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Attempts to measure thermally stimulated currents in chalcogenide glasses*

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The thermally stimulated currents (TSC) in a number of amorphous chalcogenide glasses are studied. In order to detect small changes in conductivity, after exposure to light, two samples are used in a bridge configuration. The TSC observed are found to be independent of the heating rate and the decay times are of several hours at 300 K. We find that our observations cannot be explained in terms of thermally stimulated currents. Models are discussed to explain the phenomena observed. We suggest that the observed changes in conductivity are caused by the same photoinduced defects which give rise to the reversible light-induced shifts of the optical-absorption edge in a number of chalcogenide glasses.

I. INTRODUCTION

An important technique for studying the localized states in semiconductors is the method of thermally stimulated currents (TSC).[1–24] In this method, traps are filled by the photoexcitation of the semiconductor, at a low enough temperature, such that upon ceasing the illumination the trapped carriers cannot be freed by the thermal energy available at that temperature. The temperature is then raised at a constant rate. The liberated carriers contribute in an applied field to an excess current until they recombine with carriers of the opposite type or join the equilibrium carrier distribution. This excess current, measured as a function of temperature during heating, is called a TSC curve. A TSC curve for a single trap depth has one maximum whose position depends on the trap depth, the capture cross section of the trap, and the heating rate. By varying the heating rate, the trap depth and the capture cross section can be determined.[3,5,6] If a discrete distribution of traps is present, the TSC curve may consist of several peaks, each originating from a distinct trap energy. Another technique, called step heating, is sometimes used to separate trap levels which are too closely spaced in energy to give separate peaks. This method consists of measuring the TSC while the sample is heated to successively higher temperatures in steps. After every step the sample is cooled back to the lowest temperature. This causes carriers to be liberated from progressively deeper traps. The logarithmic plot of the thermally stimulated current as a function of $1/T$ is expected to yield a straight line for each step. Its slope is directly related to the trap depth.

Other means of analyzing TSC have been proposed; some use the position of the peaks[3] and others their detailed shape.[2] Most of these depend strongly on whether the liberated carriers get retrapped by the trap centers or recombine through the recombination centers. Because of these effects the TSC is expected to depend on the transit time of the excess carrier and thus on the voltage applied. The method based on varying the heating rate and the step-heating method have been shown, however, to be independent of the recombination kinetics[5] and are therefore used most frequently.

Since the recombination kinetics of the traps in amorphous semiconductors is not known, these last two methods are the most useful techniques. In this manner Kolomiets and Mazets[22] found levels in bulk a-As_2Se_3 between 0.35 and 0.75 eV below the conduction band. Street and Yoffe[24] performed experiments on thin films of a-As_4S_4, a-As_2S_3, a-As_2Se_3, and a-Se, and interpreted their results in terms of trap levels. One of the main difficulties in observing TSC in the amorphous semiconductors which have mobility gaps of less than 2 eV is the small magnitude of the TSC currents compared to the dark currents.[22] We were able to overcome this difficulty by using two identically prepared samples in a bridge configuration. In this arrangement the dark current is largely balanced out and the offset current is proportional to the TSC current of the sample illuminated. Section II describes the experiments and the results. We find that the results cannot be explained by the conventional theory of thermostimulated currents.

In Sec. III we discuss the results in terms of light-induced bonding rearrangements and a rigid-band model. We show that a rigid-band model cannot explain the observed phenomena. The applicability of a potential fluctuation model proposed by Fritzsche[25] is also discussed.

Finally, in Sec. IV we compare our results with those obtained on amorphous semiconductors by other investigators.

