Theory of the Urbach Rule

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The two-vibrational-mode model proposed by Toyozawa and Mahr to account for the Urbach rule is considered both in the semiclassical approximation and in the full quantum theory. The semiclassical line shape accounts for both the exponential Urbach tail and the central Gaussian region of the absorption band. Quantum modifications make the semiclassical line shape incorrect for an excited state stable to odd-parity lattice distortions. The quantum line shape for an unstable excited state is shown to be qualitatively similar to the semiclassical line shape. In particular the two line shapes agree at high temperatures, but differ quantitatively at low temperatures. It is suggested that the hypothesis of an unstable excited state is consistent with recent experimental results on intrinsic luminescence in alkali halides.

I. INTRODUCTION

In a large number of insulating crystals, the low-energy tail of the fundamental absorption band, and also of impurity absorption bands, follows the Urbach rule, which states that the absorption coefficient is given by

$$\mu(\omega,T)=\mu_0 \exp[-\sigma_0(\hbar\omega_0-\hbar\omega)/kT], \qquad (1.1)$$

where $\hbar\omega$ is the energy of the incident radiation, and μ_0, ω_0, and σ_0 are constants characteristic of the crystal. Equation (1.1) applies for high temperatures. For low temperatures the temperature dependence in the exponential disappears, and T should be replaced by T_0, with T_0 an experimentally determined parameter, generally on the order of 100°K. This rule was first discovered by Urbach[1] in silver halides, and has since been found to apply to a large number of other crystals. The exponential dependence has been found to be obeyed over a remarkably wide range of the absorption constant, e.g., in[2] KI the range is seven orders of magnitude. Similar results have been obtained for[3] KCl and[4] KBr. In all three cases $\sigma_0=0.80\pm0.02$. For a typical impurity case, the absorption due to the I^- ion in KCl, the exponential dependence has been observed[5] over a range of $3\frac{1}{2}$ orders of magnitude of the absorption constant with $\sigma_0=0.77$. Other experimental results are summarized by Knox[6] and Toyozawa.[7]

By assuming that the electronic transition couples *quadratically* to one of the lattice vibrational modes, Toyozawa[8] used the semiclassical theory[9] of absorption line shapes to derive a theoretical expression which reproduces the exponential tail of Urbach's rule. Since the central region of the band is generally Gaussian, Mahr[10] and Toyozawa[7] proposed that a two-mode model is more appropriate; the first mode, with a quadratic interaction, gives the Urbach tail, and the second, with a linear interaction, gives the central Gaussian region. Such a model has been shown[10] to be capable of reproducing some observed line shapes over the whole spectral range.

In Sec. II of this work we present an exact derivation, in the semiclassical approximation, of this two-mode line shape, which has previously been treated only approximately. Recently it has been pointed out[11] that the semiclassical approximation has dubious validity for a quadratically coupled mode at low temperatures. In fact, for the case in which the excited-state adiabatic potential has a positive force constant for the quadratic mode, the semiclassical line shape is totally erroneous, possessing a low-energy tail where the quantum line shape has none. However, in Refs. 8 and 10 it was found that, in order to reproduce experimental data, it is necessary to assume a *negative* force constant in the excited state potential. Therefore in Secs. III and IV we consider the quantum line shape due to a quadratically interacting mode with an unstable excited state. We find that the quantum line shape is qualitatively similar to the semiclassical. In particular it gives an exponential low-energy tail. The details of the two line shapes differ somewhat, particularly in the low-temperature behavior of the low-energy tail.

Such a model, with the addition of a second mode with linear coupling, gives a quantum-mechanical line shape which seems capable of accounting for both the Urbach rule on the tail of the absorption band and the central Gaussian region. In addition it is suggested that the instability in the excited state of the quadratic mode is consistent with recent observation.[12–14] of the luminescence of intrinsic excitons in alkali halides.

