PHYSICAL REVIEW B VOLUME 51, NUMBER 3 15 JANUARY 1995-I

Anomalous Urbach tail in GaAs

C. W. Greeff*
Department of Physics and Liquid Crystal Institute, Kent State University, Kent, Ohio 44242

H. R. Glyde
Department of Physics and Astronomy, University of Delaware, Newark, Delaware 19716

(Received 14 December 1993; revised manuscript received 19 September 1994)

The Urbach tail in crystalline GaAs and Si due to thermal vibration is evaluated in the temperature range 0–810 K. Recent experiments suggest that there is no thermally induced Urbach tail in undoped GaAs. This is most unexpected since thermally induced tails at the absorption edge having the Urbach form and widths $E_0(T)$ linear in T are observed in a wide range of crystalline and amorphous semiconductors. Clear understanding of the tail is important in device applications. In our calculations, we obtain an absorption tail having a simple exponential energy dependence (Urbach form) in GaAs at all temperatures with $E_0(T)$ proportional to T. However, due to a very weak electron-phonon interaction, the magnitude of $E_0(T)$ is unusually small, much smaller than the temperature independent, structurally induced component $E_0 \simeq 10$ meV. As a test of the method, the tail is similarly evaluated in Si providing an $E_0(T)$ value in agreement with experiment.

I. INTRODUCTION

Optical absorption in crystalline and amorphous materials is of great intrinsic interest and has wide application in devices. Absorption begins when the incident photon energy E is large enough to excite electrons across the energy gap E_G between the valence and conduction bands. For energies E near the absorption edge, the absorption coefficient $\alpha(E)$ shows a near universal simple exponential energy dependence,

$$\alpha(E) = \alpha_0 e^{[E - E_1(T)]/E_0(T)}, \tag{1}$$

denoted the Urbach tail.[1] $E_1(T)$ is an energy close to E_G and $E_0(T)$ determines the width of the tail. Urbach tails are observed in nearly all materials and are the subject of several reviews.[2–8]

The tail is generally attributed to disorder in the material that leads to a tail in the valence and conduction bands. Disorder induced band tails are generally denoted Lifshitz tails.[9] In crystals at low temperature, dopant impurities randomly located introduce disorder for which, typically, $E_0 \simeq 10\,\text{meV}$. In amorphous materials, the disordered siting of the constituents lead to $E_0 \simeq 50\,\text{meV}$. At higher temperature, the vibrational displacements of the atoms introduce disorder. The electron sees a "snapshot" of the ions displaced from their lattice points by thermal vibration. At 50–100 °C, $E_0(T)$ due to thermal vibration is typically 10 meV in semiconductors, 50 meV in alkali halides.[10,11] The equivalence of thermal and amorphous disorder has been widely discussed.[6,12]

To evaluate band tails in crystals, a disordered potential $V(r)$ is introduced in addition to the perfect crystal potential. The correlation function $W(r) = \langle V(r)V(0)\rangle$ of the disordered potential plays a key role. If the correlation length L of $W(r)$ is of order the interatomic spacing ($L \simeq$ 2–5 Å) then the band tails take the simple exponential Urbach form (1). This can be shown generally[13,14] independent of the origin of the disorder.

For thermal disorder, $V(r)$ is assumed to be proportional to the displacements of the ions, $u_l = \sum_q(\hbar/2mN\omega_q)e^{i\mathbf{q}\cdot\mathbf{R}_l}\,(a_q + a_{-q}^{+})$, from their lattice points and a thermal average of the phonon annihilation operators a_q is taken. In addition, Miyazaki and Hanamura[15] and Grein and John[16] have considered polaronic effects in which the electron distorts the lattice. Including these effects they have obtained good agreement for band tail shapes and E_0 values in several materials.

