitly include exciton effects, and rely on short-wavelength phonons, but fail to display the dependence of the configuration coordinate on the internal motion of the exciton. The extent to which the various configuration coordinates are mostly electric-field-like (rather than "elastic"-like[38]) must be determined in each individual case. However, absorption by a self-trapped hole with an electron orbiting about it can be viewed as a configuration-coordinate mechanism somewhat analogous to the model proposed in Sec. II. The final-state hole settles partly in each of two potential troughs, tunneling from one side to the other; the electron orbits about this hydrogen molecular-ion-like V_K center.[95] In this case, the electrostatic field associated with the ions creates the potential troughs; neither the hole nor the electron is localized; the hole tunnels relative to the electron (not *vice versa*); and (in contrast with the general theory of Sec. III) the light-mass electron occupies a delocalized orbit about the self-trapped hole.

Of the microfield models from which the present work arises, Redfield's[34] neglects the Coulomb interaction between the electron and the hole by using the Franz-Keldysh form of the uniform-field absorption, which has an asymptotic form varying exponentially as the $\frac{3}{2}$ (rather than 1) power of photon energy

$$\alpha_{\text{F-K}} \propto (f^{1/3}/4\pi)(|\text{Ai}'(z)|^2 - z\text{Ai}^2(z)) \sim (f/32\pi^2|E|)\exp(-\tfrac{4}{3}|E|^{3/2}/f) \; .$$

Here we use

$$E=(\hbar\omega - E_{\text{gap}})/R, \quad a=\hbar^2\epsilon_0/\mu e^2 \; ,$$

$$R=e^2/2\epsilon_0 a, \quad f=|e|Fa/R, \quad z=E/f^{2/3} \; .$$

Dexter's Stark-shift, in the hydrogenic exciton approximation, gives an absorption

$$\alpha_{\text{Ss}} \propto \pi^{-1}\,\delta(\hbar\omega - E_{\text{gap}} + R + \tfrac{9}{8}f^2R) \; .$$

Thus, in contrast with the present model which obtains an exact exponential shape from excitonic absorption in the presence of a field,[50] the previous microfield models had to rely on the field-averaging process to obtain the exponential shape. Furthermore, for a given average field, Redfield and Dexter predict a much sharper edge than the present theory does. Comceptually, the Franz-Keldysh effect is a photon-assisted interband tunneling while the Stark shift results from polarization of the exciton. The present work unites these two different physical pictures by noting that the Franz-Keldysh effect may also be viewed as the field ionization of an exciton with zero binding energy, while polarization of the exciton is the weak-field limit of field ionization.

Dexter's calculation differs from the computation of Sec. IV in one other respect: He goes beyond the hydrogenic-exciton approximation and allows a general shape $L(E)$ for the zero-field exciton line. Such line shapes are generally due to acoustic-phonon scattering and can be incorporated into the present theory by replacing $\alpha(E,F)$ in Eq. (6) by its broadened value

$$\pi \int_{-\infty}^{\infty} \alpha(E-R-x)L(x)\,dx \quad .$$

In order to emphasize the fact that the exponential edge does not arise from any averaging process, we have not broadened the spectrum in Fig. 2 the way Dexter does. Such broadening, if it were Gaussian, would flatten the absorption near the peak while preserving the exponential tail.

Theories of exponential edges in pure, nearly covalent semiconductors have been advanced using (virtual) indirect transitions at the zone center and (real) phonon absorption sidebands.[25–32] Both these mechanisms seem to require phonon dynamics, and the indirect transition model not only is insensitive to the electric fields of the phonons, but also seems to invoke perturbations primarily of the center of mass. Neither model is capable of evaluating the many-phonon limit. Still, the phonons generally do generate electric fields and these theories may have more in common with the present theory than is apparent at first examination. For example, the trough in Fig. 1(a) could be created by many phonons opening an optical-absorption channel many phonon energies below the zero-phonon line.

