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TEMPERATURE AND PRESSURE DEPENDENCE OF THE OPTICAL
AND ELECTRICAL GAP IN CHALCOGENIDE GLASSES

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The optical absorption edge E_g and the conductivity σ of two bulk chalcogenide semiconductor glasses were measured as functions of pressure and temperature. The shift of the absorption edge $(\partial E_g / \partial T)_p$ in the absorption range $10 < \alpha < 10^3 \text{ cm}^{-1}$ is about $-7 \times 10^{-4} \text{ eV/deg}$ at room temperature. The dilatation term contributing to this value was found to be an order of magnitude smaller than the phonon term and of opposite sign. The absorption edge shifts essentially parallel with pressure, with $(\partial E_g / \partial p)_T = -(1.20 \pm 0.1) \times 10^{-5} \text{ eV/bar}$ for one material; the other was comparable. Over the temperature range $270 \text{ K} < T < 340 \text{ K}$, the pressure coefficient of the conductivity $(\partial(\ln \sigma) / \partial p)_T$ is $(4.1 \pm 0.4) \times 10^{-4} \text{ bar}^{-1}$. The pressure shift of the conductivity activation energy $\partial(\Delta E_o) / \partial p$ is approximately $-2.1 \times 10^{-5} \text{ eV/bar}$.

> 10^-4 eV/bar

1. INTRODUCTION

Many amorphous semiconductors are transparent in the infrared, and show an onset of optical absorption near a photon energy E_g close to the thermal activation energy ΔE_0 of the electrical conductivity.¹ A quantitative comparison of E_g and ΔE_0 is difficult to make because a portion of ΔE_0 may be contributed by a thermally activated mobility. Furthermore, for amorphous semiconductors the choice of E_g depends on a somewhat arbitrary procedure for distinguishing the tail and band absorption regions, in which the optical absorption shows different energy dependencies.² However, the exponential absorption edge shows an energy shift as a function of hydrostatic pressure which is substantially independent of the absorption constant ($10 < \alpha < 10^3 \text{ cm}^{-1}$). Therefore one can compare $(\partial E_g / \partial p)_T$ with $\partial(\Delta E_0) / \partial p$ without being concerned with the detailed shape of the absorption edge.

Knowing $(\partial E_g / \partial p)_T$ and the values for the compressibility and the thermal expansion coefficient, one can correct the measured temperature dependence of the absorption edge $(\partial E_g / \partial T)_p$ for the dilatation term and obtain the edge shift in the absence of dilatation, $(\partial E_g / \partial T)_V$.

For these purposes we measured the temperature and pressure dependence of the electrical conductivity and the absorption edge of bulk specimens of semiconducting glasses.

2. EXPERIMENTAL

For this study semiconducting alloy glasses were chosen which show no evidence of phase separation or of devitrification at ordinary temperatures. The samples were prepared by heating appropriate amounts of the materials in an evacuated and sealed silica tube to $T = 1250$ K in a rocking furnace for 16 hours. The ingots were water quenched. Samples were cut and polished to thicknesses varying between 30 and 7500 μm .

Electrical measurements were made with non-blocking contacts of In or carbon at dc fields below 10^3 V/cm. The transmission data were corrected for reflection losses. All pressure data were taken in an Aminco optical transmission cell with sapphire windows, using oil as a pressure medium. The temperature in the cell was monitored with a thermocouple placed in close proximity to the sample.

Table I gives the composition of the samples, the density ρ , the volume expansivity $\beta = V^{-1}(dV/dT)$, the compressibility $K_S = V^{-1}(dV/dp)$, as well as σ_0 and ΔE_0 in the equation

$$\sigma = \sigma_0 \exp(-\Delta E_0/2kT) \quad (1)$$

The values of several room temperature derivatives are also listed.