In this paper we investigate band tails due to thermal disorder in undoped GaAs and Si at several temperatures. In a recent measurement, Weilmeier *et al.*[17] found no thermal contribution to the Urbach tail in GaAs; i.e., $E_0 = 9 \pm 1\,\text{meV}$ at 32 °C and $E_0 = 10 \pm 1\,\text{meV}$ at 456 °C. This is consistent with previous measurements,[18,19] but unexpected since in a wide range of semiconductors, $E_0(T)$ is proportional to T and E_0 is dominated by the thermal tail. To investigate this unusual result in what is perhaps the most widely investigated semiconductor, we calculate $E_0(T)$ in GaAs. To test the method we also evaluate the Urbach tail in Si where $E_0(T)$ is known and is linear in T as expected. We find that $E_0(T)$ is indeed linear with T in GaAs, but its magnitude is much smaller than expected. This means that the observed $E_0 \simeq 10\,\text{meV}$ must be due to other structural disorder that dominates $E_0(T)$ and leads to an E_0 nearly independent of T. In Si we find a much larger $E_0(T)$ in agreement with other values.[16] We also show that the correlation function of the thermal disorder $W(r)$ is a Gaussian function,

$$W(r) = \xi e^{-r^2/L^2} \tag{2}$$

with a correlation length $L \simeq 2.9\,\text{Å}$ for GaAs, independent of temperature. It is for this reason that an Urbach tail linear in E is obtained.

In Sec. II we develop the model of the disordered potential $V(r)$ due to the electron-phonon interaction. We also evaluate the correlation function $W(r)$, show that is well represented by a Gaussian, and calculate the density of states $n(E)$ and $E_0(T)$ in the band tail region given ξ and L in Eq. (2). The results for $W(r)$, $n(E)$, and $E_0(T)$ in GaAs and Si are presented in Sec. III.

II. DISORDER AND DENSITY OF STATES

We assume independent, free electrons in a disordered potential, $V(r)$. All crystal effects, the electron-electron and electron-hole interactions are neglected. Particularly, with electron-hole interactions neglected, all exciton effects are ignored. This approximation is discussed below. The average of $V(r)$ is set to zero and only the correlation function, $W(r) = \langle V(r)V(0)\rangle$, of $V(r)$ is retained. For thermal disorder, we assume $V(r)$ is linearly proportional to the phonon creation operators $a_{\vec{k}}^{+}$ [$V(r)$ proportional to the ionic displacements]. The average in $W(r)$ is a thermal average over the phonon field independent of the electron so that all dynamical polaron effects are ignored. Under these assumptions $W(r)$ will be a function of r only. For this case, Sa-yakanit[20] has presented a complete theory for the density states in the band tail using Feynman path integrals. If $W(r)$ takes a Gaussian form, Eq. (2), $n(E)$ is obtained in closed form as[20]

$$n(E) = \left(\frac{E_L}{L}\right)^3 \frac{1}{\xi^2} a(\nu) \exp[-E_L^2 b(\nu)/2\xi], \tag{3}$$

where

$$E_L = \frac{\hbar^2}{2mL^2}, \tag{4}$$

$$a(\nu) = [(1+16\nu)^{1/2}-1]^{3/2}[(1+16\nu)^{1/2} +7]^{9/2}/(2^{25/2}\pi^2), \tag{5}$$

$$b(\nu) = [(1+16\nu)^{1/2}-1]^{1/2}[(1+16\nu)^{1/2}+7]^{7/2}/2^8, \tag{6}$$

and

$$\nu = -E/E_L. \tag{7}$$

The energy E is measured from the band edge, that has temperature dependence due to the disorder as well as other effects that we do not attempt to model. We show in what follows that the Gaussian model gives a good representation of the correlation function W in the phonon case.

