

DEGRADATION OF THIN FILMS OF ZINC OXIDE BY ULTRAVIOLET RADIATION

by J. D. Hayes
R. R. Mitchell

June 1970

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DEGRADATION OF THIN FILMS OF ZINC OXIDE
BY ULTRAVIOLET RADIATION

By

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June 1970

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ABSTRACT

Optical transmittance, Hall effect, and spectral photoconductivity measurements have been made on thin films of zinc oxide in vacuum for various doses of ultraviolet irradiation. The transmittance was found to be unchanged after over 1,000 equivalent Sun hours ultraviolet irradiation. Hall effect and spectral photoconductivity studies indicate that ultraviolet irradiation of zinc oxide produces infrared-sensitive defect states near the conduction band.

Approved:

A handwritten signature in dark ink, appearing to read "R C Watson Jr", with a stylized flourish at the end.

R. C. Watson, Jr.
Vice President
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1. INTRODUCTION

The degradation of white oxide-based thermal control coatings by ultraviolet (UV) radiation has been a recognized problem for several years. The degradation consists primarily of an increase in the solar absorptance of the coating. This increased absorption generally appears in two spectral regions -- near the fundamental absorption edge and in the near infrared region. For zinc oxide these two bands are located at 0.4 to 0.6 micrometer and 0.8 to 2.4 micrometers.

A great deal of effort has been put forth to determine the mechanisms by which the UV radiation causes this increased absorption. The general model which has been advanced (Ref. 1) to explain the degradation of zinc oxide is described below.

The UV photons which are absorbed near the zinc oxide surface produce free electrons and holes. Photon-produced holes which diffuse to the surface recombine with electrons localized at surface oxygen atoms, neutralizing the surface oxygen. The neutralized surface oxygen is then evolved from the zinc oxide surface if the zinc oxide is in a vacuum environment. The first oxygen to be given off is chemisorbed oxygen, but as the irradiation is continued surface lattice oxygen is also emitted. The evolution of lattice oxygen leaves the surface rich in zinc.

The mechanisms by which the above actions cause the increased visible and infrared absorption have not been clearly defined, although several speculations have been put forth. One thought is that the enhanced infrared absorption is due to additional free carrier absorption caused by a UV-induced increase in the free electron concentration. An alternate explanation is that the infrared absorption results from an increase in the density and population of defect levels lying near the conduction band.

The additional visible absorption is also not clearly understood. One speculation is that the increased visible absorption is promoted by the creation of defect centers with energy levels lying just above the valence band. Another speculation is that the excess zinc diffuses into the bulk of zinc oxide and precipitates out at dislocations, causing severe lattice strain around the dislocations. This strain would distort the energy levels and could possibly decrease the band gap in the region of the dislocations, causing increased visible absorption. Such strain-induced absorption has been shown to occur in zinc oxide as the result of precipitation of lithium along dislocation lines (Ref. 2).

The work undertaken in this study was directed at determining how the UV radiation affects the impurity energy levels responsible for the electrical transport properties of zinc oxide. It was hoped that the UV-induced optical degradation could be correlated with the UV-induced electrical degradation. The investigation was carried out in two basic phases -- study of electrical properties and study of optical properties.

The optical properties studies consisted primarily of transmission measurements. The principal goal was to observe optical degradation by UV damage and relate this damage to electrical damage. No optical damage was ever seen in transmission studies. Possible reasons for this are discussed later in this report. Another important aspect of the optical experiments was the search for optical impurity states which might be responsible for the optical degradation. Finally, the role of excitons in the degradation was to be investigated, but the failure of the first optical studies eliminated the exciton experiments.

The electrical studies were designed to demonstrate the presence or absence of defect or impurity levels, sensitive to UV radiation, which might be responsible for the UV degradation of the optical properties.

The primary experiments included conductivity and Hall-effect measurements, photo-Hall effect measurements, thermally stimulated conductivity (TSC) measurements, and photoconductivity measurements. The measurements were conducted between liquid helium temperature and 100°C.

2. SAMPLE PREPARATION

The zinc oxide samples used in these studies were prepared by evaporating 99.999 percent pure zinc pellets from a molybdenum wire-wound basket under high vacuum conditions [10^{-7} torr (10^{-5} N/m²)] onto clean sapphire substrates. The substrates were subjected to an extensive cleaning procedure prior to placement in the vacuum system. This procedure consisted of soaking the substrates in a detergent solution for 1 hour, scrubbing the substrates using the detergent solution and a soft swab, rinsing the substrates in running tap water for about 15 minutes, soaking the substrates in a sulfuric-chromic acid solution, and then rinsing them in running tap water again for 15 minutes. The substrates were then rinsed in distilled water and degreased for 30 minutes in an isopropyl alcohol degreaser. The alcohol treatment removed all traces of grease. Upon removal from the degreaser, the slides were dry and hot, thus inhibiting the condensation of water vapor from the air. The slides were mounted in aluminum substrate holders and placed in the vacuum chamber where zinc was evaporated onto them.

After the evaporation, the zinc films were removed from the vacuum chamber and placed in a quartz furnace with an oxygen or air atmosphere. The films were heated at 700°C for 24 hours. This treatment converted the zinc films into zinc oxide films. The degree of oxidation of the films could be varied by varying the time in the furnace. Twenty-four hours were sufficient to oxidize the zinc film completely, while oxidations of less than 8 hours resulted in incomplete oxidation of the zinc film. The degree of oxidation of the films was determined from electrical conductivity measurements and from optical transmission measurements around the fundamental absorption edge. The criteria used to determine the completeness of the oxidation of a film were low electrical conductivity (less than 10^{-2} ohm⁻¹ cm⁻¹) and a relatively sharp fundamental absorption edge.

To facilitate ohmic connections to the leads, aluminum was evaporated onto the ends of the sample, and fine copper wires were soldered to the aluminum using indium as solder. Aluminum and indium were chosen because of their low work functions and their ease of application. These connections gave good ohmic contact, as illustrated by Figure 2-1.

All measurements were made with the samples in vacuum. The vacuum system used to pump the various chambers consisted of a National Research Corporation Model 206 Orb-Ion pump in conjunction with two Ultek cryosorption pumps. The chamber pressure could be varied from atmospheric pressure to 10^{-7} torr (10^{-5} N/m²) and was measured with either an ion gauge or a thermocouple gauge.

For the Hall measurements a Magnion UFS-3 magnet was used with a maximum pole separation of one inch.

The source of UV radiation was either a 250-watt mercury short-arc lamp or a 200-watt Xenon short-arc lamp. A liquid filter composed of 240 gm NiSO₄ and 45 gm Cu₂SO₄ dissolved in 1 liter of water was used to filter out the long wavelength radiation. UV grade fused silica lenses were used to focus the light onto the sample through either a spectrosil window or a Vycor tube.

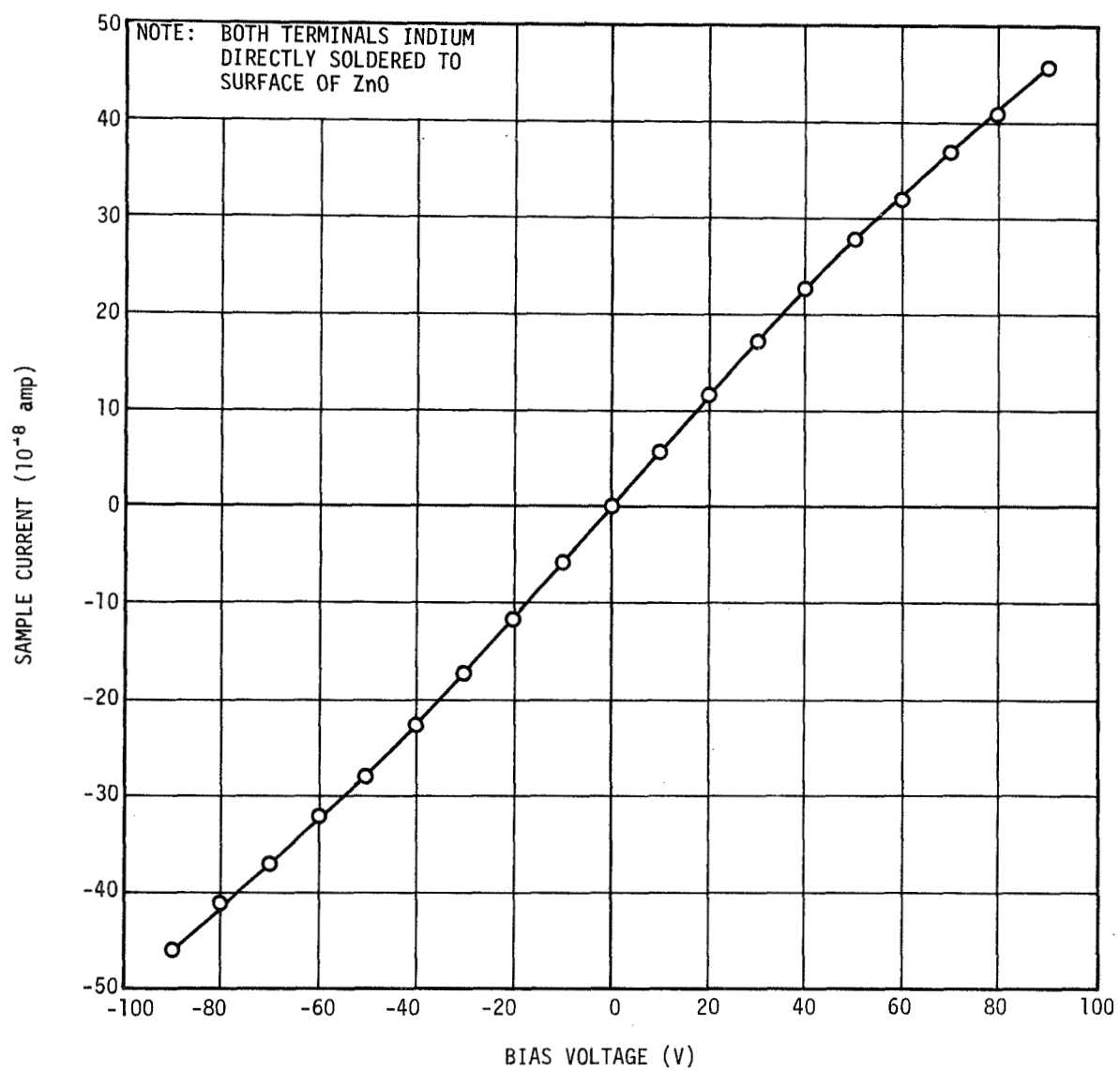


FIGURE 2-1. CURRENT-VOLTAGE CURVE FOR MELTED INDIUM CONTACT ON ZINC OXIDE FILM

3. OPTICAL PROPERTIES

PREVIOUS WORK

Heiland et al (Ref. 3) have reviewed the optical properties of zinc oxide up to 1958. Since their review, several investigators have extended the knowledge of zinc oxide optical properties. Reynolds et al (Ref. 4), Park et al (Ref. 5), Liang and Yoffe (Ref. 6), and Deitz et al (Ref. 7) have studied the role of excitons in the edge absorption of zinc oxide. Bond (Ref. 8), Park et al (Ref. 9), Burgiel et al (Ref. 10), and Vedam and Davis (Ref. 11) have measured the refractive index of zinc oxide. Hopfield and Thomas (Ref. 12) have measured polariton absorption in zinc oxide and Collins and Kleinman (Ref. 13) and Weiher (Ref. 14) have studied free carrier absorption in zinc oxide. Recently, Hengehold and Almassy (Ref. 15) have measured the reflectivity of zinc oxide in the vacuum ultraviolet spectral region.

Others, e.g., Sklensky et al (Ref. 16) and Zerlaut and Rogers (Ref. 17), have measured the change in the reflectance of powder samples of zinc oxide due to ultraviolet irradiation.

Teledyne Brown Engineering's measurements of the optical properties of zinc oxide were undertaken for two specific purposes:

- To characterize the thin zinc oxide films
- To monitor radiation damage and to correlate changes in the electronic properties with changes in the optical properties.

The transmittance of several zinc oxide films were measured in the ultraviolet, visible, and near infrared spectral ranges for various experimental situations, using the experimental arrangement depicted in Figure 3-1. Radiant energy from the monochromator was focused on the zinc oxide film or on a blank substrate mounted on the sample holder in the vacuum reflectance chamber. The sample holder was arranged

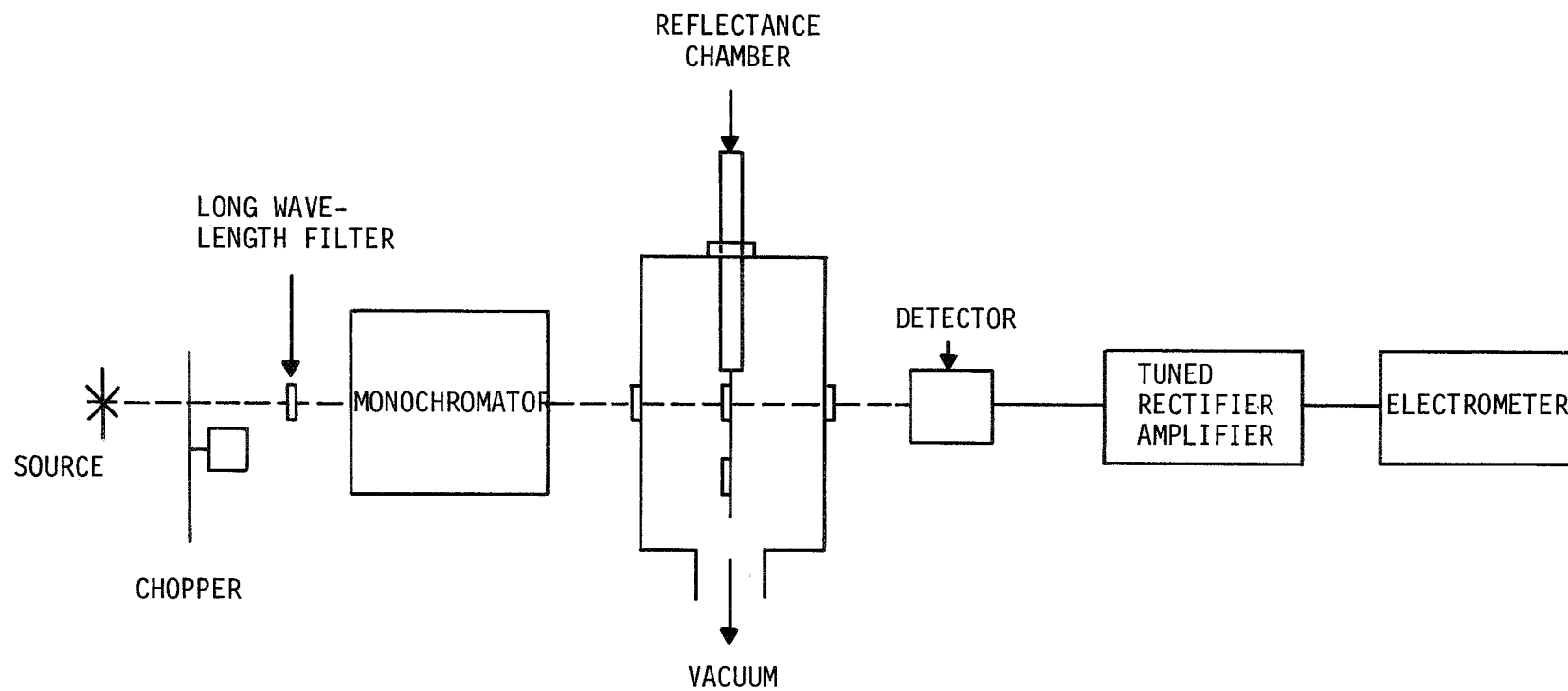


FIGURE 3-1. SCHEMATIC OF EXPERIMENTAL ARRANGEMENT FOR OPTICAL MEASUREMENTS

so that either the sample or the blank substrate could be placed in the beam from the monochromator. The radiant energy transmitted by the sample or the blank substrate was focused on the detector (a 1P28 photomultiplier or PbS cell) and the detector output processed and recorded. The data were corrected for dark current, electronic noise, and scattered radiant energy. The linearity of the electronics was calibrated regularly. The transmittance was reproducible to ± 0.002 .

Figure 3-2 shows the room temperature transmittance of a zinc oxide film in air for the spectral range from 0.24 to 2.5 micrometers. The transmittance spectra exhibited by this film are typical of all of the films that were prepared for study. The major features, other than the fundamental absorption edge, are the exciton structure immediately below the edge and the step-like absorption near 1 micrometer. The latter is possibly due to the presence of excess zinc in the film.

In characterizing the films the region of the fundamental absorption edge was primarily observed. A very sharp absorption edge was required for all the films on which further measurements were made.

From transmittance and reflectance data the thickness of zinc oxide required to absorb 90 percent of the nonreflected incident electromagnetic radiation as a function of incident photon energy was calculated. The results are shown in Figure 3-3 and are useful in visualizing the penetration depth of photons into zinc oxide. The peak absorption near 3.3 eV is due to exciton formation.

The second purpose of the optical measurements was to monitor radiation damage. To determine the feasibility of detecting radiation damage by optical transmission measurements, the following calculations were performed, based on the changes in powder reflectance measured by the Lockheed group (Ref. 16). The analysis is based on the powder reflectance model of Melamed (Ref. 18).