Table I

Composition	Ge ₁₆ As ₃₅ Te ₂₈ S ₂₁	Te ₈₀ Si ₂₀
σ_0	$1.1 \times 10^2 (\Omega - \text{cm})^{-1}$	$\sim 3 \times 10^2 (\Omega - \text{cm})^{-1}$
ΔE_0	1.10 eV	~ 1.0 eV
κ_S	$7.6 \times 10^{-6} \text{ bar}^{-1}$	$8.4 \times 10^{-6} \text{ bar}^{-1}$
β	$4.2 \times 10^{-5} \text{ deg}^{-1}$	$5.1 \times 10^{-5} \text{ deg}^{-1}$
ρ	4.60 gm/cm ³	5.05 gm/cm ³
$\frac{\partial E_g}{\partial p} (\alpha = 10)$	$-1.2 \times 10^{-5} \text{ eV/bar}$	$-1.8 \times 10^{-5} \text{ eV/bar}$
$\frac{\partial \Delta E_0}{\partial p}$	$-2.1 \times 10^{-5} \text{ eV/bar}$	$-2.8 \times 10^{-5} \text{ eV/bar}$
$\frac{\partial E_g}{\partial T} (\alpha = 10)$	$-7.2 \times 10^{-4} \text{ eV/deg}$	$-7 \times 10^{-4} \text{ eV/deg}$

3. OPTICAL MEASUREMENTS

The optical absorption α of Ge₁₆As₃₅Te₂₈S₂₁ at 300 K and normal pressure is shown in Figure 1. The data is obtained from ten samples ranging in thickness from 30 to 7500 μm . As with most amorphous semiconductors the absorption increases exponentially with photon energy

at these lower values of α . The slope $d(\ln\alpha)/d(h\nu)$ is approximately $(0.045 \text{ eV})^{-1}$ at 300 K.

Figure 2 shows, for the same material, the temperature dependence of the absorption edge, i.e., the shift with temperature of the photon energy at which a given absorption constant is observed. This photon energy decreases linearly with increasing T near room temperature. The curves are expected to approach $T = 0$ with zero slope. The similarity of these curves for different α indicates that the absorption edge shifts without appreciable change of slope in the range where α is approximately exponential. At 300 K and $\alpha \approx 10^2 \text{ cm}^{-1}$ the temperature dependence $(\partial E_g / \partial T)_p$ is $-(7.2 \pm 0.1) \times 10^{-4} \text{ eV/deg}$.

The pressure dependence of the $T = 300 \text{ K}$ absorption edge is shown in Figure 3. The shift $(\partial E_g / \partial p)_T = -(1.20 \pm 0.1) \times 10^{-5} \text{ eV/bar}$, independent of p and α in the range where α is exponential. Expressing the pressure shift in terms of strain, one obtains a deformation potential $\xi_d = 1.6 \pm 0.1 \text{ eV}$.

The pressure dependence $(\partial E_g / \partial p)_\alpha$ is found to increase with temperature in the 300-330 K range measured, with a derivative $(\partial^2 E_g / \partial p \partial T)_\alpha = -(7 \pm 3) \times 10^{-8} \text{ eV/bar-deg}$.

The temperature dependence of the absorption edge can be expressed in terms of an explicit term and an implicit or dilatation term as

$$\left(\frac{\partial E_g}{\partial T}\right)_p = \left(\frac{\partial E_g}{\partial T}\right)_V + \left(\frac{\partial E_g}{\partial V}\right)_T \cdot \left(\frac{dV}{dT}\right) \quad (2)$$

or

$$\left(\frac{\partial E_g}{\partial T}\right)_p = \left(\frac{\partial E_g}{\partial T}\right)_V - \left(\frac{\beta}{K_S}\right) \cdot \left(\frac{\partial E_g}{\partial p}\right)_T \quad (3)$$

Because of the negative sign of $(\partial E_g/\partial p)_T$, the dilatation term turns out to be positive ($+ 0.7 \times 10^{-4}$ eV/deg). It is an order of magnitude smaller than $(\partial E_g/\partial T)_p$. Thus, the dominant temperature dependence of the absorption edge is caused by the electron-phonon interaction.⁴ The magnitude observed here does not differ much from that found in other vitreous and crystalline semiconductors.^{2,5} Hence the term appears to be rather insensitive to the absence of long range order.