II. EXPERIMENTAL RESULTS

Thin films of the multicomponent chalcogenide glass $Ge_{16}As_{35}Te_{28}S_{21}$ were rf sputtered in pure argon atmosphere onto 7059 Corning glass substrates supplied with thin-film molybdenum electrodes. In the case of As_2Se_3, the chalcogenide glass films were evaporated onto similar substrates with molybdenum electrodes in a vacuum of 10^{-7}

Torr or better. For experiments on bulk a-As_2Se_3, evaporated gold was used as the electrode material. In order to be able to detect small changes in conductivity, two almost identical samples prepared at the same time were used in a bridge configuration. One was illuminated, while the other was kept in the dark. Both samples were mounted on a rotatable copper block containing a heater and were kept in a pure and dry helium atmosphere to ensure good thermal equilibrium of the samples. The geometry of the cryostat is shown in Fig. 1. Cooling was done from the outside by surrounding the cryostat with a cryogenic liquid. During cooling light was shown on the sample (1) facing up through the infrasil quartz light pipe, using a 75-W tungsten halogen lamp. At 77 K the light was switched off, and the sample holder was rotated to a vertical position using the gear arrangment shown in Fig. 1. This was found necessary to ensure that the convection currents inside the cryostat affect both samples in an identical manner. The heating was commenced after waiting at 77 K in the dark for a few minutes to allow both samples to reach thermal equilibrium.

In order to show that the bridge method is indeed required for our samples, we present the results obtained from a conventional TSC experiment, without a bridge. Figure 2 shows the logarithm of the conductivity of an approximately 1-μm-thick film of the chalcogenide alloy as a function of reciprocal temperature before and after the illumination. The difference between the two curves yields the thermally stimulated conductivity. Since the conductivity before illumination is of the same order of magnitude as after the illumination it is extremely difficult to find the position of the

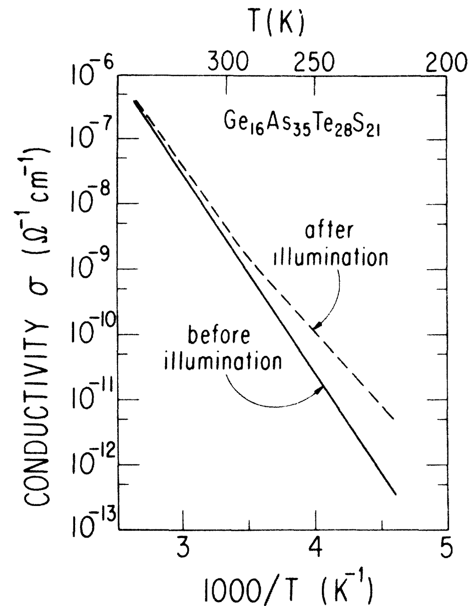

FIG. 2. Dark conductivity in a chalcogenide glass $Ge_{16}As_{35}Te_{28}S_{21}$ before illumination (solid line), and after the sample was cooled from 300 to 77 K under illumination (dashed line). The curves are independent of the heating rate.

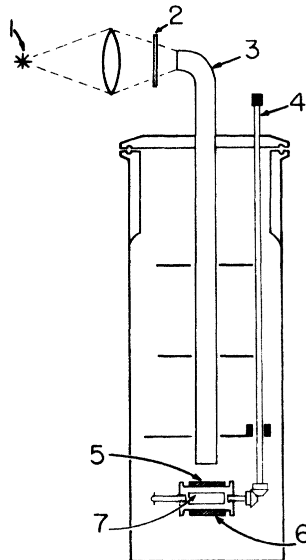

FIG. 1. Cryostat for measuring TSC. 1, Light source; 2, filter; 3, quartz light pipe; 4, gear arrangement for rotating the sample holder; 5, sample (1) to be illuminated; 6, sample (2) in the dark; 7, heater.

