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Nonequilibrium transport and slow relaxation in hopping conductivity

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We present experimental results that demonstrate the nonergodic nature of charge transport in the insulating regime of indium oxide samples. These results include an anomalous field effect described in detail by Ben-Chorin *et al.* and persistent photoconductivity created by exposure to light. The similarity of the temporal dependence of the conductance after excitation due to a burst of light and that due to charging the sample by a nearby gate suggests that in both processes the electronic system is excited and the time it takes the system to reach thermal equilibrium is much longer than the Maxwell time. We offer a simple theoretical model that ascribes all of these effects to nonequilibrium transport phenomena peculiar to the hopping regime. It is argued that exciting a hopping system out of thermal equilibrium leads to a conductivity that is higher than in equilibrium. The excited state is long lived and similar in nature to that observed in the phenomenon of persistent photoconductivity of various semiconductors measured at low temperatures. The sluggish equilibration process of the electronic system is ascribed to the inhomogeneous nature of charge transport and to the slow energy relaxation which are inherent features of disordered solids.

I. INTRODUCTION

The transport properties of Anderson insulators have been a field of active research for many years. Some of the interesting features exhibited by this class of materials show themselves in their field effect. In the context of this paper, the field effect is referred to as the dependence of sample conductance G on the voltage applied between it and a nearby metallic gate in a parallel-plate capacitor configuration. The field effect is one of the techniques routinely employed to measure density of states (DOS) in metals and semiconductors.[1] For systems where the conduction proceeds via extended states, the physics underlying the field effect is well established. By contrast, in Anderson insulators electronic states are localized and the two main issues involved in the field effect, namely, conduction and screening, are much less understood. In this respect, studies of this effect in such systems could be a useful way to elucidate their basic transport properties.

An anomalous field effect peculiar to Anderson insulators has been reported by Pepper.[2] Studying GaAs field-effect transistors (FET's) at low temperatures, Pepper noted a distinct component in G oscillating periodically with the applied gate voltage V_g. Similar conductance oscillations were reported for various other systems.[3] More recently, very prominent periodic conductance oscillations were observed in mesoscopic samples of Si,[4] GaAs,[5] and In_2O_{3-x} films[6] where the peak to valley values in $G(V_g)$ spanned several orders of magnitude in some cases. It is noteworthy that this oscillatory behavior is usually observable only when the sample conductance is lower[6] than e^2/h suggesting the relevance of localized states to the phenomenon. This observation calls attention to the process of charging an Anderson insulator (by, e.g., gating it).

Some of the peculiar features of gating an Anderson insulator were recently discussed by Ben-Chorin, Kowal, and Ovadyahu.[7] In the latter work, results of field effect in insulating films of polycrystalline and amorphous indium oxide were reported. The main results were as follows.

(a) For films with $R_\square$ smaller than $\approx 1\ \text{M}\Omega$, $G(V_g)$ was "normal" in the sense that ΔG scaled linearly with V_g as expected for a degenerate Fermi gas [cf. Fig. 1(a)]. In this regime our results agree with the field-effect measurements previously made by Fiory and Hebard[8] on amorphous indium oxide films.

(b) Deeper into the insulating regime ($R_\square \geq 10\ \text{M}\Omega$), an anomalous feature appeared: The conductance increased

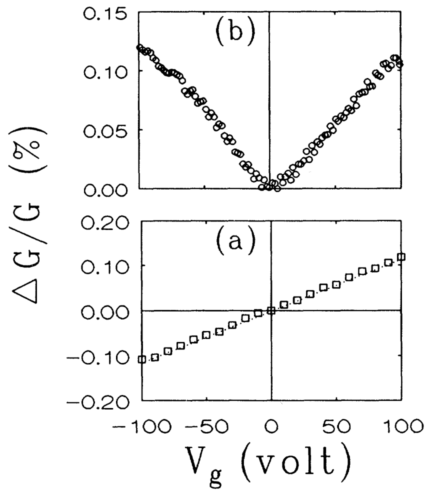

FIG. 1. The relative change of conductance vs gate voltage for (a) a $50\text{-k}\Omega/\square$ crystalline sample measured at 4.11 K, (b) a $15\text{-M}\Omega/\square$ amorphous sample (at 1.3 K).

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upon an application of a voltage on the gate for both polarities. This gives rise to a symmetrical component (SC) in $G(V_g)$. In the case of a sample cooled down while holding $V_g=0$ the SC was centered around this gate voltage [cf. Fig. 1(b)]. A similar effect in granular Au has been reported by Adkins *et al.*[9]

(c) The latter anomalous SC became more prominent with further increase in $R_\square$ but for $V_g \leq 100$ V (and gate-sample separation of a 100 μm) the SC was observable only at sufficiently low temperatures (typically lower than a few tens of degrees K).

Ben-Chorin, Kowal, and Ovadyahu suggested the possibility that the anomalous field effect as exhibited by the appearance of a SC reflects a nonequilibrium behavior of the electronic system and placed a lower bound of $\geq 10^3$ seconds on the characteristic time for relaxation involved in this phenomenon.

The purpose of the present work is to check the validity of the above conjecture by studying the temporal aspects of the anomalous field effect. The basic hypothesis that we plan to test in this paper is that the anomalies reported by Ben-Chorin, Kowal, Ovadyahu can indeed be related to nonequilibrium transport. To that end, three premises should hold true.

(1) The conductance of the sample in the excited state is always higher than in equilibrium.

(2) Adding (depleting) charge to (from) an insulating system by changing the voltage applied to the gate does indeed take it out of thermal equilibrium.

(3) The relaxation time of the excited system is very sluggish and in particular, much longer than the characteristic times of the measurements.[7]

The first premise is shown to hold true from general theoretical considerations presented in Sec. III below. The validity of the other two premises is supported by the following main findings of the present study:

(A) Exposing the sample to visible light affects the sample conductance in a similar way as charging it by applying a voltage to the gate: G rises and relaxes very slowly to its dark value when the light is switched off with a long decay rate and in a nonexponential fashion.

