Temperature-dependent tails on the density of states in noncrystalline materials

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The temperature dependence of the tails on the density of electron states in noncrystalline materials is examined theoretically. The component of this temperature dependence which is associated with two-well atomic potentials is considered for the first time. When such potentials are taken into account, one should distinguish between two types of tails on the density of states: optical and thermodynamic. These two types should be manifested in different experiments. Their shape and temperature dependence are analyzed. The temperature-dependent effect of the two-well potentials on the tails on the density of states has a certain time lag, which could give rise to long-term relaxation effects. The theory is compared with experimental data on amorphous hydrogenated silicon.

1. INTRODUCTION

The extensive experimental evidence which has now been accumulated indicates that there are tails on the density of states in noncrystalline materials: amorphous semiconductors, amorphous insulators, glasses, and polymers. States arise in the tails because of fluctuations in the random potential $U(\mathbf{r})$. These fluctuations create effective potential wells which are capable of trapping an electron or a hole (for definiteness, we will speak exclusively in terms of electrons). With decreasing energy (E) of the trapped electron, the depth $U(\mathbf{r})$ of the corresponding potential well should increase. The fluctuation probability falls off exponentially with increasing $|U|$. Correspondingly, the density of states in the tails decays exponentially with distance into the mobility gap:

$$g(E)=g_0\exp\left[-S(E)\right], \tag{1}$$

where $S(E)$ is usually a power function, and the energy E is reckoned from the mobility edge.

The theoretical description of $g(E)$ is based on the optimum fluctuation method (see the reviews[1–4]). This method allows one to seek the most probable of all possible fluctuations which would lead to a given energy E. One can thus determine the function $S(E)$. For comparatively shallow levels E in three-dimensional systems, the expression for $S(E)$ is

$$S(E)=(|E|/E_0)^{1/2}, \tag{2}$$

where

$$E_0=\frac{B_U{}^2}{4b(\hbar^2/2m)^3}\qquad B_U=\langle U^2(\mathbf{r})\rangle,\qquad b\approx 44{,}4, \tag{3}$$

and m is the effective mass of an electron. Expression (2) is valid as long as the characteristic trapping radius $r_\psi\sim\hbar(m|E|)^{-\frac{1}{2}}$ exceeds the correlation radius r_c of the random potential and the binding energy $|E|$ is much smaller than the average value of the random potential.[1]

In the present paper we analyze $g(E)$ in the region in which expression (2) is applicable, for conditions such that the disorder depends on temperature. This dependence is generated by interwell transitions of atoms in random two-well potentials (Fig. 1). The presence of such potentials is a universal property of noncrystalline systems. They make the heat capacity a linear function of the temperature ($C\propto T$), and they make the thermal conductivity a quadratic function of the temperature ($\chi\propto T^2$). They give rise to distinctive features in the acoustic and microwave absorption, cause an unusual thermal expansion, and cause yet other effects (see the reviews[5–7]). Our analysis is based on the changes which occur in the fluctuations of the electron potential $U(\mathbf{r})$ in the course of transitions of atoms between wells.

As we will show below, when the two-well potentials in these systems are taken into account, one should distinguish between tails of two types: optical and thermodynamic. These two types of tails are manifested in different experiments. We derive the shapes of these tails and their temperature dependences. We compare the theoretical results with experimental data on amorphous hydrogenated silicon.

2. QUALITATIVE CONSIDERATIONS

Following the standard description of two-well potentials in glasses,[5–7] we assume that these potentials are characterized by probability distributions of two random parameters: the asymmetry ε and the barrier height v (Fig. 1). The distribution of ε is nearly flat over a certain interval:

$$\rho_\varepsilon(\varepsilon)\approx\text{const},\quad 0\leqslant\varepsilon\leqslant\varepsilon_0. \tag{4}$$

The explicit shape of the v distributions will not be of importance in the discussion below. Wishing to stress only that it is bounded, we assume for simplicity

$$\rho_v(v)=\begin{cases}\text{const}, & v_{min}\leqslant v\leqslant v_{max},\\ 0, & v<v_{min}\quad\text{or}\quad v>v_{max}.\end{cases} \tag{5}$$

The energy of the interaction of a classical atomic particle in a two-well potential with an electron is

$$H_i=V_{0i}n_{0i}+V_i{}'n_i=V_{0i}+V_in_i,\qquad V_i\equiv V_i{}'-V_{i0}, \tag{6}$$

where the index i corresponds to the two-well potential with the parameters ε_i and v_i, n_i and $n_{0i}=1-n_i$ are the populations of the upper and lower wells of the potential, and V_{0i}

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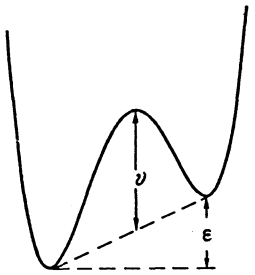

FIG. 1. Schematic diagram of a two-well potential. v—The height of the barrier; ε—the asymmetry of the wells.

and V_i' are parameters of the interaction of the electron with the atomic particle in the lower and upper wells.