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[1] F. Urbach, Phys. Rev. **92**, 1324 (1953).
[2] U. Haupt, Z. Physik **157**, 232 (1959).
[3] K. Kobayashi and T. Tomiki, J. Phys. Soc. Japan **16**, 1417 (1961).
[4] W. Martienssen, J. Phys. Chem. Solids **2**, 257 (1957).
[5] H. Mahr, Phys. Rev. **125**, 1510 (1962).
[6] R. S. Knox, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. #5.
[7] Y. Toyozawa, Institute for Solid State Physics, Tokyo Technical Report A119 (1964) (unpublished).
[8] Y. Toyozawa, Progr. Theoret. Phys. (Kyoto) **22**, 455 (1959); Suppl. **12**, 111 (1959).
[9] M. Lax, J. Chem. Phys. **20**, 1752 (1952).
[10] H. Mahr, Phys. Rev. **132**, 1880 (1963).
[11] T. H. Keil, Phys. Rev. **140**, A601 (1965).
[12] K. J. Teegarden, Phys. Rev. **105**, 1222 (1957).
[13] M. N. Kabler, Phys. Rev. **136**, A1296 (1964).
[14] R. B. Murray and F. J. Keller, Phys. Rev. **137**, A942 (1965).

II. SEMICLASSICAL LINESHAPE FOR TWO MODE MODEL

We take as the adiabatic potentials[11] for the ground and excited states, respectively,

$$\begin{aligned} U_a &= \tfrac{1}{2}m_1\omega_1^2Q_1^2+\tfrac{1}{2}m_2\omega_{2a}^2Q_2^2\,, \\ U_b &= E_{ab}+cQ_1+\tfrac{1}{2}m_1\omega_1^2Q_1^2+\tfrac{1}{2}m_2\omega_{2b}^2Q_2^2\,. \end{aligned} \tag{2.1}$$

Here Q_1 and Q_2 are the normal displacements of the linear and quadratic modes, respectively. m_1 is the mass and ω_1 the frequency of the linear mode. m_2 is the mass, ω_{2a} the ground-state frequency, and ω_{2b} the excited-state frequency for the quadratic mode. E_{ab} is the electronic excitation energy. By considering only two vibrational modes, we are essentially restricted to the impurity case. However, as Toyozawa[7] has suggested, the formalism will also apply to intrinsic excitons if self-trapping can be assumed to occur.

Following Lax[9] the semiclassical line shape for transitions from electronic state a to electronic state b in this two mode model may be written

$$I_{ab}(E)=\int P(Q_1)P(Q_2)\delta[\Delta E(Q_1,Q_2)-E]dQ_1dQ_2\,, \tag{2.2}$$

where E is the energy of the incident photon,

$$\begin{aligned} \Delta E(Q_1,Q_2) &= E_{ab}+cQ_1+\tfrac{1}{2}m_2(\omega_{2b}^2-\omega_{2a}^2)Q_2^2\,, \\ P(Q_1) &= \pi^{-1/2}(1/W_1)\exp(-Q_1^2/W_1^2)\,, \\ P(Q_2) &= \pi^{-1/2}(1/W_2)\exp(-Q_2^2/W_2^2)\,, \end{aligned} \tag{2.3}$$

and

$$\begin{aligned} W_1 &= [\hbar\coth(\hbar\omega_1/2kT)/m_1\omega_1]^{1/2}\,, \\ W_2 &= [\hbar\coth(\hbar\omega_{2a}/2kT)/m_2\omega_{2a}]^{1/2}\,. \end{aligned} \tag{2.4}$$

The δ function in Eq. (2.2) may be used to perform the integral over Q_1, and the line-shape function is

$$I_{ab}(E)=G\int_{-\infty}^{\infty}dQ_2\exp[-DQ_2^4-FQ_2^2]\,, \tag{2.5}$$

where

$$\begin{aligned} G &= (1/\pi cW_1W_2)\exp[-(E-E_{ab})^2/c^2W_1^2]\,, \\ D &= [\tfrac{1}{2}m_2(\omega_{2b}^2-\omega_{2a}^2)]^2/c^2W_1^2\,, \\ F &= 1/W_2^2+m_2(\omega_{2b}^2-\omega_{2a}^2)(E-E_{ab})/c^2W_1^2\,. \end{aligned} \tag{2.6}$$

It can be shown[15] that

$$\begin{aligned} \int_{-\infty}^{\infty}\exp[-Ax^4-Bx^2]dx &= \sqrt{2}B^{-1/2}(B^2/8A)^{1/2}\exp(B^2/8A)K_{1/4}(B^2/8A) \quad (B>0) \\ &= \sqrt{2}B^{-1/2}(B^2/8A)^{1/2}\exp(B^2/8A)K_{1/4}(-B^2/8A) \quad (B>0)\,. \end{aligned} \tag{2.7}$$

