INTERPRETATION OF URBACH'S RULE

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Urbach's observation[1] of the shape of the (electronic) optical absorption edge of nonmetallic crystals has attracted considerable attention.[2] Urbach's rule may be expressed as

$$\mu(\hbar\omega)=\mu_0(T)\exp\{\sigma[\hbar\omega-E_0(T)]/kT^*\},\quad \hbar\omega<E_0. \quad (1)$$

Here μ is the absorption coefficient, $\hbar\omega$ the photon energy, μ_0 the normalized transition strength, σ a constant of order unity, and T^* an "effective" temperature equal to T at high temperatures and to a zero-point temperature (e.g., 100°K) at low T. Typically, μ changes from an exponential to something like a Gaussian a few decades below its maximum ($\lesssim 10^6$ cm^{-1}) near $E_0(T)$. Manifested in such different materials as KBr,[3] CdS,[4] amorphous and crystalline Se,[5] and anthracene,[6] Urbach's rule has been shown to apply over many factors of 10, and evidently expresses something basic about absorption in solids. Numerous attempts have been made to explain the rule,[2] but none has been entirely satisfactory for bound transitions. In this Letter a simple and general interpretation is presented, based only on harmonic vibrational motion and second-order perturbation theory.

Suppose that in the absence of electric fields a discrete optical transition in a solid has a line shape $G(\hbar\omega-E_0)$. We would expect the usual quadratic Stark effect to occur upon application of a uniform electric field $\mathcal{E}$, resulting in a shift of E_0 to lower energy by an amount $\Delta=b\mathcal{E}^2$. Now a vibrating atom in a crystal does experience electric fields, of a magnitude determined by the degree of ionicity and/or the amount of overlapping of the charge distributions. So long as the fields remain small in comparison with $e/(\text{lattice constant})^2\sim 10^8$ V/cm, one would expect the field, and hence the matrix elements of $e\vec{\mathcal{E}}\cdot\vec{r}$ which determine the shift, to vary linearly with the atomic displacement u. Since the thermally averaged probability distribution of harmonic oscillators is a Gaussian in u, with a mean square width proportional to T^*, the probability of finding a field $\mathcal{E}$ is $\exp(-a\mathcal{E}^2)$, with $a\propto 1/T^*$. Thus the line shape becomes

$$\mu(\hbar\omega)\propto\int_{-\infty}^{\infty}e^{-a\mathcal{E}^2}G(\hbar\omega-(E_0-b\mathcal{E}^2)\,d\mathcal{E}$$
$$\propto\int_{-\infty}^{\infty}e^{-a/b\Delta}G(\hbar\omega-(E_0-\Delta))d\Delta/\Delta. \quad (2)$$

In many cases of interest a Gaussian-like line shape is observed and interpreted on the basis of interactions via the most strongly coupled, symmetrical modes[7] or the acoustic modes[8] of vibration. (Note that these modes produce no appreciable net electric field.) Accordingly let us choose the line shape G in the absence of any field to be $\exp[-\alpha(\hbar\omega-E_0)^2]$. [We expect α to vary as the reciprocal of some (different) effective temperature, and E_0 to change linearly with T at high T.] Then we may write the absorption coefficient as

$$\mu\propto\int_0^{\infty}e^{-(a/b)\Delta}e^{-\alpha[\hbar\omega-(E_0-\Delta)]^2}d\Delta/\Delta. \quad (3)$$

For a sufficiently narrow line (large α), Eq. (3) gives directly $\mu\propto\exp[(a/b)(\hbar\omega-E_0)](E_0-\hbar\omega)^{-1/2}$ with $a/b\propto 1/(kT^*)$. In the general case,

$$\mu\propto\exp(a^2/4\alpha b^2)S(c)e^{(a/b)[\hbar\omega-E_0(T)]}, \quad (4)$$

where

$$S(c)\equiv\int_0^{\infty}e^{-(x^2+c)^2}dx,\quad c\equiv a/2b\alpha^{\frac{1}{2}}-\alpha^{\frac{1}{2}}(E_0-\hbar\omega). \quad (5)$$