Mahan[31] and Dunn[32] have calculated the density of states for an interacting electron-phonon system and find an exponential dependence. Dunn's calculation, while avoiding many of the approximations of Mahan's, took constant electron-phonon coupling (i.e., deformation potential) instead of optical-phonon coupling (which varies as q^{-1}); therefore his results suggest that any electron-phonon interaction will give an exponential edge. While both these theories give the appearance that they depend on phonon dynamics, the exponential edge shape does not depend on the ionic mass. We believe that these polaron theories are quite similar in spirit to the theory presented here, that they can be extended to include exponential edges associated with electrostatic microfields, and that those theories make approximations to the electron's self-energy which are essentially equivalent to assuming a wave function of the type sketched in Fig. 1(a) (but with exciton effects omitted). While the Coulomb interaction between the electron and the hole is not included in either Mahan's or Dunn's theories, those authors do a rather good job of accounting for all the phonons (not just the long-wavelength ones). It is especially noteworthy that in Dunn's calculation, the imaginary part of the polaron self-energy near threshold seems to be somewhat less sensitive to short-wavelength phonons than the real part. This is in general accord with our result that the exciton line broadening is dominated by the long-wavelength fields while the line shift is more dependent on short-wavelength potential fluctuations.

The theoretical work on exponential edges in heavily doped semiconductors has followed quite different lines, with most of the effort devoted to understanding the density of states for various random potentials.[33] Thus, this density-of-states work is similar to the calculations of Mahan[31] and Dunn,[32] but fails to explicitly point out the importance of electric fields and electron-hole correlations.

APPENDIX C: MICROFIELD DISTRIBUTION FOR LO PHONONS

The evaluation of the probability $P(F)$ begins with the Fröhlich Hamiltonian for the electron-phonon interaction $\mathcal{H}_{ep}$

$$\mathcal{H}_{ep} = V^{-1/2} \sum_{\vec{q}} V_q e^{i\vec{q}\cdot\vec{r}} (a_{\vec{q}} - a^{\dagger}_{-\vec{q}}) \,, \tag{C1}$$

where V is the crystal volume and, for optical-phonon coupling, we have

$$V_q = -\, i\hbar\Omega_0 (4\pi\alpha)^{1/2} (\hbar/2m^*\Omega_0)^{1/4} |\vec{q}|^{-1} \,, \tag{C2}$$

where $\hbar\Omega_0$ is the optical-phonon energy, m^* is the electron effective mass, and α is the polaron coupling constant

$$\alpha = \frac{(m^* e^4/3h^3\Omega_0)^{1/2}}{\epsilon^*} \,, \tag{C3}$$

where ϵ^* can be expressed in terms of the static and optical dielectric constants ϵ_0 and ϵ_∞ as $\epsilon^* = (\epsilon_\infty^{-1} - \epsilon_0^{-1})^{-1}$. The electric field operator is

$$\vec{F}(\vec{r}) = \left(\frac{2\pi\hbar\Omega_0}{\epsilon^* V}\right)^{1/2} \sum_{\vec{q}} \frac{\vec{q}}{|\vec{q}|} (a_{\vec{q}} e^{i\vec{q}\cdot\vec{r}} + a^{\dagger}_{\vec{q}} e^{-i\vec{q}\cdot\vec{r}}) \,. \tag{C4}$$

First we wish to determine the probability $P_z(F'_z)$ that a particular component of the field, say the z component, has a value between F'_z and $F'_z + dF'_z$.[96] This can be done by constructing the characteristic function of the distribution $\phi_z(u)$ and Fourier transforming.[96] The nth moment of the distribution is

$$\int_{-\infty}^{\infty} (F'_z)^n P_z(F'_z)\, dF'_z = \mathrm{Tr}(\rho_0 F_z{}^n) \,, \tag{C5}$$

where ρ_0 is the density matrix for the canonical ensemble. The characteristic function is

$$\phi_z(u) = \mathrm{Tr}(\rho_0 e^{iuF_z}) \,, \tag{C6}$$

which leads to a simple expression for P_z

$$P_z(F'_z) = (2\pi)^{-1} \int_{-\infty}^{\infty} \phi_z(u) e^{-iuF'_z}\, du \,. \tag{C7}$$