In the present work we consider the electron-phonon interaction in the adiabatic approximation. That is, we regard the ionic displacements as giving rise to a static disorder field that is felt by the electrons as a random potential. In this case we can calculate the correlation function $W(r)$ from the electron-phonon interaction. In general, the potential energy of an electron in the presence of the phonon field can be expressed[24,25] in the form

$$V(r) = \sum_{\vec{k}} F(k) a_{\vec{k}} e^{i\vec{k}\cdot\vec{r}} + \text{H.c.}, \tag{8}$$

where $a_{\vec{k}}$ is the destruction operator for a phonon of wavevector $\vec{k}$, and of a particular polarization that we do not explicitly indicate. Then we can write the correlation function $W(r)$ as

$$\begin{aligned} W(\vec{r}-\vec{r'}) = \sum_{\vec{k}}\sum_{\vec{k'}} &[F(k)F^*(k')\langle a_{\vec{k}} a_{\vec{k'}}^{\dagger}\rangle e^{i\vec{k}\cdot\vec{r}-i\vec{k'}\cdot\vec{r'}} \\ &+F^*(k)F(k')\langle a_{\vec{k}}^{\dagger} a_{\vec{k'}}\rangle e^{-i\vec{k}\cdot\vec{r}+i\vec{k'}\cdot\vec{r'}}] \\ = \sum_{\vec{k}} &|F(k)|^2(2n_k+1)e^{i\vec{k}\cdot(\vec{r}-\vec{r'})}. \end{aligned} \tag{9}$$

The sum over $\vec{k}$ extends over one Brillouin zone. For simplicity we replace the Brillouin zone by a sphere of equivalent volume. This leads to a spherical cutoff $|\vec{k}| < k_c$ where $k_c^3/6\pi^2 = V_c^{-1} = 4/a^3 = (\frac{1}{2})(N/V)$. Here V_c is the volume of the fcc primitive cell, a is the lattice constant, and N/V is the Si atom number density. Then we have

$$W(r) = \frac{\Omega}{2\pi^2}\frac{1}{r}\int_0^{k_c} dk \coth(\hbar\omega_k/2k_BT)|F(k)|^2 k \sin(kr), \tag{10}$$

where Ω is the system volume. In what follows, we consider two forms for the electron-phonon interaction. First is the deformation potential interaction,[24,25] which relates the electron energy to local dilations and compressions of the crystal, which occur in the presence of longitudinal acoustic vibrations. For this case,

$$F(k) = \left(\frac{\hbar}{2\rho\Omega\omega_k}\right)^{1/2} kA, \tag{11}$$

where ρ is the mass density of the crystal, and A is the deformation potential parameter. From this form of the interaction, we obtain

$$W(r) = \frac{\hbar A^2}{2\rho c}\frac{1}{2\pi^2 r}\int_0^{k_c} dk \coth(\hbar ck/2k_BT)k^2 \sin(kr), \tag{12}$$

where c is the longitudinal sound velocity and we have assumed linear dispersion, $\omega_k = ck$.

In III-V semiconductors the bonding is partially ionic and we must also consider that the electron interacts with the dipole fields that arise from the relative displacement of the anion and cation. This leads to an interaction of the electron with the longitudinal optical phonons[24,25] with

$$F(k) = 4\pi i \left(\frac{e^2\hbar}{2\gamma\omega_o\Omega}\right)^{1/2} \frac{k}{k^2+Q^2}, \tag{13}$$

where ω_o is the optical phonon frequency, Q is the reciprocal screening length, and γ is the coupling constant,

$$\frac{1}{\gamma} = \frac{\omega_o^2}{4\pi}\left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0}\right), \tag{14}$$

where ϵ_0 is the static dielectric constant and ϵ_∞ is the dielectric constant at frequencies that are large compared to ω_o. In this case we obtain

$$W(r) = \frac{16\pi^2 e^2\hbar}{2\gamma\omega_o}\coth(\hbar\omega_o/2k_BT)\frac{1}{2\pi^2 r} \times \int_0^{k_c} \frac{k^3}{(k^2+Q^2)^2}\sin(kr). \tag{15}$$

When more than one type of electron-phonon interaction takes place, their contributions to $W(r)$ are additive.