The interwell transitions which iccur in the two-well potential affect the electron states because the interaction parameters V_{0i} and V_i' are different in the two atomic configurations. These configurations differ in energy by an amount whose absolute value is ε_i (by definition, $\varepsilon_i \geqslant 0$) and whose sign is random. Consequently, the larger of the two quantities V_{0i}, V_i' may correspond to either the upper well or the lower one; it is natural to assume $\langle V_i \rangle = 0$. The density of electron states is affected by the fluctuations δn in the populations of the two-well potential, not by the mean values of these populations. At a nonzero temperature, there are thermal fluctuations δn in the occupation numbers; these fluctuations lower the energy of the electron. As a result, the tail on the density of states should increase in size with increasing T. This increase reduces to a increase in the variance B_U of the electron potential in (3). The reason is that the statistical independence of the fluctuations of the original potential $U(\mathbf{r})$ and the temperature-dependent potential $V\delta n$ allows us to add their variances. Assuming

$$\langle (V\delta n)^2 \rangle = \langle V^2 \rangle \langle \bar{n}(1-\bar{n}) \rangle = {}^1/_2 \langle V^2 \rangle \pi \rho_\varepsilon T, \qquad (7)$$

we find

$$B = \langle U^2(\mathbf{r}) \rangle + {}^1/_2 \langle V^2 \rangle \pi \rho_\varepsilon T. \qquad (8)$$

In (7) we have used $\bar{n} = [1 + \exp(\varepsilon/T)]^{-1}$ as the equilibrium population of the upper well, and we have assumed that the parameters V and ε are statistically independent (this simplifying assumption is not of fundamental importance; where necessary, it can be abandoned). In Sec. 3 we verify the result in (8) through a calculation of $S(E)$ by the optimum-fluctuation method.

We have been tacitly assuming that the trapped electron does not have an inverse effect on the occupation numbers n_i of the two-well potential. The fluctuations in n_i which arise without the involvement of the electron are important if the time scales for electron transitions are much shorter than those for atomic transitions in the two-well potential. The fluctuations responsible for the tails in the optical absorption, for example, are of this type. The absorption coefficient for electron transitions to states with an energy E is proportional to the density of states $g_{\text{opt}}(E)$ determined without consideration of the interaction of the electron with the mobile atoms. The function $g_{\text{opt}}(E)$ could naturally be called an "optical density of states."

The interaction of an electron with mobile atoms in a two-well potential may lead to a displacement of these atoms and to the formation of a self-sustaining fluctuation δn, which lowers the energy of the electron and that of the system as a whole. This distinctive type of self-trapping can occur only over a sufficiently long time interval determined by the rates of atomic transitions in the potential. This self-trapping must be taken into consideration when (for example) we are dealing with thermodynamically equilibrium states. In this case the probability for finding an electron in a tail state with an energy E is proportional to $g_{\text{th}}(E)$, where the self-trapping is taken into account in the determination of the density of states $g_{\text{th}}(E)$. The function $g_{\text{th}}(E)$ could naturally be called the "thermodynamic density of states."

To clarify the qualitative behavior $g_{\text{th}}(E)$, we specify some radius r_ψ of the trapping state, and we examine the two-well potential in a volume r_ψ^3 with asymmetries in an energy layer $\varepsilon < \Delta$. Roughly half of the total number (on the order of $\rho_\varepsilon r_\psi^3 \Delta$) of two-well potentials have that sign of V which lowers the energy of the electron upon a transition of an atomic particle from the lower well to the upper one. These transitions provide an energy benefit on the order of $\langle V^2 \rangle^{1/2} r_\psi^3 \psi^2(\mathbf{r}), \rho_\varepsilon \Delta \propto \langle V^2 \rangle^{1/2} \rho_\varepsilon \Delta$, where ψ is the electron wave function. In addition, there is an energy disadvantage $\frac{1}{2} r_\psi^3 \rho_\varepsilon \Delta^2$, which is equal to the work ($\Delta/2$ per two-well potential, on the average) which must be performed in order to move the atomic particles from the lower wells to the upper ones. The resultant change in energy upon self-trapping can then be estimated to be

$$-\rho_\varepsilon \langle V^2 \rangle^{1/2} \Delta + {}^1/_2 \rho_\varepsilon r_\psi{}^3 \Delta^2. \qquad (9)$$

Expression (9) is formally the same as that which describes the self-trapping of an electron in an elastic medium; Δ is playing the role of the strain. On this basis we might expect the problem of determining the function $g_{\text{th}}(E)$ to reduce to the problem of the tail on the density of states in a disordered system with an ordinary polaron effect. The latter problem has been solved by Kusmartsev and Rashba.[8] They showed that, when a polaron effect is operating, the tail on the density of states has a sharp cutoff, so there is a gap in the spectrum below a certain energy. The reason for this cutoff is that the fluctuation states are unstable with respect to polaron collapse at sufficiently small values of $r_\psi \sim \hbar(m|E|)^{-1/2}$. This collapse occurs if the reduction of energy which occurs as a result (the polaron shift) at $r_\psi \sim a$ is greater in absolute value than the work $\hbar^2/ma^2$ which would be required to trap the electron in a region of atomic size, a.

