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TEMPERATURE DEPENDENCE OF THE FUNDAMENTAL OPTICAL ABSORPTION EDGE IN CRYSTALS AND DISORDERED SEMICONDUCTORS

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We present a first principles theory of the temperature dependence of the Urbach optical absorption edge in crystals and disordered semiconductors which incorporates the effects of short range correlated static disorder and the non-adiabatic quantum dynamics of the coupled electron-phonon system. At finite temperatures the dominant features of the Urbach tail are accounted for by multiple phonon absorption and emission side bands which accompany the optically induced electronic transition and which provide a dynamic polaronic potential well that localizes the electron. Excellent agreement is found with experimental data on both crystalline and amorphous silicon.

THE URBACH optical absorption edge [1] in crystalline and amorphous semiconductors and insulators has posed a long standing unsolved problem in theoretical solid state physics. This involves optically induced electronic transitions from the valence-to conduction-band tail of the solid. For photon energies $\hbar\nu$ below the band gap energy, the optical absorption coefficient takes the form

$$\alpha(\nu) \sim \exp\left[(\hbar\nu - E_G(T))/E_0(T)\right] \qquad (1)$$

where E_G and E_0 are temperature dependent fitting parameters. Here E_G is comparable to the band gap energy and E_0 is typically in the range 10–100 meV for amorphous semiconductors. Although a theoretical foundation [2–15] for understanding this simple and universal behavior has been established, many fundamental issues remain. The observed linearity of the edge may be accounted for by the proper incorporation of short range order in the disorder whether static or dynamic. The sensitivity to short range correlations was first reported by Sritrakool *et al.* [11] and studied in depth in [15]. For a Gaussian random potential $V(x)$ with autocorrelation of the form $B(x) \equiv \langle V(x)V(0)\rangle_{\text{ens}} = V_{\text{rms}}^2 \exp(-|x|/L)$ it was shown by Halperin and Lax that the one-electron density of states (DOS) does not exhibit a significant Urbach tail for reasonable choices of the correlation length L. On the other hand, the function $B(x) = V_{\text{rms}}^2 \exp(-x^2/L^2)$ *does* give rise to a linear exponential edge over five decades in an energy range up to 0.5 eV for L close to the interatomic spacing of the solid [9, 11, 15]. The simplicity of Urbach's rule is manifest in a simple potential well picture [9] for electronic localization. The universality of the linear exponential edge is essentially the universality of short range order in disordered solids. These results are also consistent with the pioneering work of Dow and Redfield who showed that in a different class of solids with *long* range correlated randomness entirely new physics associated with exciton formation must be added to this simple one-electron picture to understand the optical absorption edge.

Based on this foundation, some aspects of the temperature dependence of the Urbach edge can be heuristically explained by modelling the quantum and thermal lattice vibrations by means of a classical frozen field [5, 6]. This provides a good description at high temperatures. The physical picture is that thermal fluctuations prepare the lattice polarization and that the resulting static potential wells localize the electron in band tail states as before. In this Letter we present a more fundamental solution to this issue which goes beyond this static picture. By properly incorporating the quantum dynamics of the lattice and the possibility of the electron to drive quantum mechanical phonon absorption and emission processes we find that three salient features of the absorption edge can be simultaneously accounted for with essentially no free or truly adjustable parameters. These are (i) linearity of the exponential edge over 5 decades, (ii) the linear relationship between $E_G(T)$ and $E_0(T)$ and (iii) the temperature independent Urbach focus. (see Fig. 1 and 2). Our theory predicts the existence of Urbach tails in both direct and indirect gap crystals at finite temperature and also suggests that a fundamental change may occur in the effective electron–phonon coupling between crystals and amorphous semiconductors.