Here $K_{1/4}(x)$ is the Bessel function of the second kind with imaginary argument. Defining

$$\begin{aligned} \epsilon &= E-E_{ab}\,, \\ \sigma &= \frac{2\omega_{2a}}{\omega_{2a}^2-\omega_{2b}^2}\left[\hbar\coth\frac{\hbar\omega_{2a}}{2kT}\right]^{-1}, \\ \tau^2 &= \frac{1}{C^2}\left[\frac{m_1\omega_1}{\hbar\coth(\hbar\omega_1/2kT)}\right], \end{aligned} \tag{2.8}$$

and applying Eq. (2.7) to Eq. (2.5), we obtain for the line-shape function

$$\begin{aligned} I_{ab}(\epsilon) &= \tau\left(\frac{\sigma}{2\pi^2}\right)^{1/2}\left[\frac{\sigma}{2\tau^2}+\epsilon\right]^{1/2}\exp\left[\frac{\sigma^2}{4\tau^2}\right] \\ &\times\exp\left[-\frac{\tau^2}{2}\left(\epsilon-\frac{\sigma}{2\tau^2}\right)^2\right]K_{1/4} \\ &\times\left[\pm\frac{\tau^2}{2}\left(\epsilon+\frac{\sigma}{2\tau^2}\right)^2\right]. \end{aligned} \tag{2.9}$$

If $\omega_{2b}^2<\omega_{2a}^2$ the minus sign applies when $\epsilon<-\sigma/2\tau^2$.

Using the asymptotic forms for the Bessel function

$$\begin{aligned} K_{1/4}(x) &\sim (\pi/2x)^{1/2}e^{-x}\,, \\ K_{1/4}(-x) &\sim -(\pi/2x)^{1/2}ie^{+x}\,, \end{aligned} \tag{2.10}$$

we can obtain the line shape in the low-energy tail,

$$\begin{aligned} I_{ab}(\epsilon) &= (\sigma/2\pi)^{1/2}[2\hbar\omega_0-\epsilon]^{-1/2} \\ &\times\exp[-\sigma(\hbar\omega_0-\epsilon)]\,(\epsilon\ll 2\hbar\omega_0) \end{aligned} \tag{2.11}$$

and in the region of the peak absorption,

$$\begin{aligned} I_{ab}(\epsilon) &= (\sigma/2\pi)^{1/2}[\epsilon-2\hbar\omega_0]^{-1/2} \\ &\times\exp[-\tau^2\epsilon^2]\,(\epsilon\gg 2\hbar\omega_0)\,. \end{aligned} \tag{2.12}$$

Here $\hbar\omega_0=-\sigma/4\tau$. Since at high temperatures

$$\sigma\approx\omega_{2a}^2/(\omega_{2a}^2-\omega_{2b}^2)kT=\sigma_0/kT \tag{2.13}$$

Eq. (2.11) reproduces the exponential dependence of the Urbach rule, Eq. (1.1), except for an unimportant square-root factor. Equation (2.12) gives the central Gaussian region of the band. In addition Eq. (2.11) contains the low-temperature cutoff of the Urbach rule, since, for low temperatures, $\coth(\hbar\omega_{2a}/kT)=1$ and the temperature dependence in the low-energy exponential tail disappears. Using an approximate form of Eq. (2.9), Mahr[10] has shown that the two-mode model is capable

[15] T. H. Keil, thesis, University of Rochester, 1965 (unpublished).

of fitting the experimentally observed absorption in KCl:KI over a wide range of photon energies and at several temperatures.

One slight extension of the two-mode model is of interest. Suppose we add a third mode, which also interacts quadratically, but whose ground and excited-state frequencies are the same as those of the first quadratic mode. The adiabatic potentials are now

$$U_a=\tfrac{1}{2}m_1\omega_1^2Q_1^2+\tfrac{1}{2}m_2\omega_{2a}^2(Q_2^2+Q_3^2)\,,$$
$$U_b=E_{ab}+cQ_1+\tfrac{1}{2}m_1\omega_1^2Q_1^2+\tfrac{1}{2}m_2\omega_{2b}^2(Q_2^2+Q_3^2)\,. \quad (2.14)$$

