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Exactly exponential band tail in a glassy semiconductor

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Transient-photocurrent measurements in glassy As_2Se_3 reveal an accurate power-law behavior spanning more than eight decades of time. In the multiple-trapping model this requires a density of valence-band-tail states varying exponentially with energy over almost five decades. The accuracy of this exponential and its continuation deep into the gap are inconsistent with existing models for band tails based on short-range potential fluctuations, but show a remarkable degree of perfection in the electronic structure of this ostensibly random material.

Careful observations of semiconductor band edges generally show more or less exponential tails, rather than perfectly sharp edges. This behavior is well known, for example, in the optical-absorption spectrum of a wide variety of materials, both crystalline and amorphous. Years of attention have generated a plethora of reasonable theories, most relating this behavior to exponentially improbable fluctuations associated with thermal or frozen-in disorder. Unfortunately, there is still no consensus on the mechanism; it is not even clear whether a single mechanism is involved in the various cases.

In this Rapid Communication we will not address the question of universality, but we will describe experiments that severely restrict the models that should be applied to one particular material. We report an investigation of glassy As_2Se_3 that overcomes three traditional limitations of experimental tests: (1) Our data show exponential behavior in a single band tail. In contrast, optical absorption measurements reflect the *joint* density of states (DOS) of the valence and conduction bands and are also sensitive to interband matrix elements, which can by themselves give exponential behavior.[1] (2) The inferred DOS is accurately exponential over almost five decades of density, sufficient to eliminate theories predicting only approximately exponential behavior. (3) The observed exponential extends almost to the middle of the band gap of As_2Se_3, invalidating theories which use the effective-mass approximation.

We base our discussion on transient-photocurrent (TPC) measurements, in which one monitors the current $i(t)$ resulting from a short (10-ns) light pulse at time $t=0$. Our results, shown in Fig. 1, were obtained on a single $0.5\times0.5\times0.7$-cm^3 parallelepiped sample of glassy As_2Se_3 with graphite electrodes on opposite faces. Data for times shorter than 10 s were taken with pulsed light having a photon energy of 1.6 eV, while the data at longer times used 1.4-eV light to avoid bimolecular recombination. (Earlier work[2] revealed the surprising fact that the transients are independent of photon energy above 1.4 eV.) This curve is a composite of several transients, each obtained with the apparatus optimized for a particular time range. The high signal-to-noise ratio allowed the transients to be matched unambiguously by overlapping neighboring transients: No preconception of the overall form influenced the matching.

Although some of these data have been presented elsewhere, the full extent and accuracy of the power-law decay had not been appreciated. The data follow a power-law behavior over almost nine decades of time. A least-squares fit of a straight line to the log-log plot yields an exponent of -0.48 ± 0.01 (the error bars are one standard deviation). Fitting a quadratic shows that the second derivative, which we denote $K\equiv d^2\ln i/d(\ln t)^2$ is -0.002 ± 0.004, that is, zero within experimental error. This simple time dependence, surprising in a disordered material, clearly demands an equally simple explanation.

Over the past few years the explanation for power-law photocurrent transients commonly observed in amorphous semiconductors has come to be accepted as a process known as multiple trapping (MT). The history of the ideas, as well as the extensive evidence for the model in glassy As_2Se_3 are discussed by Orenstein, Kastner, and Vaninov.[3] In this model the current monitors the occupancy of the shallow, high-mobility transport states, while the decay of the current reflects the trapping of carriers in progressively deeper states (traps) in the band tail. The current at time t is determined

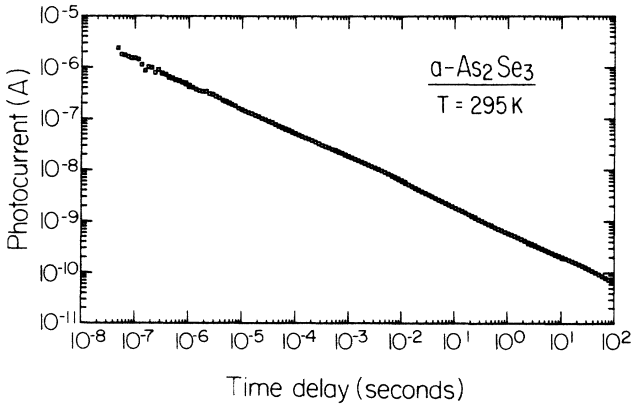

FIG. 1. Photocurrent at room temperature in glassy As_2Se_3, resulting from a 10-ns-long pulse of light at $t=0$.