4. CONDUCTIVITY MEASUREMENTS

The conductivity of the quaternary alloy increases exponentially with increasing pressure as shown in Figure 4. If one attributes this pressure dependence solely to change of the electrical activation energy ΔE_o , then one obtains $\partial(\Delta E_o)/\partial p = -2.1 \times 10^{-5}$ eV/bar, which is significantly larger than the shift $\partial E_g/\partial p = -1.2 \times 10^{-5}$ eV/bar of the optical absorption edge. Comparable results were obtained for the binary alloy. A similar discrepancy between the electrical and optical results was observed in As_2Se_3 .⁵

5. DISCUSSION

It is possible, however, that part of the observed increase of σ with pressure is caused by an increase of σ_0 . The temperature interval covered by this investigation is too small to allow a separation of the contributions of the preexponential factor and of the exponent to the conductivity change. A parallel shift of the conductivity curve with pressure without a change of slope was observed in $V_2O_5 - P_2O_5$ glasses,⁶ and was attributed to a decrease of the average separation of the vanadium atoms.

It should be noted that $(\partial E_g / \partial p)_T$ was obtained from the exponential tail of the absorption edge, whereas ΔE_0 is believed to govern the conductivity near the mobility edges.⁷ It remains to be seen whether the higher absorption region of non-direct transitions shows the same pressure shift as the tails. Furthermore, the shift $(\partial E_g / \partial p)_T$ of the absorption edge is the result of the net shift of both the valence and the conduction bands with their tails of localized states. $(\partial(\Delta E_0) / \partial p)_T$ on the other hand is the pressure shift of the separation between the Fermi level E_F and the mobility edge of the dominant carrier. If E_F is immobilized by a substantial density of localized states, $(\partial(\Delta E_0) / \partial p)_T$ reflects the pressure shift of one band only. This will differ in general from the net shift of both bands.

We wish to point out that ΔE_0 is not the mobility gap at $T = 0$ but significantly larger than that, since $\Delta E(T)$ will approach $T = 0$ with zero

slope, similar to $E_g(T)$ of Figure 2. If a comparison of the electrical gap with the optical gap is attempted at $T = 300$ K, one should correct ΔE_o , obtained from the slope of the conductivity curve at T , by the quantity $T\partial(\Delta E)/\partial T$. Although $\partial E_g/\partial T$ is the net temperature shift of both bands, it might be taken as a measure of $\partial(\Delta E)/\partial T$. For the quaternary alloy, 0.21 eV should be subtracted from ΔE_o , yielding 0.9 eV for ΔE at 300 K.

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* This research was supported in part by the Advanced Research Project Agency of the Department of Defense, under Contract No. DAHC 15-70-C-0187.

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- 3) The adiabatic compressibility was calculated from shear and longitudinal sound velocities kindly measured for us by Professor D. E. Bowen. The 10 MHz shear velocity was 1.22×10^5 cm/sec and the longitudinal velocity was 2.20×10^5 cm/sec at 300 K for the quaternary alloy, and 1.11×10^5 cm/sec and 2.00×10^5 cm/sec respectively for the binary alloy.
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FIGURE CAPTIONS

- FIGURE 1.** Optical absorption constant of bulk Ge-As-Te-S alloy vs. photon energy, at room and nitrogen temperatures. Small arrow on energy axis indicates twice slope of conductivity plot at room temperature.
- FIGURE 2.** Photon energy at which designated value of absorption constant is observed vs. temperature, for bulk Ge-As-Te-S alloy.
- FIGURE 3.** Optical absorption constant of bulk Ge-As-Te-S alloy vs. photon energy, for three values of hydrostatic pressure.
- FIGURE 4.** Electrical conductance of bulk Ge-As-Te-S alloy vs. hydrostatic pressure, at three different temperatures.