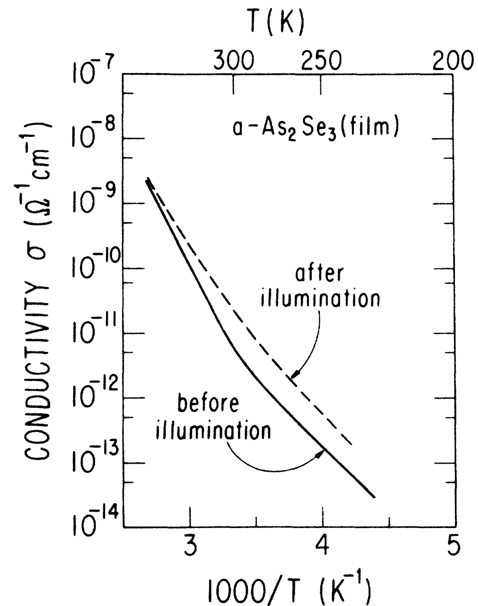

FIG. 3. Dark conductivity in a-As_2Se_3 film before illumination (solid line), and after the sample was cooled from 300 to 77 K under illumination (dashed curve). The curves are independent of heating rate.

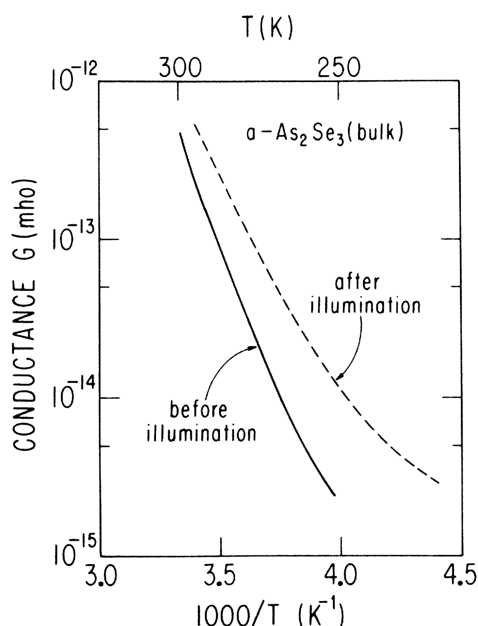

FIG. 4. Dark conductivity in bulk a-As_2Se_3 before illumination (solid line) and after the sample was cooled down from 300 to 77 K under illumination (dashed line). The curves are independent of the heating rate.

peak from such a measurement. Figures 3 and 4 show a similar situation for TSC experiments performed on a thin evaporated film of a-As_2Se_3 and bulk a-As_2Se_3, respectively. These curves were found to be independent of the heating rate between 30°/min and less than 1°/min. This observation is contrary to the expected behavior of thermally stimulated currents.

The success of the bridge method depends on the degree of dark-current cancellation throughout the whole temperature range. Figure 5 shows the tracking error between the two samples when the bridge had been balanced at room temperature. The tracking error is smaller than the dark current by several orders of magnitude at all the temperatures. This enables one to measure the thermally stimulated currents quite accurately even when the dark conductivity before exposure is of the same order of magnitude as after exposure. However, when a TSC experiment was performed on a pair of chalcogenide alloy samples in the bridge configuration, no TSC peak was observed. Instead, the thermally stimulated current was found to increase monotonically up to 400 K. In an attempt to determine the trap depth, a procedure known as step heating[6] was followed. After illuminating the sample at room temperature and during cooling to 195 K the illumination was switched off and the sample was warmed up in steps. Between every heating step to successively higher temperaature the sample was cooled back to 195 K. The temperature dependence of the conductivity is shown in Fig. 5. The curves are numbered to indicate the sequence of the heating steps.

The slope of the conductivity curves for each step is the same as that of the unexposed sample, despite the fact that the magnitude of the excess conductivity $\Delta\sigma$ decreases after each step. If was found that the conductivity curves could be traced back and forth repeatedly with essentially no change as long as the maximum temperature reached on the previous step was not exceeded.

These results do not resemble TSC reported in the literature. The equilibration times are unusually long for a semiconductor having a band gap of approximately 1.2 eV. For this reason we studied the decay of the excess conductivity $\Delta\sigma$ at fixed temperatures. Following the normal fast decay of photoconductivity, a residual excess conductivity is observed which lasts for several hours at 300 K and much longer at lower temperatures. Figure 6 shows the decay of $\Delta\sigma/\sigma$, where σ is the dark conductivity before exposure, as a function of time, after an exposure time of 4 min, at 195, 243, and 300 K, respectively.