(B) The equilibrium state achieved at low temperatures (where the sample is measured) is determined, among other things, by the specific value of the V_g applied to the gate at high temperatures (and maintained throughout the cooling process). The SC is generally centered around V_{gc}, the gate voltage held on the sample (which can be of either sign) in the process of cooling it to low temperatures.

(C) Both the minimum in $G(V_g)$ and ΔG (the extra conductance due to an application of a gate voltage on the cold sample) relax to an equilibrium value with extremely long time periods that are many orders of magnitude larger than both the characteristic experimental time, and the Maxwell time (which is equal to $\epsilon\rho/4\pi$ where ϵ is the dielectric constant and ρ is the sample bulk resistivity).

We give arguments that suggest that the glassy behavior, gate anomalies, and persistent photoconductivity all follow from the nonequilibrium properties of Anderson insulators, and discuss the generality of these phenomena. The next section describes sample preparation and characterization and the experimental techniques employed in measuring them. Section III includes some general theoretical considerations pertinent to the behavior of electronic systems in the hopping regime when driven away from thermal equilibrium. Section IV depicts our main experimental results discussed in light of our theoretical considerations.

II. EXPERIMENT

Details of sample fabrication, characterization, and the measurement techniques employed in this study were described elsewhere.[7,10] For completeness, we give here a brief description of those issues with emphasis on some auxiliary measuring techniques that were not described in the previous reports. The indium oxide films were prepared by *e*-gun evaporation of 99.999% pure indium oxide onto a 100-μm-thick glass substrate, using an oil diffusion vacuum system capable of maintaining a base pressure better than 6×10^{-6} mbar. During deposition, 99.99% pure oxygen was bled into the vacuum chamber, maintaining an O_2 partial pressure of 2×10^{-5} mbar. During the process the pressure inside the chamber rose to 4×10^{-5} mbar. Typical evaporation rates were 0.7 ∓ 0.1 Å/s. Evaporation rate and film thickness were measured *in situ* using a quartz oscillator thickness monitor, which was calibrated against a Tolanski interferometer. All films were 200 Å thick with typical lateral dimensions of 5×5 mm. A thick ($\approx10^3$ Å) copper film was evaporated from a Knudsen source onto the opposite side of the glass. This copper electrode was used as a gate in our experiments. Indium contacts were pressed onto two opposing sides of the sample ("source" and "drain") for conductance measurements and another one was connected to the gate. A schematic description of the sample geometry is given in the inset to Fig. 2.

The as-deposited films were amorphous and typically had sheet resistances of $R_\square=10-100$ kΩ at room tem-

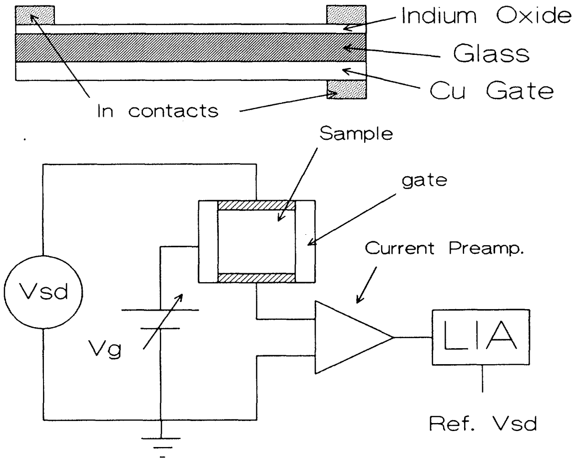

FIG. 2. A schematic description of the electronic circuit used for measuring the field effect. The inset shows the sample geometrical configuration.

perature. The $R_{\square}$ of a given sample could be fine-tuned by thermal annealing as described elsewhere.[10] Most of the measurements reported here were made on these amorphous films. However, the main findings were also reproduced using polycrystalline indium oxide samples. The latter were obtained from amorphous films that were crystallized by placing them on a 250 °C hot plate for 10–60 min. Also, we have made and measured several samples using a 1-mm-thick glass substrate instead of the nominal 100 μm and verified that the effects of the gate voltage scale with the gate-to-sample separation as they should for a field effect.

The field-effect measurements were done using the setup illustrated in Fig. 2. The source-drain voltages used were of the order of 100 mV rms at 2–10 Hz. The current was amplified and filtered (using an Ithaco 1211 current preamplifier), then measured by a lock-in amplifier (PAR 124 or 5204). The output of the phase-senstive detector was measured by a digital voltmeter. The various measuring devices were connected to a personal-computer-controlled data acquisition system. This technique for conductance measurement was dictated by the requirements of the experiments. Many of the samples measured in this study had sheet resistances of the order of 10^9 Ω and the relative changes in them due to the application of a gate voltage were small (of the order of a few percent). The use of an ac technique helped to increase the signal-to-noise value. More importantly, it alleviated the problem of possible (dc) spurious currents leaking from the gate to the sample. Several measurements were repeated using a standard dc four-terminal technique to ascertain that the main results are not due to contact problems.

The high resistance of the samples and the need to minimize the effects due to parasitic capacitances forced us to use very low frequencies for the phase-sensitive measurements. This, in turn, dictated fairly long integration times (3–10 sec) which slowed the response time of the conductance measurement. We have checked the instrumental response time of the system by studying the step response of the measuring setup and found it to be of the order of $\simeq 100$ sec for a 0.1% resolution on a 10-GΩ load. This slow response time is still much smaller than the relaxation rates relevant for this study as will become clear below.

The field-effect measurements were done by time sweeping a voltage applied between the sample and the gate. The maximum voltage swing used was 100 V and sweeping rates were in the range 0.02–2 V/sec (with 0.2 V/sec being the most commonly employed). Some measurements were done while the system was excited with electromagnetic radiation. The source of light was a red light-emitting diode (LED) with a wavelength of about 6350 Å. The excitation current was less than 1 mA and the voltage drop on the diode was $\simeq 2$ V. The diode was immersed in the liquid helium about 0.5 cm above the surface of the sample.