In the case under consideration here, the polaron shift, which is equal to the absolute value of the minimum energy in (9), is

$${}^1/_2 \rho_\varepsilon \langle V^2 \rangle r_\psi{}^{-3}. \qquad (10)$$

This quantity increases with increasing $|E|$. At $r_\psi \sim a$ (with suitable parameter values), it may be greater than the work $\hbar^2/ma^2$. In contrast with the ordinary polaron effect—the case in Ref. 8—however, a gap does not form in the density of states in the case at hand. The reason is that among other fluctuations in this system there are some at which the polaron effect is relatively small, because of random small values of the local concentration of two-well potentials with the sign of V which is favorable for self-trapping. This circumstance is not reflected in (9) and (10), which incorporate only the average concentrations of the two-well potentials and are therefore valid only at sufficiently large values of r_ψ. In other words, the polaron effect fluctuates in this system. It follows that for any energy there exist fluctuation states with a polaron effect small enough that collapse does not occur.

Summarizing, we can say that at low energies, at which expressions (9) and (10) hold, the behavior $g_{\rm th}(E)$ should be qualitatively the same as the behavior of the tails in disordered systems with an ordinary polaron effect.[8] However, the states in the high-energy region are approximately the same as the fluctuation states without a polaron effect, and there is no gap in the spectrum.

3. OPTIMUM FLUCTUATION METHOD

Our problem is to find the explicit functions $g_{\rm th}(E)$ and $g_{\rm opt}(E)$ in the region of an exponentially small density of states, $g(E)\ll g_0$. We consider the Gaussian part of the spectrum, in which the density of states is still of appreciable magnitude. This region is dominated by fluctuations which result from relatively small deviations of the parameters from their average values.

We begin with an analysis of the optical density of states. If self-trapping is ignored, the electron energy is

$$E=\min_{\psi}\left\{\frac{\hbar^2}{2m}\int(\nabla\psi)^2d^3r+\int U\psi^2\,d^3r+\sum_i\int V_i\,\Delta N_i\psi^2\,d^3r\right\},\tag{11}$$

under the condition $\int\psi^2d^3r=1$. The quantity $\Delta N_i=N_i-\bar{N}_i$ in (11) is the deviation from the average concentration of two-well potentials of type i in the excited state. Here we are using

$$\sum_i V_iN_i=\langle V\rangle=0$$

The random quantities fluctuating in (11) can be described in the Gaussian approximation by a probability distribution $\exp(-S)$, where

$$S=\int\frac{U^2}{2B_U}d^3r+\int\sum_i\frac{(\Delta N_i)^2}{2B_{ni}}d^3r.\tag{12}$$

The variance B_{ni} can be found directly from a binomial distribution:

$$B_{ni}=c_i\bar{n}_i(1-\bar{n}_i),\tag{13}$$

where c_i is the local concentration of two-well potentials of type i. In the Gaussian approximation we can set $c_i=\bar{c}_i$ in (13).

The problem of optimizing the functional S under condition (11) is equivalent to that of seeking an absolute extremum of the functional

$$\Phi=S-\lambda\left(E-\nu\int\psi^2\,d^3r\right),\tag{14}$$

where ν and λ are undetermined Lagrange multipliers. A variation of Φ with respect to the variables U, ΔN_i, and ψ leads to the equations

$$U=B_U\lambda\psi^2,\quad \Delta N_i=V_i\psi^2B_{ni},\tag{15}$$

$$-\frac{\hbar^2}{2m}\Delta\Psi+\lambda\Big(B_U+\sum_i V_i^2B_{ni}\Big)\psi^3=\nu\psi.\tag{16}$$

Comparing (16) and (11), we verify that the equality $\nu=E$ holds. Substituting (15) into (12), we find

$$S=\frac{\lambda^2}{2}\Big(B_U+\sum_i V_i^2B_{ni}\Big)\int\psi^4(\mathbf{r})\,d^3r.\tag{17}$$

A nonlinear Schrödinger equation of the type in (16) has been studied in detail in papers on the standard optimum-fluctuation method.[1-4] The results of importance to the present discussion can be summarized by the expressions

$$\int\psi^4\,d^3r=-4b\left(\frac{\hbar^2}{2m}\right)^3\lambda^{-3}\Big(B_U+\sum_i V_i^2B_{ni}\Big)^{-3},$$

$$E=-b\left(\frac{\hbar^2}{2m}\right)^3\lambda^{-2}\Big(B_U+\sum_i V_i^2B_{ni}\Big)^{-2}.\tag{18}$$

Using these expressions, we find expressions (2) and (3) again, except that B_U is replaced by the quantity

$$B=B_U+\sum_i V_i^2B_{ni}.\tag{19}$$

Since the second term in (19) is the average value of $V^2\bar{n}(1-\bar{n})$, we arrive at the result (8).

In the expressions written above, the the energy E is in all cases reckoned from the mobility edge, as renormalized by the random potential. As was shown in Ref. 3, this renormalization reduces to a downward shift

$$\Gamma=-Bm/2\pi\hbar^2a\tag{20}$$

of the mobility edge. Our analysis thus predicts not only the temperature dependence of the tails on the density of states but also a shift, which is linear in the temperature, of the edges of the mobility gap.