The magnitude of $\Delta\sigma/\sigma$ and the decay time τ for the long tail increase with decreasing temperature. Furthermore, higher light intensity I and longer exposure times (t) yield larger $\Delta\sigma/\sigma$ and longer τ.

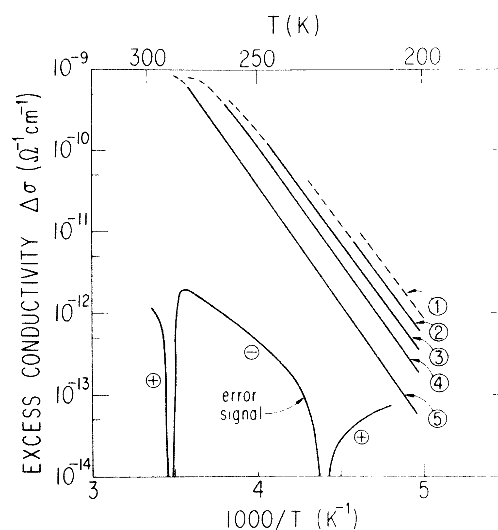

FIG. 5. Step heating performed on the chalcogenide samples in the bridge configuration. The numbers on the curves indicate the sequence of steps. The solid part of the line on each curve could be traced back and forth without any noticeable change. The tracking error between two unexposed samples in bridge configuration when the bridge had been balanced at room temperature is also shown. ⊕ means the error should be added and ⊖ that it should be subtracted from the observed signal. The error is, however, quite small as compared with the signal.

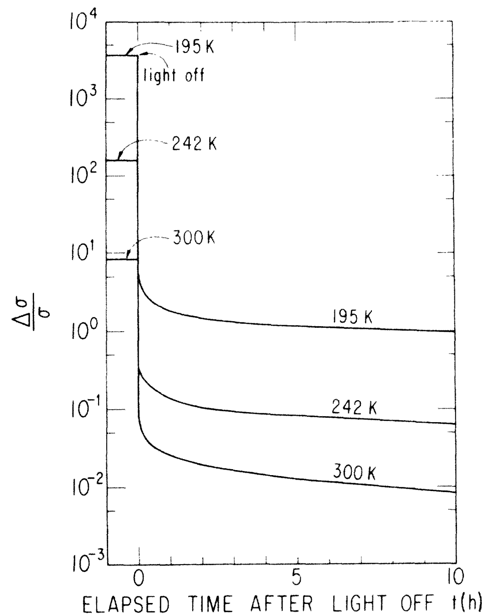

FIG. 6. Decay of excess dark conductivity, after a 4-min exposure at 195, 242, and 300 K.

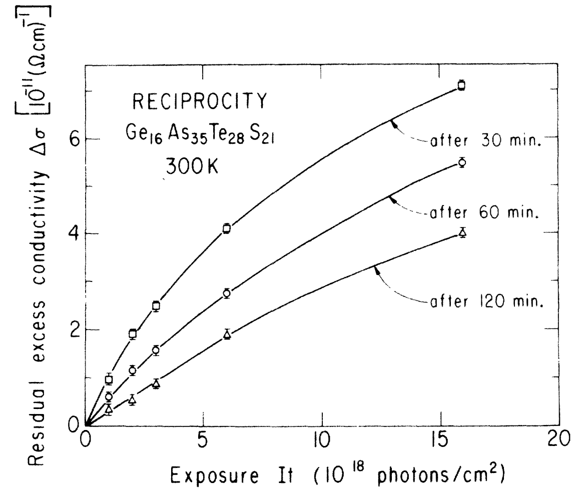

FIG. 8. Excess dark conductivity $\Delta\sigma$, measured after 30, 60, and 120 min after the exposure, plotted as a function of exposure. Exposure E is defined as the product of intensity I and time of exposure t. The reciprocity of I and t holds, i.e., the same $\Delta\sigma$ is obtained provided $E \times t$ is kept constant.