by traps that have a release rate ν to the transport states of order $1/t$. Assuming an Arrhenius form for the release rates $\nu = \nu_0 \exp[-(E_0^* - E)/kT]$, the energy E of the important traps at time t is $E_d(t) = E_0^* - kT\ln(\nu t)$. Here E_0^* is the energy of the transport states.

For the band tail, the form of the current decay is directly related to the DOS at E_d, $g(E_d)$:

$$i(t) = \frac{C}{tg(E_d)} \quad . \tag{1}$$

This reflects the decreasing number of states available at $E_d(t)$ as the carriers get deeper. A power-law decay corresponds to an exponential density of states $g(E) = \exp(E/kT_0)$ with an exponent $-1 + T/T_0$. Careful analysis[3,4] allows calculation of the prefactor C, which depends weakly on the power-law exponent at a given time. This dependence should, in principle, be included in deducing the DOS from the current, but for the present data the exponent is constant so corrections are unnecessary. Our data extend from 50 ns to 100 s, so, using[3] $\nu_0 = 2\times 10^{12}$ s^{-1}, $kT\ln(\nu_0 t)$ ranges from 0.3–0.86 eV, more than a quarter of the 2-eV gap of As_2Se_3. Thus a substantial region of the gap in this material is apparently inhabited *only* by the well-behaved, presumably intrinsic states comprising the band tail.

The calibration of the energy scale depends on the assumption that the trapping rate is the same for all states, as reflected in the constant prefactor ν_0. It would not be surprising if ν_0 were smaller for the deepest states, since transitions to or from these states involve a large number of phonons. Such variation in ν_0 would change[4,5] the *effective* DOS by a proportionate factor, and the smaller release rate would mean that $E_d(t)$ would be shallower than if ν_0 were constant. For example, if ν_0 varies exponentially[6,7] with energy $\nu_0(E) = \nu_p \exp(E/kT_p)$, $E_0^* - E_d(t)$ is reduced by a factor $[T_p/(T+T_p)]$. Since the effective DOS at E is proportional to $g(E)\nu_0(E)$, the power-law exponent is $-1 + T(T_0+T_p)/T_0(T+T_p)$. (Following the cited authors, we neglect any temperature dependence of T_p.) In glassy As_2Se_3, however, the consistency of the observed temperature dependence of the exponent with the constant-ν_0 prediction $-1 + T/T_0$ shows that any such effects are negligible: Comparison of the slope of 0.48 ± 0.01 at 295 K and 0.72 ± 0.04 at 390 K requires[3] that T_p be at least 1400 K, so the correction factor for the energy scale $T_p/(T+T_p)$ must be within 20% of unity.

We stress that these arguments have been addressing the *extent* of the exponential. For *any* value of T_p, the observation of an accurate power-law decay requires an accurately exponential DOS. If ν_0 varied in a more complicated way with energy, one would still have to explain why the *combination* of the DOS and ν_0 should conspire to give an exponential dependence.

We now compare our measured band-tail DOS with a form we denote g_n:

$$g_n(E) = g_0 \exp\left[-\left(\frac{E - E_0}{w}\right)^n\right] \quad . \tag{2}$$

Most theories predict a DOS of this general form, with various values of the exponent n. For example, if the length scale of the potential fluctuations is much larger than the localization length, the kinetic energy will be negligible, and the DOS will track the potential distribution; for Gaussian potential fluctuations,[8] n will be 2. In the opposite limit of short-range Gaussian fluctuations the kinetic energy changes the exponent to $n = 2 - d/2$, which is $\frac{1}{2}$ for a three-dimensional solid.[9]

To compare with experiment, we calculate the second derivative of the various g_n:

$$K_n \equiv \frac{d^2 \ln i_n}{d(\ln t)^2} = \frac{(1-n)kT_0}{E_0 - E} \quad , \tag{3}$$

where we have used the constraint that the local exponent $d\ln i/d\ln t$ is the experimental quantity $-1 + T/T_0$. For comparison with the data of Fig. 1, the energy E is evaluated as $E_0^* - kT\ln(\nu_0 t)$ at the center of the log scale, which is roughly $E_0^* - 0.5$ eV.