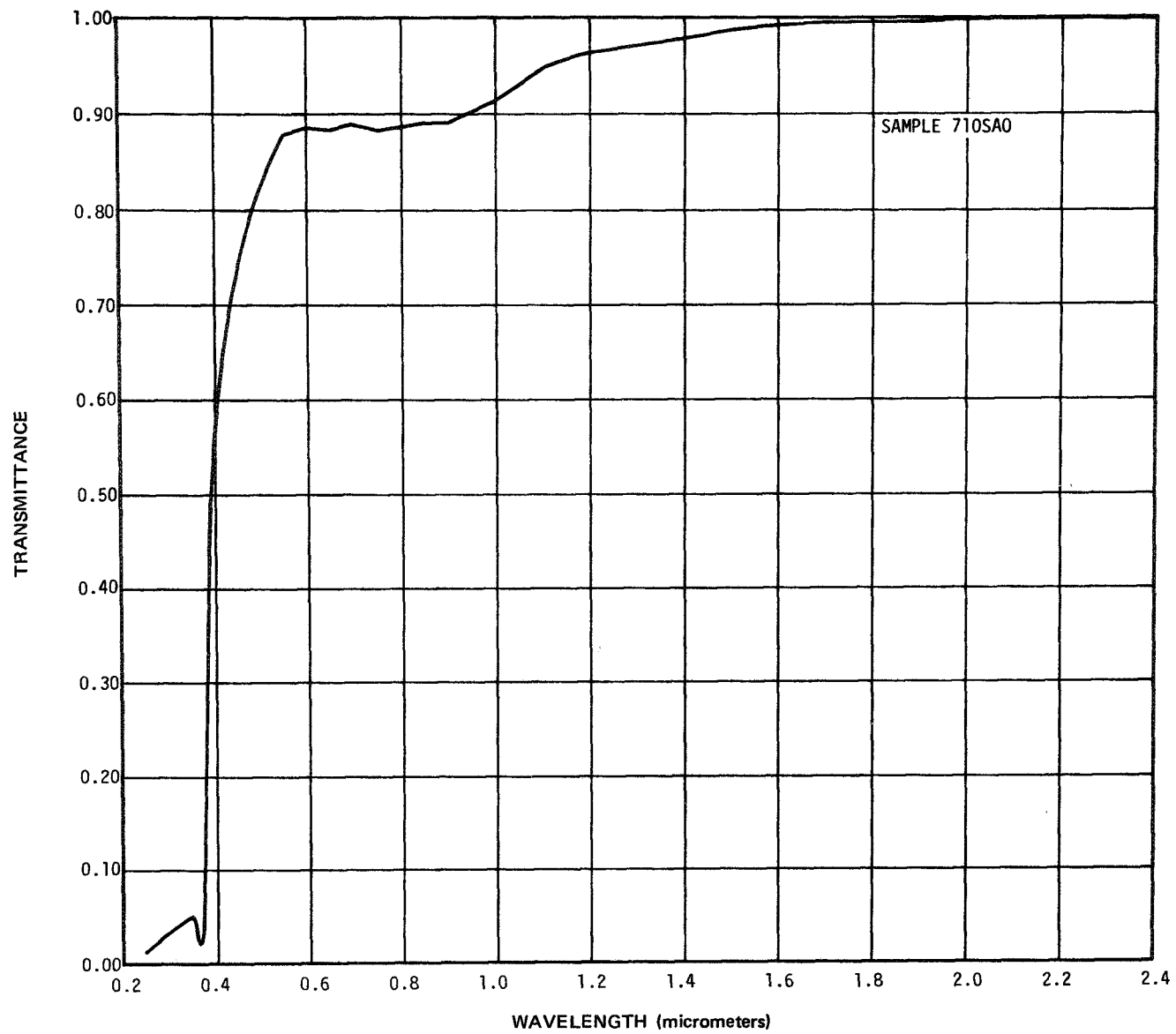
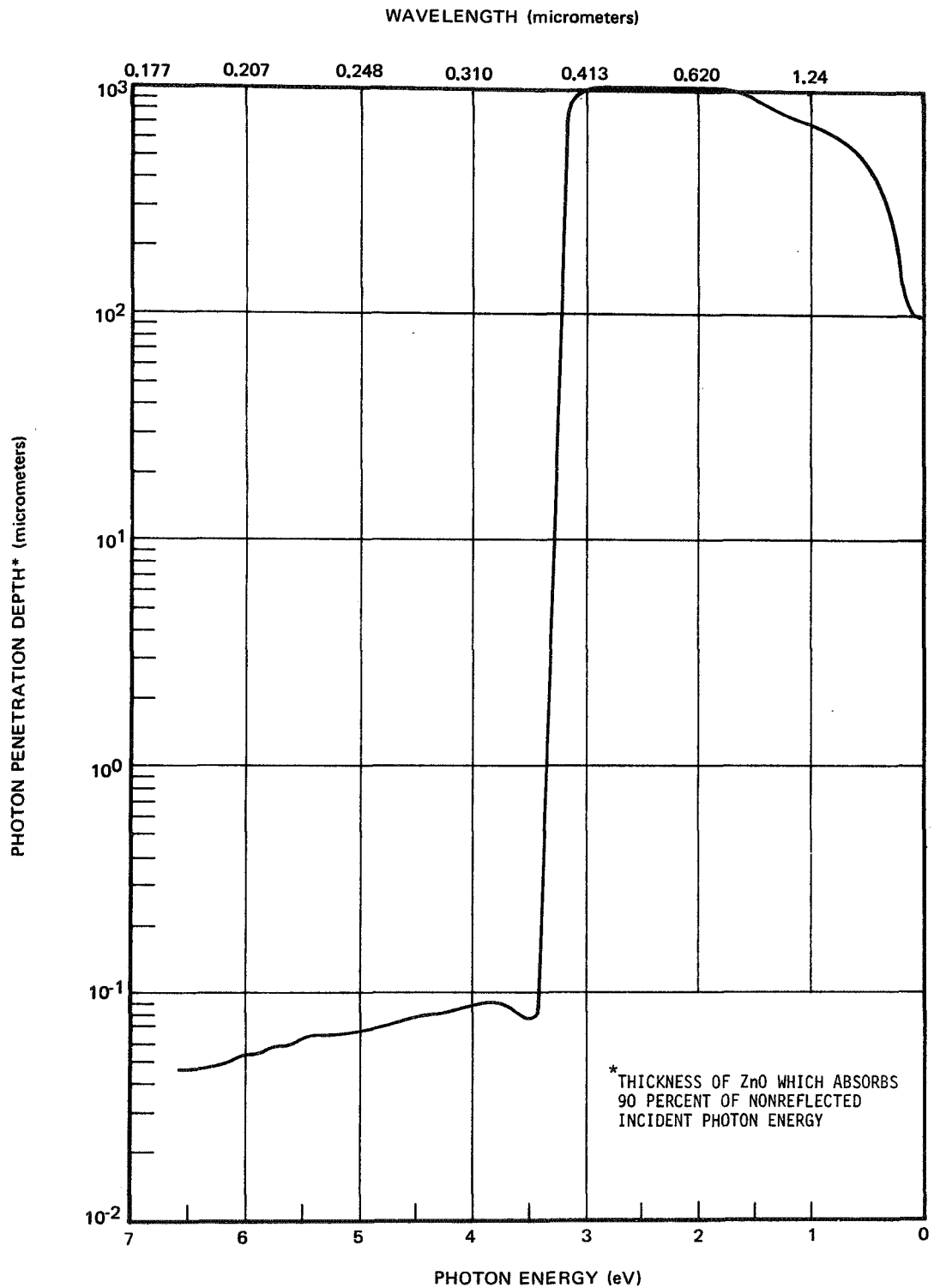


FIGURE 3-2. ROOM TEMPERATURE TRANSMITTANCE OF ZINC-OXIDE FILM



PHOTON PENETRATION DEPTH AS A FUNCTION OF PHOTON ENERGY

FIGURE 3-3. PHOTON PENETRATION DEPTH IN ZINC OXIDE AS A FUNCTION OF PHOTON ENERGY

Before ultraviolet irradiation, the absorption of infrared radiation by zinc oxide will be uniform throughout the zinc oxide and can be described at a particular wavelength, e.g., 2.0 micrometers, by the absorption coefficient at that wavelength, $\alpha_{2\mu}^{\circ}$. During ultraviolet radiation the absorption at 2 micrometers increases, with the change in the absorption proportional to the amount of ultraviolet radiation absorbed per unit thickness of sample.

For the ultraviolet radiation

$$I_{uv}^t(x) = I_{uv}^{\circ} \exp (-\alpha_{uv} x) \quad (3-1)$$

where

- I_{uv}° - incident ultraviolet radiation intensity
- $I_{uv}^t(x)$ - transmitted ultraviolet intensity at depth x
- α_{uv} - absorption coefficient of zinc oxide for ultraviolet radiation with $\lambda < 0$
- x - depth in zinc oxide measured from irradiated surface,

and

$$\frac{dI_{uv}^t(x)}{dx} = -\alpha_{uv} I_{uv}^{\circ} \exp (-\alpha_{uv} x) \quad (3-2)$$

The term $\{[(-dI_{uv}(x))/(dx)]\}$ represents the ultraviolet energy absorbed per unit time in increment dx at a depth x from the zinc oxide surface, so that

$$\alpha_{2\mu}(x) = \alpha_{2\mu}^{\circ} + \rho \alpha_{uv} I_{uv}^{\circ} \exp (-\alpha_{uv} x) \tau \quad (3-3)$$

where

- $\alpha_{2\mu}(x)$ - absorption coefficient of zinc oxide for radiation of $\lambda = 2.0$ micrometers after ultraviolet irradiation
- $\alpha_{2\mu}^{\circ}$ - absorption coefficient of zinc oxide for radiation of $\lambda = 2.0$ micrometers prior to ultraviolet irradiation
- ρ - efficiency of production of infrared absorption centers by the ultraviolet radiation
- τ - total time the sample is irradiated at intensity I_{UV}° .

ρ and α_{UV} are constant, and for fixed I_{UV}° and τ , a constant

$$A' = \rho \alpha_{UV} I_{UV}^{\circ} \tau \quad (3-4)$$

can be defined so that

$$\alpha_{2\mu}(x) = \alpha_{2\mu}^{\circ} + A' \exp(-\alpha_{UV} x) \quad (3-5)$$

describes the absorption coefficient as a function of depth after ultraviolet irradiation for τ time units at incident ultraviolet intensity I_{UV}° .

To determine the transmittance at 2 micrometers after irradiation, the absorption coefficient must be integrated.

$$I_{2\mu}^t(x) = I_{2\mu}^{\circ} \exp \left[- \int_0^x \alpha_{2.0}(x) dx \right] \quad (3-6)$$

or

$$\begin{aligned} T_{2\mu}(x) &= \exp \left[- \int_0^x \alpha_{2\mu}^{\circ} dx - \int_0^x A' \exp(-\alpha_{UV} x) dx \right] \\ T_{2\mu}(x) &= \exp \left[-\alpha_{2\mu}^{\circ} x + \frac{A'}{\alpha_{UV}} \exp(-\alpha_{UV} x) - 1 \right] \quad (3-7) \end{aligned}$$

By using Equation 3-7 and knowing α_{uv} , x , $\alpha_{2\mu}$, and A' , $T_{2\mu}(x)$ can be calculated. The only real unknown then is A' . This constant is determined by the ultraviolet irradiation dose and the efficiency of production of infrared absorption centers. Here the data of Reference 16 and the model of Reference 18 can be used to approximate A' . From these two sources, it appears that for 0.1-micrometer-diameter zinc oxide particles ultraviolet irradiated, α_{IR} increased from 60 cm^{-1} to $3,000 \text{ cm}^{-1}$. Now this increase actually occurs in uneven distribution rather than homogeneously as apparently measured.

From application of the mean value theorem α_{apparent} is given by

$$\alpha_{2\text{apparent}} = \frac{\int_0^{10^{-5} \text{ cm}} \alpha_{2\mu}(x) dx}{x \Big|_0^{10^{-5} \text{ cm}}} = 3000 \text{ cm}^{-1} \quad (3-8)$$

or

$$\begin{aligned} (3000 \text{ cm}^{-1})(10^{-5} \text{ cm}) &= 0.03 = \int_0^{10^{-5}} \left[\alpha_{IR} + A' \exp(-\alpha_{uv} x) \right] dx \\ 0.03 &= \alpha_{2\mu} x \Big|_{x=0}^{10^{-5}} + \int_0^{10^{-5}} A' \exp(-\alpha_{uv} x) dx \\ &= (60 \text{ cm}^{-1})(10^{-5} \text{ cm}) - \frac{A'}{\alpha_{uv}} \exp(-\alpha_{uv} x) \Big|_{x=0}^{10^{-5}} \\ &= 0.006 + \frac{A'}{3 \times 10^5 \text{ cm}^{-1}} \left\{ 1 - \exp \left[-(3 \times 10^5 \text{ cm})(10^{-5} \text{ cm}) \right] \right\} \end{aligned}$$

or

$$(0.03)(3 \times 10^5 \text{ cm}^{-1}) = A'(1 - 0.05) = 0.95 A'$$

so that

$$A' = \frac{9000}{0.96} \text{ cm}^{-1} \approx 10^4 \text{ cm}^{-1} \quad . \quad (3-9)$$

Substituting Equation 3-9 into Equation 3-7 and assuming that 10 percent of incident intensity is reflected and the film is 3×10^{-5} cm thick, then

$$T_{2\mu}(3 \times 10^{-5} \text{ cm}) = (0.9) \exp \left[- \int_0^{3 \times 10^{-5}} \alpha_{\text{IR}}^\circ dx - 10^4 \text{ cm}^{-1} \int_0^{3 \times 10^{-5} \text{ cm}} \exp -(3 \times 10^5 \text{ cm}^{-1})x dx \right] \quad (3-10)$$

$$= (0.9) \exp -(60 \text{ cm}^{-1})(3 \times 10^{-5} \text{ cm})$$

$$\exp -[(10^4 / 3 \times 10^5)][1 - \exp (-9)]$$

$$T_{2\mu}(3 \times 10^{-5} \text{ cm}) = (0.9) \exp (-0.002) \exp (-0.033) \quad (3-11)$$

$$T_{2\mu}(3 \times 10^{-7}) = 0.87 \text{ (after irradiation)} \quad . \quad (3-12)$$

The second factor on the RHS of Equation 3-11 multiplied by (0.9) would be the $T_{\text{IR}} (3 \times 10^{-5} \text{ cm})$ before irradiation; i. e., approximately 0.9 so that the change in T_{IR} with irradiation would be 0.03.

$$\Delta T_{\text{IR}} = 0.03 \quad . \quad (3-13)$$

The effect of evacuation on the transmittance of zinc oxide films was undetectable.

The effect of ultraviolet irradiation on the transmittance of zinc oxide films was studied extensively. The sample was mounted on the sample holder, and the transmittance of the sample in air was measured. Next, the reflectance chamber was evacuated and the sample transmittance again measured. After this, the sample was ultraviolet irradiated in the chamber in a dynamic, high-vacuum environment. After irradiation, the in situ transmittance of the sample was again measured. No change in transmittance was detected as illustrated by Figure 3-4, which shows the room temperature transmittance of a zinc oxide film 0.33 micrometer thick before and after 1,000 equivalent Sun-hours (ESH) of ultraviolet irradiation. Similar results were obtained for all other films measured including several films with approximately 2,000 ESH ultraviolet irradiation.

Several of the smoother-surfaced films were measured for specular reflectance before and after irradiation in vacuum. However, the reflectance values were so low that the measurement uncertainty was as great as the expected damage level; therefore, these measurements were discontinued.

The equipment is capable of measuring changes in transmittance of less than 0.01, so a change of 0.03 should have been readily observable.

FREE CARRIER ABSORPTION IN ZINC OXIDE

In the classical treatment of free carrier absorption in semiconductors, the equation of motion of an electron in an electromagnetic field of frequency ω subject to no restoring force is

$$m \frac{d^2 x}{dt^2} + m g \frac{dx}{dt} = e E \exp (i \omega t) \quad (3-14)$$

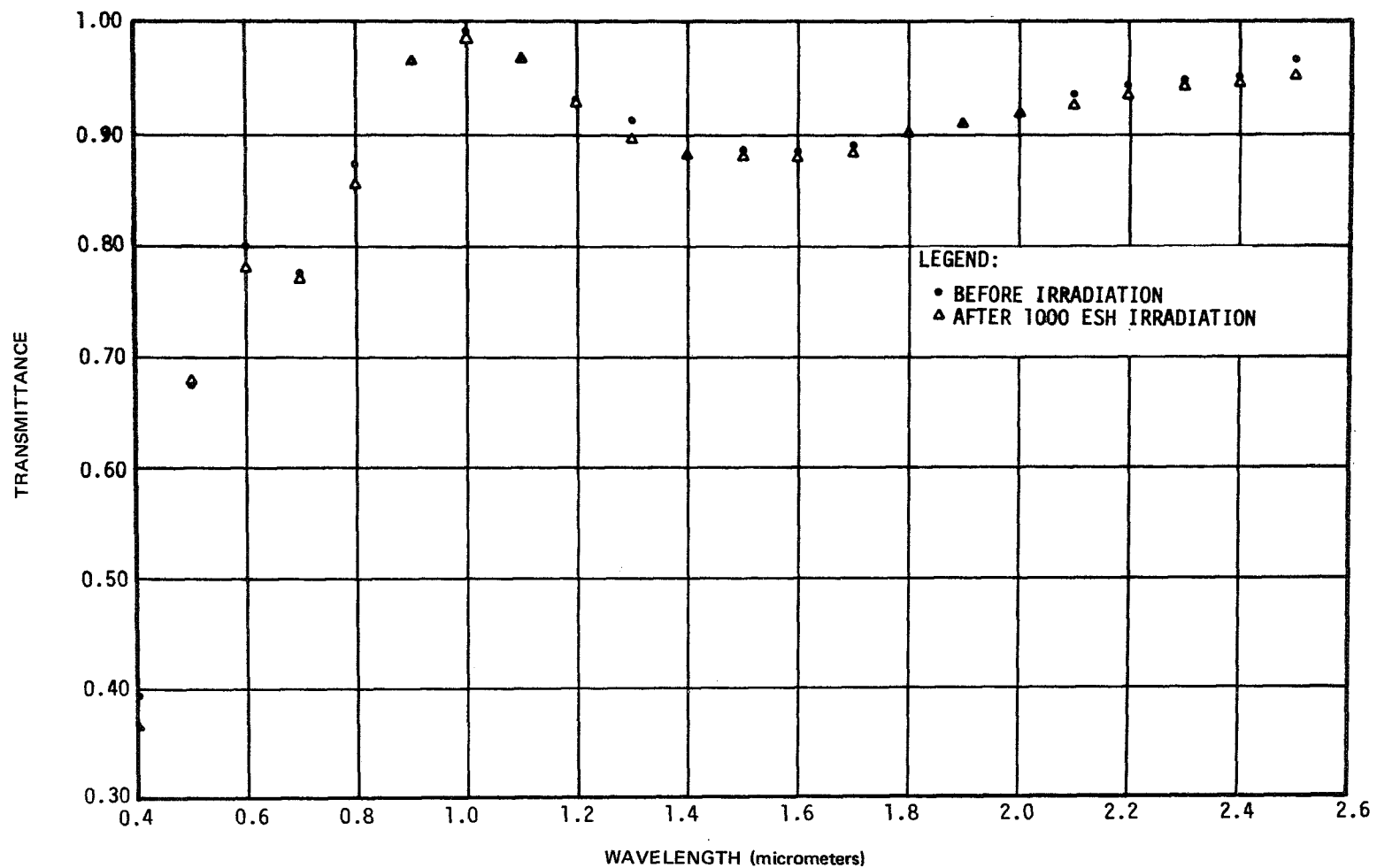


FIGURE 3-4. IN SITU TRANSMITTANCE OF ZINC-OXIDE FILM BEFORE AND AFTER 1,000 ESH IRRADIATION

where

- e - electronic charge
- E - peak field amplitude
- m - electron mass
- $(n - i k)$ - complex refractive index
- ϵ - permittivity .

Then

$$x = \frac{-e E/m}{\omega^2 - i \omega g} \quad (3-15)$$

where $g = 1/\tau = e/\mu m$ and μ is the electron mobility.

If there are N electrons per unit volume, the polarizability will be $P = N e x / E$ and the dielectric constant, K , will be given by $1 + P/\epsilon$.

$$K = (n - i k)^2 = 1 - \frac{N e^2 / m \epsilon_0}{\omega^2 - i \omega g} \quad (3-16)$$

and

$$n^2 - k^2 - i 2 n k = 1 - \frac{N e^2 / m \epsilon_0}{\omega^2 + g^2} - i \left(\frac{N e^2}{m \epsilon_0} \right) \left(\frac{g/\omega}{\omega^2 + g^2} \right) \quad (3-17)$$

so that

$$n^2 - k^2 - 1 = - \frac{N e^2 / m \epsilon_0}{\omega^2 + g^2} \quad (3-18)$$

and

$$2 n k = \frac{N e^2}{m \epsilon_0} \left(\frac{g/\omega}{\omega^2 + g^2} \right) \quad (3-19)$$

Since

$$k = \frac{\lambda \alpha}{4\pi} = \frac{\alpha c}{2\omega} \quad (3-20)$$

$$2n k \omega = c n \alpha = \frac{Ne\mu}{\epsilon_0} \left[\frac{1}{1 + (\omega \mu m/e)^2} \right] \quad (3-21)$$

or

$$c n \alpha = \frac{\sigma_0}{\epsilon_0} \left[\frac{1}{1 + (\omega \mu m/e)^2} \right], \quad (3-22)$$

then

$$\alpha = \frac{\sigma_0 e^2}{c n \epsilon_0 \omega^2 \mu^2 m^2} \quad (\text{for } \omega \mu m \gg e) \quad (3-23)$$

and

$$\alpha = \frac{\lambda^2 e^3}{4\pi^2 c^3 n \epsilon_0} \left(\frac{N}{m^2 \mu} \right) \quad (\text{for } \omega \mu m \gg e) . \quad (3-24)$$

From Equation 3-24 it is easily seen that when $\omega \mu m \gg e$, the free carrier absorption coefficient increases as λ^2 and as (N/μ) .