We can see that Eq. (3) does not give linear (Urbach) exponential behavior for the one-electron density of states in general. Indeed, the function $b(\nu)$ behaves like $\nu^{1/2}$ for $\nu \ll 1$ and ν^2 for $\nu \gg 1$. However, Sritrakool *et al.*[13] have shown that for values of L such that $\nu = E/E_l \sim 1$ (e.g., $L \sim 5$ Å and E in the experimentally accessible energy range), the exponent $b(\nu)$ is linear in ν, $b(\nu) \sim \nu$. Linear behavior of the exponent $b(\nu)$ will be observed when the logarithmic derivative $d\ln(b(\nu))/d\nu$ is close to 1. This gives a value of $\nu_0 = 3/2$. Expanding b to first order in $\nu - \nu_0$ gives a slope parameter of

$$E_0 = \frac{2\xi}{E_L}\left(\frac{db}{d\nu}\right)^{-1}_{\nu=\nu_0} = \frac{\xi}{9\sqrt{3}E_L}. \tag{16}$$

This is the definition used in the subsequent analysis. The parameter E_0 is often found to have a temperature dependence of the form[21,22]

$$E_0(T) = \alpha\coth\left(\frac{\hbar\omega_P}{2k_BT}\right), \tag{17}$$

where ω_P is a typical phonon frequency. We show subsequently that the correlation length L, and, therefore, E_L is essentially independent of temperature, being primarily determined by the lattice spacing through k_c. Thus the temperature dependence of E_0 is determined by the temperature dependence of ξ. For the dispersionless model of optical phonons we indeed have

$$\xi \propto \coth\left(\frac{\hbar\omega_o}{2k_BT}\right) \tag{18}$$

as shown in Eq. (15). However, for phonon spectra without a gap, it will be important to account for dispersion at low temperatures. In this case, as in Eq. (12), the factor $\coth(\hbar\omega_k/2k_BT)$ cannot be taken outside of the k integration, and the simple form, (18) for $\xi(T)$ will not hold. At high temperatures, however, $\coth(\hbar\omega_k/2k_BT) \rightarrow 2k_BT/\hbar\omega_k$ and the T dependence will come outside of the k integration. Thus, for $T > \hbar\omega_{k_c} \approx \theta_D$, ξ will be proportional to T. We, therefore, expect that a linear dependence of E_0 on T will be a general behavior at high T. However, the detailed form $E_0 = \alpha\coth(\hbar\omega_P/2k_BT)$ is characteristic of a system in which the dominant electron-phonon interaction is with optical phonons. This is likely to be the case for systems with strongly ionic bonding, such as AgBr (Ref. 21) and alkali halides,[22] for which measurements have shown this behavior.

III. RESULTS

In Fig. 1 we show our results for $W(r)$ over a range of temperatures using the electron-phonon interaction parameters for GaAs. In this case $W(r)$ is the sum of terms of the type given by Eq. (12) for longitudinal acoustic phonons and that given by Eq. (15) for longitudinal optical phonons. We use the parameters[23]

$$\begin{aligned} A &= 7.0 \text{ eV}, \\ \rho &= 5370 \text{ kg m}^{-3}, \\ \omega_o &= 5.37 \times 10^{13} \text{ s}^{-1}, \\ \epsilon_\infty &= 10.82, \\ \epsilon_0 &= 12.53. \end{aligned} \tag{19}$$

Using the elastic constants quoted in Ref. 23 we obtain

$$c = 5.11 \times 10^5 \text{ cm/s} \tag{20}$$

and we take as the lattice constant, $a = 5.654$ Å. Figure 2 shows the Gaussian fit of the form $\xi e^{-(r/L)^2}$ to $W(r)$, where