For large positive c, $S(c)$ varies rapidly, approximately as $e^{-c^2}(\pi/2c)^{\frac{1}{2}}$, combining with the exponential term in $\hbar\omega-E_0$ to give an (unchanged) absorption coefficient proportional to $\exp[-\alpha(\hbar\omega-E_0)^2]$ at energy $\gtrsim E_0$. For c small or negative (low energy), $S(c)$ is insensitive to c, and Urbach's rule is exhibited. [For c large and negative, $S\propto(E_0-\hbar\omega)^{-1/2}$.] Figure 1 shows the shapes of the resulting absorption spectra for several sets of parameters.[9] It is apparent that the three curves (2, 3, and 4) for which $\alpha=100$ eV^{-2} are all about the same near the origin, and approach the exponential shape more rapidly as a/b decreases. For curve 4 the downward curvature is still evident at 10^{-5} of its maximum. In curves 2 and 5, for which $a/\alpha^{1/2}b$ is small, the effect of the reciprocal square root of $E_0-\hbar\omega$ is evident on

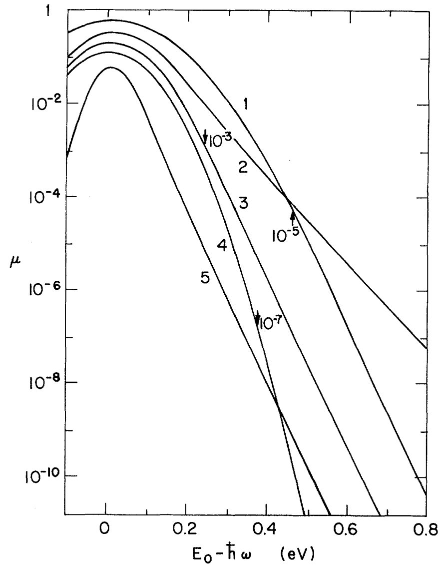

FIG. 1. Predicted shapes of absorption spectra. Curve 1, $\alpha = 49$ eV^{-2}, $a/b = 40$ eV^{-1}; Curve 2, $\alpha = 100$, $a/b = 20$; Curve 3, $\alpha = 100$, $a/b = 40$; Curve 4, $\alpha = 100$, $a/b = 80$; Curve 5, $\alpha = 400$, $a/b = 40$. $E_0(T)$ is defined as zero, and the significance of the arrows is described in the text.

close inspection.

Urbach's rule has also been observed for impurities in alkali halides, namely KCl:Br[10] and KCl:I,[11] similar to Fig. 1, Curve 3, whereas for others, e.g., Tl^+ (the *F* center) in KCl,[12] a Gaussian-like low-energy tail extends for at least 3 (4) decades, as in Fig. 1, Curve 1. It is clear from Fig. 1 that a continuous but rapid change occurs: As $a/b\alpha^{1/2}$ is changed by a factor of only 2, as in going from Curve 3 to Curve 4 in Fig. 1, the range over which μ remains substantially Gaussian increases by orders of magnitude. In the case of impurities for which b is small and/or a large, it would be relatively difficult to measure μ in the exponential region unless one were dealing with a nery narrow line (large α). It would be interesting to see if there is not an exponential tail on the narrow absorption lines of rare-earth impurities, and also on KCl:Tl at values of μ less than 10^{-3} of its maximum. Color centers in ionic crystals may represent a special case, since it is fictitious to refer to the vibration of a vacancy or vacancies. Nevertheless the long-wavelength tails of the zero-phonon absorption lines of the *R* centers in alkali halides should be investigated to see if they also exhibit an exponential increase of μ.