Equation 3-24 will be valid for zinc oxide for wavelengths shorter than $\lambda_{\max}$ where

$$\lambda_{\max} = \frac{2\pi c \mu m^*}{e} . \quad (3-25)$$

where m^* is the effective mass of electron.

If $m^* =$ free electron mass, then

$$\lambda_{\max} = \left(1.18 \frac{\text{micrometer}}{\text{cm}^2/\text{V-sec}} \right) \mu . \quad (3-26)$$

Thus, for powders and thin films, undamaged, $\lambda_{\max}$ is less than 1 micrometer. Rewriting Equation 3-22

$$\alpha = \frac{Ne\mu}{c n \epsilon_0} \left[\frac{1}{1 + \left(\frac{m\omega\mu}{e} \right)^2} \right] \quad (3-27)$$

$$\frac{m\omega\mu}{e} = \frac{2\pi c m \mu}{\lambda e} = 1.18$$

$$\begin{aligned} \alpha &= \frac{Ne\mu}{c n \epsilon_0} \left[\frac{1}{1 + (1.18)^2} \right] = \frac{Ne\mu}{c n \epsilon_0} \left(\frac{1}{1 + 1.39} \right) \\ &= \frac{670}{53.1} \text{ cm}^{-1} = 12.6 \text{ cm}^{-1} \end{aligned} \quad (3-28)$$

This value of α is very close to the value determined from thin film measurements of Hayes and Mitchel (Ref. 19) ($\alpha = 11 \text{ cm}^{-1}$) and crystal measurements of Arneth (Ref. 20) ($\alpha \approx 10 \text{ cm}^{-1}$).

For crystals $\mu \approx 100 \text{ cm}^2/\text{V-sec}$. This would make $\lambda_{\max} = 100$ micrometers. The value of σ_0 for crystals is approximately $1 \Omega^{-1} \text{ cm}^{-1}$. Then

$$\alpha = \frac{\sigma_0}{c n \epsilon_0} \frac{1}{(\omega \mu m/e)^2}$$

$$\alpha = 1.35 \times 10^{-2} \text{ cm}^{-1}$$

Thus, free carrier absorption in crystals should not be appreciable in the near infrared region, unless it occurred at the surface.

From Equation 3-24 it is seen that the free carrier absorption is proportional to (N/μ) rather than to N only, as is usually considered. for most materials where μ is constant. However, when studying

irradiation effects on materials, the mobility should not be assumed constant. As shown in Figures 4-17 and 4-18, the mobility actually changes more than the carrier concentration.

From the zinc oxide data, the free carrier absorption should actually decrease with ultraviolet irradiation. Consequently, the increased IR absorption observed by other workers must be due to an increase in the concentration and/or population of IR-sensitive defect centers.

DISCUSSION

The optical transmittance studies showed no change in the transmittance of a film after 1000 ESH ultraviolet irradiation. As stated earlier, a change in transmittance of 0.03 was expected from applying the powder reflectance models of Melamed (Ref. 18) and Johnson (Refs. 21 and 22) to the data of Sklensky et al (Ref. 16). The lack of transmittance change is inconclusive. It is possible that the powder reflectance models used were not descriptive of the zinc oxide powders, since the mean diameter of a particle of SP-500 zinc oxide is less than the wavelength of the light considered in the analysis. However, the reflectance before ultraviolet irradiation of the zinc oxide powder matches very closely the reflectance predicted by the Melamed model using the measured absorption coefficient before irradiation and the mean particle diameter of the SP-500 powder. It does not seem likely that the Melamed model could predict the reflectance so accurately and not describe the change in absorptance.

A second explanation is that the zinc oxide thin films do not damage optically to the extent that the powder samples damage. It is noteworthy that the zinc oxide films show no traces of $(OH)^{\cdot -}$ radical absorption in the near infrared spectral region whereas the powder

samples of Farnsworth and Buckley (Ref. 23) and of Gilligan et al (Ref. 24) show considerable $(\text{OH})^-$ infrared absorption. Farnsworth and Buckley (Ref. 23) found that high temperature calcining of the powders decreased the $(\text{OH})^-$ absorption and increased the stability of the sample to ultraviolet irradiation. The absence of any infrared absorption bands in the zinc oxide films may be related to their lack of optical damage.

4. ELECTRICAL PROPERTIES OF THIN FILMS

PREVIOUS WORK

Heiland et al (Ref. 3) have reviewed the electronic properties of zinc oxide. Since their review, numerous papers have been published on the electrical properties of zinc oxide. A partial list of these later papers is included as References 25 through 44. None of these papers has dealt with detecting energy states arising from ultraviolet irradiation. Several of the papers dealt with the change in conductivity caused by ultraviolet irradiation. Those studies were mainly concerned with the chemisorption of oxygen on the zinc oxide surface.

ELECTRICAL STUDIES

Measurements of the basic transport properties of a solid can yield valuable information about the electronic properties of the material. Two of the most important parameters are the free carrier concentration and the free carrier mobility. Studies of the carrier concentration give information about the activation energy and the location of the Fermi level. From these the degree of degeneracy, the influence of donors and acceptors and the effects of trapping may be inferred.

Studies of the mobility give information about the scattering mechanisms in the material. These studies can be related to

- The concentration of defect centers
- The degree of ionization of donors and acceptors
- The influence of space charge regions, including surface effects, grain boundaries, and dislocations
- The influence of lattice scattering
- The free carrier relaxation time.

The principal objective of these electrical measurements was to determine the mechanisms that cause a large conductivity increase in zinc oxide when it is ultraviolet irradiated, and to gain a better understanding of the electronic energy levels and transport processes which may be associated with ultraviolet-induced IR absorption.

The particular objectives of these studies were:

- To study the effects of ultraviolet irradiation on the free carrier concentration
- To look for defect centers sensitive to ultraviolet irradiation by means of mobility measurements
- To determine if ultraviolet irradiation creates and populates defect states with energy levels near the conduction band
- To determine to what extent surface band-bending affects the population of defect centers with energy levels near the conduction band.

To achieve these objectives the basic electrical measurements -- temperature dependence of conductivity, Hall mobility, and carrier concentration -- were made on zinc oxide films at various levels of degradation. The variation of the Hall mobility and the carrier concentration with photoexcitation was measured, and IR photoconductivity measurements were performed.

Experimental Procedures

The general experimental arrangement for the conductivity and Hall measurements is shown in Figure 4-1. The Hall signal was processed by using the circuitry depicted in Figure 4-2. The sensitivity of this arrangement was limited by sample noise and was approximately 1 millivolt for a sample current of 10^{-7} amperes. Bias voltages were kept as low as possible. However, a maximum of 300 volts was used for very high resistance films in order to achieve measureable Hall potentials.

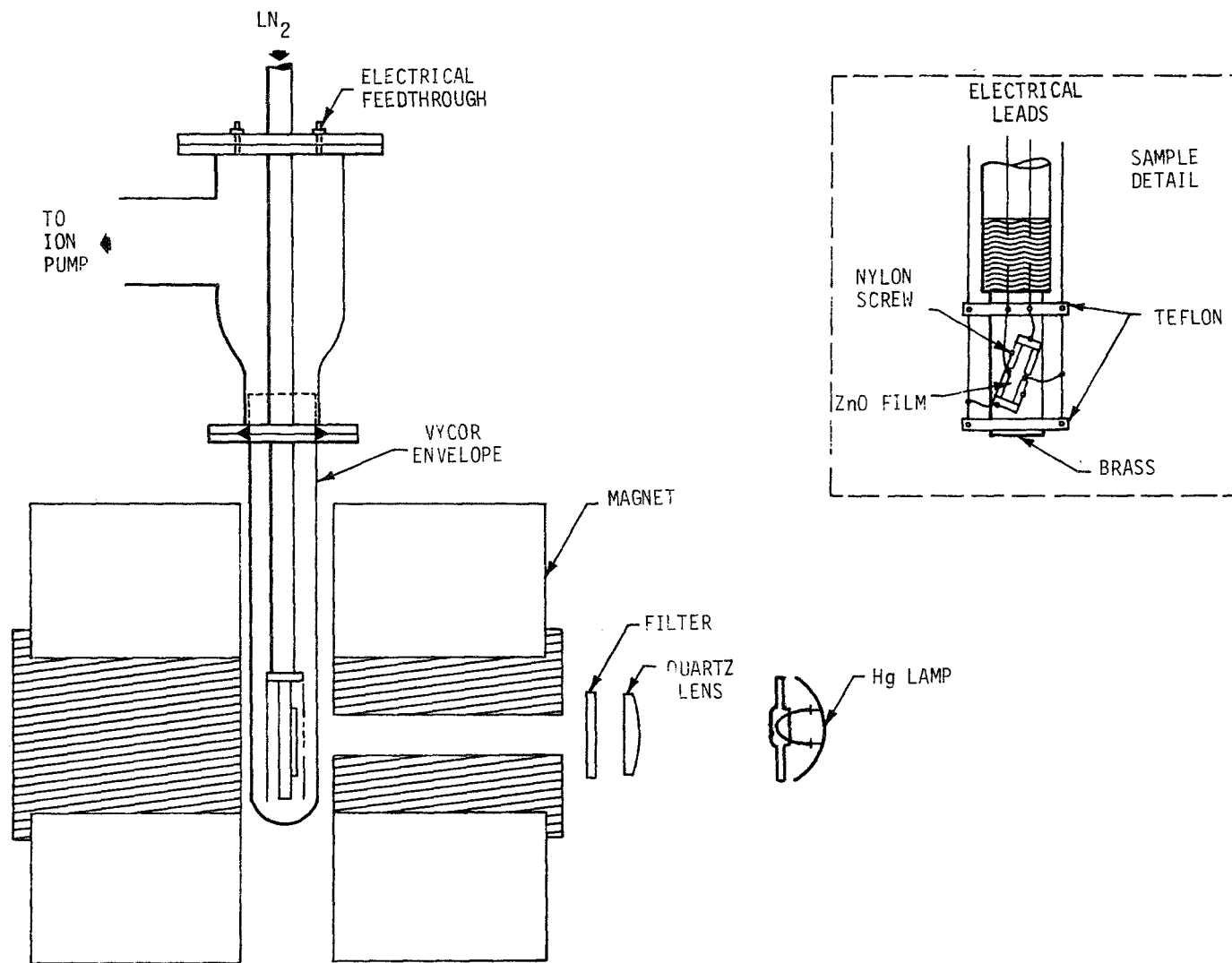
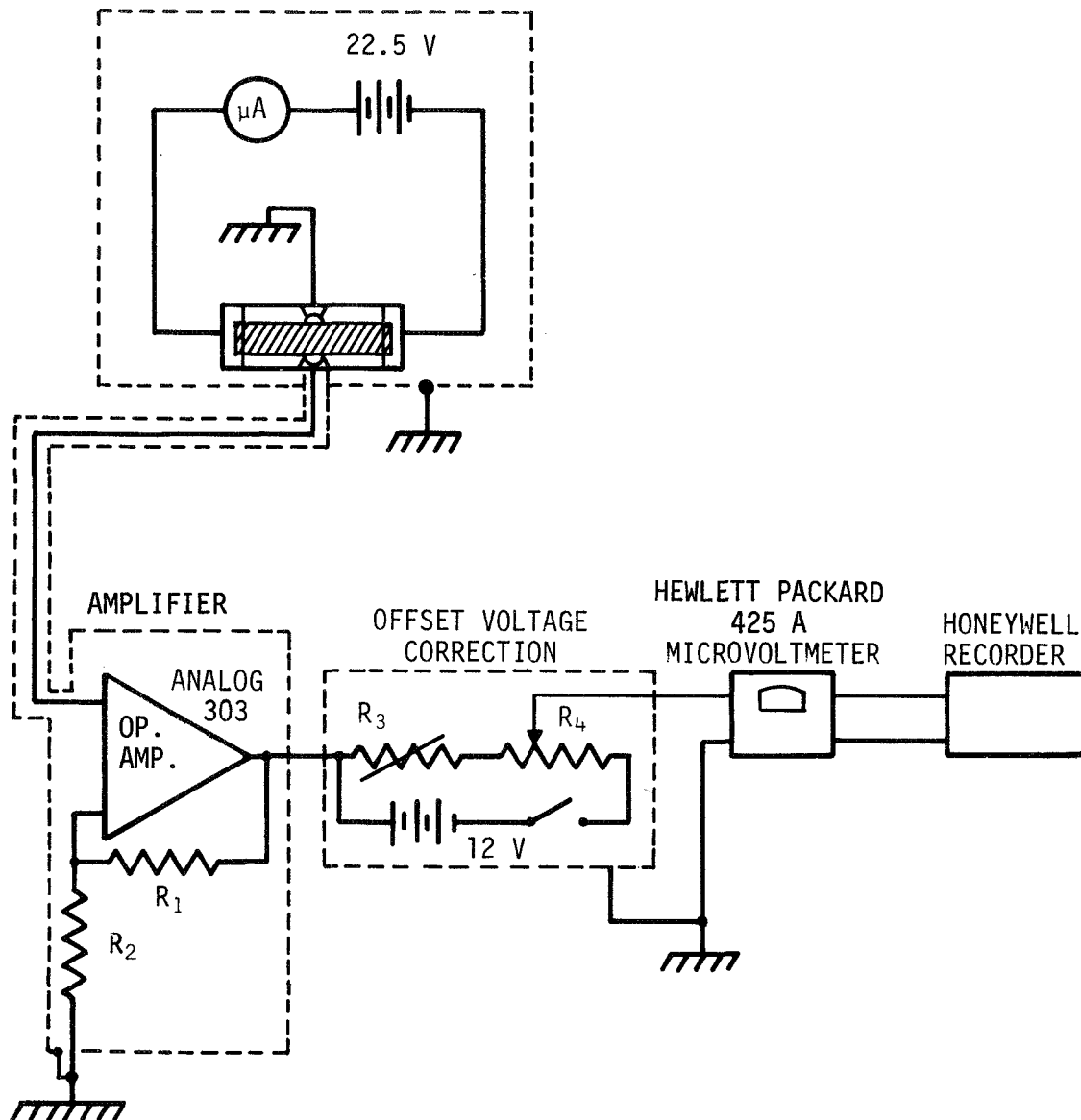


FIGURE 4-1. EXPERIMENTAL ARRANGEMENT FOR HALL EFFECT MEASUREMENTS



NOTES:

1. R_1 - FEEDBACK, 1,000-OHM METAL FILM RESISTOR
2. R_2 - 1,000-OHM METAL FILM RESISTOR
3. R_3 - 100 OHMS, 10 TURNS
4. R_4 - 1,000 OHMS, 1 TURN

FIGURE 4-2. SCHEMATIC OF HALL SIGNAL PROCESSING CIRCUIT

A Sulfrian Select-a-Stat dewar with a special tail assembly was used as the sample holder during the low temperature studies. An iron-constantan thermocouple affixed to the sample holder was used to measure the temperature of the sample down to 77°K. Below 77°K a 1/8-watt Allen-Bradley carbon resistor was used to indicate sample temperature. The resistor was affixed directly to the brass sample holder by means of Shell Epon epoxy.

All measurements were made with the sample in an ion-pumped vacuum of approximately 6×10^{-7} torr.

Temperature Variation of Conductivity

For sample temperatures down to 77°K, the experimental arrangement shown in Figure 4-1 was used. After the sample was affixed to the holder and the chamber was evacuated to 10^{-6} torr, the sample was cooled to approximately 100°K and maintained at this temperature for about 15 minutes. The sample was then slowly warmed to a maximum temperature of about 400°K, and the sample resistance was measured as a function of temperature using a General Radio Model 1230-A electrometer. Normally, two or more runs were made without additional treatment to check the repeatability of the experiment. The chamber pressure usually increased to about 5×10^{-6} torr during the warming cycle of the first run, but this pressure increase was not observed during successive runs. Consequently, the second run was taken as the control. After the control run the sample was again cooled to 100°K and then irradiated a few seconds with low intensity ultraviolet light and another temperature variation measurement made. Such slight irradiation was adequate because of the high sensitivity of the zinc oxide film. Usually, an order of magnitude decrease in sample resistance at 100°K was attempted for each successive measurement cycle. After each irradiation the sample was held at 100°K in the dark for approximately 15 minutes to allow the sample resistance to stabilize before a

new temperature variation of conductivity measurement was made. Figures 4-3, 4-4, 4-5, and curves A of Figures 4-6 and 4-7 illustrate the temperature dependence of the resistance of typical zinc oxide films in vacuum before irradiation. Figure 4-7 shows the temperature dependence of the sample resistance for the control run (A) and for three successive runs after increasing radiation doses. These figures indicate that the conductivity is extrinsic with an activation energy, ΔE , defined by

$$\sigma = \sigma_0 \exp (-\Delta E/kT) \quad ,$$

of the order of 0.1 eV. The curves of Figure 4-8 indicate the existence of some type of trapping action. Since the resistance of Sample 726SH-1 was so high, it was believed that this film would be amenable to TSC measurements to probe the trapping action. Consequently, curves B, C, and D of Figure 4-8 were taken after the film was irradiated at 100°K for increasingly greater successive doses of ultraviolet radiation. However, these TSC measurements failed to provide enough information to determine the nature and energy levels of the trapping centers.

For sample temperatures below 77°K, a modified Sulfran dewar was used as the sample chamber. After the sample was securely mounted on the tail of the dewar, the dewar was evacuated to the 10^{-7} torr range and precooled with liquid nitrogen to 77°K. The tail assembly was then cooled with liquid helium. The resistance of the unirradiated films at the lowest temperatures exceeded the maximum resistance of the vacuum-electrical feedthroughs and the electrometer input. This is evident in Figure 4-7 where the sample resistance appears constant for values greater than 4×10^{14} ohms.