$$\xi = W(0) \tag{21}$$

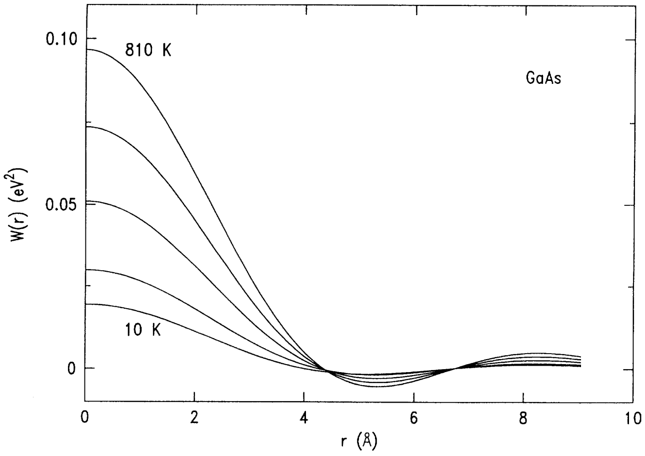

FIG. 1. The correlation function $W(r) = \langle V(r)V(0)\rangle$ of the disorder potential $V(r)$ due to electron-longitudinal (12) and electron-optical (15) phonon interactions in GaAs for temperatures 10 K, 210 K, 410 K, 610 K, and 810 K.

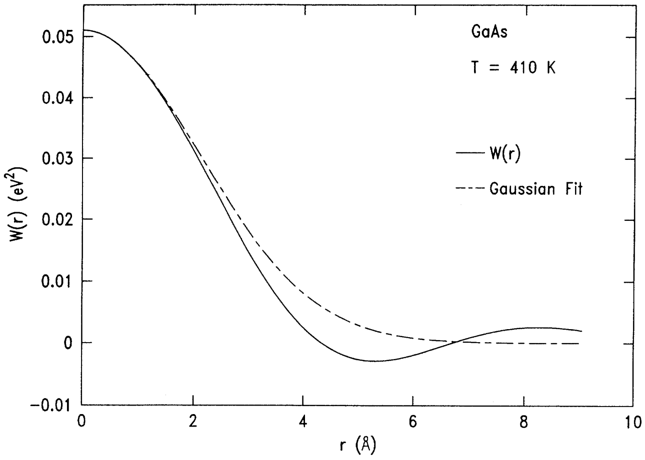

FIG. 2. Fit of a Gaussian function to the calculated correlation function $W(r)$ in GaAs at 410 K.

and

$$L = -2W(0)/W''(0). \tag{22}$$

We see that the Gaussian gives an excellent representation of the actual $W(r)$. In calculating the density of states we use the Gaussian model for W, allowing us to take advantage of the results of Sa-yakanit[20] for this case. The two parameters ξ and L are extracted from the full W as indicated above. It can be seen from Fig. 1 that the correlation length is not strongly dependent on the temperature. In fact, our numerical values are constant at $L = 2.9$ Å to within 1% over the whole temperature range from $T = 10$ K to $T = 810$ K.

We would like to comment on the relation of our calculated W to exciton formation. From Fig. 1 we see that even at 10 K, the electrons move in a potential field that fluctuates in magnitude by $\sqrt{\xi} \approx 40$ meV and becomes uncorrelated on a length scale of $\lesssim 5$ Å, whereas the exciton in this system has a binding energy ~ 3 meV and a radius $\sim 10^3$ Å. Thus, the electron moves in a field that has large fluctuations over lengths that are very short in comparison to the energy and length scales relevant to exciton binding. Under these circumstances the conventional picture of a free Wannier exciton must clearly be modified. However, these considerations do not fully justify neglecting electron-hole correlations as has been done in the present calculation. Indeed, an exciton peak, although substantially broadened, is clearly seen in the data of Ref. 19 for temperatures up to $\sim$ 185 K. We, therefore, take the point of view that the present calculation is valid at room temperature and above, where no sign of an exciton peak is observed.

Turning to Si, in Fig. 3 we show the density of sates, calculated from Eq. (3), in the tail below the conduction band for crystalline Si. In this case we have calculated ξ and L from (21) and (22), using the deformation potential interaction, Eq. (12). We have used the parameters,

$$\begin{aligned} A &= 11.3 \text{ eV}, \\ \rho &= 2.33 \text{ gm/cm}^3, \\ c &= 8.4 \times 10^5 \text{ cm/s}, \\ a &= 5.43 \text{ Å}. \end{aligned} \tag{23}$$

E_L is calculated using $m^* = 1.1 m_e$. In this case $\xi(T)$ was approximately three times larger, but $L \approx 2.7$ Å independent of temperature. In Fig. 4 we show the Urbach energy parameter E_0 as a function of temperature. In Ref. 16 a value of $E_0 \approx 7$ meV was found at a temperature of 200 K, which is less than but consistent with our result of $E_0 \approx 12$ meV.