In general, any value of n could produce an arbitrarily straight line if E_0, the reference energy in the DOS, were far enough away. For example, with $n = 2$, keeping $K_n < 0.002$ requires that $E_0 - E_0^* > 10$ eV, while for $n = \frac{1}{2}$, keeping $|K_n| < |-0.006|$ requires $E_0 - E_0^* > 1.1$ eV. This requires that E_0, the reference energy in the DOS, be deeper in the band than E_0^* by *at least* 9.5 or 0.6 eV, respectively. Of course, for exponents near unity, the limitation imposed by Eq. (3) is not particularly restrictive.

To understand the implications of these limits, one should note that E_0 has an important physical interpretation in the models discussed: It is simply the energy the band edge would have if the random potential were replaced by a uniform potential with the same mean. For weakly disordered systems like amorphous semiconductors, this effective-medium band edge will be close to the mobility edge; strong disorder moves the mobility edge even further into the band. In either case, the quantity $E_0 - E_0^*$ should be zero or *negative,* rather than the positive values required to fit $n = \frac{1}{2}$ or $n = 2$. We therefore conclude that the exponent of the DOS must be quite close to unity; a value of $n = \frac{1}{2}$ is only remotely plausible, and $n = 2$ is totally implausible. A similar conclusion was reached by Kastner[10] by considering only the temperature dependence. Of course, these detailed arguments simply add numerical weight to the obvious conclusion that the data in Fig. 1 represent an accurate power law, corresponding to an exactly exponential DOS.

It has recently been suggested[11] that the thermal excitation responsible for MT occurs not to the mobility edge, but to a transport energy within the band tail. However, although the energy to which carriers hop is not the mobility edge, the smaller wave-function overlap for tail states makes the prefactor smaller than it would be at the mobility edge. These two effects cancel approximately,[11] and the effective value of E_0^* is the energy where the wave functions would just overlap, which is presumably within a few kT_0 of the mobility edge. Thus the inclusion of hopping does not substantially alter the preceding argument requiring the exponent to be essentially unity.

In some models[12,13] of band tails, the DOS is not of the form g_n in Eq. (2), and the *apparently* exponential DOS results from a crossover between two different asymptotic behaviors. For example, if the length scale for a Gaussian potential is comparable to the localization length, the exponent will change gradually from $\frac{1}{2}$ to 2. In these models

the exponent of unity is merely a coincidence; the present experiments show dramatically how extreme this coincidence must be.

There are better reasons for believing these models to be inapplicable, however, based on the large extent of the exponential—to a depth of 0.86 eV from the mobility edge (20% less if we relax the constant cross-section assumption). At these energies the critical fluctuations in the wave functions near the mobility edge[14] are certainly unimportant. Moreover, the wave-function size[12,15] is of the order of one angstrom. Obviously the use of the effective-mass approximation is inappropriate for these states, so most models for the exponential DOS, which use this approximation, are simply irrelevant to the present measurements.

Nonetheless, the exponential DOS extends smoothly into this region, strongly suggesting that a single mechanism is determining the DOS throughout the tail. It could be some as yet unspecified local mechanism, presumably specific to glassy As_2Se_3. Because of the ubiquity of exponential tails, however, the opposite explanation seems more likely: The potential fluctuations which cause the tails are *long* range, so that the kinetic energy required to localize the electron within the fluctuation is small compared to the potential energy.[16–20] Such a potential would also explain the observed weakness of the electron-phonon coupling, since large states couple weakly to phonons.