Most measurements were done in the temperature range of 1.3–4.2 K. We used an immersion-type cryostat in which the temperature could be varied by pumping on the helium vapor. In addition to the field effect, the dependence of each sample resistance on temperature was recorded using the same low-temperature rig and electronics described above. At the liquid-helium range, all samples reported below exhibited hopping conductivity. For amorphous films the specific form of $R_{\square}(T)$ was of the Arrhenius type, namely, $R_{\square}(T) \sim \exp[T_0/T]$ with $T_0 = 5-15$ K. Insulating films of crystalline indium oxide exhibited variable range hopping, $R_{\square}(T) \sim \exp[T_*/T]^{1/3}$ consistent with Mott's law in a two-dimensional (2D) system. Further details on the $R(T)$ of such samples can be found elsewhere.[10]

In a previous paper,[7] several possible artifacts were ruled out as an explanation for the anomalous field effect described in Sec. I above. The findings in this paper and the physical interpretation of them make these earlier attempts somewhat obsolete. Nevertheless, the interested reader is referred to the work by Ben-Chorin, Kowal, and Ovadyahu[7] for a discussion of technical pitfalls in these types of measurements.

III. THEORETICAL CONSIDERATIONS

We begin this section by presenting some general theoretical considerations that are pertinent to nonequilibrium charge transport in highly disordered systems. These will be shown to be relevant to the experimental findings discussed in Sec. I. Our basic approach to the problem hinges on the following claims.

(1) Exciting an insulating system far from thermodynamic equilibrium *always increases its conductivity.* We show here that this holds true in the case of hopping for noninteracting electrons. The presence of interactions is expected to further enhance this effect.

(2) At low temperatures, the system of localized electrons can become nonergodic,[11] i.e., the time to relax to equilibrium can be longer than any realizable experimental time. Such a situation is well documented for random magnetic systems with interacting spins, e.g., spin glasses.[12] Several papers suggest that it may also be expected for localized electrons in disordered systems with Coulomb interactions.[11] In fact, even noninteracting localized electrons can exhibit nonergodic behavior.[11]

(3) Injecting charge into the system (either electrons or holes) may take the system out of equilibrium. These premises will be shown to be sufficient for accounting for all the experimental observations of Ben-Chorin, Kowal, and Ovadyahu[7] and the further results will be presented in Sec. IV below.

We now show that the conductance is smaller in equilibrium than in an excited thermodynamic state far from equilibrium, namely, when some microscopic states of the system are appreciably more probable than they are in equilibrium (at the same temperature T). We first show this to be so without interactions, when the conductivity can be evaluated from one-particle excitations. This is commonly done by applying percolation theory to the random resistance network. The resistances R_{ij}, connecting sites i and j, can be obtained by calculating the current generated by a voltage V applied between i and j. V causes a change in the transition rates w_{ij} from i to j. In the linear response regime

$$w_{ij}=w_{ij}^0+\left[\frac{eV}{k_BT}\right]\left[\frac{dw_{ij}^0}{d\epsilon_{ij}}\right], \quad \epsilon_{ij}\equiv\frac{(E_j-E_i)}{k_BT}; \tag{1}$$

the superscript 0 denotes equilibrium values, E_k is the site energy of site k, and

$$\begin{aligned} w_{ij}^0&=\nu\exp(-2r_{ij}/\xi)(e^{\epsilon}-1)^{-1} \quad \text{for } \epsilon\equiv\epsilon_{ij}>0, \\ w_{ij}^0&=\nu\exp(-2r_{ij}/\xi)[(e^{\epsilon}-1)^{-1}+1] \quad \text{for } \epsilon<0. \end{aligned} \tag{2}$$

r_{ij} is the distance between sites, ξ is the localization radius, and ν is an attempt frequency of the order of the phonon frequency. It is easily shown that the derivative in Eq. (1) is $\nu\exp(-2r_{ij}/\xi)/\sinh^2(\epsilon/2)$. Notice that the denominator restricts ϵ to be not much greater than 1. The current induced by V is then

$$\begin{aligned} I&=e[f_i^0(1-f_j^0)w_{ij}(V)-f_j^0(1-f_i^0)w_{ji}(V)] \\ &=V\left[\frac{e^2}{k_BT}\right]\nu\exp\left[\frac{-2r_{ij}}{\xi}\right] \\ &\quad\times\frac{[f_i^0(1-f_j^0)+f_j^0(1-f_i^0)]}{\sinh^2(\epsilon/2)}, \end{aligned}$$

where f_i is the occupation number of the state i, and so

$$\begin{aligned} (R_{ij})^{-1}=\frac{I}{V}=\left[\frac{e^2}{k_BT}\right]\nu\exp\left[\frac{-2r_{ij}}{\xi}\right] \\ \times\frac{[f_i^0(1-f_j^0)+f_j^0(1-f_i^0)]}{\sinh^2(\epsilon/2)}. \end{aligned} \tag{3}$$

Equation (3) expresses the resistances near equilibrium. Exciting the system from equilibrium alters the f^0's say to f^e's, such that

$$f_k^e<f_k^0 \quad \text{for } E_k<E_F, \quad f_k^e>f_k^0 \quad \text{for } E_k>E_F. \tag{4}$$

The excitation does not alter the site energies or, by assumption, the temperature, and therefore the w's. Thus the nonequilibrium resistances differ from Eq. (3) only in the last factor (the term in square brackets), where the superscripts e replace the superscripts 0. The changes in R_{ij} due to excitation are

$$\begin{aligned} \delta(R_{ij})^{-1}=\left[\frac{e^2}{k_BT}\right]\nu\exp\left[\frac{-2r_{ij}}{\xi}\right]\sinh^{-2}\left[\frac{\epsilon}{2}\right] \\ \times[f_i^e(1-f_j^e)-f_i^0(1-f_j^0) \\ +f_j^e(1-f_i^e)-f_j^0(1-f_i^0)]. \end{aligned} \tag{5}$$