Temperature Variation of Mobility and Electron Concentration

The temperature variation of the mobility of a zinc oxide film prior to irradiation was not obtained because of the low mobility and excessive noise of the unirradiated films. The noise was a function

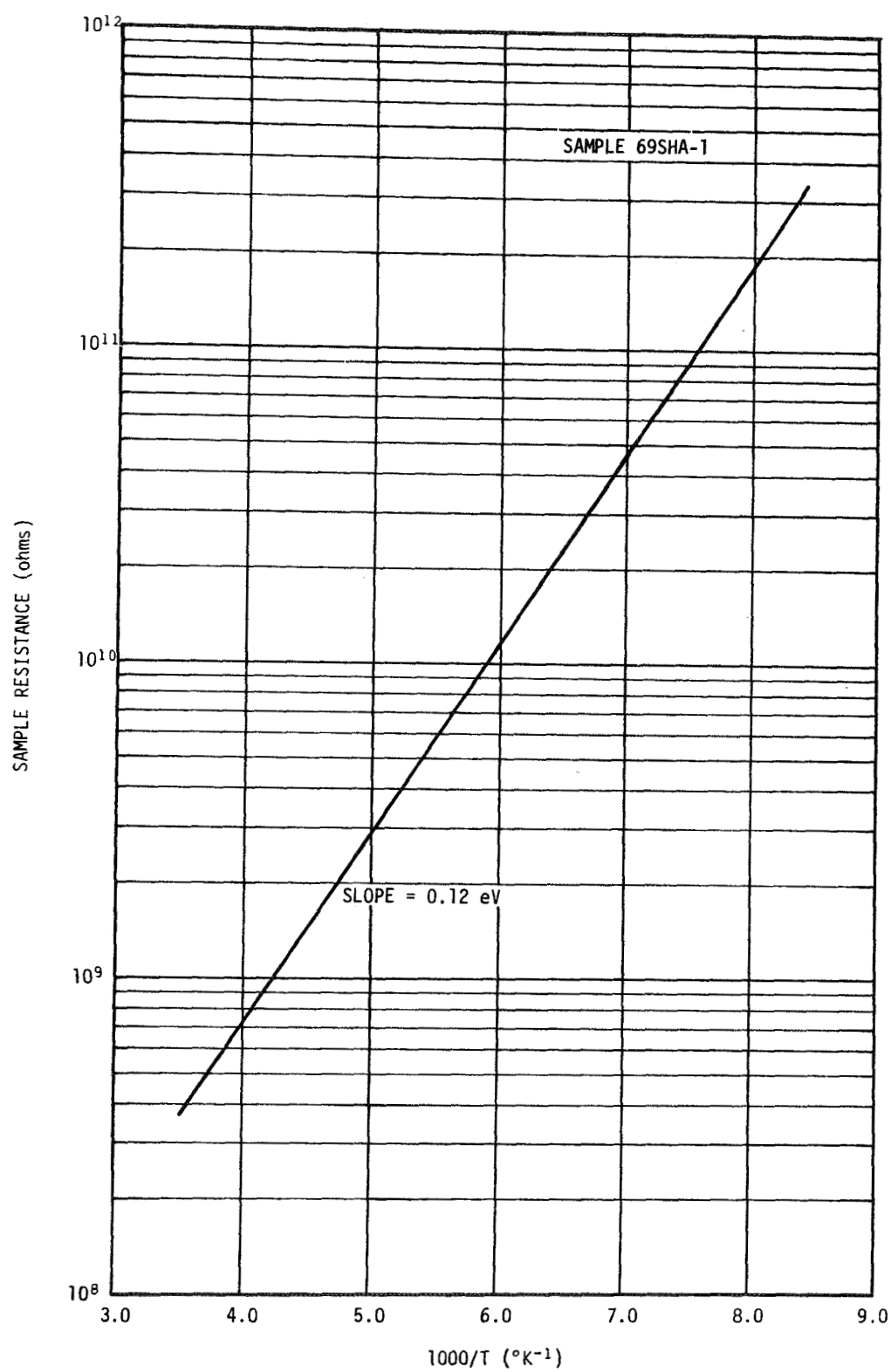


FIGURE 4-3. TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF SAMPLE 69SHA-1 BEFORE IRRADIATION

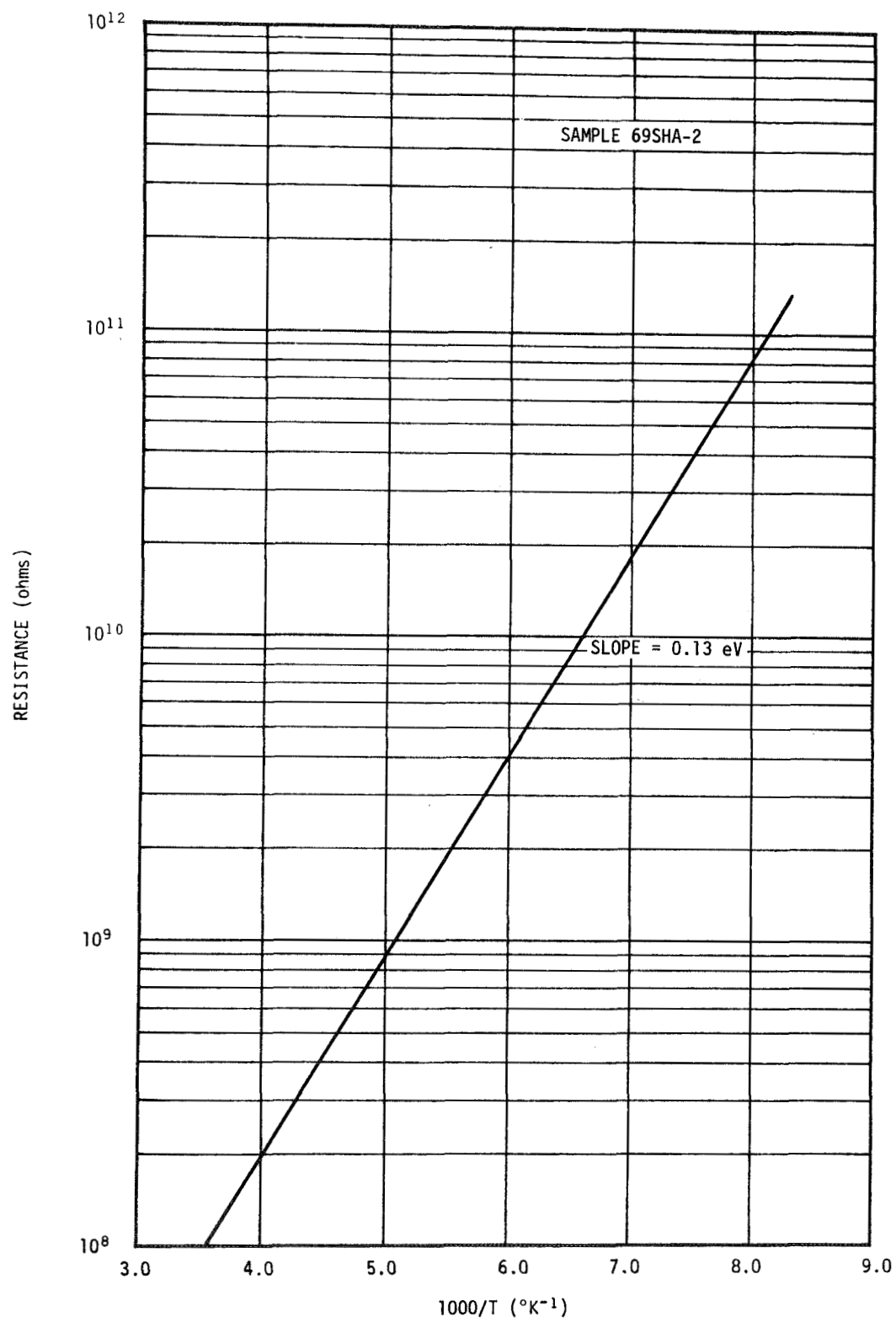


FIGURE 4-4. TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF SAMPLE 69SHA-2 BEFORE IRRADIATION

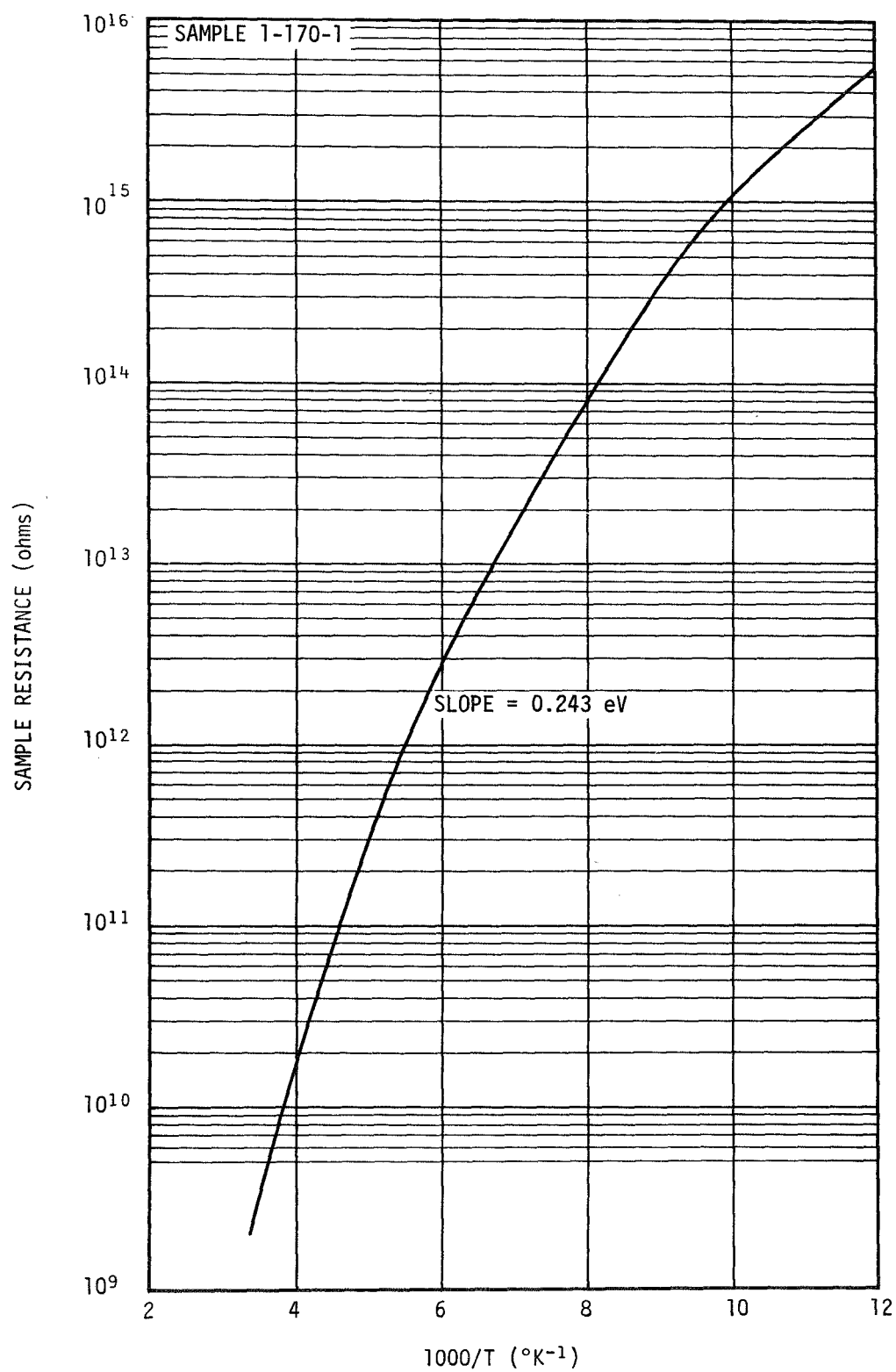


FIGURE 4-5. TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF SAMPLE BEFORE IRRADIATION

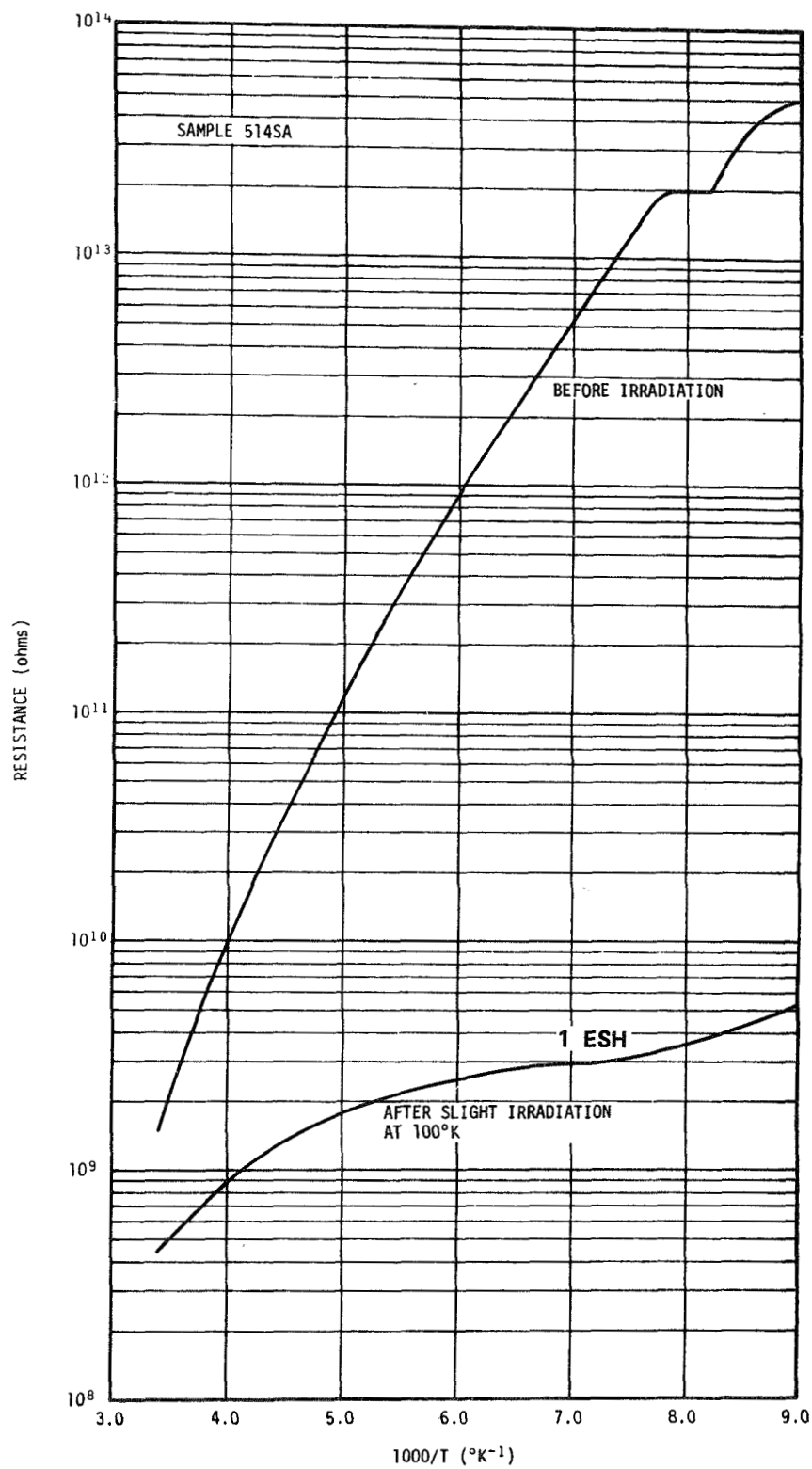


FIGURE 4-6. TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF SAMPLE 514SA BEFORE AND AFTER SLIGHT IRRADIATION AT 100°K

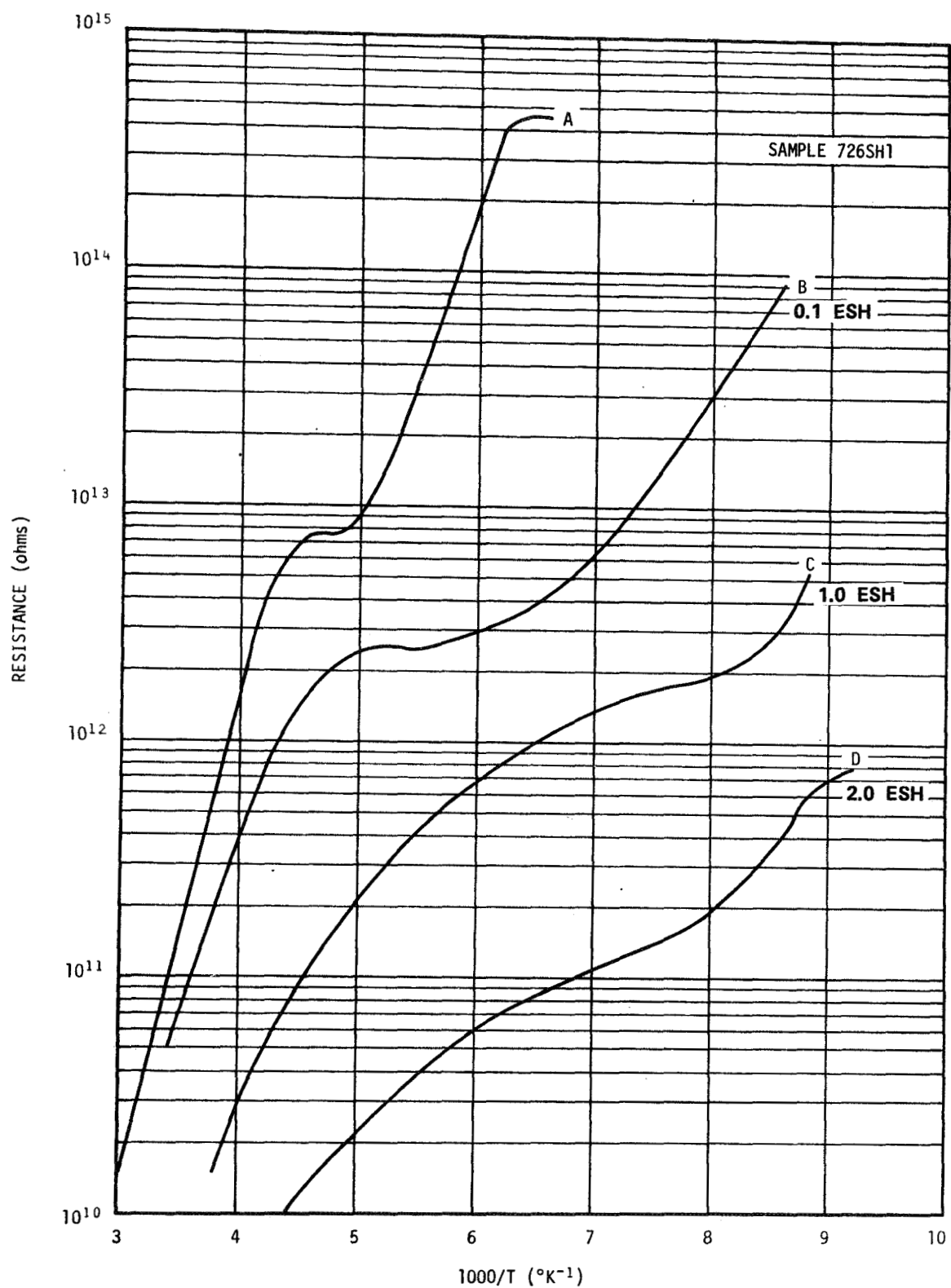


FIGURE 4-7. TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF SAMPLE 726SH-1 BEFORE AND AFTER VARIOUS DOSES OF IRRADIATION

of sample resistance; by reducing the resistance with illumination, the noise was reduced to an acceptable level.

The initial experimental procedure involved evacuating the sample chamber, cooling the sample to approximately 100°K, and irradiating the sample to a resistance of 10^9 to 10^7 ohms at 100°K. This irradiation was very slight and was administered in small steps to allow the measurement of the smallest Hall signal detectable. Generally, the minimum signal measureable was 0.1 millivolts for a sample resistance of 10^9 ohms.

After the irradiation of the sample, two measurement alternatives were available. The sample could be allowed to recover in the dark at 100°K and the temperature dependence of the mobility, μ , and the electron concentration, η , measured as the sample was warmed to room temperature; or the sample could be warmed to room temperature, recooled to 100°K and the temperature dependence of μ and η then measured as the sample was again warmed. Both methods were tried, and the results were quite different for the two cases.