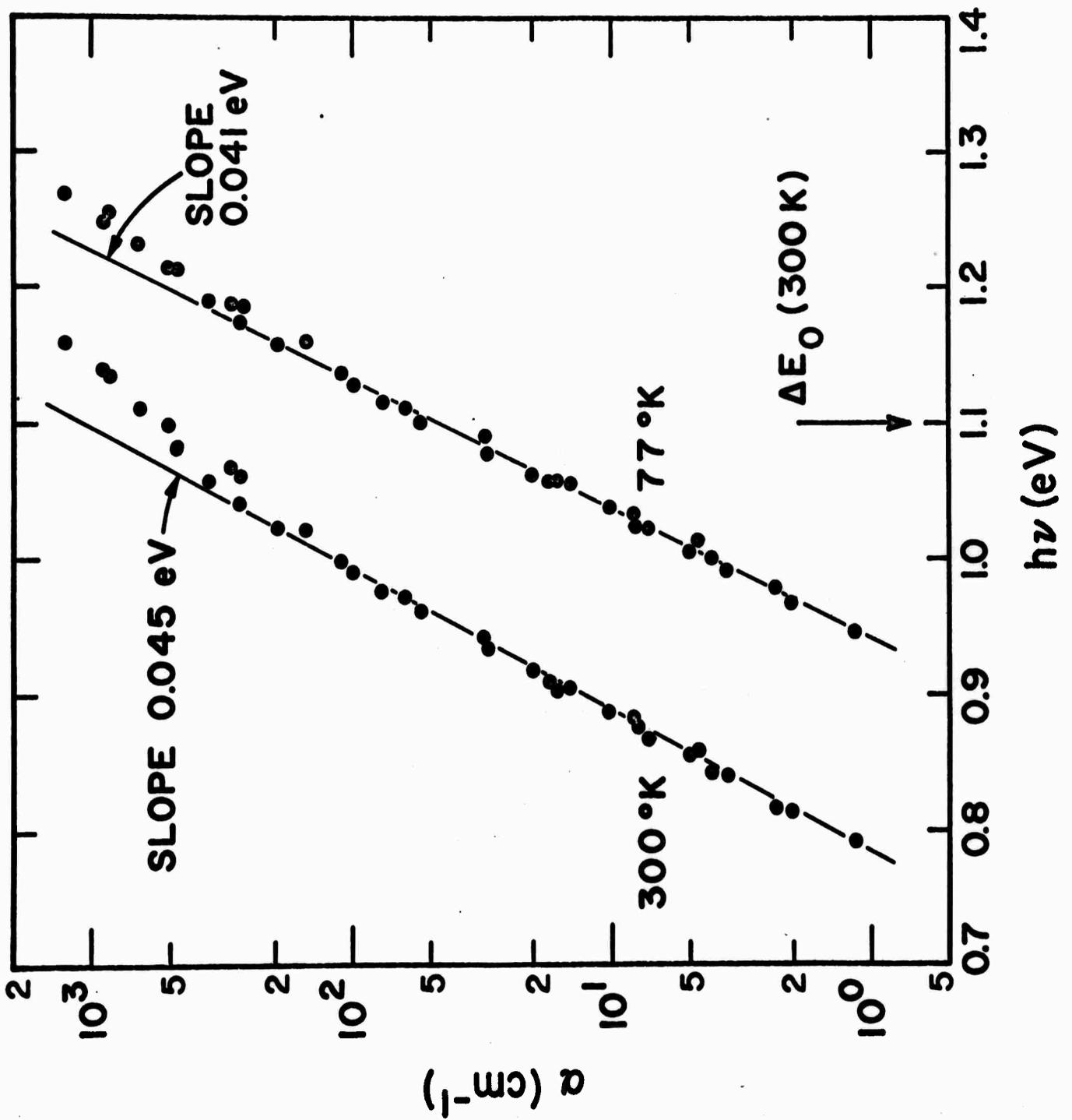


FIGURE 1.