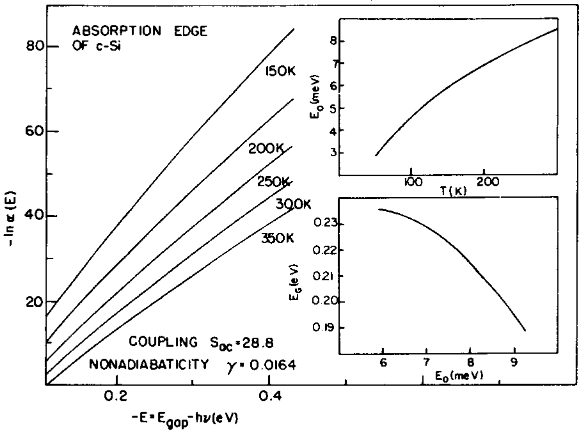

Fig. 1. Absorption coefficient in crystalline silicon (relative to its value at $\hbar\nu = 1.1$ eV for c–Si at 350 K) as a function of energy below the shifted indirect continuum edge at $E \simeq -0.1$ eV for various temperatures. Accurate linear exponential Urbach behavior begins to occur only at $E \simeq -0.3$ eV at 350 K and at the unobservably low energy $E = -0.5$ eV at 150 K. Theoretically it extends at least 0.5 eV below these energies. The upper insert shows E_0 vs temperature. The lower insert contains a plot of the downshift E_G of the continuum edge vs Urbach slope E_0. For high temperatures their relationship becomes linear.

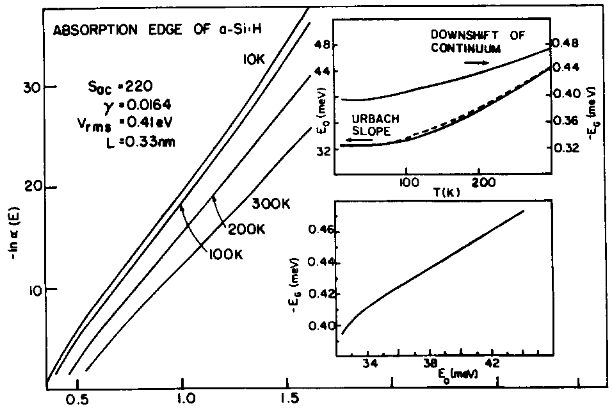

Fig. 2. Absorption coefficient for various temperatures in hydrogenated amorphous silicon. The continuum edge occurs approximately at the left of each curve. Linear Urbach behavior occurs over energy ranges $-0.6 \gtrsim E \gtrsim -1.1$ eV at 10 K and $-0.8 \gtrsim E \gtrsim -1.3$ eV at 300 K. The solid curve at the bottom of the upper insert is the computed Urbach slope E_0 vs temperature K for a-Si:H. Superimposed (dashed curve) is the experimentally observed slope (Tiedje *et al.*). The energy scale for these curves is at the left of the insert. Also shown is the downshift of the continuum E_G (energy scale on right of insert). The lower insert shows E_G vs E_0 displaying a linear relationship for $T \gtrsim 100$ K.

In the present context we neglect electron-hole correlations, excitonic effects and the associated energy dependence of the optical dipole transition matrix elements. Final state interactions, although of importance in materials such as the alkali-halides [4], play only a minor role in the determination of the absorption edge in crystalline silicon (c–Si) and hydrogenated amorphous silicon a–Si:H. In general, whenever the exciton binding energy is small compared to the scale of disorder, whether static or dynamic, the exciton line is smeared by the shift of the conduction band continuum.

In a continuum effective mass approximation for the electron dynamics, we take as our Hamiltonian for the coupled electron lattice system $H = p^2/2m^* + V(x) + H_{e-ac} + H_{ac}$ where p and m^* are the electron crystal momentum and average effective mass respectively in the conduction band, $V(x)$ is a correlated Gaussian random potential with mean value zero and a Gaussian autocorrelation function $B(x) \equiv \langle V(x)V(0)\rangle_{\text{ens}} = V_{\text{rms}}^2\, e^{-x^2/L^2}$. The electron-acoustic phonon interaction is taken to be

$$H_{e-ac} = \frac{E_d}{u}\sum_k \dot{q}_k \frac{e^{ik\cdot x}}{\sqrt{N_a}} \tag{2a}$$

where E_d is the deformation potential energy, u is the speed of sound, q_k is a normal coordinate of the lattice describing the amplitude of a longitudinal acoustic disturbance with wavevector $\boldsymbol{k}$, $\boldsymbol{x}$ is the electron coordinate and N_a is the total number of atoms in the crystal. Here the wavevector sum runs over the Brillouin zone of the crystal. Finally, H_{ac} represents the harmonic lattice Hamiltonian for atoms of mass M and for acoustic phonons with a linear dispersion relationship $\omega_k = uk$. In the continuum approximation it is convenient to replace the wavevector sum by a Brillouin zone volume preserving integral [16]. For a cubic crystal of lattice constant a, the wavevector cut-off function may be chosen to be $\exp(-\pi/4(k/k_0)^2)$ where $k_0 \equiv \pi/a$. This choice is particularly suitable for the description of disordered systems in which there is a smearing of the crystalline Brillouin zone.