We turn now to the thermodynamic tails on the density of states, $g_{\rm th}(E)$. According to the discussion in Sec. 2, the inverse effect of the electron on the two-well potential is important in this case. The resultant energy of the system consisting of the electron and of the two-well potentials interacting with it differs from (11) by an amount equal to the minimum work required to create fluctuations. The latter is equal to the change in the free energy of the system of two-well potentials upon the appearance of a fluctuation. Adding this quantity to (11), we find

$$E=\min_{\psi}\left\{\frac{\hbar^2}{2m}\int(\nabla\psi)^2\,d^3r+\int U\psi^2\,d^3r+\sum_i\int V_i\,\Delta N_i\psi^2\,d^3r+T\sum_i\int\frac{\Delta N_i^2}{2B_{ni}}d^3r\right\}\tag{21}$$

under the condition $\int\psi^2d^3r=1$. From this point on, the procedure for optimizing and determining the exponent for the density of states is similar to that described above, with (11) replaced by (21). As a result we find

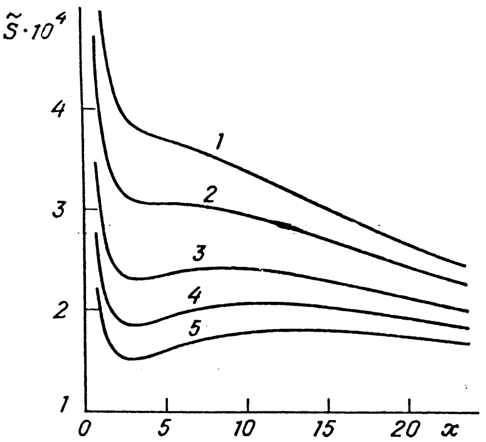

FIG. 2. The dimensionless exponent of the density of states, $\tilde{S}$, versus the parameter x for various values of the parameter β: *1*—5; *2*—5.8; *3*—7; *4*—8; *5*—9.

$$\tilde{S}\equiv\frac{S}{s}=\frac{(1+x)[(1+x)^2+\beta]}{x(1+x+\beta)^3}, \tag{22}$$

$$\tilde{E}\equiv\frac{E}{\Theta}=\frac{(1+x)[(1+x)^2+\beta(1-x)]}{x^2(1+x+\beta)^3}, \tag{23}$$

where

$$x=-\lambda T,\quad \beta=\frac{1}{B_U}\sum_i V_i^2B_{ni},$$

$$s=2b\left(\frac{\hbar^2}{2m}\right)^3\frac{T}{B_U^2},\quad \Theta=b\left(\frac{\hbar^2}{m}\right)^3\frac{T^2}{B_U^2}. \tag{24}$$

Expressions (22) and (23) constitute the final result, in parametric form. They relate in the appropriate way the dimensionless exponents of the density of states $\tilde{S}$ and the energy $\tilde{E}$.

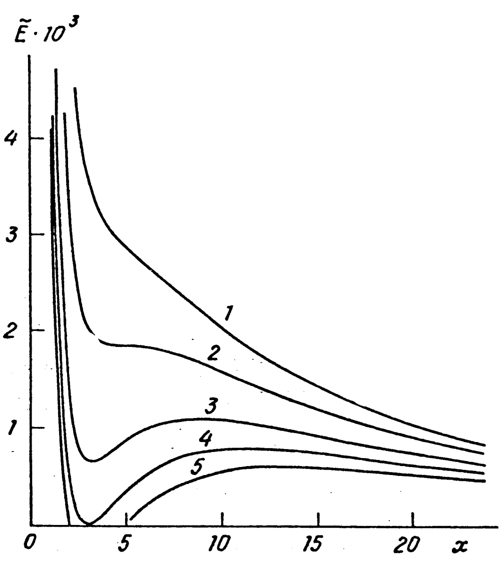

FIG. 3. The dimensionless energy $\tilde{E}$ versus the parameter x for various values of the parameter β (the curve labels have the same meaning as in Fig. 2).

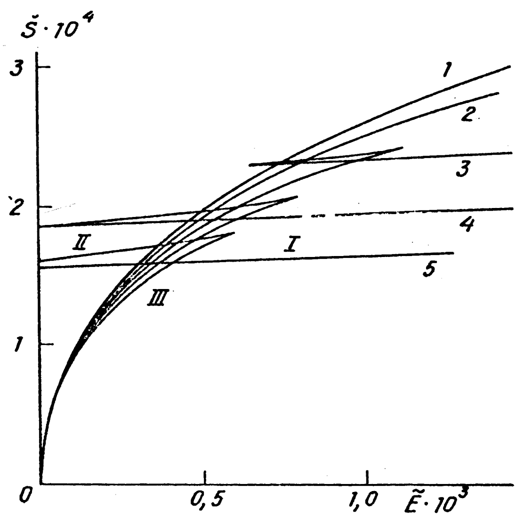

FIG. 4. Energy dependence of the exponent of the density of states, $\tilde{S}$, versus the energy $\tilde{E}$ for various values of the parameter β (the curve labels have the same meaning as in Fig. 2). The Roman numerals correspond to various branches of the functional dependence (see the text proper).