Using the previous method it is straightforward to show that the line shape is given by

$$I_{ab}(\epsilon)=\sigma\pi^{-1/2}\exp\left[\frac{\sigma^2}{4\tau^2}+\sigma\epsilon\right]\int_{\alpha}^{\infty}\exp[-x^2]dx\,, \quad (2.15)$$

where $\alpha=\tau\epsilon+\sigma/2\tau$. Equation (2.15) is identical with Mahr's[10] proposed empirical shape formula (noting that Mahr's $\hbar\nu_0$ is not the same as our $\hbar\omega_0$). The asymptotic expansions of Eq. (2.15) are easily found. For $\epsilon\ll 2\hbar\omega_0$

$$I_{ab}(\epsilon)=\sigma\exp[-\sigma(\hbar\omega_0-\epsilon)] \quad (2.16)$$

and for $\epsilon\gg 2\hbar\omega_0$

$$I_{ab}(\epsilon)=\frac{\sigma}{2\tau\pi^{1/2}}[\epsilon-2\hbar\omega_0]^{-1}\exp[-\tau^2\epsilon^2]\,. \quad (2.17)$$

The three-mode model then has essentially the same features as the two-mode model.

Note that, according to Eq. (2.11) and Eq. (2.16), the two models have exactly the same behavior on the low-energy exponential tail. It is easy to see that the addition of more quadratic modes (with the same frequencies) will not change this behavior. If an arbitrary number of vibrational modes with (possibly) different frequencies are included in the calculation, the low-energy exponential dependence will be characteristic of the quadratic mode with the *lowest* value of σ. This fact allows us to confine our attention to just one of the vibrational modes which may interact quadratically with the center, at least as far as considerations of the Urbach tail are concerned.

The line shape Eq. (2.9) can be regarded[11] as the convolution of the semiclassical line shape due to the linear model with that due to the quadratic mode. As pointed out in Ref. 11, the semiclassical line shape for a quadratic mode with $\omega_{2b}^2>0$ is incorrect at low temperatures. At $T=0$ the quantum line shape is given by

$$I_{ab}(\omega)=\frac{(\omega_{2a}\omega_{2b})^{1/2}}{\omega_{2a}+\omega_{2b}}\sum_{l=0}^{\infty}\delta(2l\omega_{2b}-\omega)\times\frac{2l!}{2^{2l}(l!)^2}\left(\frac{\omega_{2a}-\omega_{2b}}{\omega_{2a}+\omega_{2b}}\right)^{2l}\,, \quad (2.18)$$

where $\omega=(E-E_{ab})/\hbar+\frac{1}{2}\omega_{2a}-\frac{1}{2}\omega_{2b}$. The line shape Eq. (2.18) has *no* low-energy tail, and in fact has a sharp cutoff on the low-energy side of $\hbar\omega=0$. This is in direct contrast to the corresponding semiclassical result.[11] Hence the semiclassical two-mode line shape Eq. (2.9) will be incorrect for $\omega_{2b}^2>0$ at low temperatures.

However Toyozawa[7] and Mahr[10] found that to account for some experimental results it was necessary to assume that $\sigma_0<1$. The semiclassical line shape Eq. (2.9) still applies for this case, but the quantum line shape Eq. (2.18) is no longer valid. Thus it is of interest to examine the quadratic-mode quantum line shape in the case of an unstable excited state ($\omega_{2b}^2<0$).

III. QUANTUM LINE SHAPE FOR AN UNSTABLE QUADRATIC MODE: $T=0$

In this section we will confine ourselves to the quantum line shape due to the quadratic mode alone. Since the semiclassical line shape for the linear mode is expected[9] to be valid in most interesting cases, we can find the line shape for the two-mode model by taking the convolution of the semiclassical linear-mode line shape with the quantum quadratic-mode line shape.

The adiabatic potentials for the quadratic mode are

$$U_a=\tfrac{1}{2}m\omega_a^2Q^2\,, \quad (3.1)$$
$$U_b=E_{ab}+\tfrac{1}{2}m\omega_b^2Q^2\,.$$

These are plotted in Fig. 1. The dashed portion of the excited-state potential represents the region where higher than quadratic terms become important. We will assume that the temperatures considered are low enough so that these terms exert a negligible influence on the line shape. Ordinarily in computing a quantum line shape, it is necessary to evaluate overlap integrals between ground and excited vibrational states (Frank-Condon factors). Because of the nature of the excited-state potential, it is difficult to obtain excited-state vibrational wave functions. However, we can make use of the results of Lax,[9] which allow us, by using the Fourier transform of the line shape, to eliminate the need for an explicit knowledge of these wave functions. In this way we can obtain an "exact" result for the line shape.

