CHAPTER IV

C H A P T E R - IV

REFLECTIVITY MEASUREMENTS AND OPTICAL CONSTANTS OF MOLYBDENUM SULPHIDE THIN FILMS

4.1 Introduction :

In order to utilize large amount of light incident on semiconducting photoelectrode in electrochemical photovoltaic cells, its reflection coefficient must be less. Reflection coefficient of any material can be determined from reflectivity measurements. Molybdenum sulphide is predicted to be one of the good photoelectrodes in ECPV cells. Hence in the present investigation reflectivity of molybdenum sulphide films is studied. The optical phenomena such as absorption, reflection, transmission and emission exhibited by any material depend basically on the various ways in which light interacts with matter. The optical characteristics of thin films can be easily understood from a knowledge of the optical constants of the films. The refractive index (n), the absorption index (k) and absorption coefficient (α) are interesting optical constants. The refractive index is an important parameter in understanding the chemical bonding and for analysing the photoemission leading to the information about the band structure. Therefore, main goal of this chapter is to measure reflectivity of molybdenum sulphide films and to determine its optical constants from the reflectivity measurements.

4.2 Theoretical Background :

If a perfectly smooth and flat interface exists between two homogeneous media the ratio of the reflected to the incident intensity of light striking the surface is called the reflectivity.

A real surface however, is not ideally smooth and undistorted so that the situation is complicated by surface conditions such as films, roughness and disorder in the crystal lattice at the surface. The measured ratio is thus usually termed the reflectance to distinguish it from the former. The reflectivity of a material is intimately connected with its band gap structure. If the highest occupied energy band is not completely full, electrons may absorb energy from the incident light and be raised to higher energies in the band, thus affecting the reflectivity of the material. These intraband transitions of the conduction electrons, or in case of a nearly filled band, holes largely determine the reflectivity of metals and semi-conductors. At shorter wavelengths, the light has sufficient energy to raise the electrons from one energy band to the another and the reflectivity is then also affected by these interband transitions.

The determination of refractive index, absorption index from measurement of reflected intensities has been described in general terms by Tousey[1]. In principle the method consists in measuring some characteristics of the reflection at different angles of incidence. If the measured values of the characteristics at angles of incidence ϕ_1, ϕ_2, ϕ_3 .... etc. for plane polarized light of aziuth Θ, be R_1, R_2, R_3 ... etc.

We have

$$\left.\begin{aligned} R_1 &= F(n,K,\Theta,\phi_1) \\ R_2 &= F(n,K,\Theta,\phi_2) \\ R_3 &= F(n,K,\Theta,\phi_3) \end{aligned}\right| \qquad \ldots (4.1)$$

where the function F is obtained from the appropriate Fresnel's equation for the reflection. The Fresnel's equations for reflectance and transmittance are given as follows :

For the general case of light incident at angle ϕ on a film of index n_1 and thickness d, lying on a plane substrate of index n_2, the reflectance and transmittance may be determined in terms of the Fresnel's coefficient of reflection and transmission at the n_o / n_1 and n_1 / n_2 interfaces. The amplitudes of reflectance and transmittance are obtained by assuming multiply reflected and transmitted beams respectively as

$$R = \frac{\gamma_2 + \gamma_1 \exp(-2i\delta)}{1 + \gamma_1\gamma_2 \exp(-2i\delta)} \qquad \ldots (4.2)$$

and

$$T = \frac{t_1 t_2 \exp(-i\delta)}{1 + \gamma_1\gamma_2 \exp(-2i\delta)} \qquad \ldots (4.3)$$

where γ_1, γ_2 and t_1, t_2 are the Fresnel's coefficients at the n_o / n_1 and n_1 / n_2 interfaces respectively.

$$\delta = (2\pi/\lambda) n_1 d \cos\phi \qquad \ldots (4.4)$$

is the phase thickness of the film and λ is the wavelength in vacuum. The reflectivity and transmitivity are given by

$$R = \frac{\gamma_1^2 + \gamma_2^2 + 2\gamma_1\gamma_2 \cos 2\delta}{1 + \gamma_1^2\gamma_2^2 + 2\gamma_1\gamma_2 \cos 2\delta} \qquad \ldots (4.5)$$

$$T = \frac{n_2 t_1^2 t_2^2}{n_o 1 + 2\gamma_1\gamma_2 \cos 2\delta + \gamma_1^2 \gamma_2^2} \qquad \ldots (4.6)$$

For the special case of normal incidence and transparent media these expressions can be evaluated. But for an absorbing film, the refractive index is replaced by $n^* = n + iK$, and the resulting expressions are complicated and evaluation of n and K is usually done by programming in a computer.