The optical absorption coefficient is related to the imaginary part of the dielectric constant by the relation $\alpha(\nu) = \nu/c(\varepsilon_2(\nu)/n)$, where n is the real part of the refractive index. In a one-electron model this is given by [17]

$$\varepsilon_2(\nu) = (2\pi e)^2 \frac{2}{V}\sum_{i,f} \varrho_i(\beta)|R_{i,f}|^2\delta(\hbar\nu + E_i - E_f). \tag{3}$$

Here $\beta \equiv 1/(k_BT)$ and we have introduced the Boltzmann weight $\varrho_i(\beta) = e^{-\beta E_i}/(\Sigma_i\, e^{-\beta E_i})$ describing the probability that the system is in an initial state i.

The dipole matrix element takes the form $R_{i,f} = \langle \psi_f | \boldsymbol{\tau} \cdot \boldsymbol{x} | \psi_i \rangle$ where $\boldsymbol{x}$ is the electron coordinate and $\boldsymbol{\tau}$ the polarization vector of the photon. It is straightforward to generalize this one-electron expression to approximate the many-body dynamics of a coupled electron-phonon system. This simplest model which contains the relevant physics is obtained by choosing the initial state manifold to consist of a single strongly localized electronic level at energy $-E_{gap}$ which is completely decoupled from the phonons described by the Hamiltonian H_{ac}. We do not consider electron dynamics in the initial state. The final state manifold consists of the electron in the conduction band coupled to the phonon field and the static random potential. The energy E_f is an eigenvalue of the full Hamiltonian H. The dipole matrix element is interpreted in an adiabatic approximation: the many body wavefunction in the final state may be factored into a product of the lattice wavefunction and the electronic wavefunction $\psi_f(\boldsymbol{x})$. In the remainder of the calculation, however, the full nonadiabatic quantum dynamics of the many body system will be incorporated. In our model, the physical mechanisms for the production of valence and conduction band tails are the same. If the magnitude of the electron effective masses, the deformation potentials, and static disorder strengths and correlation lengths were the same in the valence and conduction bands this model would predict a DOS due to valence and conduction band tails which is symmetrical about the middle of the band gap. In recognition of the fact that some materials have their optical absorption dominated by a single band tail, a consequence of different physical parameters in the two band tails, our model considers absorption dominated by the conduction band tail. Due to the symmetry of the DOS about the middle of the gap, our model should also be valid for materials such as Si in which the absorption is dominated by the valence band tail.

Evaluation of (3) is facilitated by the integral representation of the energy conserving delta function:

$$\alpha(\nu) \sim \int_{-\infty}^{\infty} \frac{\mathrm{d}t}{2\pi\hbar} \, \mathrm{e}^{\mathrm{i}(\nu - E_{\mathrm{gap}}/\hbar)t} g(t) \tag{4a}$$

where the generating function

$$g(t) = \sum_{i,f} \langle i | \mathrm{e}^{-(\beta - \mathrm{i}t/\hbar)H_{ac}} R | f \rangle \langle \mathrm{f} | \mathrm{e}^{-\mathrm{i}tH/\hbar} R | i \rangle. \tag{4b}$$

A Feynman path-integral representation of $g(t)$ follows from a coordinate space representation $|\boldsymbol{x}; \{q_k\}\rangle$ of the state vectors. In a true many-electron formulation, the operator R would include the effect of electron-hole correlations. In our simple one-electron model the electron is initially localized at the origin and since we are considering optical excitation into localized conduction band tail states, the dominant effect of R is to restrict the electron coordinate to $\boldsymbol{x} = 0$ in the final state. Neglecting all other dependence of $R_{i,f}$ on f, it may be factored out of the summation in (4b). The first matrix element is that of a free harmonic oscillator and may be evaluated exactly. The second matrix element involving the full Hamiltonian H may be represented by a path-integral. Integrating over phonon coordinates yields, after a straightforward but tedious calculation:

