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Amorphous Semiconductors

Details of illustrations in this document may be better studied on microfiche

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SUMMARY

The study of glasses under pressure has been extremely rewarding insofar as the conventional (oxide) glasses are concerned. The study of semiconducting glasses has only begun. This project is concerned with the correlation of electrical properties with the thermodynamic state of the system. We hope to identify the electrical conduction mechanism and to determine the equation of state. The former will permit the better utilization of these materials in electronic devices and the latter will enable the potential military user to better assess the behavior under extreme conditions.

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NARRATIVE

The primary effort during the past six months was to acquire the necessary apparatus and skills to perform the measurement program described in the proposal. This segment of the project is now substantially complete.

The heart of the apparatus is the 10 kbar press designed and built by F.C. Sawin and D.S. Hughes. Much of the operational procedure died with Professor Hughes last year, and a substantial effort has been directed toward reacquisition of the understanding lost with him. We now operate the press successfully, routinely, and (we hope) safely. Thermal excursions have been limited to a few hundred degrees, but furnace operation to higher temperatures will not be a problem. Pressure measurement is carried out by manganin gauges made in our laboratory. In view of the strong dependence of resistance on pressure in the chalcogenide alloys it seems highly probable that we will be able to develop secondary standards from the materials we are studying. The insensitivity to impurity, etc., which contributes to the general attractiveness of amorphous chalcogenide alloys in electronics, also makes pressure sensors made from these alloys of wide potential usefulness. Temperature measurements are currently made using Pt vs. PtRh thermocouples.
Samples have been fabricated from the Ge:Te:As alloy system as shown on the accompanying graph (Figure 1). Samples are made by filling a quartz tube with weighed amounts of material in a He-filled glove box. The tube is then sealed off under vacuum, placed in a furnace and heated to 800°C for 12 to 24 hours. It is quenched by ejecting it into a tub of iced brine. Sectioning and shaping is then done with an air-driven drill and conventional polishing apparatus.

D.C. resistivity data have now been taken 0-10 kbar and 20-100°C. The trends reported by the ECD group are confirmed. There are signs, however, of curvature in the \( \ln \sigma \) vs \( P \) curves. All data must still be regarded as preliminary. AC data are yet to be taken.

Sound velocity data have been taken 0-2kb at room temperature and 30-200°C at atmospheric pressure. The actual experimental parameter is, of course, transit time for the sound pulse in the sample. Conversion of this datum to sound speed requires estimates of the change in sample lengths with pressure. We hope soon to measure this quantity directly but currently employ a calculational procedure due to Cook in our analysis. If we assume the material to be isotropic and consider a sample of length \( \ell \), then the compressibilities are

\[
\kappa_T = -\frac{3}{\ell} \frac{\partial \ell}{\partial P} \left|_T \right. = \gamma \kappa_S = \frac{3\gamma}{\ell} \frac{\partial \ell}{\partial P} \left|_S \right.
\]

where subscripts \( T \) and \( S \) refer to isothermal and adiabatic
Air-quenched glass-forming region.

Tg isotherms

samples
conditions, respectively; \( \gamma \) is the ratio of the specific heats. If the pressure changes the length from \( l_0 \) to \( l = l_0/s \) then

\[
\kappa_T = \left( \frac{3}{3} + \frac{\gamma s}{\gamma P} \right) T \quad \text{and} \quad \rho = s^3 \rho_0,
\]

where \( \rho \) is the density.

The sound speeds are

\[
v^2 = \frac{1}{\kappa_s} + \frac{4\rho'}{3} = \frac{l_0^2}{s^2 t^2},
\]

and

\[
\nu_s^2 = \frac{\mu'}{\rho} = \frac{l_0^2}{s^2 t_s^2},
\]

where subscripts \( l \) and \( s \) denote longitudinal and shear velocities or transit times, adiabatic shear modulus is \( \mu' \). We determine \( \mu' \) from \( v_s \) and solve for \( \kappa_s \)

\[
\kappa_s = s^3 \rho_0 l_0^2 \left[ \frac{1}{t^2} - \frac{4}{3 t_s^2} \right]^{-1}
\]

then

\[
\frac{ds}{s} = \frac{\gamma}{3} \kappa_s dP
\]

may be evaluated upon inserting \( \kappa_s \) to yield

\[
s = 1 + \frac{\gamma}{3 \rho_0 l_0^2} \left[ \int_{P_1}^{P_2} \left( \frac{1}{t^2} - \frac{4}{3 t_s^2} \right)^{-1} dP \right]
\]

At present we have only made longitudinal velocity
measurements and lack a value for $\gamma$. We have therefore assumed $t_s = 1.3t_\ell$, and solved for $s$ as a function of $\gamma$, then computed $v_\ell = l_0/st_\ell$. Figure 2 shows the extreme answers for $\gamma = 1.0$ (harmonic oscillator) and $\gamma = 1.5$ (gas); the transit times were found to be linear in the pressure. We expect to shortly have $\kappa_T$ directly.

The ease of measuring transit time vs pressure prompted us to consider this parameter as a way of measuring the pressure. Heydemann\textsuperscript{3} has suggested temperature compensated pressure gauges using quartz and Al in series so that variations in sound speed with temperature will cancel. We nevertheless intend to further explore the chalcogenide alloys for this purpose.

We have also looked at the change in sound speed at the glass transition of one Ge:Te:As alloy. One normally sees a sound speed which decreases linearly with increasing temperature and an abrupt decrease in sound speed has been reported at the glass transition of Arochlor.\textsuperscript{4} Figure 3 shows our results which are in excellent agreement with Hilton's\textsuperscript{5} early report. We expect to extend these measurements above atmospheric pressure and to higher frequencies.
REFERENCES


PERSONNEL

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