According to Eqs. (4) and (16), the greatest broadening will occur for the heaviest band. Accordingly, in Fig. 5 we show the density of states extending above the heavy hole band of GaAs. This band will have the widest tail and thus make the dominant contribution to the observed Urbach tail. Figure 6 shows the resulting

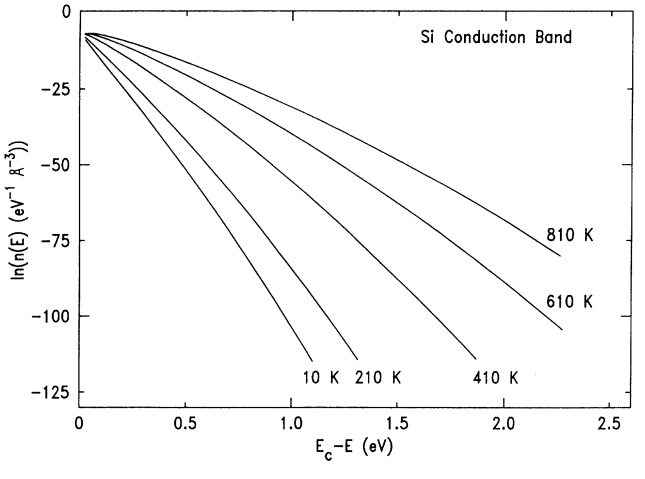

FIG. 3. Density of states in the band tail of the conduction band in Si.

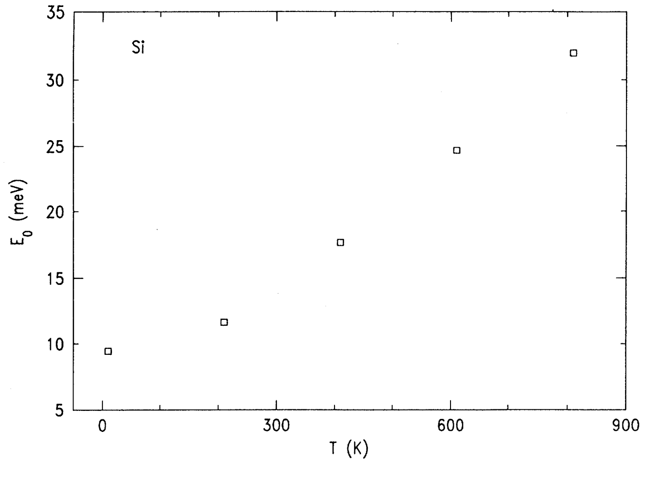

FIG. 4. The Urbach tail width parameter $E_0(T)$ due to electron-longitudinal phonon interactions in Si at temperatures 10 K to 810 K.

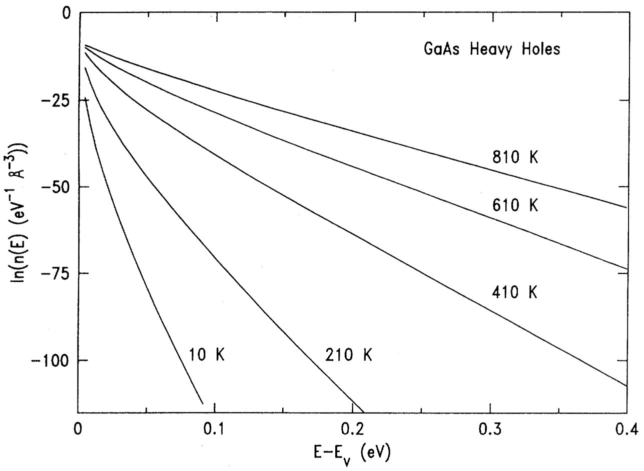

FIG. 5. Density of states in the band tail of the heavy-hole valence band in GaAs.