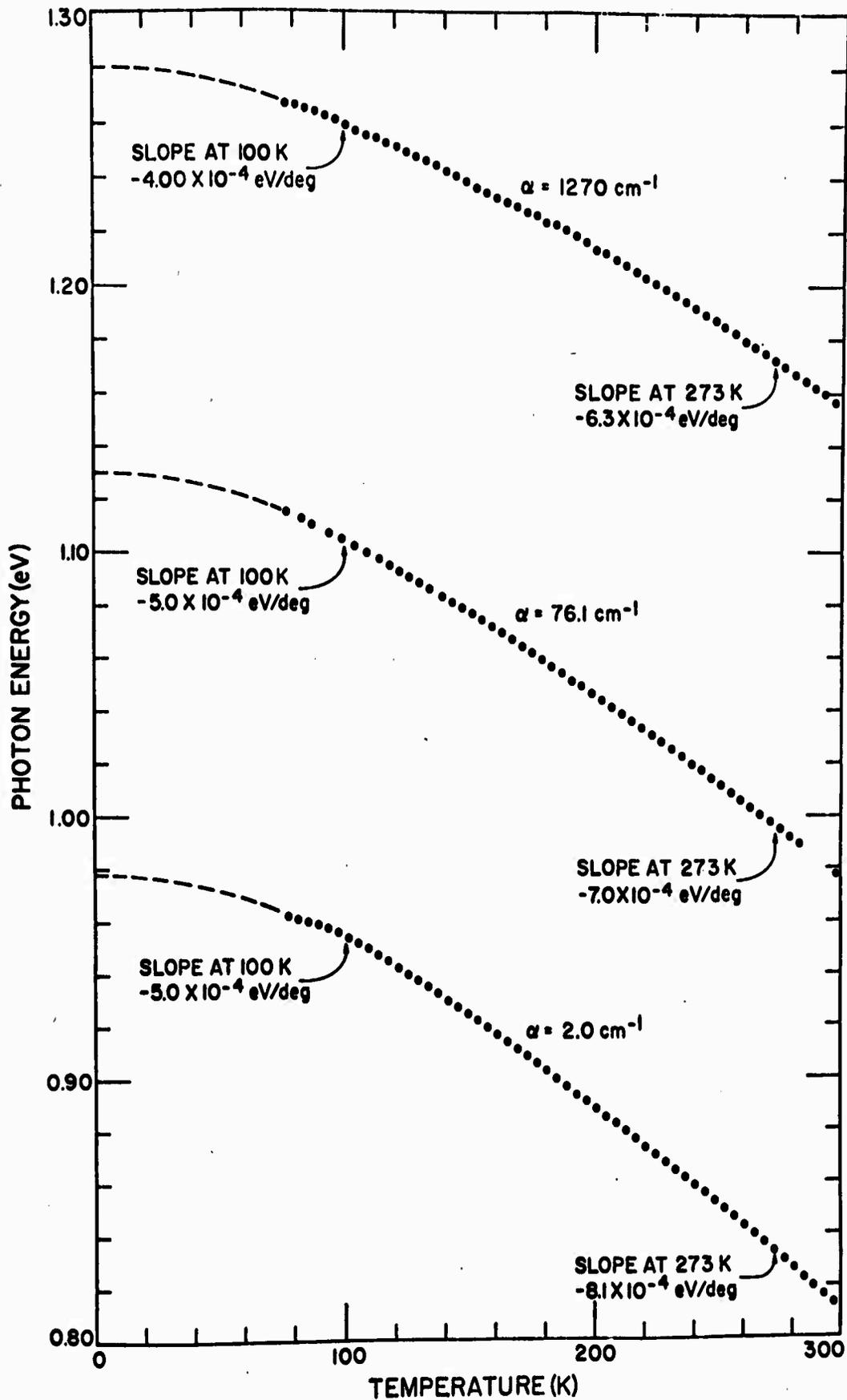


FIGURE 2.

