PHYSICAL REVIEW B VOLUME 18, NUMBER 10 15 NOVEMBER, 1978

Frequency dependence of conductivity of bulk amorphous selenium and tellurium-doped selenium

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(Received 9 August 1977)

The dc conductivity and ac conductivity of bulk amorphous selenium and selenium tellurides have been measured in the temperature range 150 to 310 °K. The ac conductivity is found to follow the relation $\sigma_{ac} \alpha \omega^n$. The value of n is found to increase with the decrease in temperature and with the increase of doping of tellurium in selenium. The value of the density of states at Fermi level, $g(E_F)$ is also found to increase with the increase of tellurium doping. The results have been discussed with the existing theories for ac and dc conduction.

I. INTRODUCTION

The frequency variation of the electrical conductivity of noncrystalline solids (NCS) has been a subject of extensive studies since the first measurements on frequency-dependent conductivity were reported by Pollak and Geballe[1] on compensated silicon. However, the measurements on NCS have been made on an extremely wide range of systems[2-5] and the physical insight into the mechanism of the ac conduction process is still inadequate. Even a correlation between the dc and ac components of the conductivity is not yet established. A distinction between dipolar conduction and conduction due to a hopping process cannot be made with the help of conductivity vs frequency variation alone because a sufficiently broad distribution of relaxation times in a dipolar system or interfacial polarization effects[6] can produce a frequency variation similar to that proposed by Pollak and Geballe for hopping conduction. To distinguish between these two processes and even to identify the nature of the hopping mechanism, measurements have to be made over a wide temperature range in the appropriate frequency region in materials having closely similar structure. Heterogeneity[7] of the materials and contacts[8] may also affect the frequency dependence of the conductivity.

The present paper reports ac and dc conductivity measurements on bulk amorphous selenium and tellurium-doped selenium samples over a wide temperature range. The ac conductivity has been found to be proportional to ω^n. The exponent n has been found to be dependent on temperature and percentage of tellurium in selenium. The results have been discussed in the light of existing theories for ac conduction.

II. EXPERIMENTAL DETAILS

Various samples of high-purity (99.999%) Se and Se_xTe_{1-x} of different composition were prepared. The exact proportions of Se and Te were weighed by using a microbalance. The samples were sealed in evacuated (~10^6- Torr) quartz ampoule of about 6 mm diameter. The ampoule containing Se was first heated at about 200 °C for 1–2 h and then heated to 525 °C in an electric oven. The temperature was kept constant for a period of 10–15 h. The ampoule containing Se_xTe_{1-x} was heated to 900 °C and held at that temperature for 20–24 h and was constantly agitated during heating to ensure complete mixing. The molten samples were then rapidly quenched in cold water. The quenched samples were taken out from the ampoule by dissolving the ampoule in solution of $HF + H_2O_2$ for about 16–20 h. Samples of different thickness were cut with a wire cutting machine and finally they were lapped and mirror polished. X-ray diffractometer traces of the samples were taken. Absence of sharp peaks in these traces reveals the amorphous nature of the samples.

Four samples used for the present work were having the following compositions:

Sample	Thickness
(1) pure Se	0.091 cm,
(2) $Se_{0.9}Te_{0.1}$	0.073 cm,
(3) $Se_{0.8}Te_{0.2}$	0.093 cm,
(4) $Se_{0.7}Te_{0.3}$	0.055 cm.

Aluminum was evaporated on entire area of the opposite faces of the samples. The samples were placed in a metallic cell (which provides proper shielding) in sandwiched configuration and the current through it was measured by noting the voltage across a standard resistance with a Keithley nanovoltmeter. Observations were also taken using silver electrode material, but no difference in the experimental results was found.

ac conductance of the samples was measured by using a capacitance bridge (Model No. GR 716-C) provided with external generator along with a null detection system. The measurements were made in the frequency range 10^2–10^4 Hz. The lower limit of the frequency was limited by the sensitivity of the bridge.