Figures 2 and 3 are plots of $\tilde{S}(x)$ and $\tilde{E}(x)$. They exhibit a critical behavior; β plays the role of the control parameter. At $\beta>\beta_0\approx 5.8$, extrema appear on both plots, at identical values of x, which are the roots of the equation

$$x^4+2x^3(2-\beta)+6x^2+4(1+\beta)x+(1+\beta)^2=0. \tag{25}$$

When extrema are present, the function $\tilde{S}(\tilde{E})$ has three branches (Fig. 4). Two of them, I and III, correspond to a minimum of functional (12), while branch II corresponds to a maximum of this functional and has no direct physical meaning. If we ignore branch I, we see that the functions $\tilde{S}(\tilde{E})$ found here correspond entirely to the functions found by Kusmartsev and Rashba[8] in an analysis of the tails on the density of states in a disordered system with an ordinary polaron effect. The presence of branch I guarantees that there is no gap in the density of states.

The physical meaning of the solutions found here corresponds to the discussion in Sec. 2. The behavior of $\tilde{S}(\tilde{E})$ at sufficiently small values of $\tilde{E}$ turns out to be the same as in systems with an ordinary polaron effect (branch III). There is a cutoff in the spectrum (the point at which branches II and III intersect). However, the fluctuation states with a small polaron effect which correspond to branch I begin to play a leading role even before this cutoff occurs. Near the intersection of branches I and III, the dimensionless derivative $d\,[\ln g_{\text{th}}(\tilde{E})]/d\tilde{E}$ changes by a finite amount, approximately equal to $\beta^2/2$ (for $\beta>\beta_0$). In the limit $E\to 0$, the behavior $g_{\text{th}}(E)$ is described by (2), and (3) (the two-well potentials have only a minor effect). As $|E|\to\infty$, the behavior $g_{\text{th}}(E)$ approaches the behavior $g_{\text{opt}}(E)$.

4. PHONON CONTRIBUTION

A temperature dependence of the disorder may stem not only from transitions of atoms in two-well potentials but also from vibrations of these atoms corresponding to phonon degrees of freedom. We will calculate the effect of these vibrations for high temperatures at which phonons can be treated as a source of classical fluctuations of the electron potential. In this case the phonon contribution can be dealt with by the optimum fluctuation method, which we have already used. We restrict the discussion to the deformation interaction with phonons, which is important for typical amorphous materials with predominantly covalent bonds (*a*-Si:H, *a*-SiO, etc.).

In the adiabatic approximation the energy of an electron changes by an amount

$$E_{ph}=\int \psi^2(\mathbf{r})Qu(\mathbf{r})\,d^3r, \tag{26}$$

upon a dilatation $u(\mathbf{r})$, where Q is the strain-potential constant. The probability for a classical fluctuation corresponding to the dilatation $u(\mathbf{r})$ can be expressed in terms of the entropy in the standard way:

$$\exp(-S_{ph})=\exp\left\{-\int \frac{u^2(\mathbf{r})}{2\langle u^2\rangle}\,d^3r\right\}. \tag{27}$$

The variance is

$$\langle u^2\rangle=T/K,$$

where K is the elastic modulus.

To calculate $g_{\text{opt}}(E)$ by the optimum fluctuation method, it is sufficient to add (26) to functional (11) for the energy and to incorporate the phonon contribution S_{ph} in the entropy in (12). The functional found in place of (14),

$$\Phi=S+S_{ph}-\lambda\left(E+E_{ph}-\nu\int\psi^2\,d^3r\right) \tag{28}$$

should be varied with respect to the variables U, ΔN_i, ψ, and u. The result for the optical density of states again reduces to expressions (2) and (3). However, instead of (19) the role of the variance is played by the quantity

$$B=B_U+\sum_i V_i^2B_{ni}+WT,\qquad W\equiv\frac{Q^2}{K}. \tag{29}$$

When this replacement is made, expression (20) remains in force.

In the limiting case $B=WT$ the result found for $g_{\text{opt}}(E)$ is the same as the corresponding result of Refs. 9, in which a study was made of the shape of a tail due exclusively to phonons (no structural disorder was involved) on the optical absorption. The case under consideration here, of classical fluctuations, corresponds to the static regime found in Ref. 9.

As for $g_{\text{opt}}(E)$ above, we can incorporate the phonon-disorder component of the thermodynamic density of states $g_{\text{th}}(E)$. For this purpose we should again include the phonon contribution S_{ph} in the entropy. In the functional for the energy, however, we need to add [in addition to (26)] the energy of the deformed medium:

$$\int\frac{Ku^2(\mathbf{r})}{2}\,d^3r=TS_{ph}. \tag{30}$$

The problem then reduces to one of finding the absolute extremum of the functional

$$\Phi=S+S_{ph}-\lambda\left(E+E_{ph}+TS_{ph}-\nu\int\psi^2\,d^3r\right), \tag{31}$$

where the functional E is given by (21). The results of this calculation again lead to expressions (22)–(25) and to Figs. 2 and 3, in which the role of β is played by the quantity