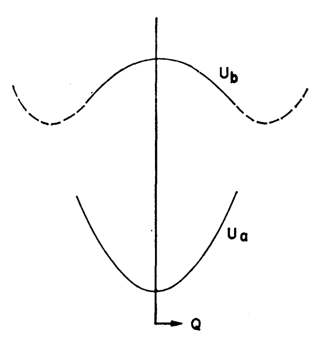


FIG. 1. Adiabatic potentials for an odd-parity, quadratically coupled vibrational mode with an unstable excited state. We assume that the temperature is low enough so that regions in which higher than quadratic terms are important (dotted lines) do not affect the line shape.

Previously the properties of this line shape have been sketched roughly by Eagles[16] and Halperin.[17]

Following Lax[9] we may write the line shape as

$$I_{ab}(E)=\frac{1}{2\pi\hbar}\int_{-\infty}^{\infty}\exp\left[\frac{-i(E-E_{ab})t}{\hbar}\right]g(t)dt, \quad (3.2)$$

where

$$g(t)=\mathrm{Av}_\alpha\langle a\alpha|\exp(-iH_at/\hbar)\exp(iH_bt/\hbar)|a\alpha\rangle, \quad (3.3)$$

and

$$\begin{aligned}H_a&=-(\hbar^2/2m)\partial^2/\partial Q^2+U_a,\\ H_b&=-(\hbar^2/2m)\partial^2/\partial Q^2+U_b;\end{aligned} \quad (3.4)$$

$|a\alpha\rangle$ is the ground-state vibrational wave function and Av_α stands for a thermal average over the ground vibrational states. Using the methods of Refs. 9 and 11, we can show that the line shape for $T=0$ is

$$I_{ab}(\omega)=\frac{(\omega_a\omega_b)^{1/2}}{\pi}\int_{-\infty}^{\infty}dte^{-i\omega t}[\Omega_+{}^2-\Omega_-{}^2e^{2i\omega_bt}]^{-1/2}, \quad (3.5)$$

where

$$\begin{aligned}\omega&=(E-E_{ab})/\hbar+\tfrac{1}{2}\omega_a-\tfrac{1}{2}\omega_b,\\ \Omega_+{}^2&=(\omega_a+\omega_b)^2,\\ \Omega_-{}^2&=(\omega_a-\omega_b)^2.\end{aligned} \quad (3.6)$$

Since we are interested in the case in which $\omega_b{}^2<0$, we let $\omega_b=ix$, where x is real, and rewrite Eq. (3.5) as

$$I_{ab}(\omega')=\frac{(i\omega_ax)^{1/2}}{\pi}\int_{-\infty}^{\infty}dt\exp[-i\omega't-\tfrac{1}{2}xt]\times[\Omega_+{}^2-\Omega_-{}^2e^{-2xt}]^{-1/2}. \quad (3.7)$$

Here $\omega'=(E-E_{ab})/\hbar+\frac{1}{2}\omega_a$.

The integral in Eq. (3.7) may be performed explicitly. However, the result is inconvenient for purposes of analysis; so we consider a somewhat different case which is analytically simpler but has the same features. Assume that there are two quadratic modes present, with the two ground-state frequencies ω_a and the two excited-state frequencies $\omega_b=ix$. The line shape for this case will be just the convolution of the line shape Eq. (3.7) with itself[11] and is thus given by

$$I_{ab}(\omega')=\frac{ix\omega_a}{\pi}\int_{-\infty}^{\infty}dt\exp[-i\omega't-xt]\times[\Omega_+{}^2-\Omega_-{}^2e^{-2xt}]^{-1}. \quad (3.8)$$

Here $\omega'=(E-E_{ab})/\hbar+\omega_a$. As in the semiclassical case, this two quadratic mode line shape will not differ essentially from the single-mode line shape, at least as far as the low energy tail is concerned. The integral in Eq. (3.8) may be performed using[18]

$$\int_{-\infty}^{\infty}\frac{e^{-\alpha x}}{(e^{\beta/\gamma}+e^{-x/\gamma})^\nu}e^{-ixy}dx=\gamma\exp\left[\beta\left(\alpha+iy-\frac{\nu}{\gamma}\right)\right]\times B[\gamma(\alpha+iy),\nu-\gamma(\alpha+iy)], \quad (3.9)$$

where $B(x,y)$ is the beta function and Eq. (3.9) holds when $\mathrm{Re}(\nu/\gamma)>\mathrm{Re}\alpha>0$ and $|\mathrm{Im}\beta|<\pi\,\mathrm{Re}\gamma$. Using Eq. (3.9) and rewriting the beta function in terms of more familiar functions, we obtain a line shape

$$I_{ab}(\omega')=\frac{\omega_a}{2|\Omega_-|^2}\exp\left[-\frac{\omega^1}{x}\left(2\tan^{-1}\frac{x}{\omega_a}-\tfrac{1}{2}\pi\right)\right]\times\left[\cosh\frac{\pi\omega'}{2x}\right]^{-1}. \quad (3.10)$$