Consider now an excitation of electrons from some group of states A below E_F to a group A' above E_F, as indicated in Fig. 3. Then, for i in A, $f_i^e=f_i^0-\delta_i\approx 1-\delta_i$, $\delta_i>0$. The approximate equality expresses the condition far from equilibrium. For i in A'. $f_i^e=f_i^0+\delta_i\approx\delta_i>0$. For i and j in either A or A', Eq. (5) gives

$$\begin{aligned} \delta(R_{ij})^{-1}\approx\left[\frac{e^2}{k_BT}\right]\nu\exp\left[\frac{-2r_{ij}}{\xi}\right]\sinh^{-2}\left[\frac{\epsilon}{2}\right] \\ \times(\delta_i+\delta_j+2\delta_i\delta_j)>0. \end{aligned} \tag{6}$$

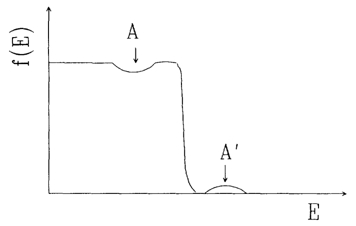

FIG. 3. The energy distribution of the electrons for an excited state of the system (when $\Delta E > k_BT$).

The main conclusion is that all changes in $\delta(R)^{-1}$ are positive, i.e., that the *conductivity increases when excited from equilibrium*. Physically, the increase in conductivity arises from the addition of Miller-Abrahams (MA) conductances that are virtually inaccessible to charge transport in equilibrium. We refer to those resistors that connect sites far from E_F to or from which excitations occur. In equilibrium, such sites have extremely large resistors associated with them because for them, either $f=0$ or $1-f=0$. This situation is altered by the excitation.

We now present a qualitative argument that this effect is expected to be stronger in the presence of interactions. Single-particle considerations are not adequate to describe the ensuing many-body effects, so we shall consider the microscopic states of the system. Their density is shown schematically in Fig. 4, in comparison with a similar density for the system without interactions. The interactions cause the density at low energy to fall well below that of the noninteracting case but at higher energies it gradually becomes steeper.[13,14] The first feature is an immediate consequence of the lowering of entropy by the interactions. The second feature is then imposed by the requirement that the total number of states be the same with and without interactions. These two features are also clearly borne out by recent computer simulations.[13,14] In equilibrium, the two systems differ in that the number of accessible microscopic states (within k_BT) with interactions is much smaller than without them. This is a manifestation of the Coulomb gap which reflects the fact that relatively few low-energy excitations are possible. Furthermore, many of these are collective excitations which have transition rates that are smaller than those for single-particle transitions. The result is a small-

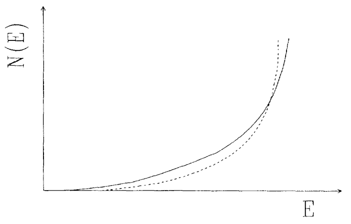

FIG. 4. Schematic description of the system density of states of an Anderson localized electron system: For noninteracting electrons (solid line): with Coulomb interactions (dashed line).

er conductivity of the interacting system relative to the noninteracting one. When an excitation by some energy E takes the system out of equilibrium, the numbers of accessible microscopic states increase much faster for the interacting system as a result of the steeper rise of the density of states with energy. This makes one expect that the relative increase in conduction due to the excitation is much larger for the interacting system. In addition, computer simulations indicate that the collective nature of the transitions decreases with increasing E thus enhancing the transition rates. Such an effect must also enhance the conductivity.

It should be noted that Fig. 3, and consequently the discussion pertaining to the increase of conductivity with excitation, assumes an excitation energy larger than $k_B T$. We have not considered what happens in the opposite case and cannot predict any details about the behavior under such conditions beyond that ΔG should be much smaller.

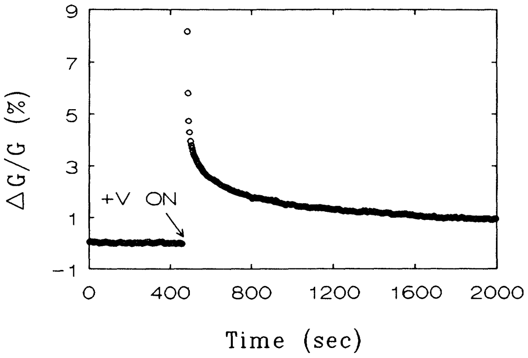

FIG. 6. The relative change of conductance of a 700-MΩ/□ (at 4.11 K) amorphous sample as a function of time after an application of a voltage step of $+100$ V to the gate. Note that the asymptotic value of $\Delta G/G$ is higher than zero presumably due to the "normal" field effect.

IV. RESULTS AND DISCUSSION

We start this section by addressing another aspect of the anomalous field effect, namely, its temporal behavior. Figure 5 depicts the time dependence of G following the application of a voltage step to the gate. Note that a similar behavior is observed in $G(t)$ for both gate-voltage polarities. The conductance rises sharply and then decays in a peculiar way. The symmetry with respect to the sign of V_g is just another way to observe the SC. The new feature that calls attention in this figure is the evanescent nature of the extra conductance that resulted from the application of V_g. As illustrated in Fig. 6 this ΔG seems to vanish[15] after a sufficiently long time. Interestingly, the qualitative features of $G(t)$ following an application of $|V_g|$ bear a striking resemblance to the $G(t)$ reported for GaAs samples excited by visible light.[16] The present system behaves in a similar way in this regard. Figure 7 describes the behavior of $G(t)$ following a brief exposure to a light-emitting diode. Note that the relaxation of the conductance in this case, as well as in Ref. 16, is very much like that observed in the gating experiments. Since the peculiar $G(t)$ that results from exposure to light is ascribable to hot-electron transport,[16] we take this similarity as an empirical indication that applying a gate voltage induces a nonequilibrium situation in the system.