$$\beta=\frac{1}{B_U}\left(\sum_i V_i^2B_{ni}+WT\right). \tag{32}$$

In analyzing the optimum fluctuation of the strain energy above we actually assumed that the typical lifetime of such a fluctuation, τ_{ph}, is long enough that the energy of the electron can adjust the altered potential. A necessary condition here is that the time scale (τ_e) of the inelastic interaction of the electron with the phonons (the time scale for relaxation of the electron phase) be much shorter than τ_{ph} (this condition corresponds to the condition for a static regime in Ref. 9). The time τ_{ph} can be estimated as the time it takes a sound wave to propagate across a fluctuation region of size r_ψ, i.e., $\tau_{\text{ph}}\sim\omega_D^{-1}r_\psi/a$, where ω_D is the Debye frequency. The estimate of τ_e is extremely sensitive to the details of the electron-phonon interaction and of the phonon spectrum. We will use the estimate from Ref. 10 for the deformation interaction, with a violation of the selection rules in terms of momenta in amorphous materials (see also Ref. 11). We find $\tau_e\sim\hbar\omega_D^2/WT$. As a result, the inequality $\tau_e\ll\tau_{\text{ph}}$ leads to the condition $T\gg(\hbar\omega_D)^2a/Wr_\psi$. This condition is no more stringent than $T\gg\hbar/\tau_{\text{ph}}$, which is the condition under which a phonon fluctuation is of a classical nature.

5. TIME LAG IN THE TEMPERATURE-DEPENDENT DISORDER

It follows from the discussion above that the temperature dependence of the disorder (and of the tails on the density of states) stems from atomic degrees of freedom which correspond to (first) two-well potentials and (second) phonons. An important feature of the component associated with the two-well potentials is its time lag, which exists because the barriers between wells must be overcome. The time scale τ_b for the tunneling through the barriers or for surmounting them in an activation process may be much longer than the experimental times involved (e.g., the times over which the temperature changes). In this case, one should observe effects stemming from a long-term relaxation of the measured quantities. A well-known example of this situation is the dependence of the low-temperature specific heat of amorphous materials on the measurement time.[5-7] The observation of time-lag effects might make it possible to experimentally distinguish a contribution from two-well potentials and from that of phonons.

With an eye on the experimental data to be described in the following section of this paper, we look at a simple problem concerning the time-lag properties of atomic particles in an ensemble of random two-well potentials. We assume that the system of two-well potentials is initially at thermodynamic equilibrium at the temperature T_i. We are to determine the average change in the variance of the populations of the wells, $\langle[\Delta n(t)]^2\rangle$, at a time t after an abrupt lowering of the temperature to a value $T<T_i$. It follows from (7) and (8) that the slow component of the variance of the electron potential also varies in proportion to this quantity.

Since the values of T are fairly high (>300 K), we consider only the activation mechanism for the surmounting of the barrier:

$$\tau_b=\tau_0 \exp(\upsilon/T)\,. \qquad (33)$$

The condition $\tau_b \leqslant t$ determines that fraction of the total number of two-well potentials,

$$[T \ln(t/\tau_0)-\upsilon_{min}]\,(\upsilon_{max}-\upsilon_{min})^{-1}, \qquad (34)$$

which has undergone randomization over the time t. According to (7), the average change in the equilibrium population is $\frac{1}{2}\pi\rho_\varepsilon(T-T_i)$. Multiplying this quantity by the factor in (34), we find $\langle[\Delta n(t)]^2\rangle$. As a result, the slow component of the variance of the electron potential changes by an amount

$$\Delta B={}^1/_2\pi L\langle V^2\rangle\rho_\varepsilon(\upsilon_{max}-\upsilon_{min})^{-1}(T-T_i)(T-T_t) \qquad (35)$$

over a time t after an instantaneous lowering of the temperature. Here

$$L\equiv\ln(t/\tau_0), \quad T_t\equiv\upsilon_{min}/L. \qquad (36)$$

An interesting aspect of the behavior in (35) is that it is not monotonic: Thought of as a function of T, the quantity ΔB goes through a minimum at a temperature

$$T_m={}^1/_2(T_i+T_t)\,. \qquad (37)$$

The physical origin of this minimum can be explained as follows. If the cooling (T_i-T) is sufficiently small, the freezing of two-well potentials is inconsequential. As a result, $\langle[\Delta n(t)]^2\rangle$ is basically proportional to the difference between the equilibrium variances, $\langle[\delta n(T_i)]^2\rangle-\langle[\delta n(T)]^2\rangle$. This difference increases with increasing value of the difference T_i-T. If the cooling is instead substantial, the changes in $\langle[\Delta n(t)]^2\rangle$ are dominated by the randomization over a time t. The rate of this randomization increases with increasing T. The extremum of $\langle[\Delta n(t)]^2\rangle$ is reached at the temperature T_m which corresponds to the optimum combination of rate of randomization and rate of change in the equilibrium population.

We think that observing a minimum in the temperature dependence $\Delta B(T)$ is the best bet for experimentally identifying a contribution of two-well potentials to a temperature-dependent disorder. It would be considerably more difficult to detect a slight logarithmic dependence of ΔB on the experimental time.