The behavior of Eq. (3.10) on the high- and low-energy tails is easily obtained. For $\omega'\gg0$

$$I_{ab}(\omega')=\frac{\omega_a}{|\Omega_-|^2}\exp\left[-\frac{\omega'}{x}2\tan^{-1}\frac{x}{\omega_a}\right], \quad (3.11)$$

and for $\omega'\ll0$

$$I_{ab}(\omega')=\frac{\omega_a}{|\Omega_-|^2}\exp\left[-\frac{\omega'}{x}\left(2\tan^{-1}\frac{x}{\omega_a}-\pi\right)\right]. \quad (3.12)$$

From Eq. (3.12) we see that the line shape due to two unstable quadratic modes gives, at $T=0$, a low-energy exponential tail, in qualitative agreement with the semiclassical result. However, the constants appearing in the exponential are substantially different. At $T=0$ the semiclassical result on the low-energy tail goes like [see Eq. (2.16)]

$$I_{ab}(\omega')\sim\exp[(2\omega_a/(\omega_a{}^2+x^2))\omega']. \quad (3.13)$$

For $x/\omega_a=0.5$ (which corresponds to $\sigma_0=0.80$), the semiclassical low-energy tail goes like

$$I_{ab}(\omega')\sim\exp[0.80\omega'/x] \quad (3.14)$$

while the quantum low-energy tail goes like

$$I_{ab}(\omega')\sim\exp[2.21\omega'/x]. \quad (3.15)$$

Hence there is a large difference in the steepness of the low-energy exponential tail for the two cases.

IV. QUANTUM LINE SHAPE FOR AN UNSTABLE QUADRATIC MODE: FINITE TEMPERATURES

In this section we will discuss the behavior of the low-energy-tail dependence of the line shape due to an unstable quadratic mode at arbitrary temperatures. We will see that the tail dependence is exponential, and at high temperatures agrees with the semiclassical result.

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

[17] B. Halperin, thesis University of California (Berkeley), 1965 (unpublished).

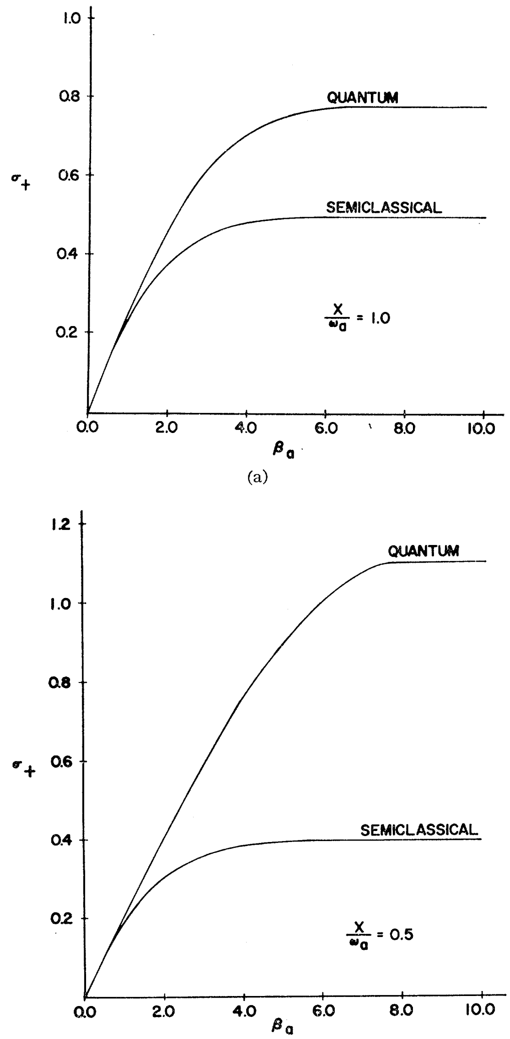
[18] *Bateman Manuscript Project, Tables of Integral Transforms*, edited by H. Erdelyi (McGraw-Hill Publishing Company, Inc., New York, 1954), Vol. I, p. 120.

As the temperature is lowered the slope of the exponential is found to be quite different for the two cases.