The evaluation of $\mathrm{Tr}(\rho_0 e^{iuF_z})$ is a straightforward problem solved by Bloch and available in Messiah's book,[96]

$$\phi_z(u)=Z^{-1}\,\mathrm{Tr}\{\exp[-\beta\hbar\Omega_0\textstyle\sum_{\vec{q}}(a^\dagger_{\vec{q}}a_{\vec{q}}+\frac{1}{2})]$$
$$\times\exp[iu\textstyle\sum_{\vec{q}}\gamma_{\vec{q},z}a_{\vec{q}}+\gamma^*_{\vec{q},z}a^\dagger_{\vec{q}}]\}\,,\qquad\text{(C8)}$$

where

$$\beta=(k_BT)^{-1}\,,$$
$$\gamma_{q,z}=(2\pi\hbar\Omega_0/\epsilon^*V)^{1/2}(q_z/|\vec{q}\,|)e^{i\vec{q}\cdot\vec{r}}\,,\qquad\text{(C9)}$$
$$Z=\mathrm{Tr}\{\exp[-\beta\hbar\Omega_0\textstyle\sum_{\vec{q}}(a^\dagger_{\vec{q}}a_{\vec{q}}+\frac{1}{2})]\}\,.$$

Algebraic manipulations reduce Eq. (C8) to

$$\phi_z(u)=\textstyle\prod_{\vec{q}}[1-\exp(-\beta\hbar\Omega_0)]\,\mathrm{Tr}\{\exp(-\beta\hbar\Omega_0a^\dagger_{\vec{q}}a_{\vec{q}})$$
$$\times\exp[iu(\gamma_{\vec{q},z}\,a_{\vec{q}}+\gamma^*_{\vec{q},z}a^\dagger_{\vec{q}})]\}\,.\qquad\text{(C10)}$$

Straightforward manipulation of exponential operators yields

$$\phi_z(u)=e^{-(1/2)u^2\langle F_z^2\rangle}\,,\qquad\text{(C11)}$$

where

$$\langle F_z^2\rangle=\mathrm{Tr}(\rho_0F_z^2)=\textstyle\sum_{\vec{q}}|\gamma_{\vec{q},z}|^2\coth\frac{1}{2}\beta\hbar\Omega_0\equiv\frac{1}{3}\langle F^2\rangle\,.\qquad\text{(C12)}$$

Fourier transformation gives

$$P_z(F'_z)=(2\pi\langle F_z^2\rangle)^{-1/2}e^{-(1/2)F'^2_z/\langle F_z^2\rangle}\,.\qquad\text{(C13)}$$

The probability $P(F)$ that there is a field of magnitude F is

$$P(F)=\int\int\int_{\infty}^{\infty}P_x(F'_x)P_y(F'_y)P_z(F'_z)$$
$$\times\delta(F-(F'^2_x+F'^2_y+F'^2_z)^{1/2})dF'_xdF'_ydF'_z$$
$$=(\tfrac{2}{3}\pi\langle F^2\rangle)^{-3/2}4\pi F^2e^{-3F^2/2\langle F^2\rangle}\,.\qquad\text{(C14)}$$

Evaluating $\langle F^2\rangle$ we find

$$\langle F^2\rangle=(\hbar\Omega_0q_c^3/3\pi\epsilon^*)\coth(\tfrac{1}{2}\beta\hbar\Omega_0)\,,\qquad\text{(C15)}$$

where q_c is the polaron cutoff wave vector and may be taken to be a Brillouin-zone radius (i.e., Debye wave vector). Expressing $\langle F^2\rangle$ in terms of the effective temperature T^* of Eq. (2), we obtain

$$\langle F^2\rangle=(2q_c^3k_BT^*/3\pi\epsilon^*)\,.\qquad\text{(C16)}$$

Defining $\langle f\rangle^2=e^2\langle F^2\rangle a^2/R^2$, where a and R are the exciton radius and rydberg, we find

$$\langle f^2\rangle=(\tfrac{4}{3}\pi)(q_ca)^3(k_BT^*/R)[(\epsilon_0-\epsilon_\infty)/\epsilon_\infty]\,.\qquad\text{(C17)}$$

---

*Work supported by the U.S. Air Force Office of Scientific Research under contract No. AF 49 (638)-1545.

[1] F. Urbach, Phys. Rev. 92, 1324 (1953); F. Moser and F. Urbach, *ibid.* 102, 1519 (1956).

[2] σ is of order unity and $\hbar\omega_0$ is approximately equal to the lowest exciton peak energy.

[3] R. S. Knox, in *Theory of Excitons*, Suppl. 5 of *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1963).

[4] H. Mahr, Phys. Rev. 125, 1510 (1962); 132, 1880 (1963).

[5] Y. Toyozowa, Progr. Theoret. Phys. (Kyoto) 22, 455 (1959); University of Tokyo Technical Report No. A119, 1964 (unpublished).

