approximation,[2] could account for the observed effect.

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Theory of Exponential Absorption Edges in Ionic and Covalent Solids*

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A calculation has been performed which yields a good fit to the exponential absorption edge of Urbach's rule in ionic crystals. The major feature of this calculation is that its underlying physical mechanism offers a unified explanation of exponential absorption edges in *all* materials: ionic, covalent, and intermediate bonding crystals, as well as amorphous semiconductors.

Fundamental optical absorption edges characterized by an exponential spectral dependence have been observed in a great variety of nonmetallic materials. Urbach first explicitly noticed this exponential dependence in ionic crystals[1] and enunciated what has become known as Urbach's rule for the dependence of the optical absorption coefficient (below the fundamental peak) on photon energy $\hbar\omega$ and temperature T:

$$\alpha(\omega)=A\exp[\sigma(\hbar\omega-\hbar\omega_0)/k_BT]; \qquad (1)$$

here σ is a constant of order unity, k_B is Boltzmann's constant, and A and ω_0 are constants. In spite of many theoretical efforts[2] to explain Urbach's rule, no completely satisfactory explanation exists—although virtually every ionic crystal exhibits an exponential absorption edge at high temperatures.[3,4] Experiments on heavily doped[5] and amorphous[6] semiconductors indicate that covalent materials also exhibit exponential edge behavior as a function of photon energy, although the temperature dependences of the edges vary widely. The presence of exponential edges in both ionic and covalent materials strongly suggests that the underlying physics is the same in all nonconducting solids. In this Letter we present the results of a simple model calculation which quantitatively reproduces the exponential absorption edges of ionic crystals. The chief significance of this result is that it is based upon a physical mechanism which is capable of explaining the data in ionic and covalent materials in a unified manner.

The model is a unification of two previous models and ascribes exponential edges to electric field ionization of the exciton—that is, field-induced tunneling of the electron away from the hole. It extends Redfield's Franz-Keldysh mechanism[7] to include the effects of the final-state Coulomb interaction between the optical electron and the hole. It also generalizes Dexter's quadratic-Stark-shift mechanism[8] to include the electric field *broadening* of the exciton as well as the shift. The unified theory thus overcomes the most serious deficiencies of the previous theories: (i) A quantitative exponential edge shape follows from the inclusion of exciton effects[9] in the Franz-Keldysh model[7]; and (ii) the breakdown of second-order perturbation theory for the exciton strong-field Stark effect is remedied by numerically solving the Stark-effect problem (including field broadening of the exciton) exactly.[9]

The principal assumption[7,8] of the present theory is that the optical absorption coefficient in the vicinity of the fundamental edge of a real crystal can be expressed as a weighted average of the absorption coefficient $\alpha(\omega, F)$ for excitons in a uniform electric field of magnitude F:

$$\alpha(\omega)=\int_0^\infty P(F;F_{\mathrm{rms}})\alpha(\omega,F)dF. \tag{2}$$

Here $P(F;F_{\mathrm{rms}})$ is the probability that there is an electric microfield[10] of magnitude F at the location of the exciton created by the absorbed photon. The dominant sources of electric microfields vary from material to material and may be optical phonons, impurities, dangling bonds, or other potential fluctuations associated with disorder. For example, in heavily doped semiconductors $P(F,F_{\mathrm{rms}})$ is a screened Holtsmark distribution[11]; the field distribution for optical phonons can be shown to be Gaussian[8,12]:

$$P(F;F_{\mathrm{rms}})=(\tfrac{2}{3}\pi F_{\mathrm{rms}}{}^2)^{-3/2}4\pi F^2 \times\exp(-\tfrac{3}{2}F^2/F_{\mathrm{rms}}{}^2), \tag{3}$$

where

$$F_{\mathrm{rms}}{}^2=[\hbar\Omega_0 q_c{}^3(\epsilon_\infty{}^{-1}-\epsilon_0{}^{-1})/3\pi] \times\coth(\hbar\Omega_0/2k_BT), \tag{4a}$$

which for high temperatures becomes

$$F_{\mathrm{rms}}{}^2=2q_c{}^3(\epsilon_\infty{}^{-1}-\epsilon_0{}^{-1})k_BT/3\pi. \tag{4b}$$

Here $\hbar\Omega_0$ is the optical phonon energy, ϵ_0 and ϵ_∞ are respectively the static and optical dielectric constants, and q_c is the polaron cutoff. [Normally $q_c{}^3$ is of order $(\pi/a_L)^3$, where a_L is the lattice constant. However, the requirements that the microfield be quasiuniform and provide sufficient phase space for the exciton to be ionized indicate that $q_c{}^3$ should be proportional to T and somewhat smaller than π/a, where a is the exciton radius.[12]] The absorption spectrum $\alpha(\omega)$ obtained using Eq. (2) with a Gaussian field distribution has been evaluated numerically and is displayed in Fig. 1 for values of F_{rms} typical of electric-field distributions due to polar phonons in alkali-halide crystals (~10^7V/cm).[13] The absorption edge is quantitatively exponential for several decades of absorption and for all photon energies more than approximately 0.5 binding energies below the lowest exciton.[12] Above this spectral region, additional broadening of the exciton peak (due, for example, to exciton scattering by acoustic phonons), which is not included in this calculation, normally dominates the line shape.[3,14]

