aftereffects, see J. E. Thun, in *Angular Correlations in Nuclear Disintegration,* edited by H. van Krugten and B. van Nooijen (Wolters-Noordhoff Publishing Co., Groningen, The Netherlands, 1971), p. 78.

[2]P. Raghavan and R. S. Raghavan, Phys. Rev. Lett. 27, 724 (1971).

[3]R. S. Raghavan and P. Raghavan, Phys. Rev. Lett. 28, 54 (1972).

[4]E. Gerdau, J. Wolf, H. Winkler, and J. Braunsfurth, Proc. Roy. Soc., Ser. A 311, 197 (1969).

[5]E. Bodenstedt, W. H. Ellis, and U. Ortabasi, Phys. Rev. B 6, 2909 (1972).

[6]D. Brandt and S. S. Rosenblum, in Proceedings of the International Conference on Nuclear Moments, Osaka, Japan, 1972 (to be published).

[7]C. H. W. Jones, J. Phys. Chem. 74, 3347 (1970).

[8]See, for example, C. H. W. Jones and J. L. Warren, J. Chem. Phys. 53, 1740 (1970); G. J. Perlow and M. R. Perlow, J. Chem. Phys. 48, 955 (1968); J. M. Friedt and J. Danon, to be published.

[9]F. D. Feiock and W. R. Johnson, Phys. Rev. 187, 39 (1969).

[10]R. S. Raghavan and P. Raghavan, Phys. Lett. 36A, 313 (1971).

[11]P. Raghavan, T. S. Raghavan, and W. B. Holzapfel, Phys. Rev. Lett. 28, 903 (1972).

Macroscopic Inhomogeneities in Amorphous Semiconductors; Contactless Conductivity

U. Strom* and P. C. Taylor
Naval Research Laboratory, Washington, D. C. 20390

(Received 26 September 1972)

Macroscopic inhomogeneities are observed in glassy $Tl_2SeAs_2Te_3$ using a contactless-conductivity technique. Electron microprobe experiments indicate that the samples are compositionally homogeneous and suggest that the inhomogeneities are structural. These inhomogeneities exhibit a thermally activated conductivity considerably greater than the dc bulk value but with an identical activation energy.

There are several universal features of amorphous semiconductors including an intrinsic, thermally activated dc electrical conductivity, a rising ac conductivity proportional to ω^{α}, where $\alpha \lesssim 1$,[1] a linear anomaly in the low-temperature specific heat, and a nearly universal thermal-conductivity curve.[2] The current models proposed to explain these universal features assume a medium whose inhomogeneous properties are either the result of statistical fluctuations on a scale comparable to interatomic spacings[1,3,4] or due to fluctuations in local physical properties such as density or composition on a submicroscopic scale of 100–500 Å.[5,6] This Letter reports contactless electronic-transport measurements which are interpreted in terms of macroscopic inhomogeneities (on a scale greater than 1 μm in the structure of an amorphous semiconductor, which may be a general property of semiconducting chalcogenide glasses. These inhomogeneities are not detectable by electron microprobe analyses, and they appear to be outside the scope of the existing structural or transport models.

In the usual low-frequency electrical-conductivity measurement, current is generated by applying an electric field to the sample. However, one may also create currents by immersing the sample in a time-varying magnetic field. The latter method, which uses the sample as a torsion pendulum, requires no electrical contacts. In the case of homogeneous, isotropic materials, the contactless technique yields the same results as ordinary contact methods.[7,8] When the material is inhomogeneous, the current paths are altered and the two methods will, in general, yield different results.

Consider the case of a medium which is homogeneous and isotropic on a scale comparable to its dimensions, but inhomogeneous (and possibly anisotropic) on a macroscopic sale much less than the sample dimensions. The torque per unit length on an infinite cylinder of such a material in a uniformly rotating magnetic field may be divided into two additive terms. The first is a bulk contribution containing the average effect of all the inhomogeneities and yields an effective conductivity equal with that measured in a contact experiment[9]; the second term results from the local current loops created by the inhomogeneities. Let the magnetic field rotate uniformly in a plane perpendicular to the axis of the cylinder. Then the torque per unit length (neglecting magnetoresistance) is given by the following expression:

$$\Gamma = (\pi/4c^2) R^4 H^2 \omega \sigma_0 + (\pi/4c^2) R^2 H^2 \omega C, \qquad (1)$$

where R is the radius of the cylinder, H the

magnitude of the rotating magnetic field, and ω its angular frequency. The quantity σ_0 is the bulk conductivity as would be measured by a dc contact technique. The second term represents the added torque due to the macroscopic inhomogeneities in the bulk sample. The constant C has the dimensions of a conductivity times an area. The evaluation of C involves an integral containing the local conductivity tensor and is evaluated over the geometries of the macroscopic inhomogeneities. This integral includes any interactions between inhomogeneities which are not contained in the homogeneous (first) term. Although the calculation of the second term of Eq. (1) depends on the exact distribution, shape, and electrical anisotropy of the inhomogeneities, the form including the R^2 dependence is general.