It is not obvious that the multiple-trapping model would be appropriate for describing dispersive transport in such a long-range potential. Fortunately, the simulations of Overhof[19] suggest that it is primarily the distribution of states in *energy,* rather than in space, that determined the form of the transients. It is harder to see how the long-range model fits in with the observations of apparent hopping thermalization at low temperatures.[11]

If the potential is long range it is still necessary to explain the implied exponential distribution of potentials. The simplest mechanisms identify the exponential with some Boltzmann factor, for example, describing the electrostatic potential of charged defects.[3] It is intriguing that the glass transition temperature for As_2Se_3, $T_g = 450$ K, is comparable to $T_0 = 550$ K; however, this appears to be coincidental.[10] Skettrup[20] proposes another long-range Boltzmann model, in which the coupling of electrons to the fluctuating phonon density causes the tail. This model has been elaborated and adapted to amorphous materials by Roberts and Dunstan,[21] and remains the model most consistent with the present experiments.

An entirely different explanation for the exponential is that the electronic states are confined to two dimensions, with a short-range potential; the layered structure of crystalline As_2Se_3 supports this possibility. Calculated effective masses for the crystal,[15] however, are not anisotropic enough to consider the holes localized in the layers.

We now compare the present DOS with that inferred from equilibrium measurements. For simplicity we neglect the possible influence of electron-phonon coupling on the energy scale. We also assume that the 0.9-eV activation energy of the conductivity is the difference between the transport energy and the Fermi level, neglecting the shifts (of order $3kT_0$) due to the temperature dependence of the hopping process.[11] The photocurrent measurements[3] imply that the density of tail states, extrapolated to the mobility edge E_0^*, g_0^*, is at least 4×10^{21} cm^{-3}eV^{-1}. This is consistent with xerographic measurements,[22] which imply a density near the Fermi level (assumed to be at $E_0^* - 0.9$ eV) no more than $\sim10^{14}$ cm^{-3}eV^{-1}, only if g_0^* is close to this lower limit. In contrast, a density of defect levels of order 10^{17} cm^{-3} has long been used to explain experiments showing Fermi-level pinning and metastable, low-temperature, photoinduced properties; if the defect level has width kT_0, the DOS is roughly 2×10^{18} cm^{-3}eV^{-1}. Recent measurements[23] confirm this estimate and determine the energy of the centers to be roughly 0.35 eV from the Fermi level, or 0.55 eV from the mobility edge. Using the prefactor $g_0^* = 4\times10^{21}$ cm^{-3}eV^{-1} yields an estimate of 5×10^{16} cm^{-3}eV^{-1} for the DOS at this energy. Thus the defect density is expected to exceed the tail density by a factor of 40, substantially greater than the factor of 2.5 necessary[24] for observation of a feature of width kT_0.

This apparent discrepancy between the present *transient* results and *equilibrium* mesurements of the density of gap states in As_2Se_3 can be rationalized by positing a strong electron-phonon coupling at the defects, which slows transitions into and out of these states but does not change the fraction eventually occupied. Recent photo-induced absorption studies suggest the same conclusion.[25] Indeed, such electron-phonon coupling is a necessary ingredient of the negative-U model for such defects. Nonetheless, the elusiveness of these important defects, whose existence is inferred mainly from negative results, is intriguing.

Exact power-law decays are not universally observed in arsenic triselenide. In particular, evaporated films,[26] as well as doped glasses,[27] sometimes show structure on double logarithmic plots. It is conceivable that some preparation conditions enhance the density of more or less discrete states in the gap, possibly the same defects just referred to. Our focus here, however, is on the overall form of the DOS in the tail. It is extraordinarily improbable that the entire power-law decay shown in Fig. 1 results from a fortuitous combination of exponential decays associated with discrete states, since this would require both the *energies* and the *densities* of states of each type to be precisely correlated.

In summary, we have shown that the transient photocurrent in glassy arsenic triselenide obeys power law over a prodigious range of time. This requires a density of band-tail states that is *exactly* exponential over almost five decades of density. This is by far the clearest evidence to date for exponential tails, and is independent of assumptions about optical matrix elements. Furthermore, the tails extend to energies far deeper than those in which traditional models of band tails should be applicable. The accuracy of the power lay clearly shows that glassy semiconductors can exhibit a truly remarkable degree of ideality in their electronic structure.

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