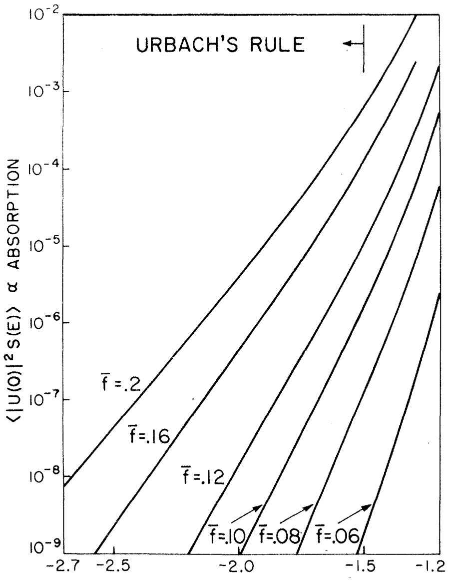

FIG. 1. Field-averaged absorption strength $\langle |U(0)|^2 \times S(E)\rangle$, which is proportional to the absorption coefficient $\langle\alpha(\omega)\rangle$ (see Ref. 9), as a function of $E\equiv(\hbar\omega-E_{\mathrm{gap}})/R$, where R is the exciton binding energy and E_{gap} is the band-gap energy. The dependence on the field F_{rms} is indicated by $\bar{f}=|e|F_{\mathrm{rms}}a/R$, where a is the exciton radius. The Urbach tails of alkali halides normally occur at energies to the left of the arrow in the figure, and for temperatures (proportional to $\bar{f}$) near and above 300°K such that $\bar{f}$ is of order 0.1.

It should be clear from Fig. 1 that the present theory is capable of explaining the spectral dependence of Urbach's rule in alkali halides using a mechanism which is also applicable to exponential edges in covalent materials. In addition, the Urbach temperature variation in ionic materials follows from a detailed analysis of the dependence of the tunneling process on phonon wavelength.[12] We believe that electric-field-induced ionization of the exciton is the only mechanism consistent with existing data which can explain exponential edges in both ionic and covalent solids in a unified manner. The details of such a unified theory (and of the present calculation) will be presented in a subsequent paper[12] in which other types of theories of exponential edges will be considered and will be found to be incapable of the generality which this model provides. Experiments supporting and testing these arguments will be cited and suggested, respectively.

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

Here $\hbar\Omega_0$ is the energy of the longitudinal optical phonon.

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Imprisonment of Resonant Phonons Observed with a New Technique for the Detection of 10^{12}-Hz Phonons

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A new technique for the monochromatic detection of 10^{12}-Hz phonons is applied to the study of 20-cm^{-1} phonons in ruby. The resolution of the phonon detector in space and time allows the observation of the local imprisonment of 29-cm^{-1} phonons in a ruby crystal that contains variable concentrations of Cr^{3+} ions in the excited $\bar{E}(^2E)$ state. The application for the determination of the lifetime of 10^{12}-Hz phonons is discussed.

We report the direct observation of imprisonment of resonant phonons in ruby using a new technique for phonon detection. The frequency of the trapped phonons (29 cm^{-1} or 0.87×10^{12} Hz) corresponds to the separation of the $\bar{E}(^2E)$ and $2\bar{A}(^2\bar{E})$ levels of the Cr^{3+} ion in Al$_2$O$_3$ [see Fig. 1(a)]. Transitions between these two excited states by the resonant phonons limit their mean free path severely and lead to the local imprisonment of these phonons reported here.

The resonant phonons are only scattered by *excited* Cr^{3+} ions, the number of which can easily be varied by changing the intensity of the exciting optical-pump radiation [see Fig. 1(a)]: Absorption of the pump light (from a mercury lamp) and subsequent radiationless transitions (RL) lead to the occupation of the metastable excited states $\bar{E}$ and $2\bar{A}$. The relative population of both levels is determined only by the 29-cm^{-1} pho-

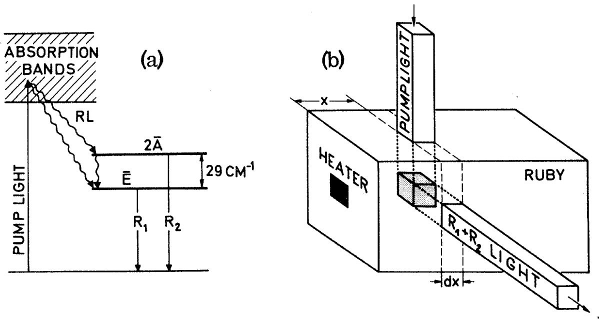

FIG. 1. Optical detector for 29-cm^{-1} phonons in ruby. (a) The energy levels of Cr^{3+} are shown schematically: The (blue and green) pump light is absorbed in the broad absorption bands. The wavelengths of the R_1 and R_2 fluorescence lines are 6935 and 6922 Å, respectively. (b) The experimental arrangement: The 50-Ω heater is evaporated on the 3×3-mm^2 surface of a 17-mm-long crystal (*a* direction). The detector volume (shaded has a size of about $1\times1\times1$ mm^3 and can be shifted relative to the heater.