Observation of Dipolar Activity in Amorphous Se and Some of Its As Alloys

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A relatively large population of bulk dipoles can be detected in amorphous selenium, a homopolar solid, via the coupling they provide between an applied ac electric field and the large-scale cooperative molecular motion thermally excited at the glass transition temperature. Although the structural-chemical origin of the contributing dipoles is not determined, their presence provides a unique opportunity to study a primary moleuclar relaxation process in an important class of amorphous semiconductors.

In a recent Letter Kastner, Adler, and Fritzsche[1] proposed a charged-defect model for gap states in amorphous selenium and chalcogenide glasses. For amorphous selenium they predict a defect density or equivalently a bulk dipole density of 10^{17}–10^{19} cm^{-3}. Street and Mott[2] also postulated a charge-defect population for chalcogenides which they argue derives from an energy-lowering interaction between lone-pair electrons and dangling bonds in the presence of atomic motion. Mott[3] proposed that the conductivity-modifying effect of certain impurity atoms on chalcogens could also be explained in terms of charged dangling bonds. A principal feature of the charged-defect states proposed for chalcogenides is their spin-paired electronic configuration which explains the well documented absence of any observable ESR signals.[4,5]

We describe in this Letter an ac technique by which bulk dipole densities in the range proposed above can be detected and demonstrate its successful application both to *a*-Se which is a homopolar solid and several of its As alloys which do have some bond ionicity. The limitation of this technique is its inability to distinguish the particular structural-chemical origin of the contributing bulk dipoles.

The experimental problem posed in the search for charged defects arises with the need to detect the incremental contribution of defect dipoles to a total dielectric permittivity which is predominantly electronic in origin.[6] The solution we propose is to detect the participation of these dipoles in a specific molecular relaxation process. The relaxation process we induce is common to all amorphous solids and involves the large-scale cooperative atomic motion which is thermally excited at the glass transition temperature. This relaxation process can always be detected by dynamic mechanical measurements but is only manifested dielectrically if there are deformable dipoles in the bulk to provide the necessary coupling of the ensuing molecular motion to an ac electric field.

In the ac measurement both components of the ac current are detected synchronously by using a lock-in amplifier system in conjunction with an operational preamplifier. The detected current components are then recorded at a selected frequency as temperature is swept linearly at a desired rate in either direction. Complementary low-frequency relaxation data are obtained from dc thermally stimulated depolarization (TSD) measurements on the same electroded samples. Other experimental and interpretative details have been fully described in a prior publication.[7]

Amorphous films were prepared by flash evaporating at 10^{-6} Torr a charge of the appropriate 99.999%-purity starting material onto an aluminum substrate held at the respective glass transition temperature to assure vitrification.[8] Uniformity of the arsenic profile was verified by energy dispersive x-ray analysis. X-ray photoemission spectroscopy does not reveal any chemically incorporated oxygen within detectable limits (0.1% monolayer) although there is appreciable physisorbed oxygen on film surfaces. The absence of room-temperature ESR in these films seems to preclude both paramagnetic oxygen-selenium charge-transfer states and the organoselenium radical complexes which are sometimes detected as a contaminant in selenium.[4]

The single dielectric relaxation detected in these films was clearly assignable to the glass transition because of its proximity to the actual dilatometric glass transition temperature,[9] its shift to higher temperature at a given frequency with As doping, and an overall frequency and temperature dependence readily distinguishable from the behavior of various local-mode processes.[10] Figure 1(a) shows the component of ac current proportional to ϵ'' which is recorded when a 100-