The finite length of the cylinder can be taken into account by an additional factor $k^{-1} \approx 1$ in the first term of Eq. (1), which depends on the radius-to-length ratio of the cylinder and may be determined empirically using known standards.[10] An effective conductivity of Eq. (1) for an infinite cylinder per unit length can be expressed as[11]

$$\sigma_{\text{eff}} = (4c^2/\pi R^4 H^2 \omega)\Gamma = \sigma_0 + C/R^2,$$

where in terms of measured quantities

$$\sigma_{\text{eff}} = (4\pi\rho\theta/H^2\tau^2\nu) \times 10^9\ \Omega^{-1}\ \text{cm}^{-1}. \quad (2)$$

In this equation ρ is the density of the sample, τ the period of the torsion pendulum in the absence of the magnetic field, ν the frequency of the rotating field in hertz, and θ the angular deflection of the pendulum in radians. In the special, if unrealistic, case where there is only one characteristic inhomogeneity size $r_{\text{eff}} \ll R$ with one characteristic conductivity $\sigma_1 > \sigma_0$, the conductivity for an infinite cylinder per unit length may be written as

$$\sigma_{\text{eff}} = \sigma_0 + v\sigma_1 (r_{\text{eff}}/R)^2, \quad (3)$$

where v is the volume fraction of inhomogeneous regions. The major contribution to σ_0 is due to current loops whose area is of order R^2. The second term of Eq. (3) is scaled down by the factor $(r_{\text{eff}}/R)^2$ because the torque exerted per unit length by all of the small current loops is proportional to $r_{\text{eff}}{}^2 R^2$, not R^4. In a dc contact measurement the conductivity is dominanted by σ_0 since the regions of conductivity σ_1 are assumed to be isolated. However, in a contact-free measurement, the conductivity will depend on $1/R^2$ whenever $\sigma_0 R^2 \sim \sigma_1 r_{\text{eff}}{}^2$.

Contactless measurements were preformed on cylindrical samples of vitreous $Tl_2SeAs_2Te_3$ and single-crystal, dislocation-free, p-type silicon standards[12] using a torsion pendulum hanging in an evacuated quartz tube centered in a uniformly rotating magnetic field. Vitreous $Tl_2SeAs_2Te_3$ was studied because it is as highly conducting as any known semiconducting glass, and does not crystallize easily. The samples were glued onto fine, polished, and straightened tungsten wire[13] (7.6 and 24 μm diam) using unfilled epoxy. Torques were recorded by measuring the deflection of a laser beam reflected from a thin aluminum-coated mica mirror which was attached to the tungsten wire well above the rotating field. A 1500-G magnetron magnet rotating between 2 and 20 Hz supplied the time-varying magnetic fields. These fields were homogeneous to within 3% over all sample sizes measured, and the rotation speed varied by less than 0.1% at all frequencies. Elevated temperatures (25–75°C) were achieved using a noninductive heater wound around the quartz vacuum chamber. Temperatures were calibrated to $\pm 1°$.

Boron-doped, p-type silicon standards were used because the conductivity is isotropic and homogeneous in these materials. A series of standards were measured whose conductivities σ and radii R spanned the ranges of the glass samples (σ between 10^{-4} and $10^{-2}\ \Omega^{-1}\ \text{cm}^{-1}$ and R between 0.48 and 1.27 cm). The radius-to-length ratio R/L of these standards was varied systematically to obtain an empirical relation for the parameter k mentioned above.

The conductivity as described by Eq. (2) is proportional to the angular deflection θ and inversely proportional to the frequency of the rotating magnetic field ν. Figure 1 is a plot of θ versus ν for two cylinders of $Tl_2SeAs_2Te_3$ glass, at room temperature, with different radii R. The zero deflection of the torsion pendulum in the rotating field was calibrated using the silicon and nonconducting standards. The data points in Fig. 1 are well represented by straight lines whose slopes are directly proportional to the conductivity. The proportionality constants are functions of the period of the pendulum τ which in turn depends on the cylinder radius [Eq. (2)]. A cylinder of As_2Se_3 glass at temperatures from 25 to 50°C yielded no observable deflection as expected since $\sigma \approx 10^{-11}\ \Omega^{-1}\ \text{cm}^{-1}$ in this material.