It is of interest to consider the magnitude of $a/b = \sigma/kT^*$, which at 300°K has been found experimentally to be between about 20 and 200 eV^{-1} in various materials. For KI, b has been measured[13] to be $\sim 3\times 10^{-15}$ eV/(V/cm)^2, and a/b is 32 eV^{-1} at room temperature.[3] Thus $a = 10^{-13}$ (cm/V)^2, or the rms field at 300°K is $\sim 2\times 10^6$ V/cm. Redfield[14] has outlined a calculation for $\mathcal{E}_{\mathrm{rms}}(300°)$ in KI in which he estimated a value of order 10^6 V/cm. Without the corrections Redfield refers to, F. T. Lee of this laboratory (private communication) obtains 7×10^6 V/cm. Thus the order of magnitude of the computed slope seems consistent with what is known of the individual parameters. (Of course, b as measured in a spatially constant field would not be expected to be precisely the same as that appropriate to lattice vibration.)

It should be emphasized that, although the exciton represents an excitation of the entire crystal, the low-energy region of the spectrum is not characteristic of the average, periodic potential. Typically less than 10^{-3} of the line strength occurs in the energy range where Urbach's rule is valid. Next to each arrow in Fig. 1 is indicated the fractional area of the absorption line which occurs at lower energy than the arrow. Absorption in this low-energy range occurs at (momentarily) vibrationally distorted sites, where a localized description is the natural one.

Finally, it should be noted that nothing in this presentation has required the existence of a periodic potential. If the broadening produced by the vibrational Stark effect should exceed that resulting from static disorder, one would still expect to see an exponential tail at low energies in vitreous media.

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[9] I am indebted to G. Gaspari, I. J. Kim, and W.-M. Shyu for their programs and assistance in the numerical integration of Eq. (5). Keil (Ref. 2) has noted the relationship between S and a Bessel function of the second kind, of imaginary argument.

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FINITE TRANSLATIONS IN SOLID-STATE PHYSICS

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Eigenvalues of finite translations are used for specifying a complete set of states in quantum mechanics. A derivation of these states is given and they are shown to be very useful in solid-state physics.

It is shown that finite translations in direct and reciprocal space can be chosen to form a complete set of commuting operators in quantum mechanics.[1] The eigenfunctions of these operators are found and are proven to form a complete orthonormal set of functions. Expressions for the basic operators $\vec{r}$ and $\vec{p}$ have been derived in the representation of these functions.

The new complete set of functions are of the Bloch-type with the ideal feature of being expressible in infinitely localized Wannier functions. This makes them extremely useful in solid-state physics. As an example, the problem of an electron in a periodic potential and a constant magnetic field is considered. This problem has attracted attention for many years, and although the results expressed in the effective-mass approximation are very simple, their derivation is "shockingly complicated."[2] It was pointed out[3-5] that the complications come about because of the set of functions one uses for expanding the solution of the mentioned problem. It turns out that the functions obtained in this paper form a very convenient set for expanding the solutions of a Bloch electron in a magnetic field and give us a very good insight into the problem. This is demonstrated by deriving an equation that was used before[4,6,7] and shown to be very useful, but never rigorously proven.

Finite translations in real space,

$$T(\vec{R}_n)=\exp(i\vec{p}\cdot\vec{R}_n), \tag{1}$$

where $\vec{R}_n$ is a Bravais lattice vector and $\vec{p}$ is the linear-momentum operator ($\hbar=1$), are known to be very important in solid-state physics. By means of them Bloch functions[8] $\psi_k(\vec{r})$ are defined:

$$T(\vec{R}_n)\psi_k(\vec{r})=\psi_k(\vec{r}+\vec{R}_n)=\exp(i\vec{k}\cdot\vec{R}_n)\psi_k(\vec{r}). \tag{2}$$

Here $\vec{k}$ is the wave vector and it defines the eigenvalues of the translation operators $T(\vec{R}_n)$. Relation (2) does not define the Bloch functions completely; it only requires that they have the form[8]

$$\psi_k(\vec{r})=\exp(i\vec{k}\cdot\vec{r})u_k(\vec{r}), \tag{3}$$

where $u_k(\vec{r})$ is an arbitrary periodic function, $u_k(\vec{r}+\vec{R}_n)=u_k(\vec{r})$. The reason that the operators $T(\vec{R}_n)$ do not define the functions ψ_k completely is because they do not form a complete set of commuting operators. It can be checked that operators

$$T(\vec{K}_m)=\exp(i\vec{r}\cdot\vec{K}_m) \tag{4}$$