Not all electromagnetic excitations lead to a state characterized by a slowly decaying extra conductance. Figure 8 illustrates the effect of exciting a sample by exposing it to a burst of an electromagnetic source at a frequency $\nu=35$ GHz. In this case, the conductance rises too, but the ensuing $G(t)$ after the generator was turned off exhibits an instantaneous decay (limited only by the measurement time, cf. Sec. II) to its dark value. We suggest that the difference between the response in $G(t)$ to the LED and the microwave excitation is due to the effective energies involved. The LED creates a nonequilibrium state since it can impart ΔE much bigger than $k_B T$ ($h\nu$ of the LED used is of the order of 2 V). An excited state with its associated slow decay of $G(t)$ could be created by exposing the samples to LED illumination at much higher temperatures. In fact, we have observed slow relaxations even at room temperatures when the

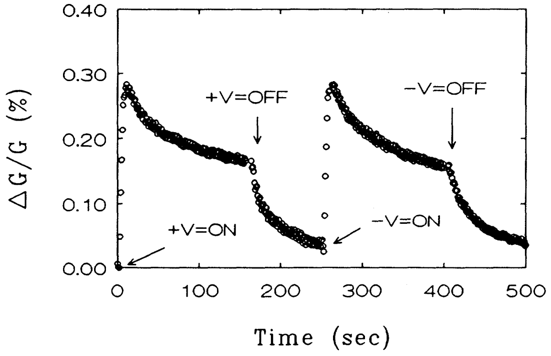

FIG. 5. The relative change of conductance of a 16-MΩ/□ amorphous sample (at 1.3 K) as a function of time following the application of voltage steps to the gate. Step voltages were 100 and -100 V.

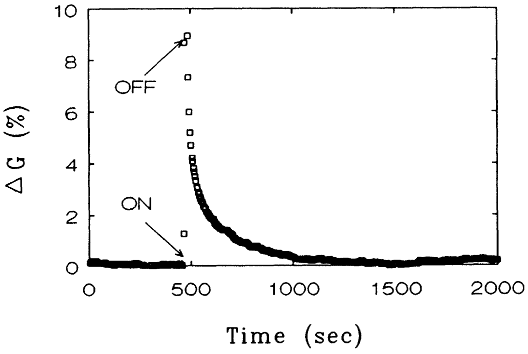

FIG. 7. The same as in Fig. 6 but following exposure to a $\simeq$10-sec pulse of light by the LED. Note the general similarity to Fig. 6.

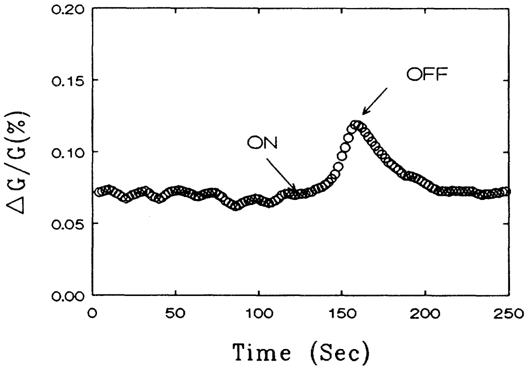

FIG. 8. The relative change of conductance of a 250-MΩ/□ amorphous sample, measured at 4.11 K, as a function of time following an exposure to a microwave radiation with a frequency of 35 GHz. Note that the decay of G after turning the generator off is essentially as fast as its increase during the "on" period in contrast with Fig. 7. The curve is shifted along the y axis for clarity.

resistance was sufficiently high. On the other hand, the microwave source, having an energy of the order of 1 K, is ineffective in this regard for a sample held at 4 K. Actually the difference in the energy quantum is not the only reason for this difference in the system response: Attempts to measure an increase in G by exposure to microwaves at temperatures below the λ point failed to detect any change above the noise level even though the samples were illuminated for a longer period of time than at 4.11 K. This is consistent with Joule heating being the main reason for the increase of G at 4.11 K following an exposure to the microwave source as opposed to the nonequilibrium situation presumably created by the LED.

As mentioned in Sec. I, the anomalous field effect (which is ascribed here to a nonequilibrium excitation) is *only* observable in our system when the temperature is lower than ≈ 10 K. No anomalous effect can be observed at 77 K even in samples with $R_{\square} \gg 1$ G Ω at that temperature. One reason could be that 77 K is always above the glass temperature. But that does not seem plausible—in the hopping regime the glassy state is intimately associated with small transition rates which are tantamount to large Miller-Abrahams resistances which, in turn, lead to high resistivities. Thus a very high hopping resistivity should yield a glassy state. We thus prefer to think that our failure to observe an anomalous effect at 77 K is due to the fact that ΔE is not larger than $k_B T$. Indeed, for the sample geometry used here (and based on Thomas-Fermi screening length[7] of $\simeq 5$ Å) we estimate that the application of $V_g = 100$ V is equivalent to $\Delta E_F \simeq 10$ K which, for a sample held at liquid-helium temperatures, should be enough to induce a far-from-equilibrium situation.

Having established the fact that gating the sample may take it out of equilibrium and that its G is then enhanced, we can immediately account for the anomalous field effect if the following statement is valid: The minimum in $G(V_g)$ corresponds to an equilibrium configuration of the electronic system.

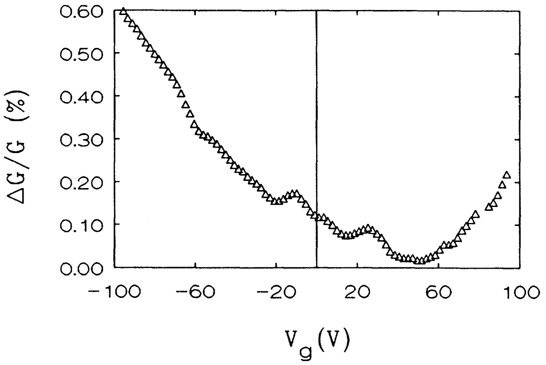

FIG. 9. The relative change of conductance of a 700-MΩ/□ amorphous film as a function of gate voltage. The film was cooled to 4.11 K while maintaining $V_{gc} = 50$ V on the gate.