III. RESULTS AND DISCUSSION

The variation of dc conductivity (σ_0) and total conductivity σ with temperature has been shown in Figs. 1–4 (for the four samples 1, 2, 3, and 4). The variation of the ac component of the conductivity ($\sigma_{ac} = \sigma - \sigma_0$) has also been shown with broken curves in these figures. It shall be seen that the dc conductivity is thermally activated with activation energies varying from 0.84 eV (for pure Se sample) to 0.68 eV (for 30% Te doped Se). The values of the pre-exponential factor (σ_1) obtained from the intercepts of these plots ranges from about 4 to 20 $\Omega^{-1}\,\mathrm{cm}^{-1}$ as the atomic concentration of Te is increased from 0% to 30%. The values of σ_1 are about three orders of magnitude lower than the preexponential factor C for conduction in the extended states, suggesting thereby that the conduction is in the localized states above the valence band via thermally activated hopping. The decrease in the values of the activation energy with

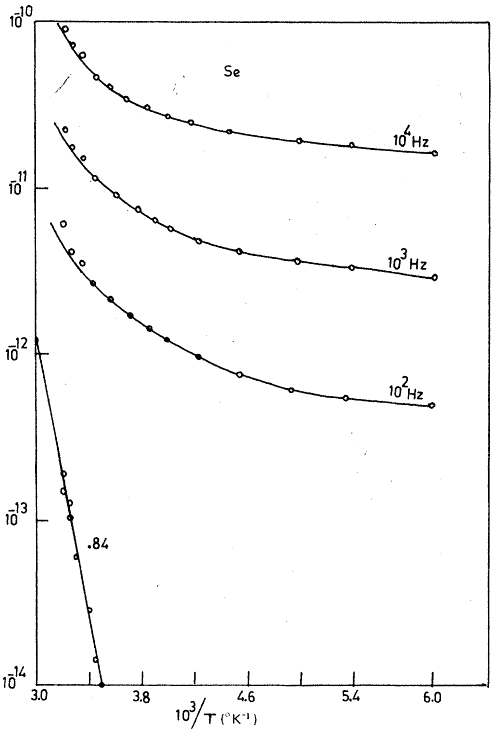

FIG. 1. Semilog plots of the conductivity vs reciprocal temperature for Se, at different frequencies.

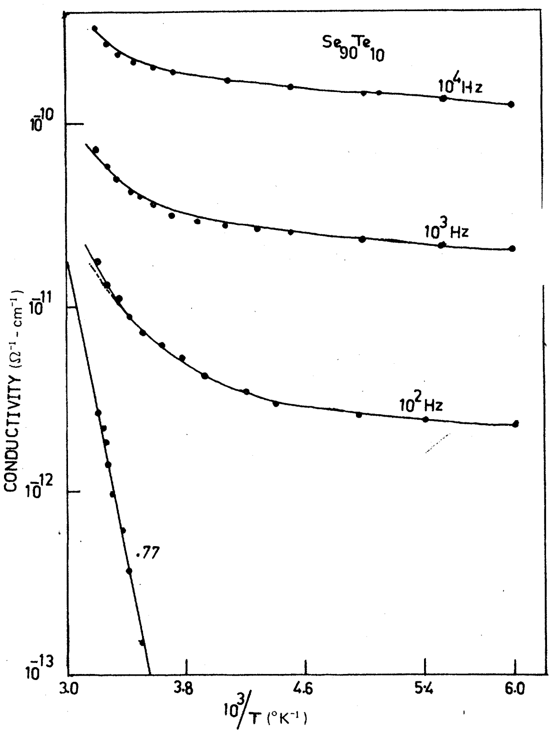

FIG. 2. Semilog plots of the conductivity vs reciprocal temperature for $Se_{90}Te_{10}$, at different frequencies.

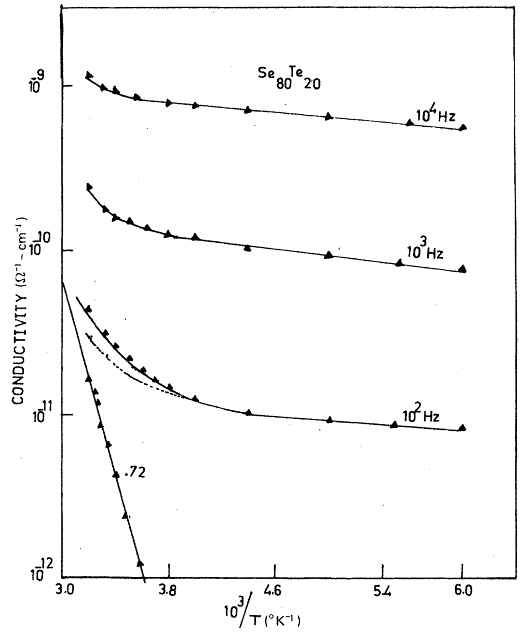

FIG. 3. Semilog plots of the conductivity vs reciprocal temperature for $Se_{80}Te_{20}$ at different frequencies.