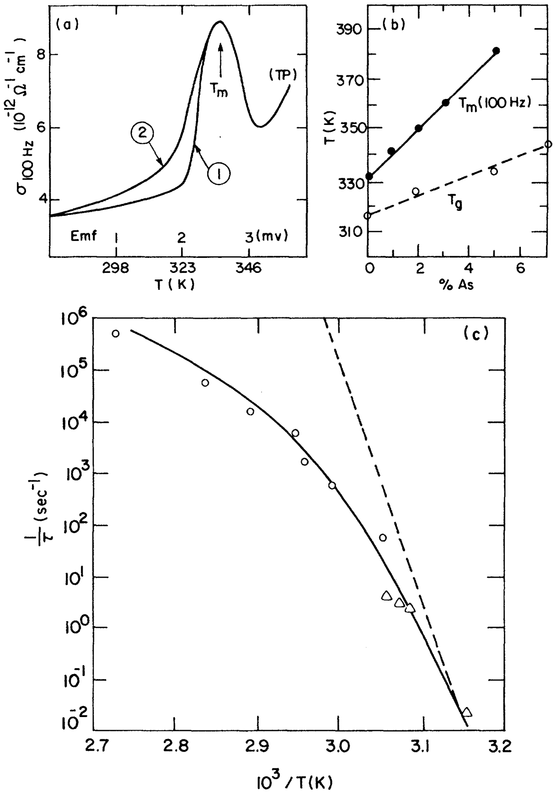

FIG. 1. (a) ac current component proportional to ϵ'' represented as an ac conductivity vs emf of copper-Constantan thermocouple. Frequency is 100 Hz and ac bias is 10 mV rms. T_m is the temperature corresponding to the current maximum. TP is the highest temperature to which the sample is continuously cycled. Trace 1 was recorded during the first thermal cycle at 4 K/min of a 26-μm a-Se film after dark rest for 1 week at 295 K. Trace 2 is recorded within 1 h after trace 1 (see text). (b) Solid line is the shift in T_m produced by As alloying. Data were recorded under conditions of (a). Dashed line is the shift of the glass transition temperature with As concentration as determined calorimetrically. (c) Relaxation rate vs $10^3/T$ (K^{-1}) from ac experiments (circles) and dc TSD measurements (triangles). Sample is 26-μm a-Se film. Solid line is calculated using the WLF equation, the standard parameters $c_1 = 40$ K and $c_2 = 51.6$ K, and $T_g = 317$ K from calorimetric data. $\tau_g = 50$ sec gives the best fit to the data. Dashed line illustrates the strong deviation of the data from simple, singly activated behavior.

Hz, 10-mV-rms bias is applied to a 26-μm a-Se sample while temperature is scanned upward at 4 K/min. The recorder X axis is driven directly by a compensated copper-Constantan thermocouple. The Y axis scale is converted to the equivalent ac conductivity. Two successive current traces are illustrated: Current trace 1 is recorded on a sample stored in the dark at room temperature for about a week and shows pronounced truncation at low temperature. The scan is terminated at the temperature designated TP and the temperature is quickly lowered at about 10 K/min to minimize the possibility of crystallization. Trace 2 is the next scan run under identical conditions and no longer shows the original truncation. All subsequent scans are identical to scan 2. If the same film is stored in the dark at room temperature for about a week after thermal cycling the first scan recorded under the conditions described above will reproduce trace 1 identically. We designate the temperature at which the current exhibits its peak value as T_m. The parameter T_m is found to exhibit a distinctive frequency dependence in the ac measurement at fixed scanning rate and a well-defined scanning-rate dependence in the dc TSD experiment. In Fig. 1(b) we show the observed increase in T_m measured at 100 Hz when we increase the As content of the amorphous selenium films. The shift in the T_g as reported from thermodynamic measurements[9] on similar films is plotted for comparison. The shift in T_m with As concentration clearly reflects the increased glass transition temperature. Molecular relaxation at the glass transition is usually modeled by using a phenomenological relaxation distribution function to describe the ensuing cooperative large-scale molecular motion.[10] Experimentally, it can often be distinguished from simpler local-mode relaxation processes by the strong deviation of its temperature-dependent central relaxation time from simple singly activated behavior. For a large class of noncrystalline solids it has been found that the behavior of the central relaxation time can be approximated by the phenomenological equation of Williams, Landel, and Ferry[11] (WLF):

$$\tau(T) = \tau_g \exp\{-c_1(T - T_g)/[c_2 + (T - T_g)]\},$$

where $\tau(T)$ is the relaxation time at temperature T and τ_g the central relaxation time at the glass transition temperature. c_1 and c_2 are empirical constants and the values $c_1 = 40$ and $c_2 = 51.6$ K have been found to fit data on a relatively large collection of noncrystalline solids.[7,10] Using unimproved values for c_1 and c_2 and taking 317 K for the glass transition temperature of Se[9] we obtain an adequate fit to the experimental data for the choice $1/\tau_g = 2\times10^{-2}$ sec^{-1}. The calculated WLF expression is represented by the solid curve in Fig. 1(c). A mapping of the temperature-dependent relaxation rate is obtained from the ac