The occurrence of a minimum in $G(V_g)$ at $V_g = 0$ reported by Ben-Chorin, Kowal, and Ovadyahu[7] immediately raises the question *"What is unique about zero gate voltage?"* We start by presenting an experimental answer to this question. The position of the minimum in $G(V_g)$ depends on the way the system is "prepared."[17] A minimum in $G(V_g)$ centered at *zero* gate voltage is an attribute of samples cooled down with *zero* gate voltage being applied in the process. That is the only thing which is unique about zero gate voltage, as we now proceed to demonstrate.

Figures 9 and 10 depict two cases involving *the same physical sample* cooled from room temperature to 4.11 K while maintaining a $V_g \neq 0$ in the process. The low-temperature scans of $G(V_g)$ exhibit two distinctly different curves[18] with the minima nearly coincident with the two different values of the respective "cooling-down" gate voltage V_{gc}. Another aspect of this phenomenon is illustrated in Fig. 11. This figure shows the evolution with time of $G(V_g)$ for a sample that was cooled down with $V_g = 0$ and then charged by applying a $V_g = 55$ V. The change with time of the field-effect trace was checked periodically sweeping the gate voltage (at a rate of 2 V/sec). The minimum of $G(V_g)$ was initially at $V_g = 0$.

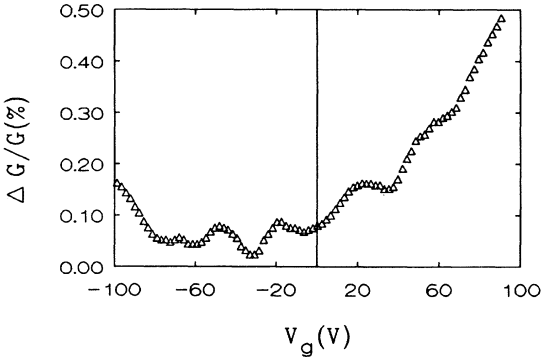

FIG. 10. The same as in Fig. 9, but with a different cooling gate voltage ($V_{gc} = -75$ V).

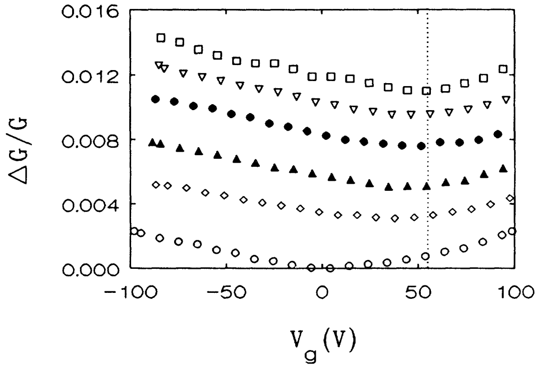

FIG. 11. Scans of $G(V_g)$ for a 90-MΩ/□ amorphous film initially cooled to 4.11 with zero applied gate voltage (lowest set of data). A constant voltage of 55 V was then applied to the gate. Consecutive "test scans" were taken at $\simeq 1$ h intervals to check for the "instantaneous" position of the minimum. The curves are displaced along the y axis for clarity by their chronological order.

Later scans showed that it shifted from 0 towards 55 V. Figure 12 depicts $\Delta G = G - G_{\min}$ as a function of $\Delta V = V_g - V_{\min}$ where $G_{\min}$ is the minimum of G for a given scan and $V_{\min}$ is the gate voltage where this minimum is observed. Note that all scans collapse onto an almost common plot of $\Delta G(\Delta V)$. This suggests that the only essential difference between the state of the system immediately after cooldown and in subsequent stages is due to an effective rescaling of V_g. Thus $V_{\min}(t)$ can be used as a "marker" delineating the momentary equilibrium configuration of the system. The change of $V_{\min}$ with time is shown in Fig. 13 (since each time sweep takes 5–10 min, which is not negligible, one should regard this plot as merely descriptive). Note that the typical relaxation time of $V_{\min}(t)$ is much longer than the experimental response time, much like that of $G(t)$ following an excitation.

There is some analogy between the phenomena described above and that exhibited by spin glasses[12,19] where the behavior of the low-temperature susceptibility depends on the value of the magnetic field applied in the process of cooling. In the present case, there is a remarkable feature that makes the observation of the glassy state easy to identify and keep track of, namely, the minimum in $G(V_g)$ and its position. The shift of the minimum is related to a creation of a "bias field" analogous to the remnant magnetization in spin glasses. When one applies V_g to the gate, the electronic system is disturbed and the system is out of equilibrium. The electron density $N(r)$ adjusts itself to cancel the applied field. The surface of the sample adjacent to the gate accumulates a charge of CV_{gc} (C is the effective sample-gate capacitance) which screens the applied field. Drawing on the analogy with other glasses, this adjustment is presumed to be faster than the time scale of the measurement when the system is at sufficiently high temperatures. However, when cooled below the glass transition temperature T_g, the readjustment of the charges in the system becomes a sluggish process. $N(r)$ remains for extended times in a configuration compatible with the high-temperature equilibrium state. This creates a persistent "bias field" proportional to V_{gc}. The electric field to which electrons in the sample respond is a superposition of the applied and bias field and thus it is proportional to $V_g - V_{gc}$. This picture accounts for the shift of the minimum with time, seen in Fig. 13. At a given moment, the "frozen" charge Q_f is dictating a local (in time) quasiequilibrium in the sense that imposing $V_g = Q_f/C$ will result in a static situation. The energy distribution of the "frozen" electrons is that conforming to the Fermi-Dirac distribution with respect to the chemical potential established through the imposed V_g.