Figures 4-8 and 4-9 show the temperature dependence of μ and η for Sample 826SH-1 for three different doses of ultraviolet irradiation at 100°K, after which the sample was not warmed before the individual measurements were taken. Curves A were obtained after very slight irradiation at 100°K, curves B after moderate irradiation at 100°K and curves C after extensive irradiation at 100°K. Note that above 250°K the temperature variation of the mobility reversed while the electron concentration also decreased rapidly. These data indicated that recovery was strongly enhanced for temperatures above 250°K. To demonstrate this cycling effect more clearly the temperature dependence of the mobility for sample 827SH-2 was measured immediately after extensive irradiation, Figure 4-10, curve A; after then warming to room temperature once and recooling, curve B; and after warming to

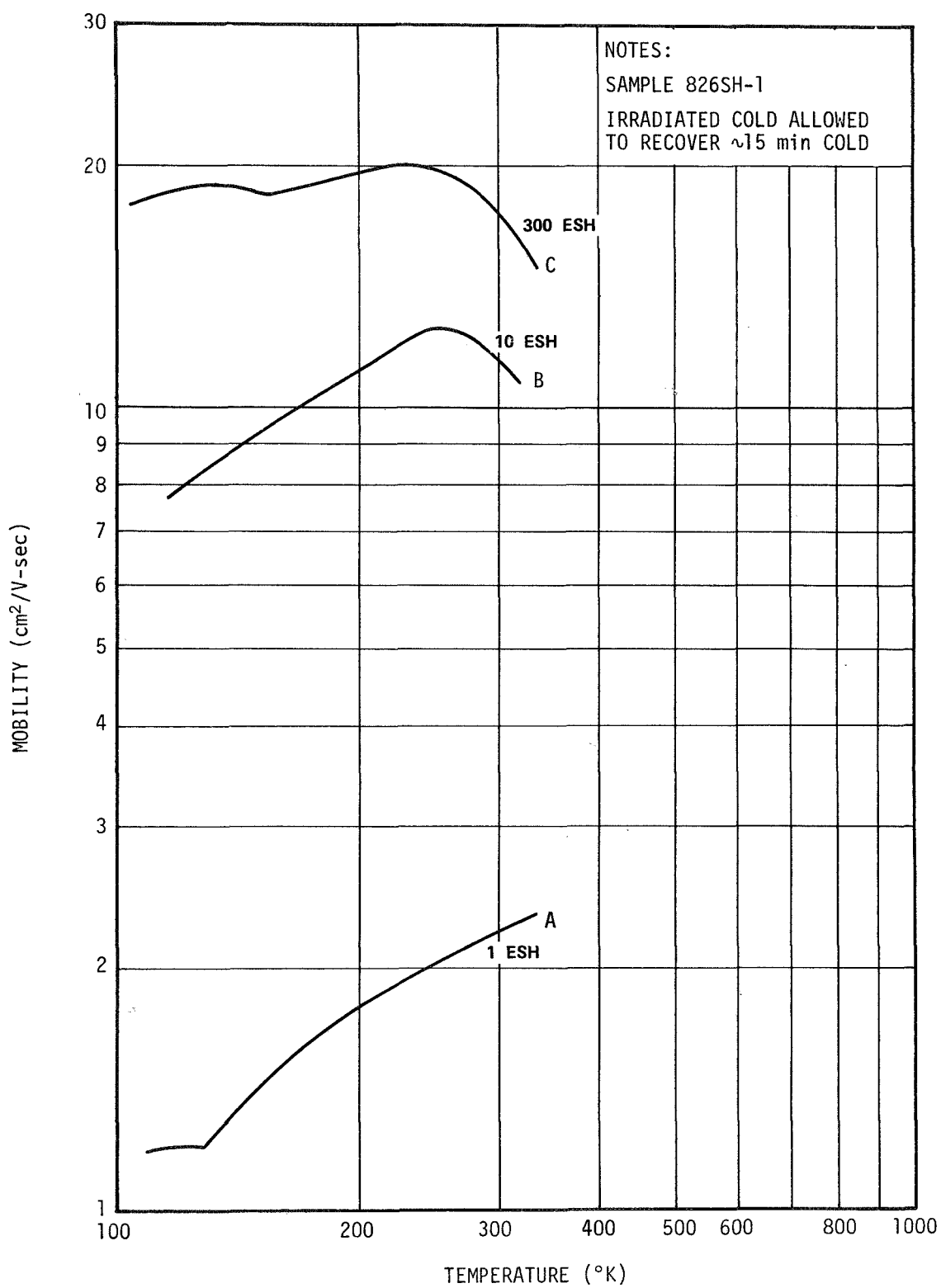


FIGURE 4-8. TEMPERATURE DEPENDENCE OF HALL MOBILITY OF SAMPLE 826SH-1

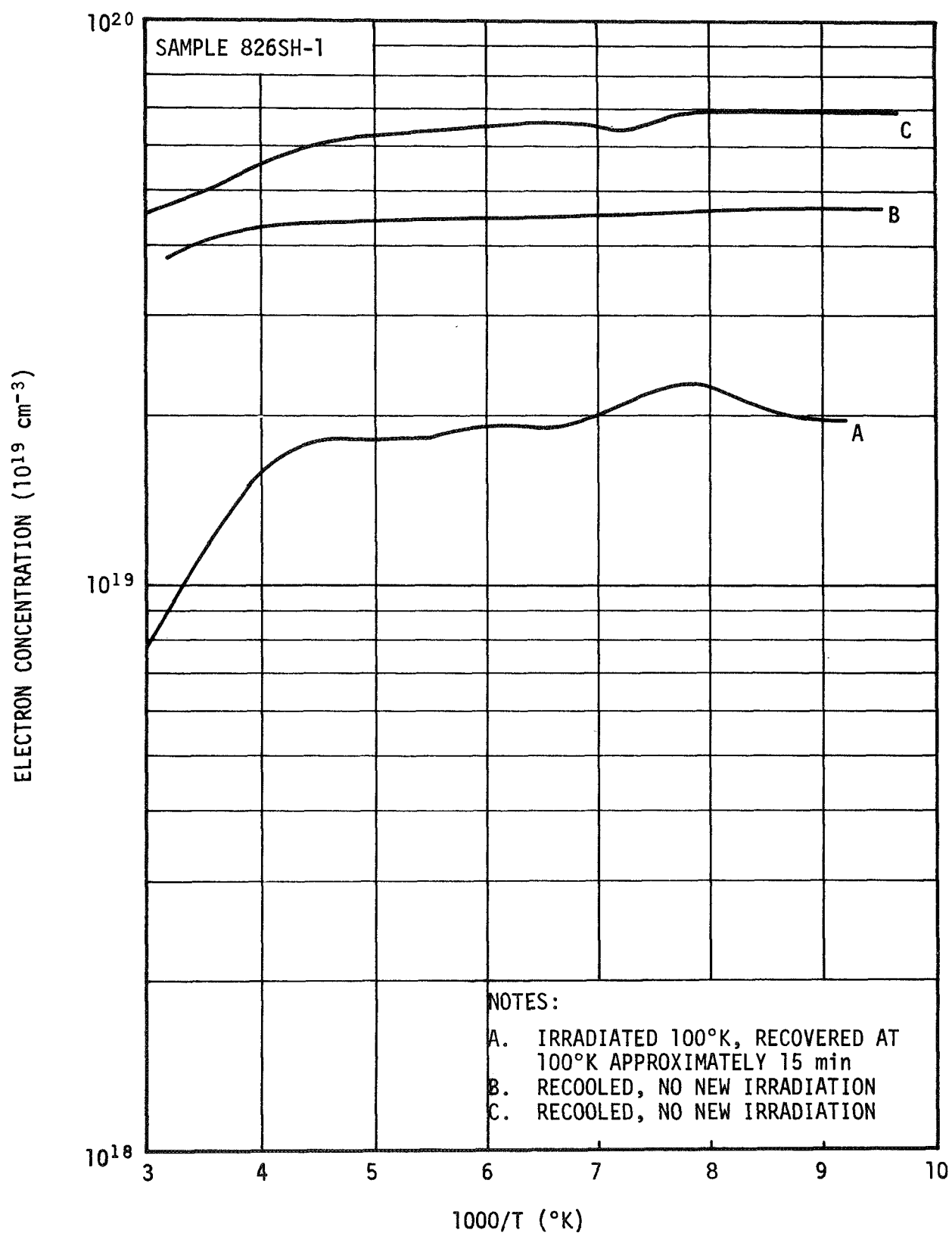


FIGURE 4-9. TEMPERATURE DEPENDENCE OF ELECTRON CONCENTRATION OF SAMPLE 826SH-1

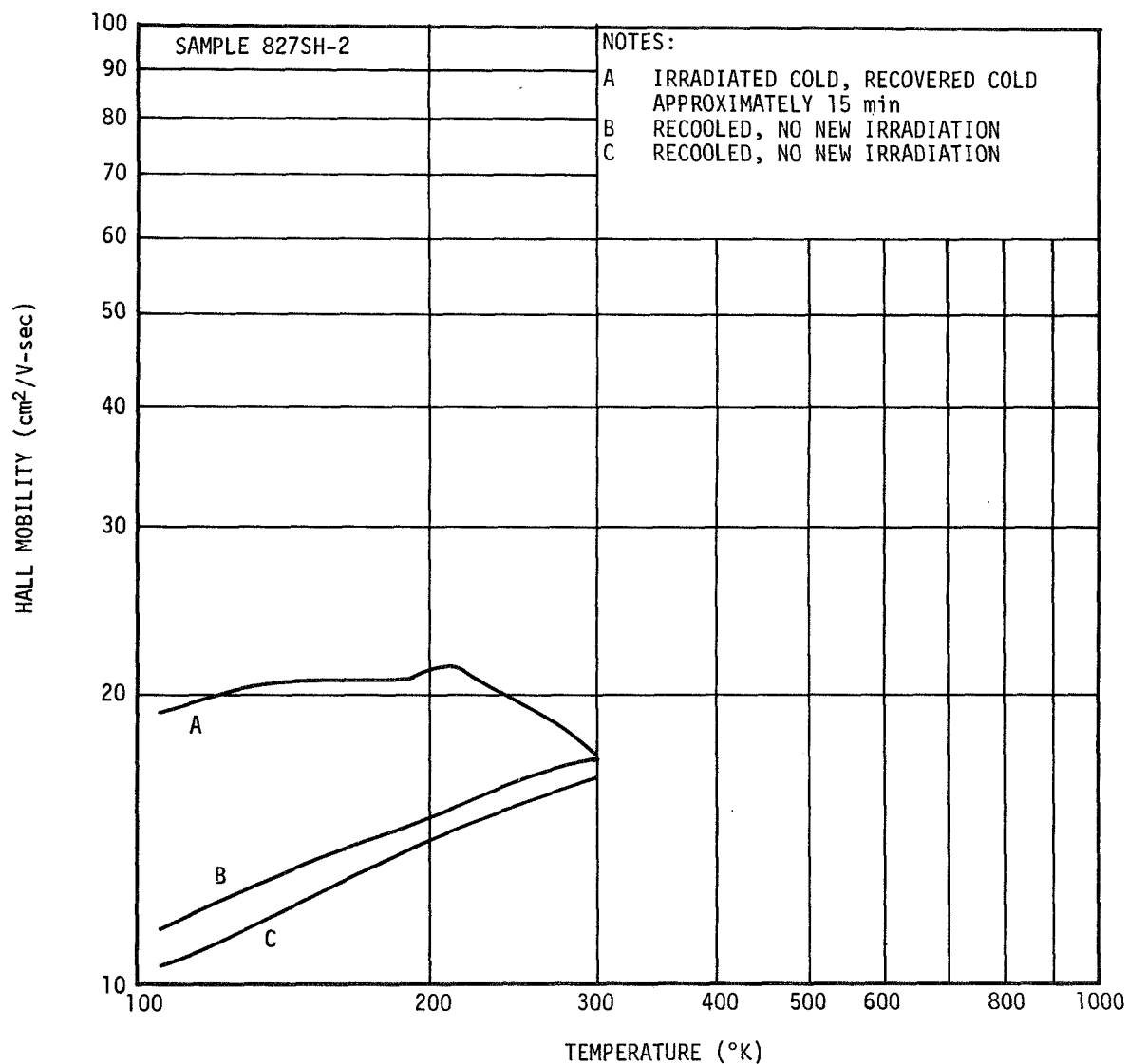


FIGURE 4-10. EFFECT OF TEMPERATURE CYCLING ON THE TEMPERATURE DEPENDENCE OF THE HALL MOBILITY

room temperature and recooling twice, curve C. These results show that recovery is extensive above 200°K during the warming cycle immediately after irradiation and that successive warming cycles continue to aid recovery but not to as large an extent. The temperature variation of the mobility does not change much after one cycling.

Figures 4-11 and 4-12 show the temperature variation of μ and η for two different doses of irradiation at room temperature. Curves A were obtained after slight irradiation and one-hour recovery in high vacuum at room temperature prior to cooling the sample and measuring the temperature dependence of μ and η . Curves B were obtained after extensive irradiation and one-hour recovery in high vacuum at room temperature prior to cooling and measurement. Curves C were obtained with no additional irradiation after overnight recovery at room temperature in high vacuum. Curves C show considerable recovery taking place overnight with the electron concentration decreasing to less than its value after slight irradiation. The slope of the mobility curves changes with irradiation and recovery.

To determine the effects of long-term vacuum recovery on the temperature dependence of the mobility, Sample 827SH-2 was irradiated and recovered in high vacuum for two days at room temperature. Figure 4-13, curve A shows the temperature dependence of μ after 1-day recovery and curve B shows the change after 2 days recovery. The recovery is seen to be virtually complete after one day. Figure 4-14 shows the recovery of the electron concentration for the same measurements.

For Hall measurements below 77°K, the samples were cooled to 77°K, irradiated, allowed to recover for 1 hour at 77°K, and then cooled with liquid helium. Figures 4-15 and 4-16 show the results for sample 1-7-2 for two consecutive runs. These results indicate that the scattering processes prominent around room temperature are also important at very low temperatures.

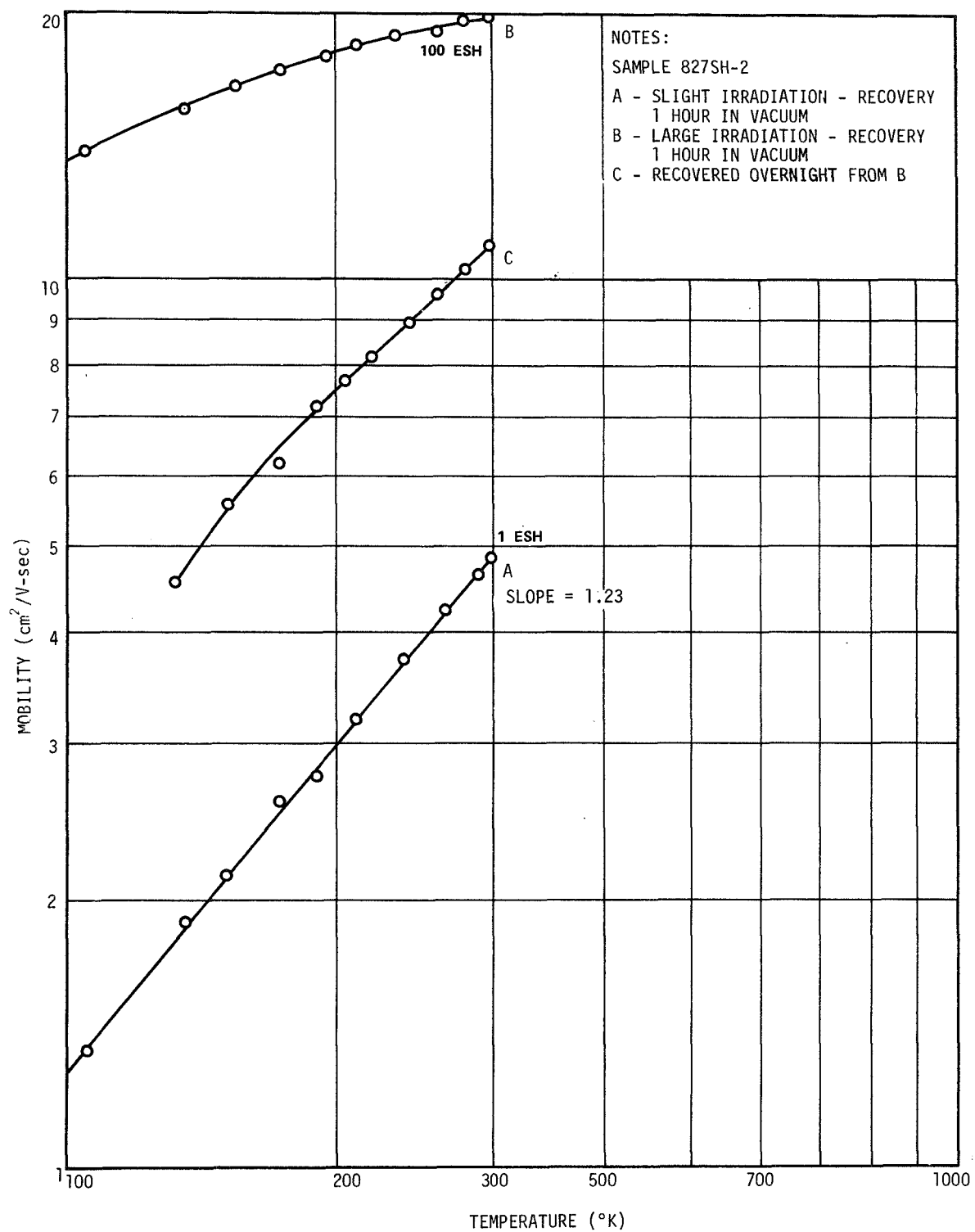


FIGURE 4-11. TEMPERATURE DEPENDENCE OF HALL MOBILITY OF SAMPLE 827SH-2 AFTER VARIOUS DOSES OF IRRADIATION AND IN SITU RECOVERY

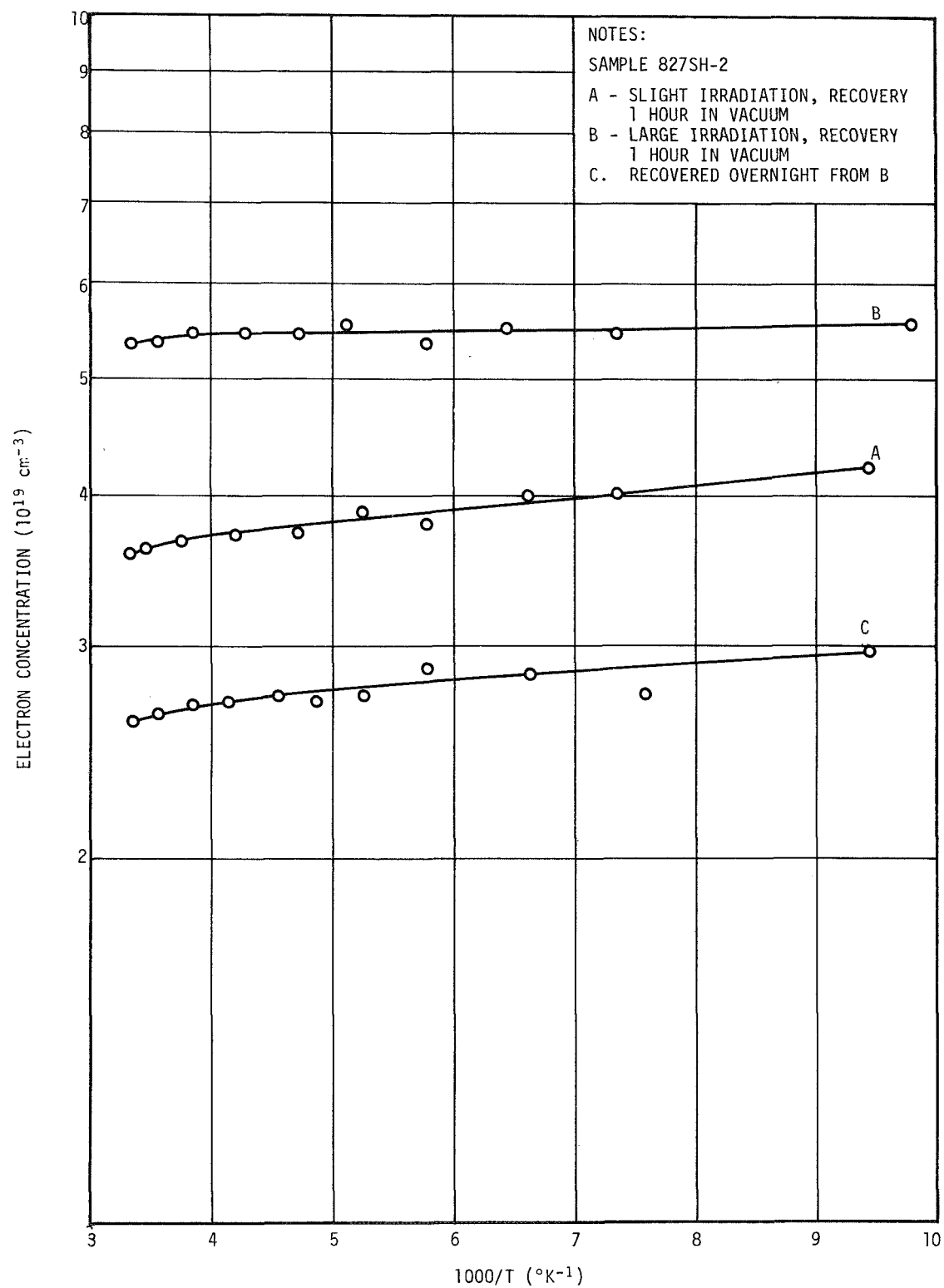


FIGURE 4-12. TEMPERATURE DEPENDENCE OF ELECTRON CONCENTRATION OF SAMPLE 827SH-2 AFTER VARIOUS DOSES OF IRRADIATION AND IN SITU RECOVERY