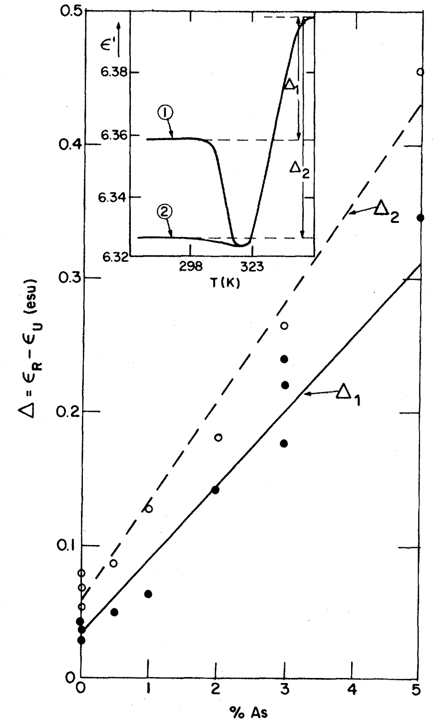

FIG. 2. Dielectric increment $\Delta = \epsilon_R - \epsilon_u$ associated with glass-transition relaxation vs As concentration determined from ac current component proportional to ϵ'. Several data sets on Se and the 3%-As alloys are included to illustrate sample-to-sample scatter. Δ_1 and Δ_2 are defined for a selenium sample by the arrows on traces 1 and 2 as shown in the inset. Traces 1 and 2 correspond to thermal histories described in Fig. 1(a) caption.

measurements by plotting the logarithm of the experimental frequency versus the reciprocal peak temperature[7] and is represented by circles in Fig. 1(c). In the TSD measurement the very-low-frequency mapping as calculated from the temperature of the current peak and the corresponding temperature scanning rate[7] is represented by triangles. Taken together this analysis provides an experimental characterization of the measured relaxation rate in Se spanning about eight orders of magnitude and demonstrates the general agreement with the WLF behavior which is characteristic of glass-transition–associated relaxation in many polymeric solids. Figure 2 is a plot of the dielectric increment $\Delta = \epsilon_r - \epsilon_\mu$ measured at 100 Hz for amorphous selenium and shows the increases that result with As doping. ϵ_r is the relative dielectric constant in esu of the relaxed sample and ϵ_μ is the room-temperature dielectric constant which is taken as the unrelaxed value. The variation with temperature of the dielectric constant at 100 Hz is represented in the inset with the trace designations paralleling Fig. 1(a) in all respects. The dielectric increment Δ_1 measured during the first thermal cycle of a well-rested sample is always smaller than the increment Δ_2 measured for all subsequent thermal cycles in a-Se and in the As-alloy samples. The systematic variation with thermal history of the dielectric properties which can be related to variation in the thermodynamic parameters of these samples is an interesting subject in its own right and will be dealt with in another article. We limit ourselves here to estimating the quantity $N\bar{\mu}_0^2$ from the dielectric increment measured during the first cycle of a well-rested selenium sample, where N is the volume dipole density and $\bar{\mu}_0$ the average unit dipole moment in vacuum. Using the expression[10]

$$\epsilon_R - \epsilon_\mu = \frac{3\epsilon_R}{2\epsilon_R + \epsilon_\mu} \frac{4\pi N\bar{\mu}_0^2}{3kT}\left(\frac{\epsilon_\mu + 2}{3}\right)^2$$

and our data we estimate $N\bar{\mu}_0^2 \approx 10^{-17}$ (esu^2 cm^{-1}) for a-Se, and choosing for $\bar{\mu}_0$ about 1 D leads to an estimate of $N \approx 10^{19}$ cm^{-3} for selenium. For the As-Se alloys one should expect some additional contribution from the bond dipoles and the dielectric increment is in fact observed to increase with As concentration. The estimated dipole density appears rather large for selenium[1] and it remains to extend these measurements to films prepared under ultrahigh-vacuum conditions (10^{-10} Torr) to minimize any contribution from impurities complexed in the structure.