In spin glasses the time scales of the dynamics have no classical estimates. This is not the case for electronic systems, the dynamics of which was widely investigated. It is interesting to compare the time it takes the system to reach an equilibrium configuration with the classical relaxation time expected from electrostatic considerations (based on Ohm's law and Maxwell equations). The latter suggests a relaxation time $\tau_M = \epsilon\rho/4\pi$ which is typically

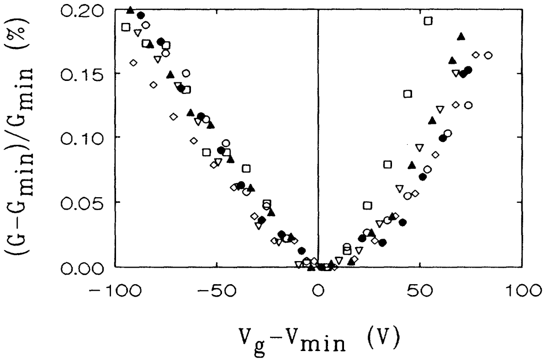

FIG. 12. The normalized change of the conductance $(G - G_{\min})$ as a function of the deviation of the gate voltage from its value at the minimum $(V_g - V_{\min})$ for the data presented in Fig. 11. Different labels are used to distinguish between different traces (as in Fig. 11).

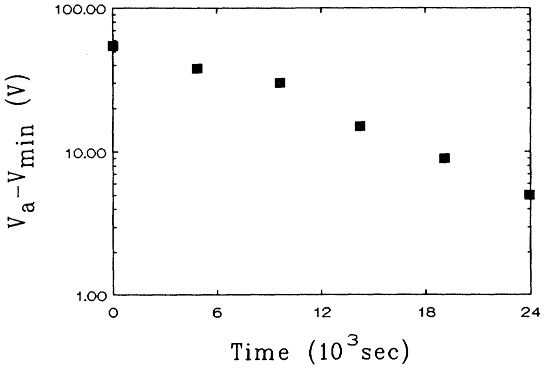

FIG. 13. The position of the minimum in $G(V_g)$ with respect to the applied voltage, $V_a = 55$ V, as a function of time. The data points are based on the traces in Fig. 11.

$\simeq 1$ μsec for our samples. The observed dependences in the position of the minimum of $G(V_g)$ can be recorded over time scales that are ten or so orders of magnitude larger than τ_M. Clearly, classical "bulk-ρ" considerations are inadequate to deal with screening in such systems.[11,20] The classical consideration leads to a gross underestimation of τ since it implicitly assumes spatial homogeneity and thus a possibility to define ρ and ϵ on *all length scales including the microscopic one.* However, in a hopping system this assumption is true only for length scales larger than the correlation length of the percolation cluster.[21] The inhomogeneous nature of such systems brings in some complications. In the first place, the classical estimate for ρ based on the macroscopic geometry is irrelevant since charge transport over short distances is quasi-one-dimensional in these systems.[21] The characteristic time for the charge transfer along such a segment is given by RC, where R is the resistance of the segment and C is a certain capacitance associated with it.[11] The fractal nature of the current-carrying network defies the simple result that $RC \sim \epsilon\rho$. Physically, this results from the fact that the effective capacitance is larger than that estimated[20] from the confined "cross section" controlling R. The resulting enhancement in relaxation times is further enhanced by Coulomb interactions.[22] It should also be pointed out the C's involved in the determination of the characteristic times may be the C's inherent in the Miller-Abrahams network rather than the geometrical C's alluded to above.[20]

The intriguing question to be addressed is this: What is the reason for the extended time of relaxation observed after gating the sample? In the following we try to give an intuitive picture of a charging process and its subsequent redistribution in the system which may account for the experimental observations. This picture is presented as a simple example of the response to the gate voltage by the hopping processes. It conveys the main idea in a clear way, but may not apply in the general case—the actual processes may be more complicated, e.g., due to interactions.

Applying a voltage between the sample and the gate results, at first, in a field normal to the sample plane. This field modifies $N(r)$ such that the current due to the field is balanced by the diffusion current proportional to $\nabla N(r)$. During this process, the system is out of equilibrium. In a homogeneous system, one expects $N(r)$ to adjust itself to the instantaneous value of V_g with a time delay given by $\epsilon\rho/4\pi$ which is usually too small to be of any practical concern. However, in the present case, there are important relaxation phenomena that, on short length scales, persist for extremely long times. Figure 14(a) illustrates the equilibrium state of the system in such a case. Equilibrium reflects itself in that E_F is spatially uniform, and electrons occupy states in accordance with the Fermi-Dirac distribution (at the temperature T). Immediately after adding charge to the two hatched regions which could be either the metallic contacts or any regions in the bulk of the system that happen to have much higher conductance than the central region in Fig. 14, the situation is as depicted in FIg. 14(b). The Fermi energy is larger in the "contacts" than in the "bulk" of the sample as electrons are just beginning to flow into the sample under the influence of the concentration gradient. The ensuing charging process is a hierarchical one.[23] The sites connected to the contacts with the smallest Miller-Abrahams resistors will be filled first. Naturally, most of them will be within a short distance from the contacts leading to an inward pointing charge gradient (i.e., from the "contacts" into the low-conductance region). To balance that, electrons admitted at high energies will make transitions to sites further inside the sample. This will be followed by more electrons flowing to the vacated sites from the contacts and so on. There are two features peculiar to this type of diffusion, the huge distribution in transition times involved on the one hand and the fact that as the electrons go down in energy the number of available states is diminished on the other. The latter causes the average distance of the transition to increase with time with a concomitant increase of the time necessary to make the transition. Note that as long as this process is going on, the local distribution of electrons is different from that of the thermodynamic equilibrium (and thus the conductance is enhanced). This is illustrated in Fig. 14(c). In the bulk of the sample the quasi Fermi energy will move towards the equilibrium value, leaving below it empty sites as well as "frozen electrons." Thermal equilibrium will be reached sluggishly due to the above considerations.[11,23] Note that the relatively higher-conductance regions in this picture (which are referred to as "contacts") could be the segments of the current-carrying network threading the bulk of the sample. Thus the relaxation time *should not* depend on the size of the sample once the latter is bigger than the percolation radius.