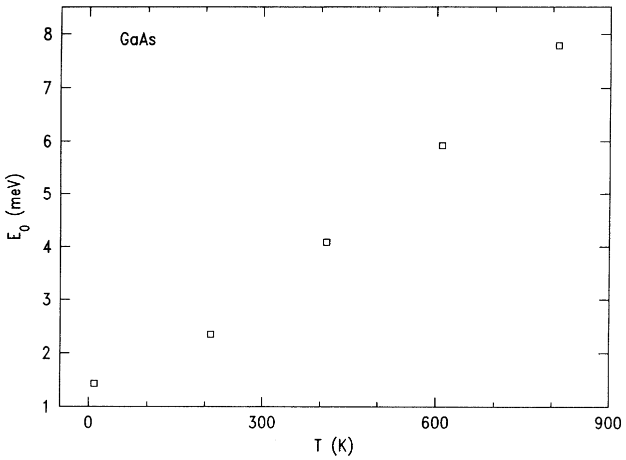

FIG. 6. Urbach tail width parameter $E_0(T)$ in GaAs due to electron-phonon interactions at temperatures 10 K to 810 K.

Urbach parameter as a function of temperature. Our calculated value of E_0 is generally smaller than what has been observed in optical absorption experiments in GaAs. E_0 has been found to be in the range 7–9 meV at room temperature, whereas our calculation gives $E_0 \approx 3$ meV at room temperature. At temperatures above room temperature, our E_0 is linear in T, with a coefficient $\Delta E/\Delta T = 0.75 \times 10^{-2}$ meV/K. The results of Ref. 18 indicate that E_0 changes from 7 to 14 meV as T varies from 24 to 600 °C, giving a coefficient of variation of 0.14 $\times 10^{-2}$ meV/K. This is only a rough estimate since the data of Ref. 18 do not show a systematic temperature dependence of E_0, and in particular the data at $T = 700$ °C seem to show a smaller E_0 than those at $T = 600$ °C. In Ref. 17 it was found that E_0 varied from 9 ± 1 meV at 32 °C to 10 ± 1 meV at 456 °C. Over this temperature range we predict a variation of E_0 of 4 meV which is not inconsistent with the data.

E_0 is often modeled as the sum of a thermal part and a structural part. If we take this approach, the above comparisons would seem to indicate that a substantial part of the observed Urbach energy E_0 in GaAs is due to structural disorder. Thermal disorder then results in a small variation of E_0 with T.

IV. CONCLUSIONS

We have considered a model for the temperature dependence of the Urbach tail in semiconductors in which the electrons move in a random field due to the presence of thermally excited phonons. This field gives rise to a tail of states in the one-electron density of states. In this way we are able to make a connection to previous theories of the Urbach tail in heavily doped and amorphous semiconductors. In this formulation the disorder is characterized by its mean squared fluctuation ξ and its correlation length L. We find that the correlation length is essentially independent of temperature, so that the temperature dependence of the Urbach parameter E_0 is determined by the temperature dependence of ξ, E_0 being proportional to ξ. ξ is, in turn, related, via the electron-phonon interaction to a Brillouin zone sum of the squared phonon amplitudes. For dispersionless phonons, this results in a temperature dependence of E_0 of the form

$$E_0 \propto \coth(\hbar\omega_o/2k_BT). \qquad (24)$$

However, this form is not general. In particular, for acoustic phonons, where dispersion is important at low temperatures, this form will not hold. At high temperatures a linear dependence of E_0 on T is expected to be general.

Using the electron-phonon interaction parameters as input, we have calculated the Urbach parameter E_0 as a function of temperature for crystalline Si and for GaAs. For Si, we find that the temperature dependence is large and that the absolute value of $E_0(T)$ at room temperature is somewhat larger than the observed value. For GaAs, we find that the temperature dependence is much smaller with $E_0(T)$ increasing by only 4 meV between 32 °C and 450 °C. We interpret this as signifying that the measured E_0 in GaAs is largely due to structural disorder, with a small temperature variation due to thermal displacement of the ions.

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[*] Present address: Department of Chemistry, University of California, Berkeley, CA 94720.

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