[6] J. R. Dixon and J. M. Ellis, Phys. Rev. 123, 1560 (1961).

[7] D. Redfield and M. A. Afromowitz, Appl. Phys. Letters 11, 138 (1967).

[8] M. A. Afromowitz and D. Redfield, in *Proceedings of the Ninth International Conference on Physics of Semiconductors, Moscow*, 1968 (Nauka, Leningrad, 1968).

[9] For a review of the theories see Ref. 3, p. 154 and Refs. 10 and 11.

[10] J. J. Hopfield, Comments Solid State Phys. 1, 16 (1968).

[11] D. L. Dexter and R. S. Knox, *Excitons* (Interscience, New York, 1965).

[12] W. Martienssen, J. Phys. Chem. Solids 2, 257 (1957); U. Haupt, Z. Physik 157, 232 (1959).

[13] D. B. Dutton, Phys. Rev. 112, 785 (1958). For a survey of these see *Proceedings of the International Conference on II-VI Semiconducting Compounds*, edited by D. G. Thomas (Benjamin, New York, 1967), Session B-II.

[14] J. I. Pankove, Phys. Rev. 140, A2059 (1965).

[15] H. C. Wolf, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1959), Vol. 9, p. 1.

[16] E. A. Davis and N. F. Mott, Phil. Mag. 22, 903 (1970).

[17] This conviction was somewhat influenced by the possibility that we might have such a general theory in hand.

[18] We reject the other two alternatives: (i) Two or more different mechanisms are responsible for the spectral behavior in different materials, or (ii) the universality of the rule is illusory and Urbach's rule is merely a manifestation of the adage that all lines plotted on semilogarithmic scales appear straight. Various careful measurements (e.g., Ref. 4) seem to preclude this latter possibility.

[19] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (Pergamon, New York, 1963).

[20] T. H. Keil, Phys. Rev. 144, 582 (1966).

[21] A. F. Lubchenko, Phys. Status Solidi 27, K73 (1968).

[22] A. S. Davydov, Phys. Status Solidi 27, 51 (1968).

[23] M. H. Reilly, J. Phys. Chem. Solids 31, 1041 (1970).

[24] D. M. Eagles, Phys. Rev. 130, 1381 (1963).

[25] D. G. Thomas, J. J. Hopfield, and M. Power, Phys. Rev. 119, 570 (1960).

[26] B. Segall, Phys. Rev. 150, 734 (1966).

[27] D. T. F. Marple, Phys. Rev. 150, 728 (1966).

[28] W. P. Dumke, Phys. Rev. 108, 1419 (1957).

[29] J. J. Hopfield, Phys. Chem. Solids 22, 63 (1961).

[30] D. E. McCumber, Phys. Rev. 135, A1676 (1964); D. Eagles, *ibid.* 130, 1381 (1963).

[31] G. D. Mahan, Phys. Rev. 145, 602 (1966).

[32] D. Dunn, Phys. Rev. 166, 822 (1968); Can. J. Phys. 47, 1703 (1969); we gratefully acknowledge conversations with Professor Dunn about his work.

[33] B. Halperin and M. Lax, Phys. Rev. 148, 722 (1966);

153, 802 (1967); E. O. Kane, *ibid.* 131, 79 (1963); V. L. Bonch-Bruevich, *The Electronic Theory of Heavily Doped Semiconductors* (Elsevier, New York, 1966).

[34] D. Redfield, Phys. Rev. 130, 916 (1963); Trans. N.Y. Acad. Sci. 26, 590 (1964).

[35] D. L. Dexter, Nuovo Cimento Suppl. 7, 245 (1958).

[36] D. L. Dexter, Phys. Rev. Letters 19, 383 (1967).

[37] J. D. Dow and D. Redfield, Phys. Rev. Letters 26, 762 (1971).