6. EXPERIMENTAL RESULTS AND DISCUSSION

Tails on the density of states in amorphous semiconductors are usually seen in the spectra of the absorption coefficient, $\alpha(\hbar\omega)$. These tails correspond to an exponential decay of $\alpha(\hbar\omega)$ with decreasing photon energy. Experimental data in the region of the exponential decay of $\alpha(\hbar\omega)$ for amorphous semiconductors are customarily described by an expression $\alpha\propto\exp(\hbar\omega/E_1)$. It is usually assumed[12-14] that this expression corresponds to the tails on the density of states in (1), for which we have

$$S(E)=|E|/E_1, \quad |E|=E_g-\hbar\omega, \qquad (38)$$

where E_g is the width of the optical gap. The values of E_1 for various materials range from 0.03 to 0.15 eV (Refs. 12–15). Strictly speaking, the dependence $\alpha(\hbar\omega)$ should reproduce the convolution of two band tails: that of the conduction band and that of the valence band. That circumstance is frequently ignored, and it is assumed that only one tail is important. This would be the larger tail, e.g., the tail on the valence band in a-Si:H (Refs. 12–15). We adopt that simplifying assumption here. We recognize that in adopting this assumption we are limiting ourselves to only an approximate comparison of theory and experiment.

The purely linear dependence in (38) cannot be derived theoretically, for any type of disorder, in three-dimensional systems.[1] The approximate nature of this dependence has been emphasized in several places.[16-19] We have analyzed by computer a family of $\alpha(\hbar\omega)$ curves fitted by expressions (2) and (38). Figure 5 illustrates the results of this analysis with the particular example of an $\alpha(\hbar\omega)$ curve from Ref. 20. Expression (38) gives a good description of the experimental curve over the $\hbar\omega$ region from 1.4 to 1.7 eV. The quality of the approximation is of course independent of the choice of E_g. When we use expression (2) for the approximation, on the other hand, the agreement with experiment is sensitive to the choice of the energy E_g. If we calculate E_g by the Tauc procedure[12] [in which $\alpha(\hbar\omega)$ is postulated to have a behavior $\alpha\propto(\hbar\omega-E_g)^2$ at values $\hbar\omega\geqslant E_g$], we find $E_g\approx1.7$ eV and $E_0\approx3.5$ meV. The description of the absorption tail by expression (2) is poorer than that by expression (38). If we instead use the value $E_g\approx2.2$ eV, on the basis of other data (e.g. the data in Sec. 3.4.4 in Ref. 12), we find a considerably improved agreement with experiment. In describing the experimental data below we give preference to expression (2), since it has a theoretical foundation.

Since the density of states in the tails is usually described by (38), as we mentioned above, the experimental data available correspond to specifically the energy parameter E_1 in expression (38). Treating that law as a linear approximation of theoretical function (2), we can write

$$E_1=2(|E|E_0)^{1/2}=\frac{B}{a^3}|E|^{1/2}b^{-1/2}\left(\frac{\hbar^2}{2ma^2}\right)^{-3/2}, \qquad (39)$$

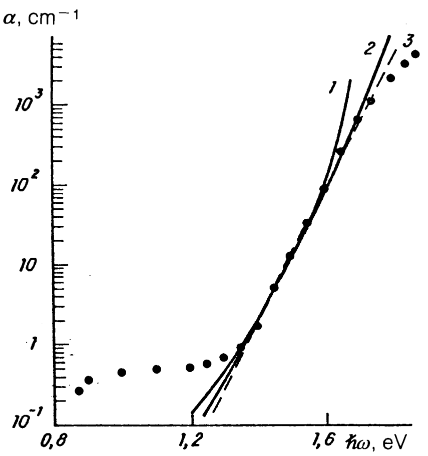

FIG. 5. Least-squares approximation of $\alpha(\hbar\omega)$ for samples of undoped a-Si:H. Points—Experimental data of Ref. 20; *1*—approximation by expression (2) with $E_g=1.7$ eV and $E_0=3.5$ meV; *2*—approximation by expression (2) with $E_g=2.2$ eV and $E_0=1$ meV; *3*—approximation by expression (38) with $E_g=1.7$ eV and $E_1=50$ meV.

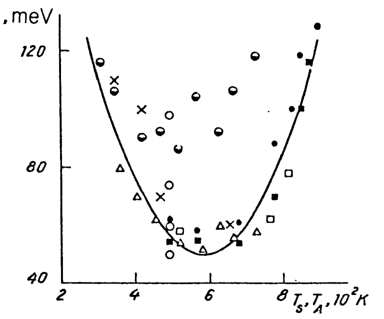

FIG. 6. The Urbach parameter E_1 versus the substrate temperature T_S or the annealing temperature T_A for amorphous silicon, from Ref. 14. The solid line corresponds to Eq. (40).

where E is the energy near which the approximation is made. We will use (39) to compare the theoretical predictions made above with experimental data.

Figure 6 shows experimental data from Ref. 14 on the parameter E_1 for a number of samples of amorphous hydrogenated silicon. The maximum temperature reached in the prior treatment of the sample, $T = \max(T_A, T_S)$, is plotted along the abscissa. The maximum temperature is either the annealing temperature T_A (the annealing was usually carried for $t \approx 10$–30 min) or the temperature (T_S) of the substrate on which the a-Si:H film was deposited from the gas mixture. In all cases, the temperature at which E_1 was measured was lower than T. It was found that the particular choice of measurement temperature had a much weaker effect than the choice of T on the value of E_1. In other words, the test samples behaved as though they were frozen at the corresponding temperature T.