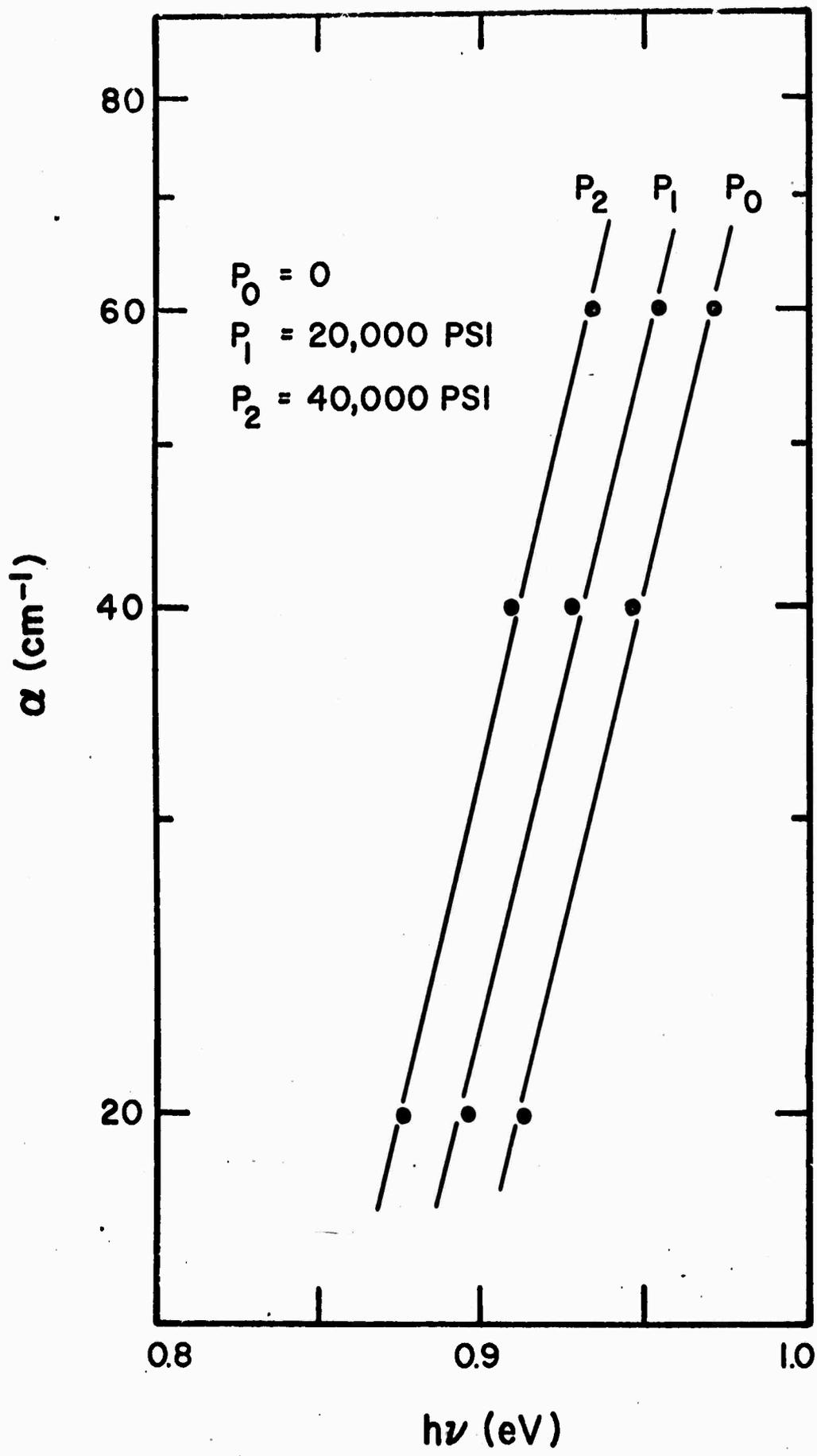


FIGURE 3.