[38] Implicit throughout this paper is the notion that the effective, single-particle interaction potential energy $V_e(e, \vec{r})$ of a charge e at position $\vec{r}$ can be decomposed into an "electrical" interaction $G(\vec{r})$, which is odd in e, and an "elastic" interaction $W(\vec{r})$ which is even. Here

$$G(\vec{r}) = \tfrac{1}{2}[V_e(e, \vec{r}) - V_e(-e, \vec{r})], \quad W(\vec{r}) = \tfrac{1}{2}[V_e(e, \vec{r}) + V_e(-e, \vec{r})].$$

Thus the (generally nonuniform) electric field $\vec{F}$ is $\vec{F} = -e^{-1}\vec{\nabla} G$. We believe that the electrical interactions are primarily responsible for exponential edges. Note that V_e is the potential energy which enters the effective-mass equation for the electron quasiparticle. Even though all the bare interactions between other electrons or ions and the test electron are Coulombic, the dressed interaction V_e can have non-"electrical" "elastic" components such as are found in deformation-potential electron-phonon interactions. The "electrical" interactions cause the valence- and conduction-band edges to be displaced parallel without locally shrinking the band gap; "elastic" interactions cause a local dilation of the band gap.

[39] The possibility that the impurities affect the exponential tail by perturbing the lattice dynamics is untenable since only the *charged* impurities cause an Urbach shape (Ref. 7). One might expect the long-range forces associated with charged impurities to alter the phonon spectrum near the zone boundary, but not by as much as a factor of 2.

[40] The importance of these naturally occurring fields causes us to adopt the term "microfield" to describe them, and to distinguish them from the atomic-scale electric field, the macroscopic field, and the local field (the latter two of which are averages over macroscopic regions of the solid). The term "microfield" is borrowed from plasma physics [see C. F. Hooper, Jr., Phys. Rev. 149, 77 (1966)] where it used to describe electric fields (averaged over atomic volumes) whose spatial variation occurs over distances large compared with atomic sizes but small compared with macroscopic dimensions (i.e., $1\ \text{Å} < |F|/|\vec{\nabla}F| \ll 10^4\ \text{Å}$). For our purposes, the microfield is the gradient of the electrostatic potential which appears in the effective-mass equation for the exciton envelope function [see J. M. Luttinger and W. Kohn, Phys. Rev. 97, 869 (1955); J. M. Luttinger, *ibid.* 102, 1030 (1956)].

[41] It is conceivable that these exponential edges are due solely to the charge-induced alteration of the band tails in the conduction- and the valence-band densities of states. However, there are good arguments against such an interpretation (see Refs. 8 and 42).

[42] J. D. Dow and J. J. Hopfield, J. Noncrystalline Solids (to be published).

[43] See Appendix C; and D. Redfield, Trans. N.Y. Acad. Sci. 26, 590 (1964).

[44] Equivalent descriptions may be given in terms of spatial fluctuations of electrical potential.

[45] R. Zallen, Phys. Rev. 173, 824 (1968).

[46] J. Tauc, Mater. Res. Bull. 5, 721 (1970).

[47] D. L. Spears and R. Bray, Appl. Phys. Letters 12, 118 (1968).

[48] L. Mandel and E. Wolf, Rev. Mod. Phys. 37, 231 (1965); M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford U.P., Oxford, England, 1954), Sec. 7.

[49] When formulated in terms of electron and hole coordinates, the one-electron Franz-Keldysh effect is a photon-assisted interband transition which occurs at photon energies less than the band gap because the conduction- and the valence-band wave functions have tails extending into the forbidden gap (see Ref. 8). In exciton language, the one-electron Franz-Keldysh effect is a field-induced ionization of an exciton of zero binding energy, and involves an intraband scattering by the electric field of a quasiparticle having the reduced mass of the electron and the hole [see Refs. 50 and 52; K. Tharmalingam, Phys. Rev. 130, 2204 (1963); F. C. Weinstein, J. D. Dow, and B. Y. Lao, Phys. Rev. B 4, 3502 (1971)].

[50] J. D. Dow and D. Redfield, Phys. Rev. B 1, 3358 (1970).

[51] By "exciton effects" we mean all effects due to the Coulomb interaction between the final-state electron and hole, not just those effects associated with the formation of bound exciton states.

[52] H. I. Ralph, J. Phys. C 1, 378 (1968); D. F. Blossey, Phys. Rev. B 2, 3976 (1970).

[53] S. E. Schnatterly, Phys. Rev. B 1, 921 (1970).

[54] R. J. Elliott, Phys. Rev. 108, 1384 (1957).

[55] For small-radius excitons (e.g., in alkali halides) the effective-mass approximation should be capable of providing a description of the qualitative physics even though there may be significant quantitative deviations from its predictions.