The pair of values of n and K which can be obtained from the simultaneous solution of these equations are the optical constants of the medium. Since the algebric relations cannot be solved directly for n and K the equations are solved graphically optical constants were evaluated from R_p and R_s components using the relations as given below[2]

$$R_s = \frac{n_o^2\cos^2\Theta + (n^2 + K^2)(a^2 + b^2) - 2\,n_o(na - Kb)\cos\Theta}{n_o^2\cos^2\Theta + (n^2 + K^2)(a^2 + b^2) + 2\,n_o(na - Kb)\cos\Theta} \quad \ldots (4.7)$$

$$R_p = \frac{n_o^2(a^2 + b^2) + (n^2 + K^2)\cos^2\Theta - 2n_o(na + Kb)\cos\Theta}{n_o^2(a^2 + b^2) + (n^2 + K^2)\cos^2\Theta + 2n_o(na + kb)\cos\Theta} \quad \ldots (4.8)$$

where n_o is the refractive index of the external medium (air) and the quantities a and b are given by the expressions

$$a = \sqrt{\frac{\sqrt{p^2 + q^2} + p}{2}}$$

$$b = \sqrt{\frac{\sqrt{p^2 + q^2} - p}{2}}$$

$$p = 1 + (K^2 - n^2)\left(\frac{n_o \sin\Theta}{n^2 + K^2}\right)^2$$

$$q = -2\,nK\left(\frac{n_o \sin\Theta}{n^2 + K^2}\right)^2$$

when $n^2 + K^2 \gg 1$, the term $\left(\frac{n_o \sin \Theta}{n^2 + K^2} \right)$ can be neglected and the above equations (4.7) and (4.8) reduce to simpler forms[3]

$$R_s = \frac{\cos^2\Theta + (n^2 + K^2) - 2n \cos \Theta}{\cos^2\Theta + (n^2 + K^2) + 2n \cos \Theta} \quad \ldots (4.9)$$

$$R_p = \frac{1 + (n^2 + K^2) \cos^2 \Theta - 2n \cos \Theta}{1 + (n^2 + K^2) \cos^2 \Theta + 2n \cos \Theta} \quad \ldots (4.10)$$

4.3 Experimental

4.3.a Reflection Spectrometer :

The reflection spectrometer designed and constructed in our laboratory consists of mainly (1) Source of light (2) Convex lens (L_1) (3) Narrow slit (4) Sample holder (5) Convex lens (L_2) (6) Polarizer (7) Photovoltaic cell. The light source used in this set-up is a 12 V, 36 W lamp (Cosmic Type 1144). The light source is mounted on a rigid stand. A convex lens (L_1) is mounted just infront and at the same height of the source of light. For the detection of incident and reflected light a photovoltaic cell with adjustable opening is used. For measuring the intensity of reflected light in terms of the current of photovoltaic cell an FET nanoammeter is used. The film coated substrate is placed in the sample holder, which can rotate about its vertical axis. The convex lens (L_1) and light source are adjusted for a concentrated and parallel beam of light. The height of the sample holder is adjusted to make all the light fall normal to the film surface. The reflected light is focussed with another convex lens (L_2) fixed in front of photovoltaic cell. The surface of photovoltaic cell is adjusted and exposed to such focussed light. The photovoltaic cell along with convex lens (L_2) can be rotated to receive the reflected light from the film surface.

A polarizer is used to separate the parallel (p) and perpendicular (s) components of the polarized light. For the p-component of the light the polarizer is fixed with its axis horizontal. It is then rotated through 90° to allow only S-component of the light incident on film surface.

One of the various characteristics of a refrection, the most generally chosen is the measurement of reflection coefficient i.e. the relative intensity after reflection under given conditions of incidence and polarization. The beam cross section used for measurement of reflection coefficient was very small. To maintain the accuracy of the experiment, one reflection coefficient is measured at 70° or even higher incidence. Care was taken that the same portion of the photosensitive surface of the photovoltaic cell was used for all angles, to avoid errors due to variation in photosensitivity across the surface. The basic requirement is that the light beam passing through Polarizer suffers no lateral shift on rotating the plane of polarization.

4.4. Result and Discussion

4.4.1 Reflectivity and Reflection Coefficient :

The factors influencing optical reflectivity are discussed in the following subsections :

a) Effect of Angle of Incidence -

The reflectivity of molybdenum sulphide thin films was studied as a function of angle of incidence of light beam. The relation between reflectivity and angle of incidence of light beam is shown in the fig.4.2. The reflectivity of the film increases with angle of incidence of light beam. At normal incidence 3 percent of the intensity of a beam of unpolarized light is reflected. At other angles of incidence the reflectivity increases with angle at first slowly and then more rapidly until at 90^{o} i.e. grazing angle, all the light is reflected.