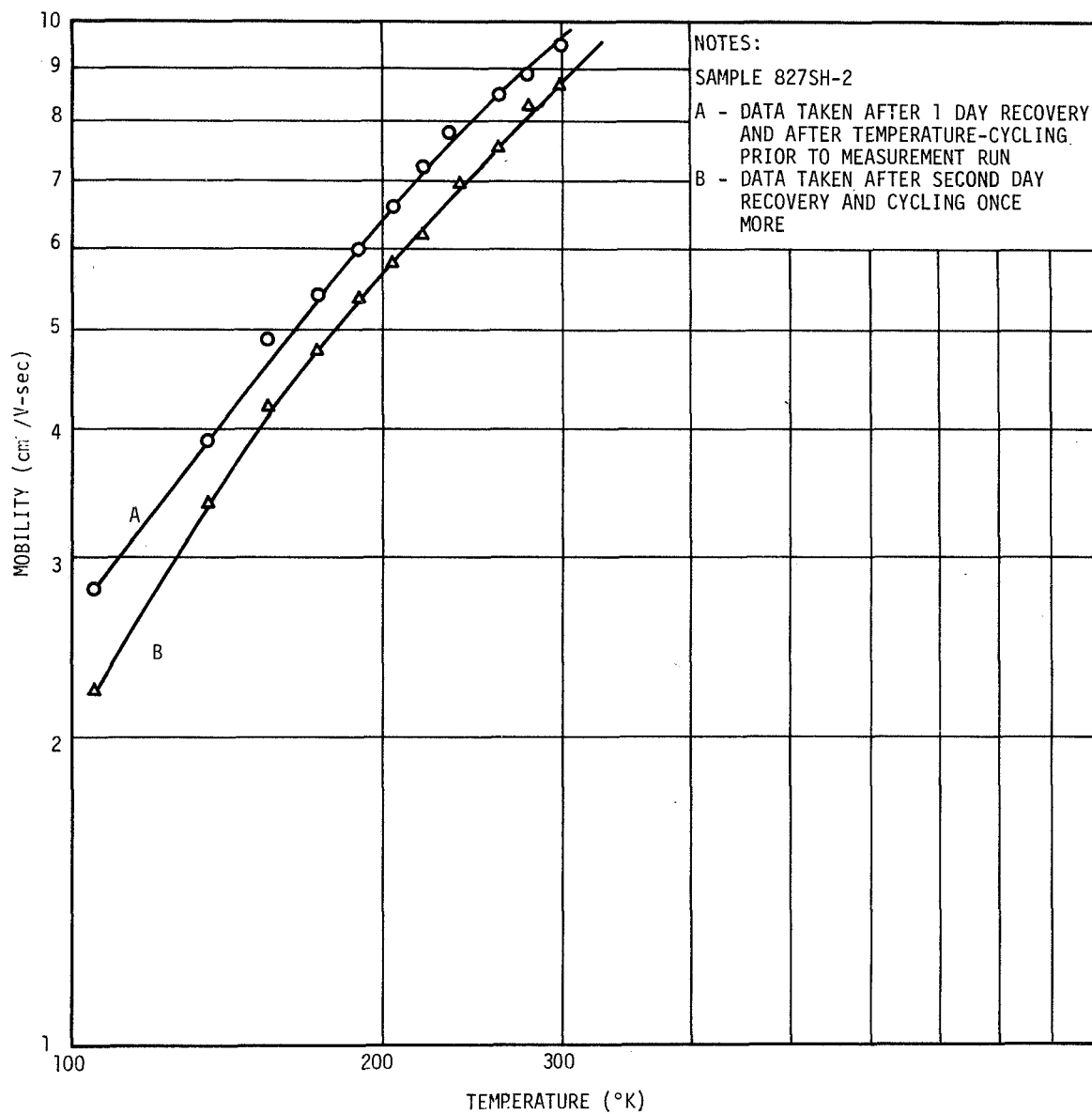


FIGURE 4-13. TEMPERATURE DEPENDENCE OF MOBILITY OF SAMPLE 827SH-2 AFTER ONE AND TWO DAYS RECOVERY IN VACUUM

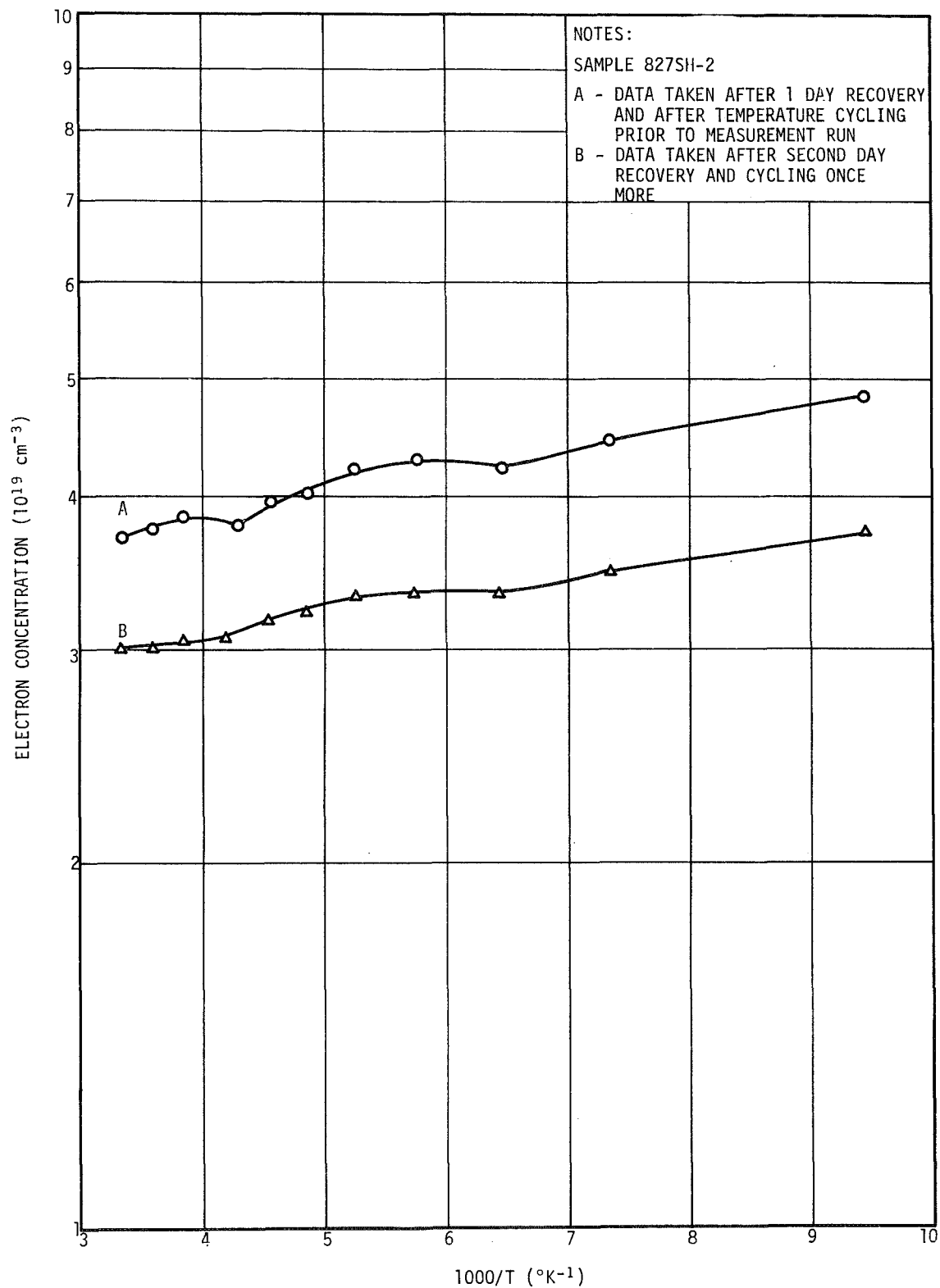


FIGURE 4-14. TEMPERATURE DEPENDENCE OF ELECTRON CONCENTRAION OF SAMPLE 827SH-2 AFTER ONE AND TWO DAYS RECOVERY IN VACUUM

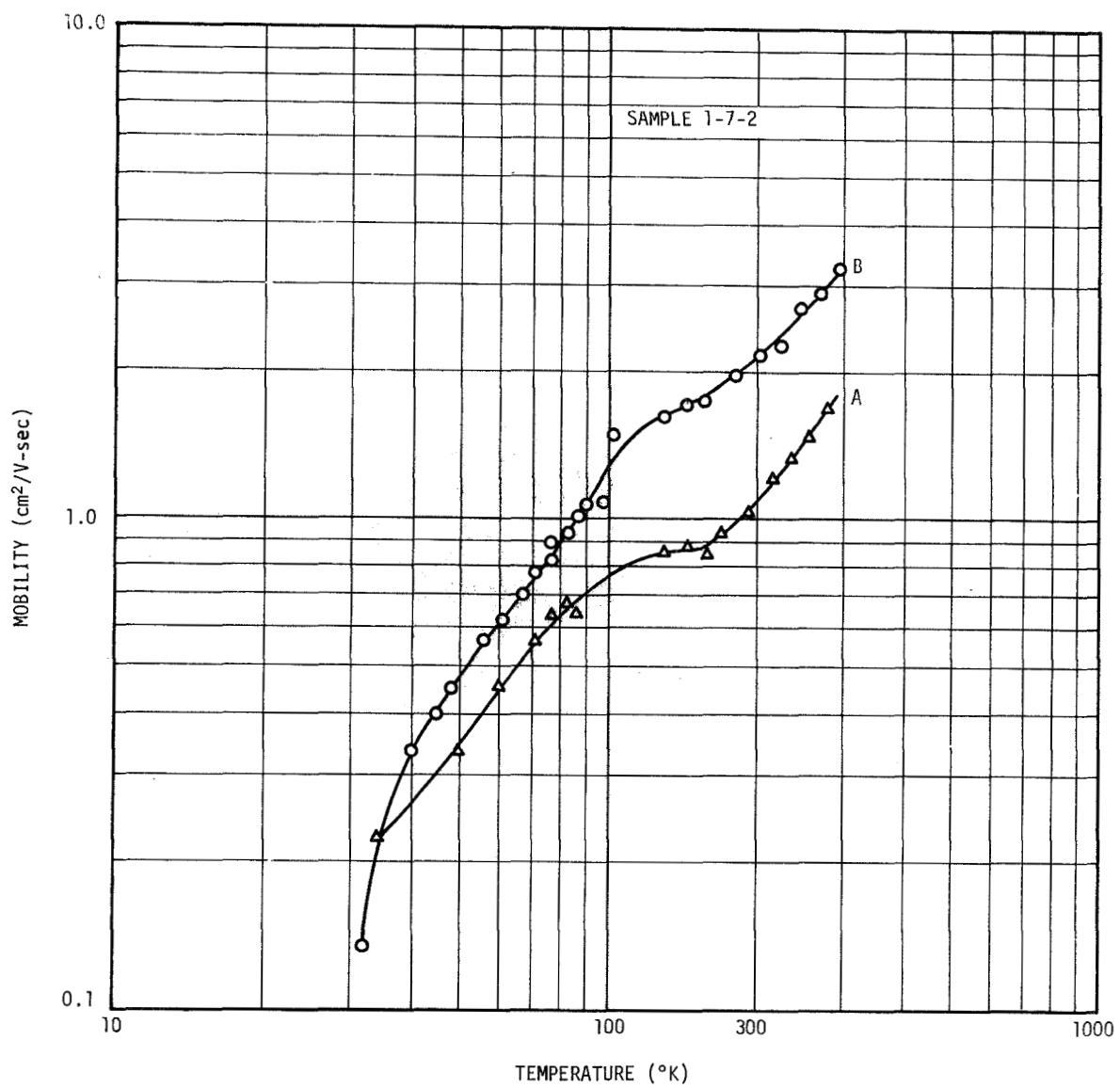


FIGURE 4-15. EXTENDED TEMPERATURE DEPENDENCE OF HALL MOBILITY OF SAMPLE 1-7-2

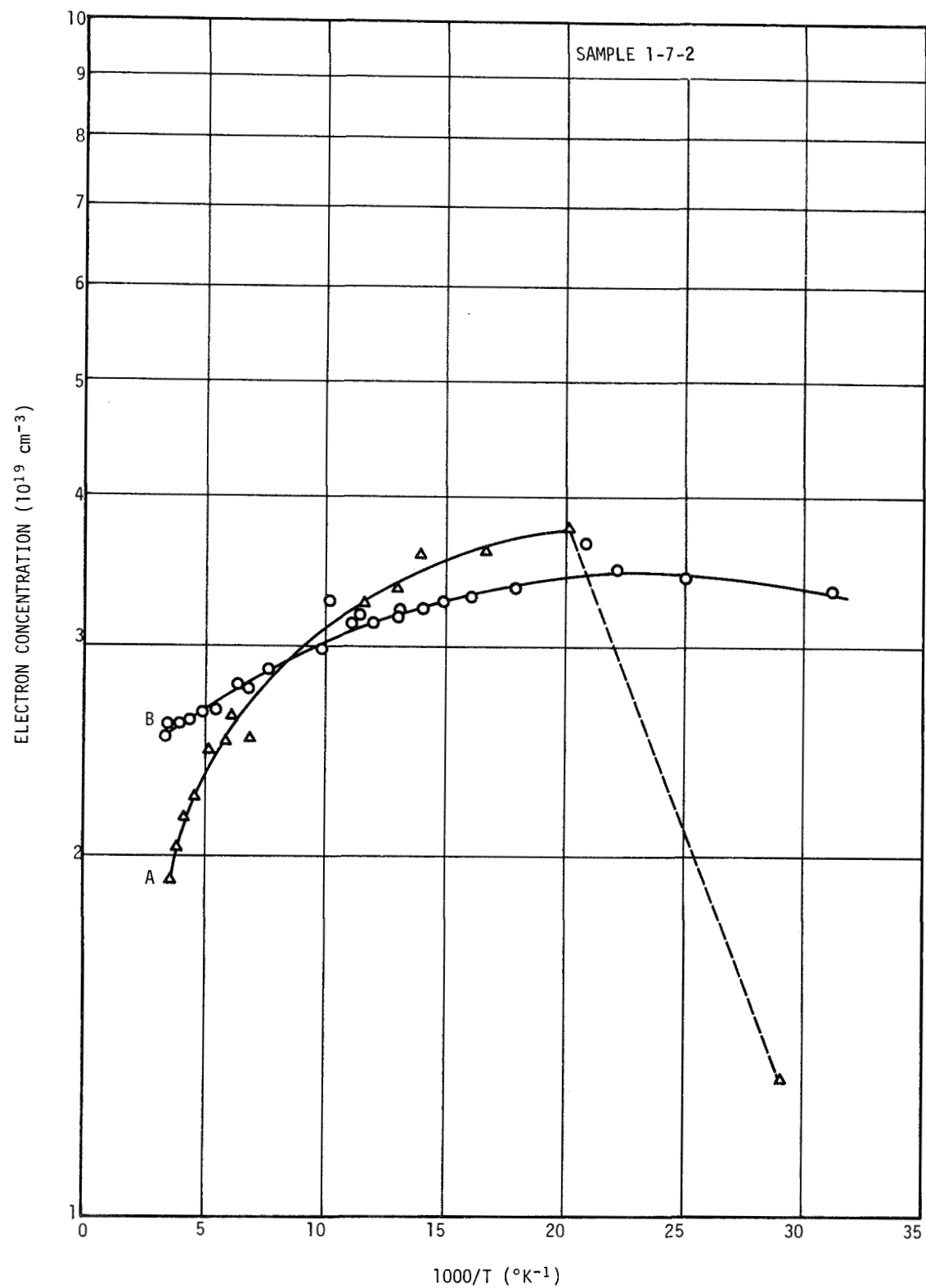


FIGURE 4-16. EXTENDED TEMPERATURE DEPENDENCE OF ELECTRON CONCENTRATION OF SAMPLE 1-7-2

Variation of Mobility with Photoexcitation

The Hall voltage measurements for this experiment were made in the manner described earlier, except that in this case the sample temperature was not varied. The sample resistance was varied by irradiating the sample with increasingly higher intensities of illumination. The Hall voltage was measured with the film in a quasi-steady-state condition under illumination, whereas the temperature dependent data were taken with the sample in the dark.

The intensity of irradiation was varied by using neutral density filters and by varying the focus of the ultraviolet light.

Figures 4-17 and 4-18 show the variation of μ and η with sample current at room temperature, as varied by increasing irradiation intensity, for two typical zinc oxide films. Both the mobility and carrier concentration increased with irradiation as previously reported (Refs. 19 and 44). The circled points represent the actual data. The curves were extrapolated beyond the data points to include the undamaged and very slightly damaged regions where Hall measurements were not possible. The curves for μ and η were extrapolated independently, without regard to sample current. However, the current calculated from the extrapolated values of μ and η matches very closely the abscissa values of the extrapolated curves. The extrapolated curves were terminated near the abscissa value corresponding to the undamaged sample resistance. It is believed that the extrapolated regions of the curves very closely match the actual η and μ values of the undamaged and very slightly damaged samples.

The same experimental data is plotted as logarithm of mobility as a function of logarithm of electron concentration in Figures 4-19 and 4-20. The mobility is proportional to η^χ for a given film for all but the greatest damaged regions. The exponent χ varies from 1 to 3 for different films.