[56] If $V_e(\vec{r}, \vec{R}_{\text{c.m.}})$ is due to the electrostatic potential ϕ, then we have

$$V_e(\vec{r}, R_{\text{c.m.}}) = e\phi(\vec{r}_e) - e\phi(\vec{r}_h),$$

where r_e and r_h are the electron and hole coordinates, respectively. Transforming to center-of-mass and relative coordinates, this becomes

$$V_e(\vec{r}, \vec{R}_{\text{c.m.}}) = e\phi(\vec{R}_{\text{c.m.}} + m_h \vec{r} M^{-1}) - e\phi(\vec{R}_{\text{c.m.}} - m_e \vec{r} M^{-1}).$$

Taylor expanding about $\vec{R}_{\text{c.m.}}$, and neglecting terms of order (exciton radius/characteristic wavelength of $\phi)^2$ we have

$$V_e(\vec{r}, \vec{R}_{\text{c.m.}}) \approx e(\vec{\nabla}_{\text{c.m.}}\phi) \cdot \vec{r} = -e\vec{F} \cdot \vec{r},$$

where $\vec{F} = -\vec{\nabla}_{\text{c.m.}}\phi$ is the microfield.

[57] J. D. Dow (unpublished).

[58] We thus imply the "semiclassical Frank-Condon principle" for ionic crystals; see Ref. 59.

[59] M. Lax, J. Chem. Phys. 20, 1752 (1952).

[60] Remember that the wave function $U(0)$ in the Elliott theory is a stationary-state function. Since the physics of the broadening is frequently more obvious in the time domain, we shall frequently talk in terms of the nonstationary wave functions as well.

[61] The uniform-field potential may be viewed as the first term in a multipole expansion as in Ref. 56.

[62] Strictly speaking, this integral would have a finite upper limit because any single region with very high fields is probably too small for a bound state. The present treatment relies on the Gaussian decrease in the field

probability at the highest fields to provide the effect of this cutoff.

[63] T. N. Morgan, Phys. Rev. 139, A343 (1965).

[64] See Appendix C.

[65] For the most part, deviations from Urbach's rule are found experimentally from the center of the exciton line to $-0.5R$ (R is the 1s exciton binding energy) below (see, e.g., Ref. 4).

[66] Although the lines in Fig. 5 are not straight, we could argue that they are sufficiently straight to be consistent with most of the observed data. Very few accurate measurements of the temperature dependence of Urbach's rule have been made, and the most extensive of these has only been made for T^* between 100 and 900 K (a factor of about 9 in $\langle F^2\rangle$ for $F_{\mathrm{rms}} \approx 0.2R/|e|a$). Still, those measurements which have been made are sufficiently impressive for us to believe that the difficulty lies with the details of the uniform-field approximation.

[67] $\langle V^2\rangle = 2\,e^2 q_c k_B T^*/\pi\epsilon^*$.

[68] A careful solution of Eq. (16) reveals that ignoring the second term cannot be quantitatively justified.

[69] Note that, in the present theory, the T in Urbach's rule does not follow directly from a Boltzmann factor, but is instead the product of two factors $T^{1/2}$: one due to the field strength, and one due to the number of available states into which the electron may tunnel.

[70] Even if a particular short-wavelength mode were to inhibit the tunneling (and thus the Stark broadening), it would still cause a shift in the energy of the lowest exciton. Dexter has shown that such shifts give an Urbach tail in the quadratic Stark-effect limit (i.e., weak uniform electric field). It is likely that the shifts due to short-wave phonons likewise contribute to an exponential spectral behavior, but that their contribution is generally overwhelmed by the tunneling.

[71] F. C. Brown, T. Masumi, and H. H. Tippins, J. Phys. Chem. Solids 22, 101 (1961); B. L. Joestin and F. C. Brown, Phys. Rev. 148, 919 (1966).

[72] M. Capizzi and A. Frova, Phys. Rev. Letters 25, 1298 (1970).

[73] M. Nagasawa and S. Shionoya, Solid State Commun. 7, 1731 (1969).

[74] In II-VI compounds, the phonon structure has been generally attributed to phonon sidebands on a direct exciton transition. In $SrTiO_3$, the transitions involved are thought to be phonon-assisted and indirect. The difficulty in distinguishing between these two cases is documented in Ref. 27.