The effect of the length of exposure on $\Delta\sigma/\sigma$ is shown in Fig. 7. Provided t is kept much smaller than the decay time, the reciprocity relation holds and $\Delta\sigma/\sigma$ is found to depend only on exposure $I\times t$. The magnitude of the residual excess conductivity $\Delta\sigma$, measured after the light has been off for a certain length of time, increases linearly for small exposures. It appears to saturate at high exposure levels. Figure 8 shows this behavior, where $\Delta\sigma$ measured 30, 60, and 120 min after the exposure has been plotted as a function of exposure (It). The magnitude of the residual excess conductivity thus depends on the total number of absorbed photons. Attempts to quench[13] the excess conductivity with infrared light ($h\nu \leq 0.6$ eV) or by applying a high electric field of about 1.5×10^4 V/cm failed.

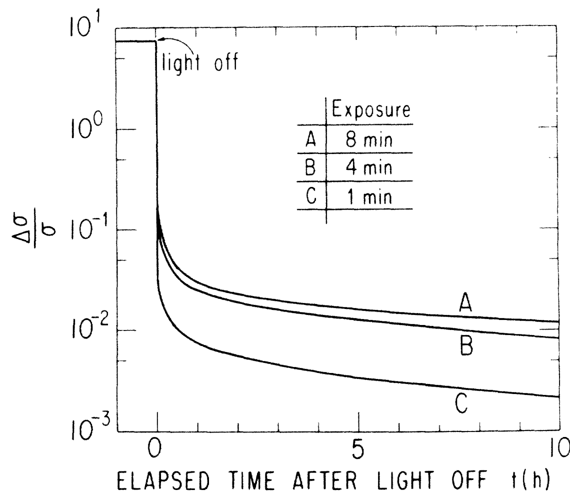

FIG. 7. Decay of excess dark conductivity at 300 K, as a function of exposure time.

III. DISCUSSION

In trying to interpret these results as TSC we have to consider two observations which are not expected for thermally stimulated currents (i) the observed currents are independent of the heating rate and (ii) the currents decay with an unusually long decay time even at temperatures as high as room temperatures. Let us try to understand this in terms of emptying of traps.

A. Rigid-band model

The activation energy of this chalcogenide glass is $E \simeq 0.55$ eV and the optical band gap is ~ 1.2 eV.[22] There are no empty electron traps deeper than 0.6 eV below the conduction edge because the Fermi energy is near the gap center.

Electron equilibration times of the order of several hours at 300 K are difficult to reconcile with a rigid-band model in which traps are at most 0.55 eV deep. This can be seen by the following argument. Neglecting retrapping, the equilibration time τ can be estimated from

$$\tau = (1/\nu)\, e^{E_t/kT} ,$$

where E_t is the trap depth. The so-called attempt to escape frequency ν is related to the effective number of band states $N_c \approx 5\times10^{19}$ cm^{-3}, the thermal electron velocity $v \sim 8\times10^6$ cm/sec and the

capture cross section S via the relation of detailed balance,

$$\nu = N_c S v \ .$$

For charged traps ($S \approx 10^{-11}$ cm^2) one obtains $\nu \approx 4 \times 10^{15}$ sec^{-1}, for neutral traps ($S \approx 10^{-15}$ cm^2) $\nu \approx 4 \times 10^{11}$ sec^{-1}. The smallest value reported[2] is approximately $\nu \approx 10^8$ sec^{-1}. Assuming this least favorable case ($\nu \approx 10^8$ sec^{-1}) the equilibration should take less than $\tau = 40$ sec at 300 K for the deepest traps $E_t = 0.55$ eV and considerably less for shallower traps.