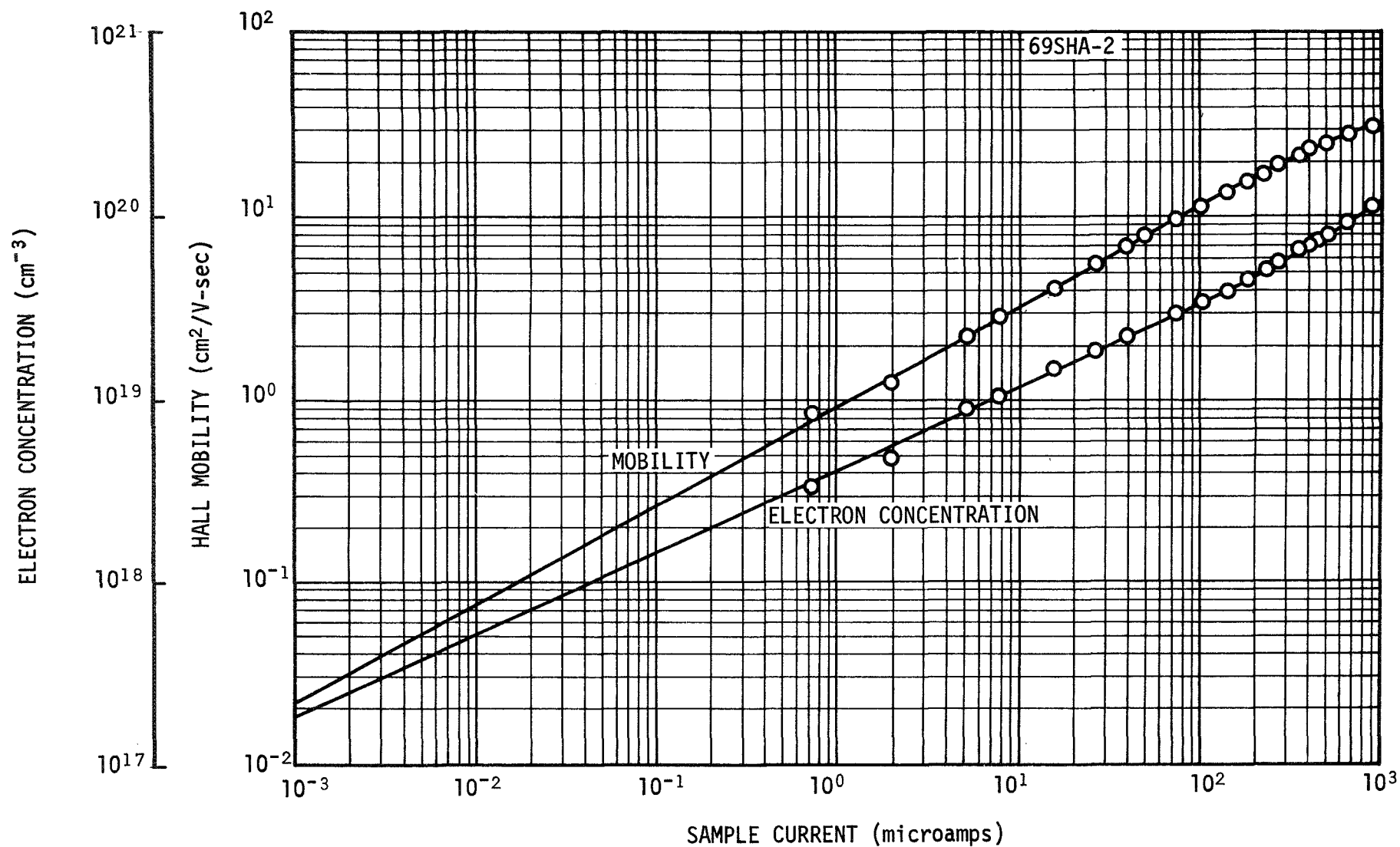


FIGURE 4-17. VARIATION OF MOBILITY AND ELECTRON CONCENTRATION WITH SAMPLE CURRENT AS VARIED BY ULTRAVIOLET IRRADIATION (SAMPLE 69SHA-2)

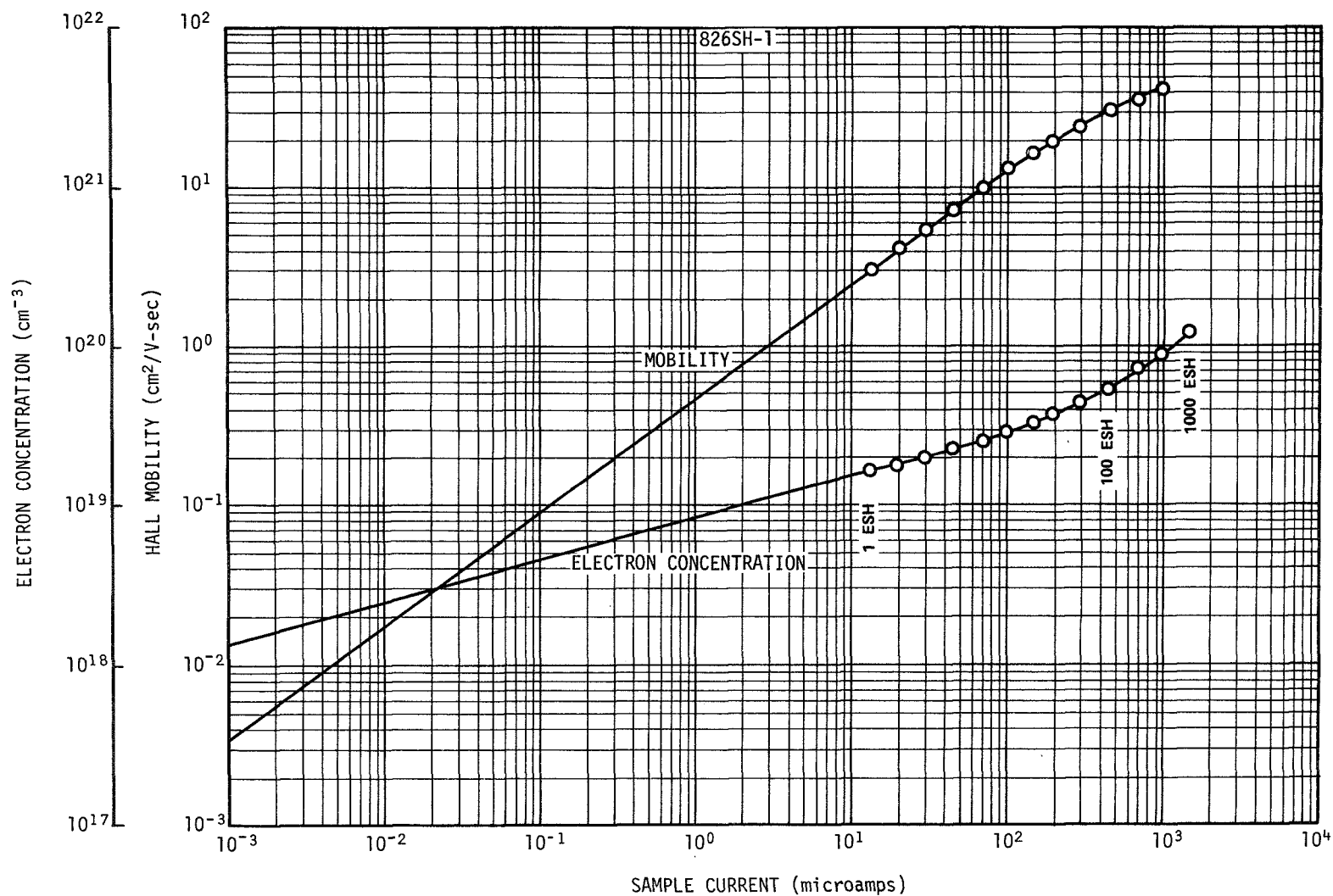


FIGURE 4-18. VARIATION OF MOBILITY AND ELECTRON CONCENTRATION WITH SAMPLE CURRENT AS VARIED BY ULTRAVIOLET IRRADIATION (SAMPLE 826SH-1)

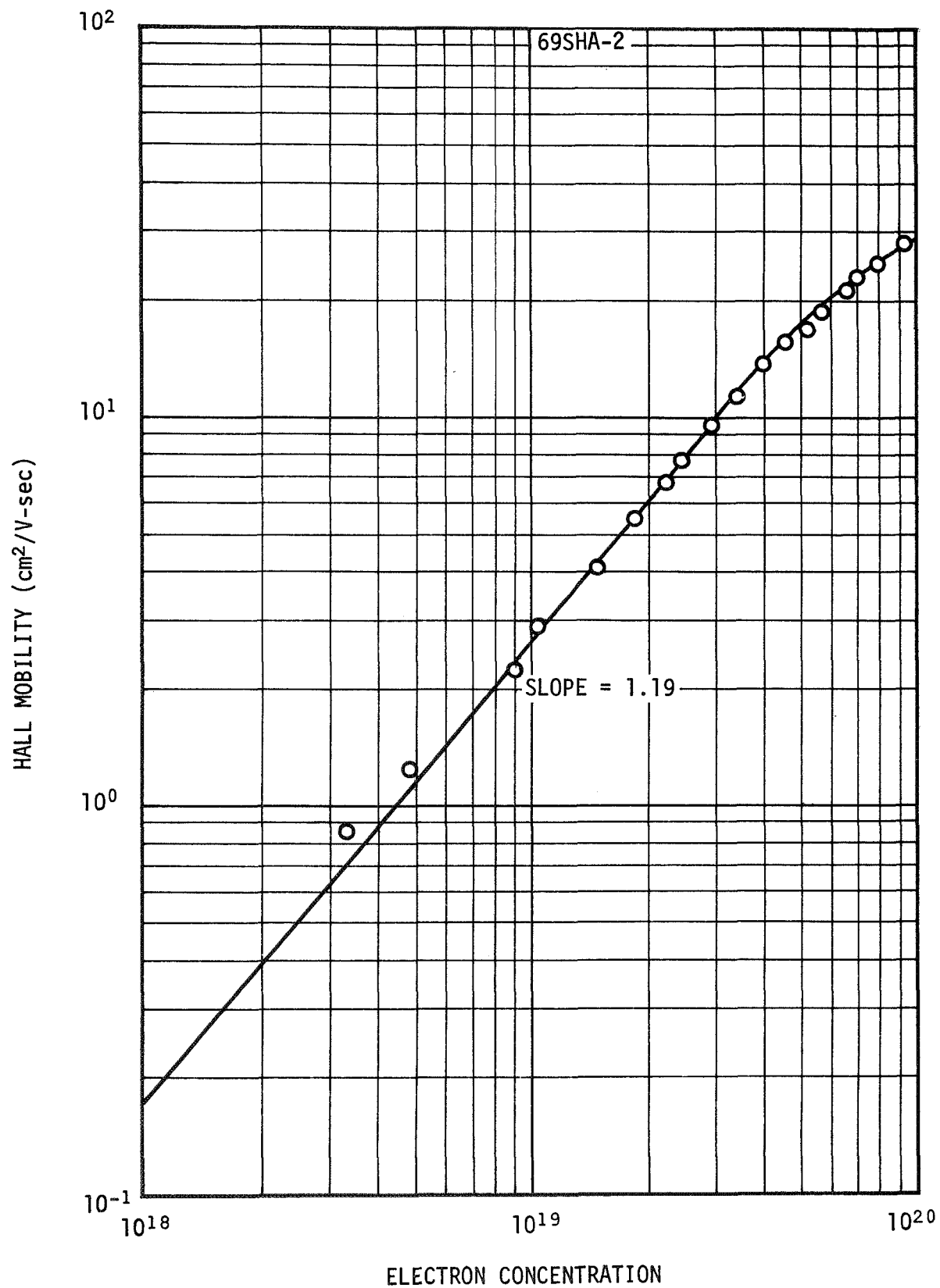


FIGURE 4-19. VARIATION OF MOBILITY AND ELECTRON CONCENTRATION WITH SAMPLE CURRENT AS VARIED BY ULTRAVIOLET IRRADIATION (SAMPLE 69SHA-2)

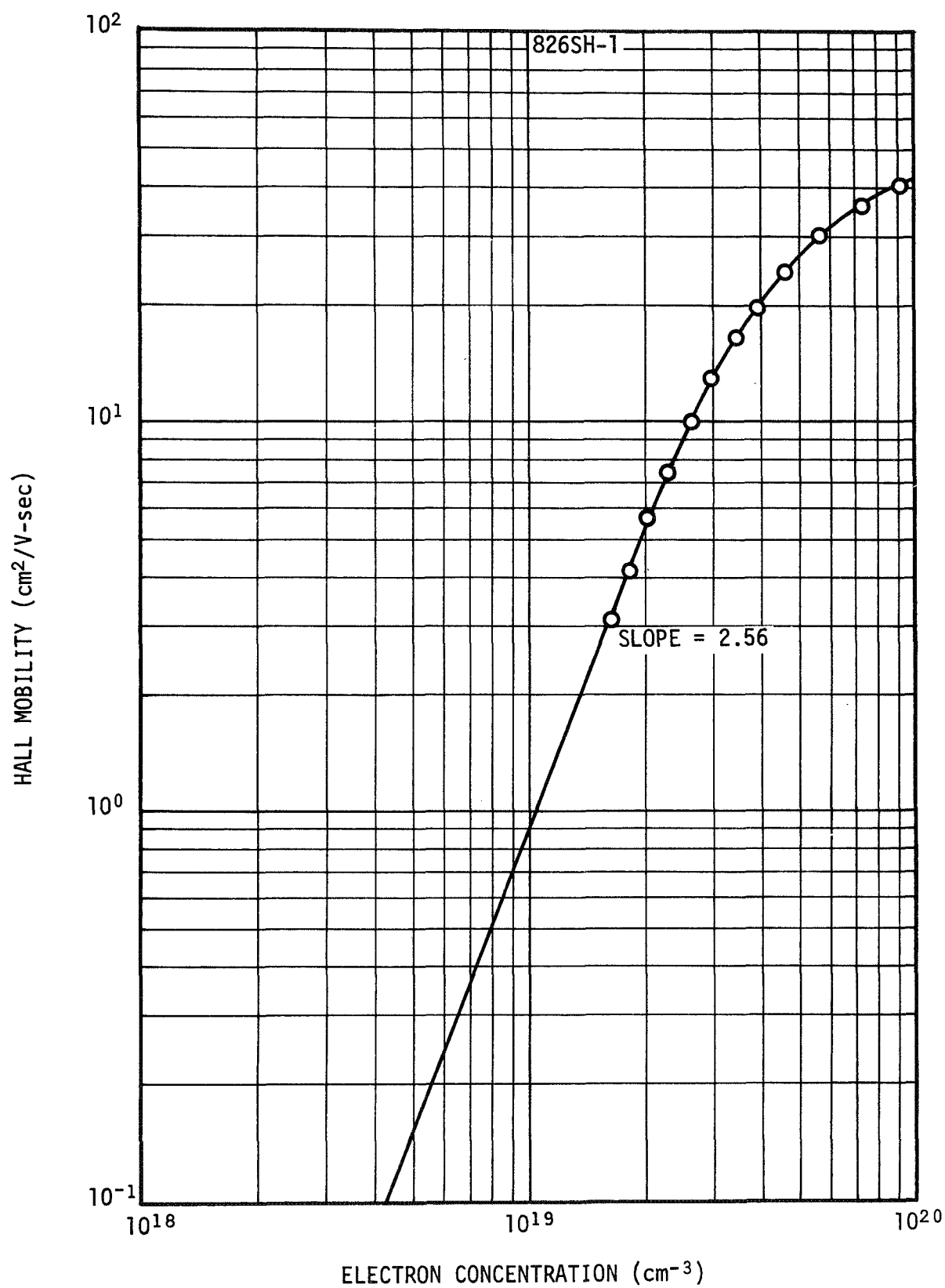


FIGURE 4-20. TEMPERATURE DEPENDENCE OF CONDUCTIVITY OF SAMPLE BEFORE IRRADIATION

These data also show that the mobility tends to saturation as the electron concentration increases above $3 \times 10^{19} \text{ cm}^{-3}$. Experimentally it was found to be very difficult to damage the samples beyond the maximum values shown on these figures.

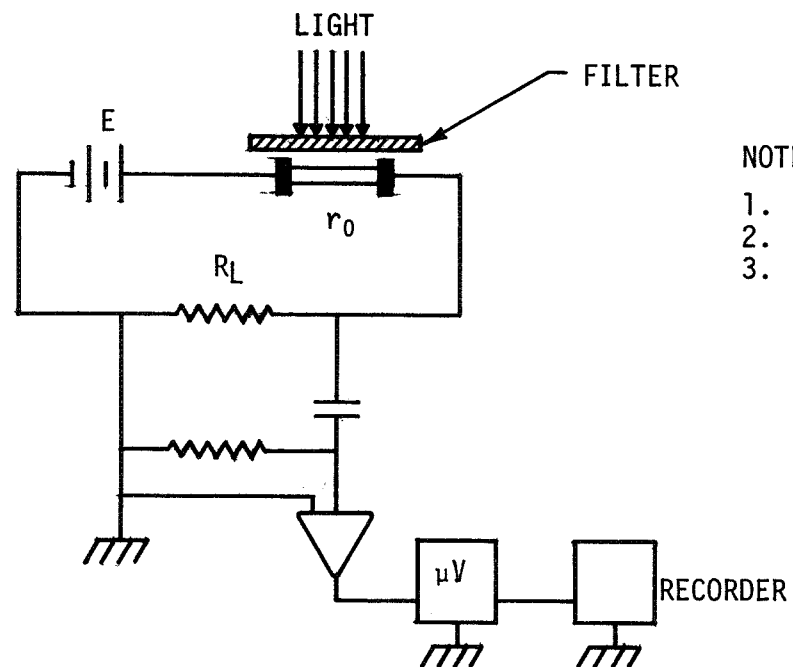
Spectral Photoconductivity

Electrons in impurity or defect levels in the forbidden band of semiconductors may be excited to the conduction band by the absorption of light. Such excitation results in an increase in the conductivity of an n -type semiconductor and the process is known as impurity photoconductivity. Since the exciting light must have energy greater than or equal to the energy separation between the impurity level and the conduction band, the energy level scheme can be probed by measuring the spectral dependence of the photoconductivity.

The number of free carriers generated by the exciting light of wavelength λ is proportional to the concentration of populated impurity centers, to the exciting light intensity, to the quantum yield, and to the capture cross section of the electron-occupied impurity center for a photon of wavelength λ . By measuring the impurity photoconductivity for different treatments of a material, one can determine how the density of populated impurity centers changes with the treatment.

The experimental arrangement for the spectral photoconductivity measurements is shown in Figure 4-21. The experiment consists of measuring the voltage change, Δv , across the load resistor, R_L , when the sample is flashed with light. It can be shown (Ref. 45) that the change in conductivity, $\Delta\sigma$, of the film is related to the measured voltage change by

$$\Delta\sigma = \frac{(R_L + r_0)^2 \Delta v}{r_0^2 E R_L - \Delta v r_0 R_L (r_0 + R_L)} \quad (4-1)$$



NOTES:

1. E - BIAS VOLTAGE
2. r_0 - SAMPLE RESISTANCE
3. R_L - LOAD RESISTANCE

FIGURE 4-21. SCHEMATIC OF SPECTRAL PHOTOCONDUCTIVITY EXPERIMENTAL ARRANGEMENT

where

E - voltage bias across the sample

$r_0 = \frac{1}{\sigma_0}$ - sample resistance before illumination.

If the load resistance is small compared to the sample resistance, then

$$\Delta\sigma = \frac{\Delta v}{E R_L} \quad (\text{for } R_L \ll r_0) \quad . \quad (4-2)$$

However, the maximum sensitivity is obtained when the load resistance is given by

$$R_{LM} = [r_0 (r_0 - \Delta r)]^{\frac{1}{2}} \quad (4-3)$$

where Δr is change in sample resistance due to illumination. For $\Delta r \ll r$

$$R_{LM} = r_0 \quad (4-4)$$

and the photovoltage, Δv , is related to the photoconductance, $\Delta\sigma$, by

$$\Delta v = \frac{E}{4} \frac{\Delta\sigma}{\sigma_0} \quad . \quad (4-5)$$

The load resistance was usually chosen such that Equation 4-2 was satisfied. For very small signal levels, the load resistance was chosen to maximize the photovoltage and Equation 4-5 was used to calculate the photoconductance.

A Xenon flash lamp with a flash duration of about 2 milliseconds was used as the source of exciting light, and narrow-bandpass interference filters were used to select the desired wavelength of exciting light.

The incident intensity of the exciting light was determined using a blackened thermocouple whose response had been calibrated with a 1000°C blackbody. The spectral photoconductivity was then corrected

for intensity and energy differences, and the normalized photoconductance was plotted as a function of wavelength of exciting light.

Figure 4-22 shows the near infrared photoconductivity of a thin film of zinc oxide at 100°K for several different sample conditions. Curve A is the IR photoconductivity of the sample before any significant ultraviolet irradiation, Curve B after 15 minutes of ultraviolet irradiation, and Curve C after 60 minutes of ultraviolet irradiation. Curve D is the response in vacuum after the film was recovered in air (note the scale expansions). Figure 4-23 shows the spectral photoconductivity of another film at 30°K before and after irradiation. Figures 4-22 and 4-23 both show an increase in IR photoconductivity due to irradiation.

Figure 4-24 shows the effect of "flashing" the sample with band gap light immediately before making the photoconductivity measurements. This "flashing" increases the IR photoconductivity by helping populate existing ionized defect centers in the forbidden band. Such additional photoconductivity is known as induced impurity photoconductivity.

Conclusions

The temperature dependence of the mobility studies for thin film of zinc oxide showed that the mobility varied as T^x with values of x between 1/2 and 3/2. Since lattice scattering of electrons varies as $T^{-3/2}$, it is obvious that this mode of scattering is unimportant in thin films.