[75] If systems exist in which the exponential absorption edge can be attributed to the center-of-mass motion of the exciton, then theorists and experimenters should attempt to explain the relative importance of the center-of-mass and relative-motion mechanisms as a function of electronegativity, dielectric constants, and other physical properties.

[76] We are grateful to J. J. Hopfield for pointing out that this method of selectively pumping $q=0$ optical phonons is now feasible.

[77] M. Cardona, in *Modulation Spectroscopy*, Suppl. 11 of *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1969).

[78] A broadening would result in a reduction of the slope of the exponential edge, without any change in the position of the first exciton peak; a shift would result in a rigid shift of both the first exciton peak and the exponential edge to lower energy.

[79] The ionized electron will undoubtedly stay in the potential valley not too far from the hole [see Fig. 1(a)]; but approximately 10^{-12} sec later (in the ionic crystals) the normal behavior of the lattice will tend to rearrange the ions and thereby may destroy the trough in which the electron lies. The presence of the excited-state electron alters this, however, so that the vibrations will probably not succeed in destroying the trough; rather the electron will probably become self-trapped and will probably deepen the electrostatic trough in which it lies. If this is so, then excitation of states in the Urbach tail should lead to creation of self-trapped electrons nearby self-trapped holes (V_K centers). In the tunneling model, the self-trapping cross section should be larger than in other models of Urbach's rule. Perhaps magnetic resonance could be used to study this situation.

[80] J. J. Hopfield, J. Phys. Chem. Solids 22, 63 (1961).

[81] D. Redfield, J. P. Wittke, and J. I. Pankove, Phys. Rev. B 2, 1830 (1970).

[82] Perhaps we should follow an idea of D. L. Dexter (private communication) and try to understand why certain extrinsic absorption lines in insulating systems do not seem to exhibit an Urbach rule. For example, the absorption line shapes of F centers in alkali halides do not have observable Urbach tails. [See C. C. Klick, D. A. Patterson, and R. S. Knox, Phys. Rev. 133, A1717 (1964).] Dexter reasons that this is due to the fact that the hole has no mass—that is, the F-center vacancy moves when the adjacent ions move, preventing a large electric field from building up at the exciton. In the tunneling model presented here, large central-cell corrections would also contribute to non-Urbachian behavior (see Ref. 83). The lack of observable Urbach tails on F bands may, however, simply be due to experimental limitations caused by the presence of other absorbing transitions which accompany F centers.

[83] Central-cell corrections put a bottom on the potential well near $r=0$, so that the exponential rise in the electron's wave function near the Coulomb well in Fig. 1(b) does not occur.

[84] J. F. Weller and D. L. Dexter, Optics Commun. 2, 399 (1971).

[85] Several compounds (GaSe, GaS, MbS_2 EuS_2, TaS_2, ZrS_2) with two-dimensional excitons seem to have non-exponential absorption edges. We are grateful to G. Roberts for bringing this fact to our attention.

[86] M. Bujatti, J. Appl. Phys. 40, 2965 (1969); D. Redfield, Phys. Rev. 140, A2056 (1965).

[87] J. E. Robinson (unpublished); J. E. Robinson and B. Bosacchi (unpublished).

[88] H. Sumi and Y. Toyozowa, J. Phys. Soc. Japan 31, 342 (1971); H. Sumi, Tech. Rpt. Inst. Solid State Phys. Univ. Tokyo, Ser. A, No. 477, 1971 (unpublished); K. Cho and Y. Toyozowa, J. Phys. Soc. Japan 30, 1555 (1971).

[89] Note that Ref. 88 (i) assumes that self-trapping by *acoustic* phonons causes the exponential tails in alkali halides, and (ii) states that the present theory predicts broader Urbach tails for shallower excitons. We disagree with these assertions. The role of acoustic phonons is inferred in Ref. 88 from low-temperature absorption data which indicate values of T^* [Eq. (2)] with $\hbar\Omega_0$ somewhat less than LO phonon energies. Even if the inference is valid (see Appendix A for arguments that low-temperature data should not be used for explanation of Urbach's rule), these experiments indicate that the *only* acoustic phonons which could possibly contribute to the Urbach tail are those

with wave vectors near the Brillouin zone boundary; such zone-boundary phonons generally have the large electric fields postulated in the present model. Assertion (ii) assumes that the internal fields are the same order of magnitude in I-VII, II-VI, and III-V compounds; in fact, the more ionic solids generally have larger internal fields. When the dependence of internal fields on dielectric function is taken into account in the Frohlich model [Eq. (c16)], we find that the Urbach exponent (which apart from numerical constants is $E/\bar{f}$) becomes

$$\frac{E}{\bar{f}}=\frac{\hbar\omega-E_{\text{gap}}}{k_B T^*}\;\frac{\sqrt{3}}{4(\epsilon_0/\epsilon_\infty-1)}\;.$$