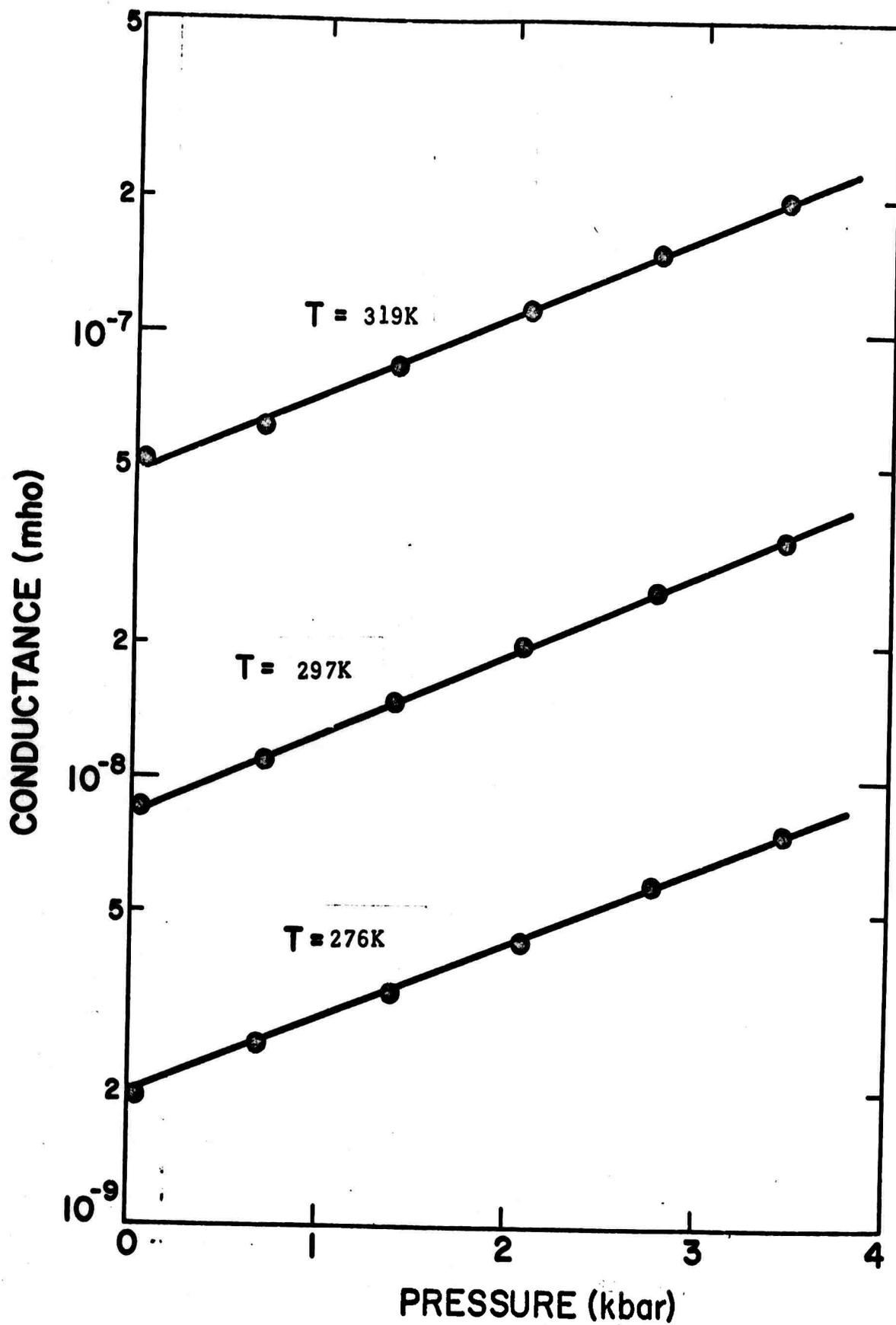


FIGURE 4.