Thus in order to obtain the observed long equilibration times with this model one should either have very efficient retrapping compared to recombination or an unusually small probability for emptying of traps. In that case, however, an excess dark conductivity should be produced if the sample is cooled very fast compared to the electronic equilibration time. No such effect was observed. We, therefore, conclude that such slow equilibration times cannot be explained by a rigid-band model.

B. Potential fluctuation

Fritzsche[25] suggested a model for amorphous semiconductor alloys with irregular spatial potential fluctuations in order to account for the discrepancy between the optical absorption edge and the electrical gap observed in these materials. These fluctuations can be divided into a symmetric part for which the valence and conduction bands fluctuate together, and an asymmetric part for which they fluctuate against one another. The symmetric part is shown in Fig. 9. Electron-hole pairs produced by light are separated by the internal fields which are associated with the symmetric part of the potential. This causes the electrons to move into positively charged regions and the holes into negatively charged regions, where they get trapped. If the internal fields are of the order of 10^5 V/cm, carriers of 10^{-8} sec lifetime and a mobility of 10^{-3} cm^2/V sec drift a distance of 10^2 Å. As a consequence the potential fluctuations are reduced, and the mobility gap is slightly decreased and the dark conductivity is increased. Equilibrium is then restored slowly by a recombination process involving spatially separated excess charges. It appears that the failure to freeze-in a detectable nonequilibrium carrier distribution by rapidly quenching the amorphous semiconductor films from 400 to 78 K also eliminates this process as an explanation for our observations.

C. Bond changes produced by light

It has been known for some time[26–32] that the optical properties of many chalcogenide glasses change upon exposure to light. In the case of a-As_2S_3 or a-As_2Se_3, for example, these changes manifest themselves as a parallel shift of the absorption edge to lower energies. Similar shifts have also been observed in a large number of multicomponent As-S-Ge and As-S-Te glasses. These light-induced changes can be divided into two categories[33,34] (i) irreversible and (ii) reversible. The first one, observed in freshly evaporated amorphous semiconductor films, is associated with photostructural changes which can be observed by x-ray diffraction.[33] The reversible light-induced changes, on the other hand, do not alter the x-ray pattern, and can be reversed by annealing at elevated temperatures.

The reversible changes may be caused by (i) defects or bond changes created by light or by (ii) trapped charge carriers which fail to equilibrate at temperatures below the annealing temperature.

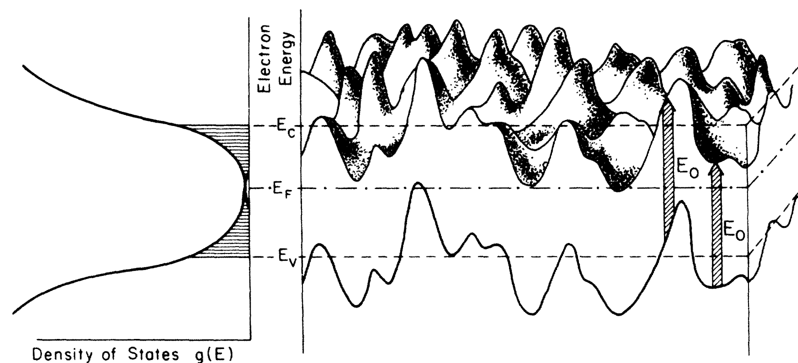

FIG. 9. Sketch of the symmetric part of long-wave-length-potential fluctuation. The short-range fluctuations, as well as variations which shift valence and conduction band states in opposite directions, are omitted for clarity. E_0 corresponds to an average optical gap. E_c and E_v are the percolation thresholds or mobility edges. The left hand side shows the density of states. The distribution of localized gap states between E_c and E_v is not necessarily smooth and monotonic (after Fritzsche, Ref. 25).