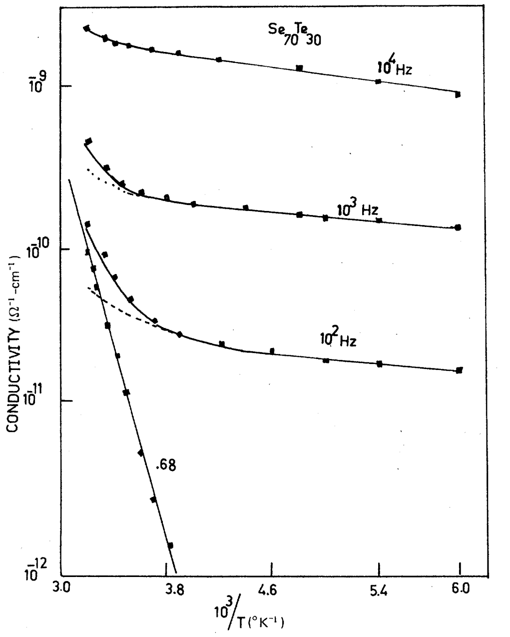

FIG. 4. Semilog plots of the conductivity vs reciprocal temperature for $Se_{70}Te_{30}$ at different frequencies.

the increase of tellurium doping can either be due to the decrease in the band gap as tellurium content increases, or due to the increase in the width of the localized-state region, or due to both the causes. The increase in the values of the preexponential factor indicates an increase in the density of localized state with the increase of tellurium, which is the main reason for such a large increase in the conductivity as has been observed in the tellurium-doped samples. The ac component of the conductivity shows a single-activation energy at low frequencies and in the high-temperature region, but the values of the activation energy are lower as compared to the dc activation energy. In the case of conduction in the localized states near valence band, the activation energy values for dc and ac conduction should be equal.[9] Although the activation energy values for ac conductivity are lower than dc conduction-activation energy, yet there is an indication that at higher temperatures, ac activation energy may increase and may tend towards dc activation energy values. As the frequency increases, the activation energy decreases and deviates from the single-activation nature. Another important feature of the results is that while both dc and ac conductivities increase with Te doping, the ratio of ac to dc conductivities (σ_{ac}/σ_0) decreases, which means that the dc conductivity increases faster with the increase of tellurium doping as compared to ac conductivity. This indicates that the dc conduction process in our samples involves localized states near the tail region, while the upper region of the localized states, where the density of the localized states is expected to be higher, is responsible for ac conduction process. The values of σ_{ac}/σ_0 obtained by us for Se-Te system at room temperature and at frequency 10^4 Hz have been shown in Table I.

Austin and Mott[10] have adopted Pollak's analysis[1] to the case of chalcogenide glasses. The hopping is considered due to phonon-assisted tunneling between the pair of sites at Fermi level and the conductivity is given by

$$\sigma_{ac}(\omega) = (\tfrac{1}{3}\pi)\omega[g(E_F)]^2 kTe^2\alpha^{-5}[\ln(\nu_{ph}/\omega)]^4 , \quad (1)$$

where ν_{ph} is the phonon frequency ($\sim 10^{13}$ sec^{-1}), α describes the decay with r of the localized-state wave function $\exp(-\alpha r)$, and $g(E_F)$ is the density of states at Fermi level.

Assuming α^{-1} to be 8 Å, the values of $g(E_F)$ have been calculated at 200°K for all the samples and have been shown in Table I. These values of $g(E_F)$ are very much larger than the values obtained by optical-induced paramagnetic states[11] and by field effect space-charge measurements.[12] This discrepancy could be due to the fact that even at temperature as low as 200 °K, the contribution to conductivity may be due to both the processes, i.e., conduction in the localized states near Fermi level and near band edge.

The frequency variation of the ac conductivity

TABLE I. Activation energy, preexponential factor, exponent n, density of states at Fermi level, and the ratio of ac conductivity to dc conductivity of Se, $Se_{90}Te_{10}$, $Se_{80}Te_{20}$, and $Se_{70}Te_{30}$.