Here we have used the relationship $q_c a \sim (V_{\text{rms}}/R)^{1/2}$, as discussed in Eq. (13). Note that this is precisely the observed Urbach dependence, with the additional prediction of the variation of σ with ϵ_0 and ϵ_∞: $\sigma \propto (\epsilon_0/\epsilon_\infty-1)^{-1}$. This slight variation of σ is the observed one (the more ionic systems have smaller values of σ). However, we caution the reader that this last prediction may depend on the *ad hoc* manner in which the wave-vector cutoff has been introduced; furthermore, the data on σ are not unambiguous on this question.

---

[90] J. D. Dow, Comments Solid State Phys. (to be published).

[91] H. Fritzsche, J. Noncrystalline Solids 6, 49 (1971); J. Tauc, *ibid.* (to be published).

[92] J. D. Dow and J. J. Hopfield (unpublished); see also Ref. 42.

[93] M. DiDomenico and S. H. Wemple, Phys. Rev. 166, 565 (1968).

[94] A. B. Fowler, W. E. Howard, and G. E. Brock, Phys. Rev. 128, 1664 (1962).

[95] T. G. Castner and W. Känzig, J. Phys. Chem. Solids 3, 178 (1957).

[96] A. Messiah, *Quantum Mechanics* (Wiley, New York, 1961), p. 449.

PHYSICAL REVIEW B VOLUME 5, NUMBER 2 15 JANUARY 1972

Photoconductivity Due to Excitonic-Energy Transfer to Crystalline Defects*

W. L. Emkey† and W. J. Van Sciver
Department of Physics, Lehigh University, Bethlehem, Pennsylvania 18015

(Received 23 July 1971)

The internal photoconductivity spectrum of single crystals of NaI was investigated over a wide range of temperatures. A photocurrent threshold was observed which is believed to be due to the onset of band-to-band transitions. Aside from this threshold, a photoconductivity band appeared on the low-energy side of the first fundamental absorption band. The existence of this response is attributed to the ionization of traps via an exciton interaction.

I. INTRODUCTION

Early work on the intrinsic photoconductivity of single crystals of KI, KBr, and KCl by Kuwabara and Aoyagi[1] indicated that, aside from photocurrents due to band-to-band transitions, a photoconductivity response appeared on the low-energy tail of the first fundamental absorption band. They attributed this response either to an absorption related to the presence of an impurity or to impurity ionization via an exciton energy transfer. Their results favored the latter mechanism. At the same time, Nakai and Teegarden[2] reported results on the photoconductivity of RbI and KI single crystals. Once again, aside from band-to-band related photocurrents, an additional band was observed on the low-energy tail of the corresponding fundamental absorption spectrum. The authors postulated the photoproduction and destruction of color centers as being responsible for this band, and they indicated the *F* center as a possible candidate. In this paper, we present the results of our photoconductivity studies of NaI and RbI in the corresponding spectral region.

II. EXPERIMENTAL PROCEDURE

Single crystals, obtained from the Harshaw Chemical Co., were cleaved in a dry box. These crystals, typically of 1.0-mm thickness, were then mounted onto the sample holder, a diagram of which can be seen in Fig. 1. The sample holder was attached to the end of a $\frac{7}{8}$-in. stainless-steel tube which was then inserted into the sample chamber of an Andonian exchange-gas cryostat. Because of the design of the cryostat, it was necessary for the signal to travel a distance of ~3 ft before the photocurrent detection system could be connected. Because of the electrical noise involved due to the generation of microphonics, a $\frac{1}{8}$-in.-brass rod was used as the signal "wire." This rod, which was held in place by Teflon spacers within the stainless-steel tube, was found to effectively reduce the microphonics.

Photocurrents were detected by a Keithley model No. 640 electrometer with the input shunted by 10^{12} Ω. An electric potential of 800 V was supplied by a combination of dry-cell batteries. Data were acquired by first recording a background current.