The data reported in Ref. 14 were a summary of the results of numerous studies, which differed significantly in the conditions under which the a-Si:H was prepared. Despite these differences, a correlation was found between E_1 and T. According to Ref. 14, this correlation can be described by

$$E_1 \geqslant 50\ \text{MeV} + 8.3 \cdot 10^{-4} (T - 590\ \text{K})^2\ \text{MeV/K}^2, \tag{40}$$

where the right side describes a parabola (Fig. 6).

The minimum in the correlation dependence $E_1(T)$ is the topic of primary interest. We can explain the origin of this minimum by using the arguments in Sec. 5 regarding the time lag in the temperature-dependent disorder. For this purpose we ignore for the time being the random scatter of points in Fig. 6, and we consider relation (40) as a functional dependence [correspondingly, we change the inequality sign in (40) to an equals sign]. Since we have a functional dependence of this sort, we can introduce a common temperature T_i (at least a fictitious one) from which the freezing to various values of T occurs. The temperature T_i corresponds to a completely thawed equilibrium system in which all the potential barriers are overcome over the experimental time. In the case of infinitely slow cooling, this system relaxes to a state with an absolute minimum of the energy. This minimum corresponds to the crystal structure. It is thus natural to identify T_i as the crystallization temperature in the a-Si:H system; i.e., we set $T_i \approx 900$ K (Ref. 21).

The mathematical description of this interpretation reduces to the problem, discussed in Sec. 5, of the freezing of atomic particles in an ensemble of two-well potentials. Using the result found there, (35), along with (39), we conclude that the functional dependence $E_1(T)$ is parabolic, with a minimum at T_m [see (37)]. The functional dependence which has been found is the same as the empirical dependence $E_1(T)$ if we ignore the random scatter of points in Fig. 6. From the standpoint presented above, this scatter results from technological factors which have been ignored and which are different in the different procedures for preparing the a-Si:H.

Our interpretation makes it possible to find an independent estimate of the temperature of the minimum in Fig. 6. For this purpose we note that for the temperature corresponding to complete freezing of the system, T_t [see (36)], there are experimental estimates over the interval $T_t \approx 300$–400 K, depending on the particular type of a-Si:H sample and the particular conditions under which it was prepared[21,22] (we are ignoring the logarithmically weak dependence of T_t on t). Taking $T_i = 900$ K, we find the estimate $T_m \approx 600$–650 K from (37). This estimate agrees well with the experimental value $T_m = 590$ K from (40).

Another possibility for testing this theory comes from the empirical relation[23] between the parameter E_1 and the width of the optical gap, E_g, in the case of thermally stimulated changes in E_g and E_1 in a-Si:H:

$$dE_g/dE_1 = \text{const} \approx -6. \tag{41}$$

Assuming for the purposes of this estimate that both edges of the mobility gap shift upon a change in the disorder and that the shifts are identical, equal to $d\Gamma$, we find $dE_g = 2d\Gamma$. From (20) and (39) we then find

$$\frac{d\Gamma}{dE_1} = -\frac{b^{1/2}}{2\pi}\left(\frac{\hbar^2}{2ma^2|E|}\right)^{1/2}. \tag{42}$$

Since $|E| \approx 0.2$ eV (Fig. 5), and we have $\hbar^2/2ma^2 \approx 5$ eV (on the order of the width of the band gap), we find the estimate $dE_g/dE_1 \approx -6$ from (42). The exact agreement with the constant in (41) is of course just fortuitous, resulting from the latitude in the choice of the parameter values in (42). However, there can be no doubt that there is an approximate agreement.

Using the parameter values adopted above, along with the data in Fig. 6, we find the estimate $\langle V^2 \rangle \rho_\varepsilon / a^3 \sim 10$ eV from (35) and (39). This energy is of atomic scale. The energy W/a^3, constructed from the atomic constants [see (29)], should be on the same order of magnitude. On this basis we conclude that the two-well potentials and the phonons make comparable contributions to the equilibrium temperature-dependent disorder in a-Si:H. However, it would hardly be possible for the ensemble of two-well potentials to reach equilibrium conditions over the actual experimental times at temperatures well below T_i. We would thus expect that the observed manifestations of the order would be sensitive to the history of the sample.

In the numerical estimates in this section of the paper we have ignored the difference between the optical and thermodynamic tails on the density of states. For the optical measurements used here, we should of course discuss only the optical density $g_{\text{opt}}(E)$. However, the data of Ref. 24, found by photoelectron spectroscopy, should probably be described by the thermodynamic density $g_{\text{th}}(E)$. The results of Ref. 24 must be compared in detail with optical data in order to identify differences between $g_{\text{opt}}(E)$ and $g_{\text{th}}(E)$. To the best of our knowledge, no such comparison has been carried out.

We also note that in discussing the experimental data above we assumed that *a*-Si:H contains two-well potentials. This assumption is supported by independent magnetic-resonance experiments.[25–27]

We conclude by pointing out a consequence of the approach presented above. The disorder in a system can be altered by applying some nonthermal agent to the two-well potentials, e.g., photons or electrons of sufficiently high energy. When such an agent is applied to the equilibrium system, the tails on the density of states should grow, and the optical gap should shrink. When a external agent is applied to a nonequilibrium frozen system, the system may undergo a relaxation as a result, accompanied by a shrinkage of the tails on the density of states and a widening of the optical gap. Effects of this sort do indeed occur in amorphous semiconductors.[15]

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