Using previous methods, it is easy to show[11] that the line shape in the case of two degenerate quadratic modes is given by

$$I_{ab}(\omega')=\frac{ix\omega_a}{\pi}[1-\exp(-\beta_a)]^2\int_{-\infty}^{\infty}dt\,\exp[-i\omega' t-xt]$$
$$\times\{\Omega_+^2[1-\exp(-\beta_a-i\Omega_- t)]^2$$
$$-\Omega_-^2[1-\exp(-\beta_a-i\Omega_+ t)]^2$$
$$\times\exp(-2xt)\}^{-1}. \quad (4.1)$$

Here $\beta_a=h\omega_a/kT$. It does not seem to be possible to evaluate the integral in Eq. (4.1) explicitly. However,



(b)

FIG. 2. Exponential dependence of the low-energy tail [see Eq. (4)–(5)] as a function of $\beta_a=h\omega_a/kT$ in the quantum and semiclassical theories for two values of the coupling constant (a) $x/\omega_a=1.0$ and (b) $x/\omega_a=0.5$.

we can obtain the behavior of the low- and high-energy tails by using a familiar result from the theory of Fourier transforms. This theorem[19] states that if (1) $f(t)\,(t=x+iy)$ is analytic in the strip $y_-<y<y_+$, with $y_+>0$ and $y_-<0$ and (2) for any strip within this strip

$$|f(t)|\sim Ae^{\tau-x}\quad(x\to\infty;\ \tau_-<0)$$
$$\sim Be^{\tau+x}\quad(x\to-\infty;\ \tau_+>0) \quad (4.2)$$

then $I(\omega)=(1/2\pi)\int_{-\infty}^{\infty}dt\exp(-i\omega t)f(t)$ (with $\omega=\mu+i\tau$) will be analytic in the strip $\tau_-<\tau<\tau_+$, and in any strip within this strip

$$|I(\omega)|\sim C\exp(y_-\mu)\quad(\mu\to\infty)$$
$$\sim D\exp(y_+\mu)\quad(\mu\to-\infty)\,. \quad (4.3)$$

Here A, B, C and D are constants.

It is easily verified that the integral in Eq. (4.1) satisfies condition (2). Hence, in order to ascertain the low- and high-energy exponential behavior of Eq. (4.1) we can simply find the poles of the integrand closest to the real axis and then apply Eq. (4.3). Note that we can now easily see why the low-energy tail is the same for a single quadratic mode and for two degenerate quadratic modes. The single-mode line shape differs from Eq. (4.1) in the appearance of a $-\frac{1}{2}$ power instead of a -1 power (and in the constants in front of the integral), which does not affect the singularities of the integrand. It does not seem to be possible to obtain the singularities of the integrand of Eq. (4.1) analytically. However, the problem is easily adapted to a digital computer, and we have written a program for the Princeton University IBM 7094 which finds the poles of the integrand closest to the real axis. The results for the singularity closest to the real axis on the positive imaginary side are shown in Fig. 2(a) and Fig. 2(b) for two values of the coupling parameter x/ω_a. In Fig. 2(a) $x/\omega_a=0.1$ and in Fig. 2(b) $x/\omega_a=0.5$, and the singularity is plotted as a function of the inverse temperature, $\beta_a=h\omega_a/kT$. The abscissa, σ_+, is related to y_+ of of Eq. (4.3) by

$$\sigma_+=\tfrac{1}{2}xy_+ \quad (4.4)$$

and the exponential dependence of the low-energy tail is thus given by

$$I_{ab}(\omega')\sim\exp[(2\sigma_+/x)\omega']\,. \quad (4.5)$$

In Figs. 2(a) and 2(b) we have also plotted the quantity σ_+ for the semiclassical line shape.

Note that, as expected,[11,17] the semiclassical and quantum exponential tails coincide for high temperatures (small β_a). Both methods give a high-temperature exponential dependence on the low-energy tail of

$$I_{ab}(\omega)\sim\exp[\sigma_0 h\omega/kT] \quad (4.6)$$

with $\sigma_0=\omega_a^2/(\omega_a^2+x^2)$. As the temperature is lowered

[19] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Vol. I, p. 459.

both methods give a line shape with a qualitatively similar behavior. At low temperatures the exponential tail goes like

$$I_{ab}(\omega)\sim\exp[\sigma_0\hbar\omega/kT_0]\,. \tag{4.7}$$

However, the semiclassical method gives

$$kT_0=\tfrac{1}{2}\hbar\omega_a \tag{4.8}$$

while the quantum result is

$$kT_0=\hbar x\sigma_0/(\pi-2\tan^{-1}(x/\omega_a))\,. \tag{4.9}$$

From Figs. 2(a) and 2(b) we see that the exponential tail at low temperatures will be considerably steeper than the exponential tail given by the semiclassical approximation.