The latter explanation, however, suffers from the same difficulties as the models *A* and *B*: the relaxation times are unusually long for normal traps in semiconductors having band gaps between 1 and 2 eV. Traps with repulsive potential barriers may explain this, but there is no independent evidence for their existence. Further, our inability to quench the excess conductivity by application of a high electric field or by exposure to infrared light is another indication that we are probably not dealing with a purely electronic phenomenon.

In view of these observations, we feel that our results suggest that light produces local bond changes which yield an increase of the dark conductivity.[35] This may result from a decrease in the mobility gap similar to the observed decrease in the optical gap referred to above or from a shift of the equilibrium Fermi level toward the more conducting band.

The fact that in these materials no unpaired electrons were observed[36] by electron-spin resonance, with a detection sensitivity of 10^{14} spins/cm^3, after strong light exposure indicates that such light-induced bond changes do not produce defect states with dangling bonds. Such bond changes appear to produce a material of higher structural energy than the metastable state of the annealed semiconductor because they relax at elevated temperature where the viscosity is decreased. Any vitreous material can exist in many disordered structural states. Of these the metastable equilibrium state has the lowest free energy. A change to a different local-bonding arrangement is favored in materials having low covalent coordination numbers and containing group VI elements with nonbonding (lone-pair) p orbitals. Band-gap light excites an electron from a lone-pair state to an antibonding state. The concommittant distortion and availability of bonding to the unpaired lone-pair state may result in a bond switching and thus a new bond arrangement among the nearby atoms. We are not able to describe this in detail but it appears reasonable[37] that such bond changes occur most easily (i) when the excitation or recombination process takes place locally so that the energy is absorbed or dissipated in a small volume, (ii) when atoms with lone-pair electrons are present, and (iii) when the average covalent coordination number is small. Such materials have usually rather low melting or glass transition temperatures in relation to the magnitude of the optical gap.[38] It is unlikely to observe such effects in three dimensionally cross-linked network glasses or in tetrahedrally bonded semiconductors. The alloy glass investigated in this work is as expected only weakly photosensitive. The shift of the optical gap in this material must be less than 0.02 eV, since we have not observed it. We predict that some of the strongly photosensitive materials mentioned at the beginning of Sec. III will show a significant change in electrical conductivity after illumination.

IV. COMPARISON WITH PREVIOUS WORK AND CONCLUSIONS

Kolomiets and Mazets[23] found one TSC peak in bulk a-As_2Se_3 near 300 K. Using step heating, they interpreted this peak as being caused by a continuous distribution of trap levels in the range 0.35 to 0.75 eV below the conduction edge. Thin films of a-As_2Se_3, as well as a-As_2S_3, a-As_4S_4 and a-Se were studied by Street and Yoffe,[24] who explained their results in terms of various trap levels. In contrast, we found that in chalcogenide glasses studied by us, including a-As_2Se_3, the excess conductivity is independent of the heating rate and persists for several hours even at temperatures as high as 300 K. We also found that it is not possible to quench the excess conductivity by exposure to infrared light or by high electric fields. These observations indicate that purely electronic processes are inadequate for explaining these results.

The above mentioned authors do not mention whether or not the heating rate affects their observations in a-As_2Se_3. Furthermore, Kolomiets and Mazets[23] use silver as the electrode material. Silver is known to diffuse readily into chalcogenide glasses upon exposure to light.[30] This will increase the conductivity and obscure the effects we have seen, or any thermostimulated currents if they were present.

Most of the materials mentioned above are known to exhibit a red shift of the optical absorption edge upon exposure to light. As discussed in Sec. III, these changes may be permanent or reversible by annealing. The physical origin of the reversible changes has not yet been determined. It is quite likely that the kinds of physical processes which give rise to the reversible shift of absorption edge also change the mobility gap and shift the Fermi level and thus cause the excess dark conductivity. One of the explanations which can account for the excess dark conductivity as well as the reversible shift of absorption edge, is that they are both caused by bonding changes upon exposure to light. A change to a different local-bonding arrangement is favored in materials having low covalent coordination numbers and containing group VI elements with nonbonding p orbitals.

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