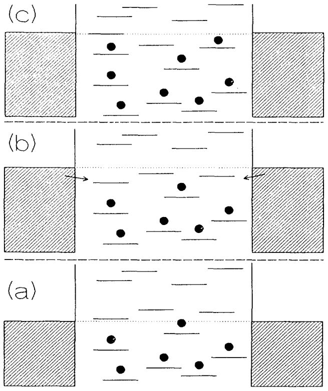

FIG. 14. A schematic description of the space-energy distribution of electrons at various stages of the charging process. The horizontal lines depict localized states and full circles are electrons occupying them. (a) At equilibrium prior to the application of a gate voltage. (b) Immediately after the application of V_g and (c) after charge enters the system and transitions are made on the way to establish new equilibrium. Dotted horizontal lines depict the position of the Fermi energy at equilibrium for the pertinent V_g. See text for more details.

The above scenario ascribes the relaxation process to a purely electronic mechanism. In particular, it disregards completely possible movements of other charges in the system during the process (this is symbolized in Fig. 14 as a rigid distribution of available sites). Given the very long times involved, the possibility that, say, ions can move should be given serious consideration. We cannot rule out this possibility. Yet, it is important to realize that even if such movement exists it does not change the qualitative conclusions of our model. The key point is that the material does have a high density of electrons per unit volume[10] which ought to screen out any internal fields thus eliminating the driving force for any charges to move in the first place. The data presented above strongly suggest that internal fields persist for extended times. The focus should then be on the fact that the electrons are manifestly responding extremely slowly rather than ruling out movements of other charges in the system.

It should be emphasized that as far as the electrostatic of the *macroscopic* sample is concerned, spatial charge homogenization may occur on a much shorter time scale than that associated with the relaxations in G discussed above. Chandrasekhar, Ovadyahu, and Webb[6] studied field effects in insulating films where both the "active" channel and the gate itself were made from high-resistance indium oxide films. The single electron charging effects reported there had a voltage periodicity which was *independent* of the sweep rates (up to 3 V/h). This enables us to place an upper bound of 10–100 sec on the time scale for the sample and gate material to become essentially equipotential objects. This does not conflict with our scenario for the following reason: Reaching a macroscopic, spatial homogeneity does *not* imply equilibrium if, as in our scenario, charge diffusion is faster than energy relaxation (which depends more strongly on microscopic disorder). In simple words, charge may spread evenly in the system (on scales larger than the percolation radius) rather quickly but that does not rule out nonequilibrium in energy. Relaxation along the energy axis involves hops on *microscopic* scales (e.g., the hopping length) which, on the average, do not change the "equipotentiality" of the sample on the *macroscopic* scale.

Finally, in the proposed picture, the increase of the conductance (relative to the equilibrium state) is due to downward hops made by electrons and holes. Clearly, a similar situation will arise if electrons are removed from the sample, as the entire picture is symmetrical with respect to replacing electrons by holes. This, we believe, is the reason for the appearance of the SC in the field effect. The nonequilibrium effect is counteracted by the underlying "normal" (essentially linear) field effect. Whether or not a minimum in $G(V_g)$ appears will depend on the interplay between these two components. It seems clear that a likely candidate for the observation of the minimum is a system with a small linear field effect. This will usually be the case in materials having a relatively high density of states. Both amorphous and crystalline indium oxide films have quite high densities of states[10] which perhaps is why this effect is observable in them. Granular systems made from metallic elements should also possess high densities of states and we suggest that they should be studied as they are likely to show the minimum in $G(V_g)$. It is interesting to note that such a feature has indeed been observed[9] in granular Au films, consistent with our picture. Adkins *et al.*[9] seem to emphasize glassy dynamics as arising from ion movement, not from electrons. In their treatment, electronic excitations from a Coulomb gap ground state are invoked (and thus nonequilibrium is implied), but the dynamics of the electronic system, essential in our model, is not considered in Ref. 9.

It is interesting to note that there is no qualitative difference in the anomalous field effect of the two types of systems: Both crystalline and amorphous indium oxide films are *structurally continuous structures*[10] while the Au samples in Ref. 9 are *granular.* It should be clear from the above considerations that sufficiently strong disorder is the *only* essential ingredient necessary for observing the anomalous effects reported here. Granular structures are one possible way to achieve that but, as we establish here, it is not the *only* way.

By contrast to the above high density-of-states systems, the density of states in most semiconductors is much smaller and strongly energy dependent. This usually causes the conductivity to be pinched off for negative gate voltages thus prohibiting the observation of the minimum. The considerations outlined in this paper are quite general though and we expect that time dependences in field effects of *any* hopping system should be observable. Experimentalists studying "dirty" metal-oxide-semiconductor field-effect transistor (MOSFET) structures are familiar with a host of problems that arise when sweeping the gate voltage "too fast" and sometimes tend to attribute these effects to "motion of ions." Though, as alluded to above, such a problem *might* exist, we maintain that slow relaxation and out-of-equilibrium situation *must* arise in a highly disordered system from a purely electronic mechanism even when the ions are effectively frozen out.

Before concluding, we wish to discuss the possible relevance of Coulomb interactions to the issues at hand. The qualitative arguments presented in Sec. III suggest that interactions should significantly influence the nature of the anomalous field effect due to their modification of the system density of states. Coulomb interactions may also strongly affect the relaxation process since the type of transitions in the presence of interactions may be altered, as is well known. At present, our model for the anomalous field effect does not include such details. It is hoped that further theoretical study of these questions will culminate in more specific knowledge of the modifications expected from interactions. In this regard the anomalous field effect may prove to be a useful tool to study Coulomb interactions.

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