Material	Activation energy ΔE (eV)	Preexponential factor σ_1 (Ω^{-1}cm^{-1})	Exponent n at 200° K	Exponent n at 300° K	Density of states at Fermi level $g(E_F)$ (eV^{-1}cm^{-3}) for α = 8 Å	Ratio of ac conductivity to dc conductivity at 300° K σ_{ac} (10^4 Hz)/σ_0
Se	0.84	4.88	0.72	0.63	4.24×10^{18}	1.9×10^3
$Se_{90}Te_{10}$	0.77	5.28	0.82	0.69	9.3×10^{18}	4.03×10^2
$Se_{80}Te_{20}$	0.72	7.52	0.85	0.76	1.8×10^{19}	1.4×10^2
$Se_{70}Te_{30}$	0.68	15.9	0.89	0.83	2.3×10^{19}	5.4×10^1

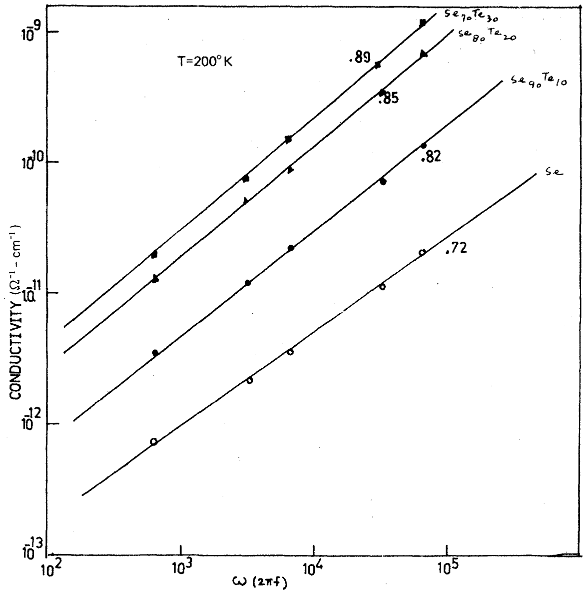

FIG. 5. Frequency dependence of the conductivity at 200 °K of Se, $Se_{90}Te_{10}$, $Se_{80}Te_{20}$, and $Se_{70}Te_{30}$.

for all the samples have been shown in Figs. 5 and 6 for 200 and 300 °K. It shall be seen from these figures that σ_{ac} follows the well-established relation $\sigma_{ac} \propto \omega^n$. The values of n (shown in Table I) are found to decrease with the increase in temperature. Such a large variation of n cannot be explained merely by considering the variation of ν_{ph} with temperature. A change in ν_{ph} as large as from 10^{11} to 10^{13} shall correspond to change in n only from 0.77 to 0.82 which is much smaller than the change of n observed by us. It may, however, be pointed out that a much larger change in ν_{ph} is possible if there is a polaron formation,[13] which is yet to be established in amorphous selenium. The decrease of n at high temperature has been explained by Pollak[14] by considering multiple hopping when paths containing different number of single-site distances contribute to ac conductivity. If multiple hopping is the only cause for change in n, then $\sigma_{ac}(300\,°K)/\sigma_{ac}(200\,°K)$ should be same for all the samples. However, the observed results are in contradiction to this. There are various other mechanisms which predict decrease of n at high temperature. Scher and Lax[15] and Moore[16] have analyzed the problem of ac conduction by adopting a continuous-time random-walk model. Pike[17] has explained the decrease of n at high temperature by considering the classical hops over statistically distributed barrier. Similar behavior is also observed in the phonon-assisted hopping with statistically distributed relaxation times with correlation effect.

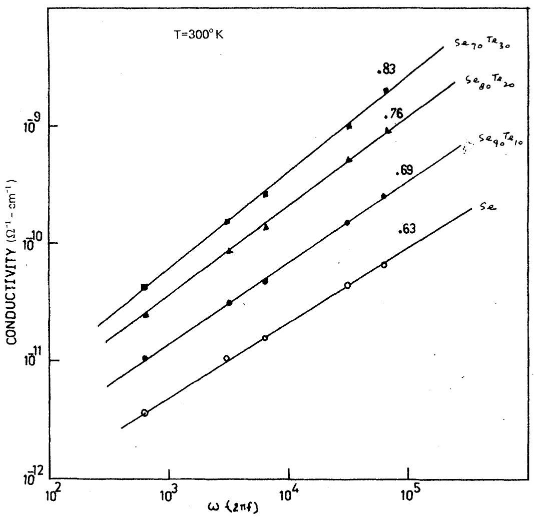

FIG. 6. Frequency dependence of the conductivity at 300 °K of Se, $Se_{90}Te_{10}$, $Se_{80}Te_{20}$, and $Se_{70}Te_{30}$.

We also see that as doping increases, the value of n increases at any temperature. This shows that n has some correlation with disorder, as Te content increases the material is expected to be more disordered. It may be pointed out that it is very difficult to establish a unique mechanism which is responsible for change in n.

ACKNOWLEDGMENT

One of us (AKK) is thankful to the Council of Scientific and Industrial Research (India) for financial assistance.

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