We conclude with four observations: (1) A similar analysis of measurements made by us on amorphous polystyrene films leads to a bulk dipole density in good agreement with published results.[12] The chemical nature and strength of the unit dipole is known in this case.[10] (2) In comparing measurements on selenium samples made from different source materials in different evaporators we could detect no significant variations in dielectric increment or dissipation at the glass transition. (3) The infrared activity of trigonal Se is produced entirely by displacement-induced charge redistribution[13] (dynamic charge). If it is this process rather than a charged-defect population which provides the effective dipolar coupling required to observe dielectric activity at the glass transition of a-Se, then the present study is in fact the first reported manifestation of this mechanism in a low-frequency relaxation measurement. (4) The existence of bulk dipoles whatever their origin provides a unique opportunity to probe a primary molecular relaxation process and any associated microstructural or conformational changes in an important class of amorphous semiconductors.

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[1] M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. 37, 1504 (1976).

[2] R. A. Street and N. F. Mott, Phys. Rev. Lett. 35, 1293 (1975).

[3] N. F. Mott, Philos. Mag. 34, 1101 (1976).

[4] M. Abkowitz, J. Chem. Phys. 46, 4537 (1967).

[5] S. C. Agarwal, Phys. Rev. B 7, 685 (1973).

[6] See, for example, A. I. Lakatos and M. Abkowitz, Phys. Rev. B 3, 1791 (1971), ~~Table~~ I.

[7] M. Abkowitz and G. Pfister, J. Appl. Phys. 46, 2559 (1975).

[8] D. G. Ast, J. Vac. Sci. Technol. 10, 748 (1973).

[9] M. B. Myers and E. J. Felty, Mater. Res. Bull. 2, 535 (1967).

[10] N. G. McCrum, B. E. Read, and G. Williams, *Anelastic and Dielectric Effects in Polymeric Solids* (Wiley, New York, 1967).

[11] M. L. Williams, R. F. Landel, and J. D. Ferry, J. Am. Chem. Soc. 77, 3701 (1955).

[12] O. Broens and F. H. Muller, Kolloid Z. 140, 121 (1955), and 141, 20 (1955).

[13] R. Zallen, Phys. Rev. 173, 824 (1968); I. Chen and R. Zallen, Phys. Rev. 173, 833 (1968); R. Zallen and G. Lucovsky, in *Selenium*, edited by R. A. Zingaro and W. C. Cooper (Van Nostrand-Reinhold, New York, 1974), p. 148.

Effects of Energy Exchange on Vibrational Dephasing Times in Raman Scattering

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It is shown that the Raman line-shape function and/or vibrational dephasing times can reflect random frequency modulation of high-frequency vibrational modes via exchange with low-frequency modes. When exchange is incorporated into the vibrational correlation function, lifetimes and scattering rates between modes can be quantitatively determined from the temperature dependence of the spontaneous Raman spectrum. Finally, some experimental results on vibrational redistribution are presented which demonstrate the salient features of the theory.

The effects of molecular interactions and molecular motion are fundamental to an understanding of vibrational relaxation and redistribution in liquids and solids. Until recently, most of the information on vibrational dephasing and relaxation has come from an analysis of the spontaneous Raman linewidth and line shape which Gordon[1] first represented as the Fourier transform of a polarizibility autocorrelation function. In general terms it is thought that contributions to the vibrational part of the correlation function decay via events which cause relaxation or redistribution of the excited vibrational population among other degrees of freedom (T_1 processes) and events which randomly modulate the vibrational phase (T_2 processes).

Recent experiments by von der Linde, Laubereau, and Kaiser[2] have separated the two contributions in the case of symmetric C-H stretching modes in a variety of liquids. The decay time of the vibrational correlation function was obtained from a convolution of their laser pulse shape with an assumed vibrational correlation function whose Fourier transform was related to a Lorentz spontaneous Raman line-shape function. Both the interpretation of the Raman line shape and the deconvolution of the vibrational dephasing time from stimulated Raman scattering assumed that all phase memory is lost during the elastic scattering process or during the inelastic scattering process and thus resulting linewidths, determined by T_1 or T_2, represent the "true" decay time of the autocorrelation function.

In this Letter we would like to demonstrate that the neglect of phase memory in the scattering process can in many instances lead to serious misinterpretations of the vibration correlation function for spontaneous and stimulated Raman scattering. Furthermore, we will demonstrate that the incorporation of intermolecular or intramolecular energy exchange into the vibration correlation function allows one to extract (i) the mechanisms responsible for vibrational dephasing and relaxation when energy exchange is im-