The contactless conductivity of vitreous $Tl_2SeAs_2Te_3$ at room temperature is found to be a function of the radius of the cylindrical sample, while the conductivities of the Si standards are

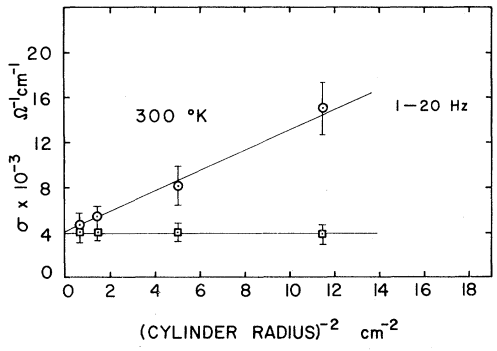

FIG. 1. Deflection of $Tl_2SeAs_2Te_3$ glass cylinders as a function of frequency of the rotating magnetic field. Circles, a sample of radius $R = 0.825$ cm with the pendulum period $\tau = 185$ sec. Squares, a sample with $R = 0.445$ cm, $\tau = 75$ sec. Conductivities are determined from the slopes of the lines using Eq. (2).

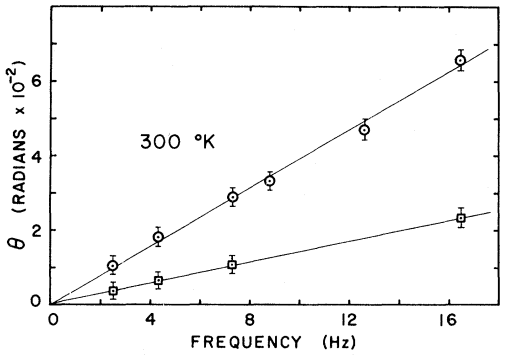

FIG. 2. Dependence of contactless conductivity in glassy $Tl_2SeAs_2Te_3$ on cylinder radius R (circles). Squares, dc contact measurements on the same samples.

independent of cylinder radius as one would expect. Figure 2 is a plot of σ_{eff} adjusted for an infinite cylinder ($k = 1$) per unit length, as measured by the contact[15] and contactless methods versus $1/R^2$. The contactless data fall approximately on a straight line and extrapolate to the dc contact value for large R as predicted by Eq. (2).[16] The slope of the line is proportional to the constant term C in Eq. (2).

The magnitude of the inhomogeneous conductivity term in vitreous $Tl_2SeAs_2Te_3$ is considerable. One may estimate this magnitude for the simple case described by Eq. (3) which assumes isolated inhomogeneities of a unique size given by r_{eff} and a unique conductivity σ_1. In this case, the slope of the line in Fig. 2 yields a value for $v\sigma_1 r_{eff}^2$ of 10^{-3} cm/Ω. Since the measured effective conductivity is thermally activated, it is reasonable to assume that σ_1 is not greater than the high-temperature–conductivity limit for amorphous semiconductors (10^3 to 10^4 Ω^{-1} cm^{-1}).[1] This assumption implies that r_{eff} is greater than 5 μm. Thus, inhomogeneities on the order of 10 to 100 μm with conductivities 10^5 to 10^4 over the bulk dc contact value provide the most plausible explanation for the magnitude of this effect.

Pearson[17] has observed phase-separated regions in freshly fractured surfaces of glassy $Tl_2SeAs_2Te_3$, which are about 0.5 μm in diameter and comprise approximately 20% of the sample volume. However, microprobe and scanning electron microscopy studies on our samples indicate glassy material with no crystalline inclusions or compositional inhomogeneities (fluctuations <3 at.%) on a scale at least as small as 200 Å. Several different samples were investigated both before and after the conductivity measurements, and compositional inhomogeneities were never observed.

Although the contactless conductivity of glassy $Tl_2SeAs_2Te_3$ varies with the cylinder radius, the activation energy for this thermally activated conductivity $\Delta\epsilon$ is independent of R as indicated in Fig. 3. In this figure the natural log of the conductivity is plotted versus inverse temperature for several glass samples. The activation energy (slope of the lines) is constant within experimental error and given by $\Delta\epsilon = 0.39 \pm 0.05$ eV. Also plotted in Fig. 3 are the dc contact conduc-

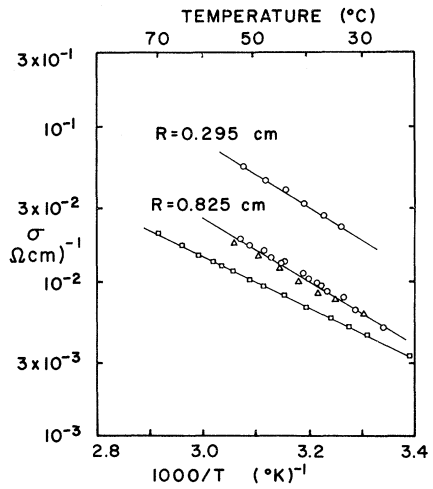

FIG. 3. Temperature dependence of the conductivity in vitreous $Tl_2SeAs_2Te_3$. Circles and triangles, contactless measurements at 17 and 7 Hz, respectively. Squares, dc contact measurements which are independent of sample radius R.

tivity data which are identical for all cylinders. These contact measurements yield an activation energy of $\Delta\epsilon = 0.36 \pm 0.03$ eV which is equal to the contactless results within experimental error.