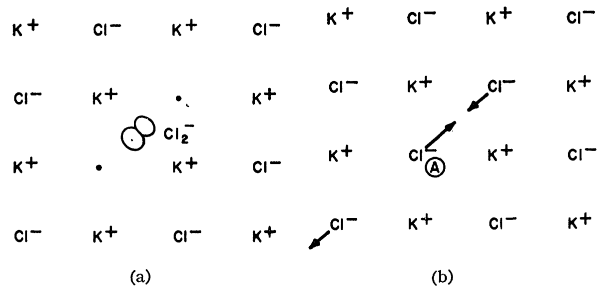


FIG. 3. (a) A V_k center in an alkali halide [see J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The Macmillan Company, New York, 1962), p. 152]. (b) An odd-parity (about the halide ion marked A) distortion which could lead to trapping of the exciton in the V_k configuration and to the low-energy exponential tail of Urbach's rule.

V. DISCUSSION

We have considered the quantum-mechanical modifications to the two-mode semiclassical line-shape theory proposed by Toyozawa and Mahr to account for the Urbach rule in insulators. We found that, in the case of a quadratic mode unstable in the excited state ($\omega_b^2<0$), the quantum line shape has many of the same features as the semiclassical line shape. In particular the exponential behavior of the low-energy tail at high temperatures is the same for both models. At low temperatures the quantum result predicts that the absorption constant will decrease more rapidly with smaller photon energies than the corresponding semiclassical result. The two-mode model in this case seems capable of reproducing the absorption constant over the entire range of interesting incident photon energies. For a stable excited state ($\omega_b^2>0$), the quantum line shape has no exponential tail for low temperatures and the two mode model fails to account for Urbach's rule.

There is some additional evidence that excitons in alkali halides are unstable to a lattice distortion which corresponds to a quadratically coupled mode. Kabler[13] and Murray and Keller[14] have shown that the luminescence observed by Teegarden[12] upon irradiation in the intrinsic exciton bands of several alkali halides is identical with the radiation obtained from recombination of an electron with the V_k center. A V_k center is shown in Fig. 3(a). This result suggests that the exciton created at the halide ion marked A is unstable to a lattice distortion such as that shown in Fig. 3(b). This distortion has odd parity (about the central halide ion marked A) and is thus a quadratic mode,[7,11] and could well be the source of the Urbach tail. Absorption on the low-energy tail corresponds to creation of an exciton at a time when the lattice is distorted and translational invariance is destroyed. Hence in this region it may not be necessary to explicitly consider the dynamics of the exciton, since it is essentially trapped at the time of creation. For absorption in the center of the band translational invariance is preserved and the dynamics of the exciton must be considered. Hence the present model must be considered as only qualitative for intrinsic excitons. It applies directly only to impurity bands. Some considerations on lattice distortion around excitons in alkali halides have been presented by Wood.[20]

Some problems remain, the major one being the interpretation of the low-temperature cutoff T_0. Martienssen[4] found that in KBr, $T_0\sim 60°$K. Using his value of $\sigma_0=0.79$ and Eq. (4.9), we find $\hbar\omega_a/k\sim 320°$K, well above the longitudinal-optical-mode frequency of KBr,[21] $\hbar\omega_l/k=230°$K. Note that if the experimental value of T_0 were 45°K, we would obtain good agreement with the longitudinal optical mode frequency. There are two other possible sources of the discrepancy. First, since quadratic cross terms in the normal-mode displacements may appear in the excited-state adiabatic potential, ω_a may be an "effective" frequency, not necessarily one of the normal mode frequencies of the ground state of the crystal. Qualitatively, the effect of cross terms will be to make the effective mass of the excited-state oscillator different from that of the ground-state oscillator. Such a mass difference will change the calculated value of ω_a. Second, since the excited electronic state is degenerate, the dynamical Jahn-Teller effect may introduce important modifications into the line shape. Neither of these effects has been successfully treated theoretically as yet.

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[20] R. F. Wood, Phys. Rev. Letters **15**, 449 (1965).

[21] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, London, 1954), p. 85.