$$g(t) \sim \int_{\boldsymbol{x}(0) = \boldsymbol{x}(t) = 0} \mathscr{D}\boldsymbol{x}(\tau) \, \mathrm{e}^{(\mathrm{i}/\hbar) S_{\mathrm{eff}}} \tag{5a}$$

where

$$S_{\mathrm{eff}} = S_e + S_{\mathrm{int}} + S_{\mathrm{dis}},$$

$$S_e = \frac{m^*}{2} \int_0^t \dot{\boldsymbol{x}}^2(\tau) \, \mathrm{d}\tau \tag{5b}$$

$$S_{\mathrm{int}} = \int_0^t \mathrm{d}\tau \int_0^t \mathrm{d}\tau' \frac{1}{N_a} \sum_{\boldsymbol{k}} \mathrm{e}^{\mathrm{i}\boldsymbol{k} \cdot (\boldsymbol{x}(\tau) - \boldsymbol{x}(\tau'))} \frac{\hbar u k_0}{2} S_{ac} \mathrm{i}\omega_{\boldsymbol{k}} \times [(N(\omega_{\boldsymbol{k}}) + 1) \, \mathrm{e}^{-\mathrm{i}\omega_{\boldsymbol{k}}|\tau - \tau'|} + N(\omega_{\boldsymbol{k}}) \, \mathrm{e}^{\mathrm{i}\omega_{\boldsymbol{k}}|\tau - \tau'|}] \tag{5c}$$

and

$$S_{\mathrm{dis}} = \frac{i}{2\hbar} \int_0^t \mathrm{d}\tau \int_0^t \mathrm{d}\tau' B(\boldsymbol{x}(\tau) - \boldsymbol{x}(\tau')). \tag{5d}$$

Here, we have introduced the phonon occupation number $N(\omega_{\boldsymbol{k}}) \equiv (\mathrm{e}^{\beta\hbar\omega_{\boldsymbol{k}}} - 1)$. An ensemble average over the static Gaussian random potential $V(\boldsymbol{x})$ has been performed to obtain S_{dis}. The dimensionless electron–acoustic phonon coupling constant is defined by the relation $\hbar u k_q S_{ac} = E_d^2/(2Mu^2)$.

The term involving $N(\omega_{\boldsymbol{k}}) + 1$ in S_{int} corresponds to optical transitions accompanied by the emission of a phonon of energy $\hbar\omega_{\boldsymbol{k}}$. Such processes cost elastic energy and the photon energy $\hbar\nu$ must be made accordingly higher. At zero temperature this emission process gives rise to polaronic states if the coupling S_{ac} is sufficiently strong. This density of coupled electron-lattice states has recently been shown to give rise to an Urbach tail in the strong coupling limit [13]. However, due to the elastic energy cost of deforming the lattice, this tail terminated at the polaron ground state. For small S_{ac}, no band tail occurs at zero temperature. Such states, however, could be nucleated by static disorder even for S_{ac} below polaron threshold, giving rise to a synergetic interplay between disorder induced localization and polaron formation [14]. It is apparent from (5c) that at finite temperature, thermal fluctuations will likewise enhance the phonon emission amplitude. The entirely new feature in our model arises from the term $N(\omega_k)\,e^{i\omega_k|\tau-\tau'|}$. This describes phonon assisted optical transitions in which a phonon of frequency ω_k is absorbed from the heat bath. Since elastic energy is provided by the heat bath, it is apparent that multiple phonon absorption can give rise to an infinite tail in the optical absorption spectrum below the conduction band edge even in the absence of static disorder. That is to say, by absorbing an appropriate set of phonons from the temperature bath and emitting them into a surrounding polaronic cloud the electron can dig its own potential well and form a localized conduction band tail state without paying the elastic energy cost it would have to at $T = 0$. A process of this nature involving n_- phonons absorbed and n_+ phonons emitted is apparent from the $(n_+ + n_-)^{\text{th}}$ order term in the power series expansion of $e^{iS_{\text{int}}/\hbar}$.

Evaluation of the path-integral (5a) is facilitated by introducing a trial harmonic action S_{trial} corresponding to the electron coupled by a classical spring of stiffness K_{trial} to a fictitious mass M_{trial} simulating the phonon cloud. This trial action implies that the phonons have a Gaussian wavefunction. A first cumulant expansion of the true action S_{eff} about S_{trial} is performed. This variational procedure as well as its high degree of accuracy in comparison to other methods has been discussed previously [10, 11, 13–16]. A detailed derivation including a comparison with most probable static potential well methods will be presented elsewhere [18].