For ionized impurity scattering, the scattering cross section, S , calculated by Brooks and Herring (Ref. 46), allowing for the screening of ions by electrons, is

$$S = \frac{2\pi e^4}{\epsilon^2 m^2 v^2} \left[\ln(1 + b) - \frac{b}{1 + b} \right] \quad (4-6)$$

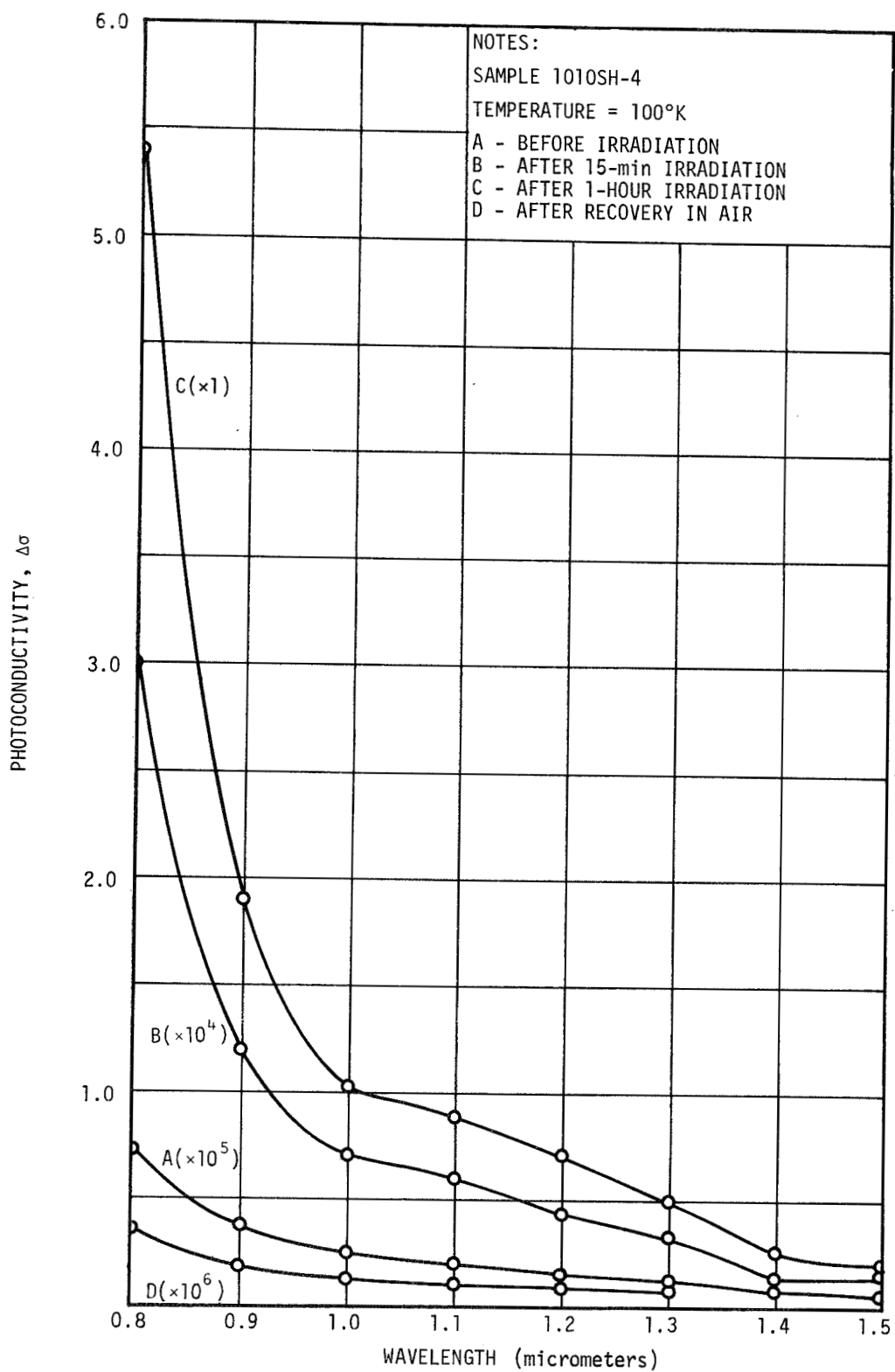


FIGURE 4-22. SPECTRAL PHOTOCONDUCTIVITY OF SAMPLE 1010SH-4 AT 100°K FOR VARIOUS IRRADIATION CONDITIONS

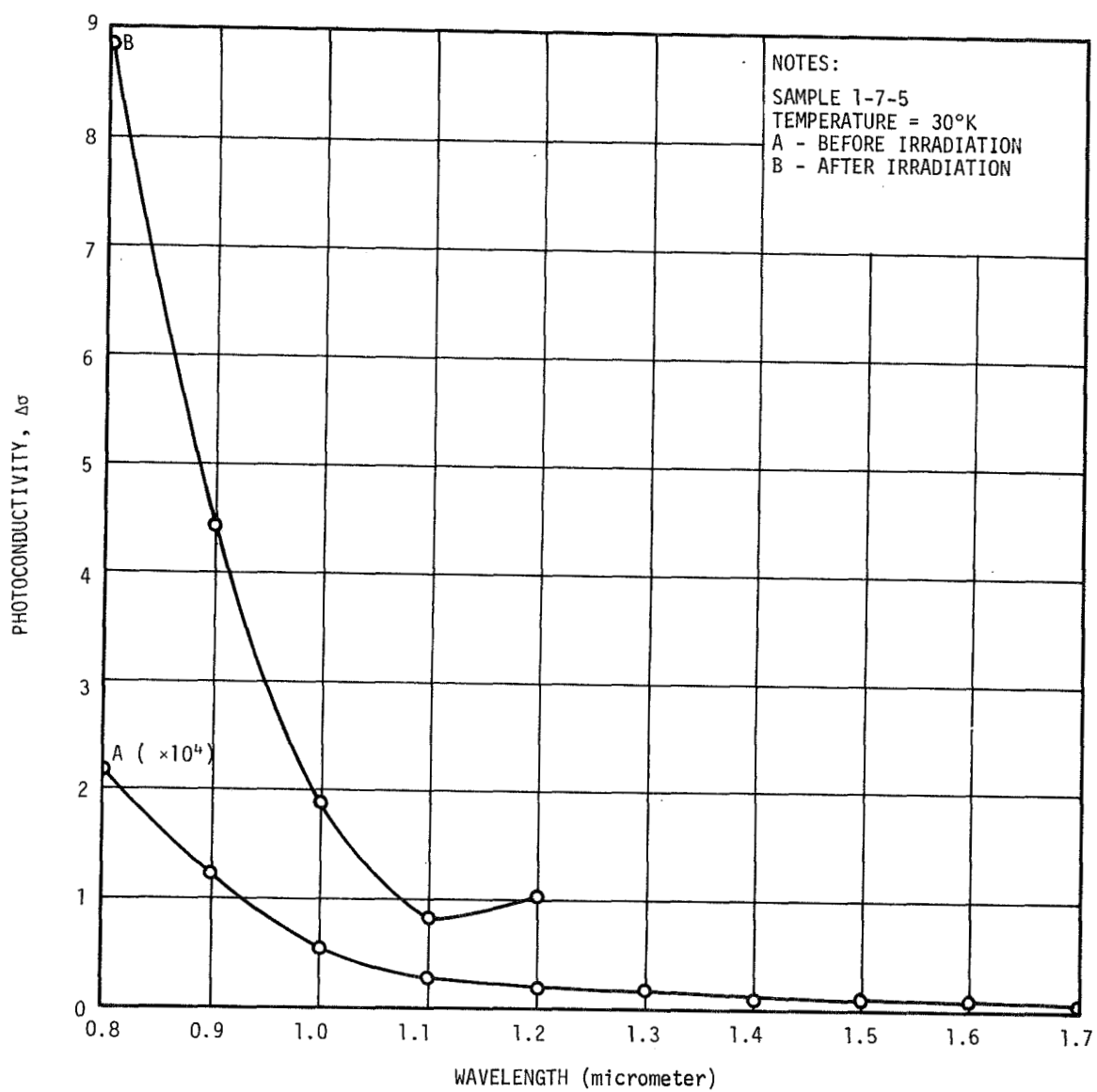


FIGURE 4-23. SPECTRAL PHOTOCONDUCTIVITY OF SAMPLE 1-7-5 AT 300°K BEFORE AND AFTER IRRADIATION

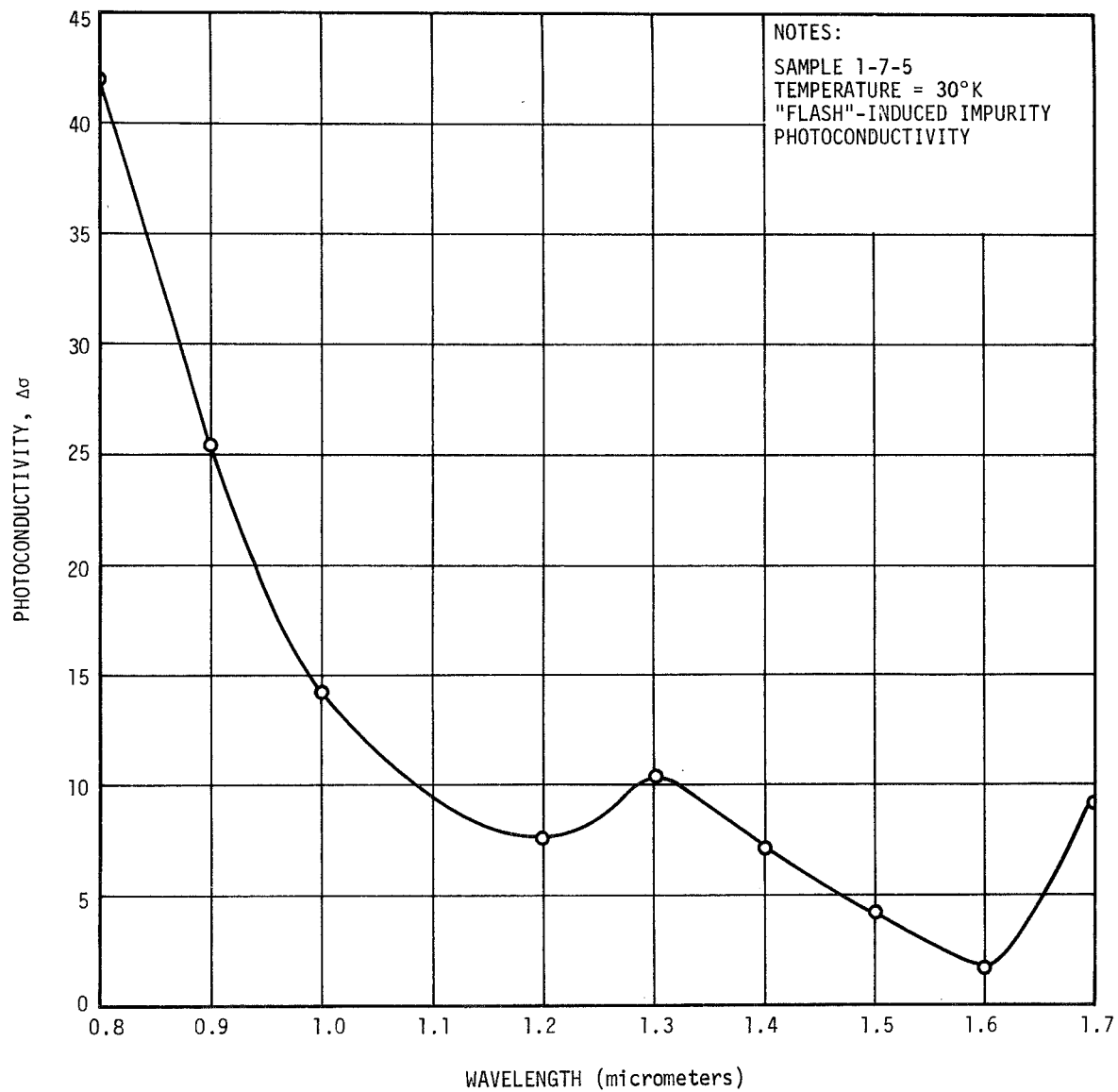


FIGURE 4-24. FLASH-INDUCED IMPURITY PHOTOCONDUCTIVITY OF SAMPLE 1-7-5 AT 30°K

where

$$b = \frac{8 m E}{\hbar^2} R_0^2 \quad (4-7)$$

ϵ - permittivity of material

v - electron velocity

E - average energy of the scattered particle.

R_0 is the screening radius, which in the absence of degeneracy is given by

$$R_0 = \frac{\epsilon k T}{4e^2 \pi n} \quad (4-8)$$

and in the strongly degenerate case by

$$R_0^2 = \frac{\hbar^2 \epsilon}{4e^2 m} \left(\frac{\pi}{3n} \right)^{\frac{1}{3}} \quad (4-9)$$

Then the mobility, μ , will be given by

$$\mu = \frac{e \tau}{m} = \frac{e l}{m N_i S v} \quad (4-10)$$

where

N_i - volume density of ionized scattering centers

τ - average time between collisions

v - electron velocity.

Substituting for S and v in Equation 4-10 leads to a solution of the form

$$\mu = \frac{A}{N_i} \left(k T \right)^{3/2} \ln [B(N_i, n)] \quad (4-11)$$

where A is a constant and B is a complex function of the ionized donor density and the electron concentration.

Equation 4-11 shows that the variation of mobility due to ionized impurity scattering should go as $T^{3/2}$.

Other scattering processes which must be considered are charged surface scattering and dislocation scattering. Petritz (Ref. 47) has shown that for surface scattering, μ varies as $T^{1/2}$.

Mobility scattering due to dislocation space charge regions varies as

$$\mu = e [N_s (2 m k T)^{\frac{1}{2}} A]^{-1} \quad (4-12)$$

where

N_s - volume density of space charge regions

A - area of the space charge region.

The two modes of scattering which are described by the experimental data on temperature dependence are surface scattering and ionized impurity scattering with ionized impurity scattering the dominant mode.

It should be pointed out that due to the degeneracy of the samples, the logarithmic term in Equation 4-11 will alter the temperature dependence somewhat. Also, due to the large carrier concentration, the screening radius will be described better by Equation 4-9 rather than Equation 4-8, and the screening of the charged ions by the free carriers will be more effective.

The temperature dependence of the electron concentration showed that the samples were degenerate after irradiation. The degeneracy is probably the result of the formation of a broad band of donor levels near the bottom edge of the conduction band.

The temperature dependence of the in situ recovery of the mobility implies that the recovery is dependent on the diffusion of scattering centers.

The variation of mobility and electron concentration with phot-excitation showed that the mobility actually increased more rapidly than did the carrier concentration until the mobility began to saturate at about $40 \text{ cm}^2/\text{V-sec}$.

The variation of mobility with electron concentration could be described by

$$\mu \propto n^x$$

with values of x between 1 and 3 for the various samples measured.

It has been suggested (Ref. s 1 and 16) that the visible damage observed in irradiated zinc oxide may be due to the precipitation of excess zinc at dislocations.

When a metallic precipitate is formed in a dielectric such as zinc oxide, then a barrier layer should exist around the precipitate with a thickness, d , given by

$$d = \left(\frac{e \phi}{2\pi \epsilon n} \right)^{\frac{1}{2}} \quad (4-13)$$

where

ϕ - electric potential

ϵ - dielectric constant of the zinc oxide

n - electron concentration.

Substituting Equation 4-13 into 4-12 shows that for a spherical space charge region

$$\mu \propto \left[\frac{2\pi \epsilon n}{\phi N_s (2m k T)^{\frac{1}{2}}} \right] , \quad (4-14)$$

while for a cylindrical space charge region

$$\mu \propto \frac{e}{N_s} \left(\frac{2\pi \epsilon n}{e \phi 2m k T} \right)^{\frac{1}{2}} \quad (4-15)$$

Equations 4-14 and 4-15 indicate that precipitation alone is not enough to explain the experimental dependence of mobility on electron concentration.

In an earlier paper (Ref. 44) Teledyne Brown Engineering showed that the mobility varied linearly with the electron concentration for neutralization of ionized donor levels due to decrease in band-bending. The results obtained in this work can be explained by a combination of these effects.

The increase in mobility with photoexcitation is attributed to the population and neutralization of charged scattering centers, to the increased screening of ions by electrons, and to the precipitation of excess zinc at dislocation centers.

The increased mobility recovery at higher temperatures is believed to be due to the diffusion of excess zinc to dislocation centers where it is precipitated, reducing the space charge at the dislocation.

The photoconductivity studies have demonstrated the existence of a strong infrared absorption edge near 1.0 micrometer (approximately 1.25 eV) which is greatly enhanced by ultraviolet irradiation -- the photo-current increases by a factor of 10^6 due to ultraviolet irradiation. Another

infrared absorption band is produced near 1.3 micrometers (approximately 0.95 eV) by ultraviolet irradiation. Still another band is produced by the ultraviolet irradiation near 1.7 micrometers. The energy states associated with these three absorptions are believed to be donor states with energy levels approximately 1.2, 0.9, and 0.7 eV below the conduction band.

5. SUMMARY

The optical transmittance studies showed no change in visible or infrared transmittance of zinc-oxide films after 1,000 ESH ultraviolet irradiation. No infrared absorption bands were observed in the spectra of thin zinc-oxide films for wavelengths between 1.0 and 2.5 micrometers.

The temperature dependence of the electron concentration in irradiated films indicated that the Fermi level for the irradiated films was either above the bottom of the conduction band or that the donor centers were so dense that impurity band conduction was significant.

The temperature dependence of the mobility indicated that the dominant scattering mechanisms for thin films in the temperature range 30°K to 400°K were surface scattering and ionized impurity scattering. The variation of the mobility with photoexcitation indicated that the ultraviolet radiation neutralized scattering centers. It is believed that this neutralization was accomplished by the elevation of the Fermi level and the subsequent population of ionized donor centers.

The photo-Hall effect studies showed that both the mobility and the free electron concentration increased due to ultraviolet irradiation. The increase in electron concentration is believed to be due to the desorption of chemisorbed oxygen and the resultant decrease in electronic energy band-bending and to the creation of additional zinc donors by lattice photolysis at the surface.

The photoconductivity data shows that there exists an absorption at 1.0 micrometer prior to ultraviolet irradiation but that this absorption is greatly enhanced by the ultraviolet irradiation.

Absorptions near 1.4 and 1.7 micrometers are induced by ultraviolet irradiation. The energy states associated with these three absorptions are believed to be donor states with energy levels approximately 1.2, 0.9, and 0.7 eV below the conduction band.

These studies have shown that ultraviolet irradiation of zinc-oxide results in the production and population of defect centers with energy levels near the conduction band and that these centers are sensitive to infrared radiation.

Although the ultraviolet irradiation increases the electron concentration, the large increase in mobility should prohibit any increase in free carrier infrared absorption.

6. RECOMMENDATIONS

The absence of observable infrared structure in the zinc-oxide films and the lack of observable damage in the film transmittance after irradiation, contrasted with the occurrence of (OH^-) bands in powder samples which damage heavily, suggest that (OH^-) absorption may enhance the degradation of zinc-oxide pigment material.

Infrared absorption centers related to hydroxyl radical content have been observed in several of the white oxides used as pigments in thermal control coatings. Infrared absorptions related to hydroxyl radical bands are seen in the reflectance spectra of nearly all the zinc-oxide powder specimens used in thermal control coating degradation studies. These absorptions decrease as the samples are degraded, indicating that the hydroxyl radicals are dissociated by the irradiation. Since the presence of the hydride ion has been shown to greatly reduce the energy required form an F-center in the alkali halides it is reasonable to expect the same effect in zinc oxide, and because of the strong OH^- absorptions observed in the spectra of the zinc-oxide powders, the dependence of the degradation on the OH^- content should be investigated thoroughly.

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