One possible explanation of these results envokes the local bonding characteristics of the glass. Several of the semiconducting compounds containing Se, S, As, Tl, and Te consist of layers or chains. These layers and chains are highly anisotropic bonding configurations whose anisotropies are manifested in the conduction processes. If the conductivity in the $Tl_2SeAs_2Te_3$ glass is highly anisotropic locally, it is possible than an increased conductivity could arise in the contact-free method from the random orientations of layers or chains, while the activation energy could remain nearly identical with the contact value.

The present results suggest experiments which, if performed carefully, should provide additional information about the structural inhomogeneities in semiconducting $Tl_3SeAs_2Te_3$ glass. Ideally, ordinary dc contact measurements across thin films should yield conductivities much greater than the bulk value measured along the sample. In practice, it is difficult to obtain thin films which are indicative of the structure of the bulk and free of contact effects. The effects of inhomogeneities must also show up in careful scattering measurments. Although scattering in the infrared region is known to exist in chalcogenide glasses,[18,19] careful measurements on glassy $Tl_2SeAs_2Te_3$ are complicated by the strong thermally activated infrared absorption observed in this material.[19]

The authors have benefited greatly from many helpful discussions with D. L. Mitchell. F. W. Frazer is thanked for technical assistance in the electron-microscopy experiments. L. H. Slack is thanked for providing the glass samples.

---

*National Research Council Postdoctoral Research Associate.

[1]N. F. Mott and E. A. Davis, *Electronic Processes in Non-Crystalline Materials* (Clarendon Press, Oxford, 1971).

[2]R. C. Zeller and R. O. Pohl, Phys. Rev. B 4, 2029 (1971).

[3]M. H. Cohen, H. Fritzsche, and S. R. Ovshinsky, Phys. Rev. Lett. 22, 1065 (1969).

[4]P. W. Anderson, B. I. Halperin, and C. M. Varma, Phil. Mag. 25, 1 (1972).

[5]F. Williams, J. Non-Cryst. Solids 8-10, 516 (1972).

[6]H. Fritzsche, J. Non-Cryst. Solids 6, 49 (1971).

[7]A. Z. Chaberski, J. Appl. Phys. 42, 940 (1971).

[8]J. S. Lass and A. B. Pippard, J. Phys. E: J. Sci. Instrum. 3, 137 (1970).

[9]L. D. Landau and E. M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon, New York, 1960), p. 194.

[10]J. LePage, A. Bernalte, and D. A. Lindholm, Rev. Sci. Instrum. 39, 1019 (1968).

[11]When the cylinder is of finite length, the first term only of Eq. (2) is multiplied by the factor k. In this case σ_0 must be determined separately from dc contact measurements in order to determine uniquely the second term. In the present experiment finite cylinder length ($k \neq 1$) was a significant factor for only one sample (the sample of largest radius in Fig. 2, $R = 1.27$ cm).

[12]Dislocation-free, boron-doped, single-crystal Si samples were obtained from Dow Corning Semiconductor Products and from High Performance Technology, Inc. These samples underwent float zoning for several passes in vacuum.

[13]Straightened and polished tungsten wire was obtained from Sylvania Electric Products, Inc.

[14]An upper limit of $10^{-4}\,\Omega^{-1}\,\mathrm{cm}^{-1}$ can be placed on the contact-free conductivity of vitreous As_2Se_3 in contrast to results previously reported: V. P. Pozdnev, Fiz. Tverd. Tela 4, 946 (1972) [Sov. Phys. Solid State 4, 693 (1962)].

[15]The dc contact measurements were performed on samples of varying geometries to eliminate surface and contact effects.

[16]The dependence of conductivity on cylinder radius in $Tl_2SeAs_2Te_3$ is not due to a conducting surface layer or to crystallized regions in the glass. A conducting surface layer of identical thickness for all samples would yield a radial dependence of $1/R$, whereas the experimental data depend on $1/R^2$ (Fig. 2); crystallized regions in the glass are not observed by electron microscopy. In addition, neither of these two mechanisms would yield the appropriate activation energy (Fig. 3).

[17]A. D. Pearson, J. Non-Cryst. Solids 2, 1 (1970).

[18]D. L. Wood and J. Tauc, Phys. Rev. B 5, 3144 (1972).

[19]D. L. Mitchell, P. C. Taylor, and S. G. Bishop, Solid State Commun. 9, 1833 (1971).