For the case of crystalline silicon, we set $V_{\text{rms}} = 0$. A straightforward rescaling of all lengths by k_0^{-1} and time by $(uk_0)^{-1}$ reveals that the dimensionless input parameters in the evaluation of the generating function $g(t)$ are the electron-phonon coupling constant S_{ac} and the non-adiabaticity parameter $\gamma \equiv (\hbar uk_0)/(\hbar^2 k_0^2/2m^*)$. For c–Si $\hbar uk_0 \simeq 0.054\,\text{eV}$ [19], the average speed of sound $u \simeq 8.4 \times 10^3\,\text{m}\,\text{s}^{-1}$ [20] and the conduction band average effective mass is $m^* \simeq 1.1\,m_e$ [21] where m_e is the bare electron mass. Also the valence band deformation potential is known to be $E_d \simeq 11.3\,\text{eV}$ [22]. It follows that $S_{ac} \simeq 28.8$ and $\gamma \simeq 0.016$. Figure 1 shows numerically evaluated Urbach tails in the range $T = 150$ to $350\,\text{K}$. Comprehensive measurements of $\alpha(\nu)$ by Cody *et al.* [23] at 300 K in c–Si reveal an Urbach slope of $E_0 = 8.5 \pm 1.0\,\text{meV}$ in the vicinity of the indirect edge $1.0 \lesssim \hbar\nu \lesssim 1.1\,\text{eV}$. Our theory, which contains no free parameters, yields accurate linear exponential behavior with a slope of $E_0 = 8.6\,\text{meV}$. The electron crystal momentum $\boldsymbol{k}$-selection rule has been suppressed here since the electronic wavefunctions are strongly localized. It would be nevertheless be of interest to generalize this continuum effective mass model to capture both the direct and indirect edge of *c*–Si.

For amorphous semiconductors in the static limit, for high temperatures and static disorder correlation length close to the phonon correlation length, we can analytically solve for the absorption coefficient (1) in the Urbach regime, obtaining $E_G(T) \approx E_{\text{gap}} - V_{\text{rms}}^2/2\varepsilon_L - \pi S_{ac}\gamma k_B T/\sqrt{2}$ and $E_0(T) \approx V_{\text{rms}}^2/14.5\varepsilon_L + S_{ac}\gamma k_B T/3.26$, where $\hbar uk_0 = \hbar\omega_0$ is the Debye energy, and $\varepsilon_L \equiv \hbar^2/2m^*L^2$. These results are in close agreement with those in [9]. These expressions give an approximation to α, however the greatest lower bound to the true absorption coefficient can only be obtained numerically through the relaxation of the above limiting assumptions.

For a-Si : H, independent measurements of all of the input parameters are not yet available. For convenience we choose γ to have the same value as in c–Si and the correlation length L for the static random potential to be equal to the lattice constant. S_{ac} and V_{rms} of a–Si : H were then uniquely determined by matching the observed temperature dependence of E_0 with our theoretical model, yielding $V_{\text{rms}} \simeq 0.41\,\text{eV}$ and $S_{ac} \simeq 220$. A detailed comparison between our theory and measurements of Tiedje *et al.* [24] is presented in Fig. 2. The Urbach focus is temperature independent and E_0 and E_G are linearly related at high temperatures. At low temperatures our theory predicts deviations from linearity characteristic of the true quantum nature of the lattice vibrations.

We note finally the large change in the coupling S_{ac} from its crystalline value. Although some amount of freedom is available in the choice of γ and hence V_{rms} and S_{ac}, we find that for all choices, the effect of disorder is to move the electron-phonon coupling closer to small polaron threshold than in the corresponding crystal. Whether or not this represents a fundamental physical difference between amorphous and crystalline materials is an interesting open question. Resolution of this question requires a better understanding of the role of real band structure effects, higher order corrections in the electron-phonon coupling and the effects of disorder on the phonon spectrum which our simple model neglects. It is nevertheless noteworthy that even a very simple model when solved accurately with highly controlled approximations can quantitatively account for many experimentally observed features of these complex materials.

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