The increase in reflectivity with angle of incidence (ϕ) can be explained with the help of equations (4.2) and (4.4). In equation 4.2 the Fresnels coefficient γ_1 and γ_2 are very small hence $\gamma_1 \gamma_2 e^{-2i\delta} << 1$ and can be neglected. This simplifies the relation (4.2) as

$$R = \gamma_2 + \gamma_1 \exp(-2 i\delta) \qquad \ldots (4.11)$$

From equation (4.4) when $\phi = 0$, $\cos 0 = 1$ and

$\delta = (2\pi/\lambda)\, n_1 d$

As angle of incidence (ϕ) increases the magnitude of $\cos \phi$

decreases and hence δ decreases. When δ decreases equation (4.11) predicts that reflectivity (R) increases.

Our result is in confirmation with the work of Jain[4] on reflectivity of tellurium thin films.

b) Thickness Effect -

The reflectivity of molybdenum sulphide thin films deposited at different thicknesses was studied as a function of angle of incidence. Three films having different thicknesses (t_1 = 0.20 micron, t_2 = 0.55 micron and t_3 = 0.74 micron) deposited at substrate temperature 300°C were used for reflectivity measurements. Fig.4.2 shows the change in reflectivity of molybdenum sulphide films as a function of angle of incidence for three different film thicknesses. For a particular angle of incidence it was found that reflectivity decreases as film thickness increases.

This result can also be explained from equations (4.4) and (4.11). For particular angle of incidence ($\emptyset$), magnitude of cos $\emptyset$ is constant and when film thickness increases δ increases, equation (4.11) states that as δ increases reflectivity decreases.

c) Effect of Substrate Temperature -

The change in reflectivity of molybdenum sulphide film as a function of angle of incidence, prepared at different substrate temperatures is shown in fig.4.3. It was observed that as substrate temperature increases the reflectivity increases. This is because the films formed at lower substrate temperatures are thicker and as substrate temperature increases film thickness decreases.

d) Variation of R_p and R_s with $\emptyset$ -

The variation of R_p and R_s components with angle of incidence ($\emptyset$) for a molybdenum sulphide film is shown in Fig.4.4 and 4.5 respectively. It is seen that initially R_s increases slowly whereas there is decrease of R_p component. At higher angles of incidence R_s component increased steadily. R_p, on the other hand, passed through a minimum corresponding to the Brewster angle and then increased rapidly. These results are in fair agreement with the work of Goswami and Rao[2] on the optical properties of cuprous sulphide films.

It was shown that there is one angle of incidence for which the reflected light is completely plane-polarized, with its electric vector perpendicular to the plane of incidence. At angles different from this the reflected light is only partially polarized. The relations in this case are described in terms of the reflection of the two plane-polarized components of the incident unpolarized light, the vibrations of which are, parallel and perpendicular to the plane of incidence. The curves of fig.4.4 and 4.5 are represented by theoretical equations. The reflection coefficient R_p and R_s are given by

$$R_s = \frac{\sin^2 (\emptyset - \emptyset'')}{\sin^2 (\emptyset + \emptyset'')} \quad \ldots (4.12)$$

and

$$R_p = \frac{\tan^2(\phi - \phi'')}{\tan^2(\phi + \phi'')} \quad \ldots (4.13)$$

the angles ϕ and ϕ'' are angles of incidence and refraction respectively. From the relations (4.12) and (4.13) it is evident that both the components are the function of angle of incidence (ϕ).

Case - I : Normal Incidence :-

At normal incidence, where $\phi = 0$, the parallel and perpendicular components are equally reflected because here plane of incidence is undefined and the two components are not distinguishable. Here $R_p = R_s = 1$

Hence

$$R = \frac{(n_2 - n_1)^2}{(n_2 + n_1)^2} \quad \ldots (4.14)$$

For air conductor interface

$n_1 = 1$ and $n_2 = n - iK$

where n is real part of the refractive index and K is extinction coefficient.

The reflectivity at normal incidence

$$R = \frac{(n-1)^2 + K^2}{(n+1)^2 + K^2} \quad \ldots (4.15)$$

... Conducting media

For non conducting media there is no absorption i.e.

$$\alpha = 0$$

$$\alpha = \frac{4\pi K}{\lambda} = 0$$

hence $K = 0$

Therefore
$$R = \frac{(n-1)^2}{(n+1)^2} \quad \ldots (4.16)$$

... Non absorbing media

Case II : Non-Normal Incidence $\phi \neq 0$:

With increasing ϕ, R_p drops and R_s rises upto the polarizing angle. At grazing angle ($\phi = 90^o$) both the components are totally reflected. For a critical situation when $\phi + \phi'' = 90^o$ then $R_p = 0$ because $\tan^2 (\phi + \phi'') = 0$ however when $R_s \neq 0$ i.e. $R_s = \sin^2 (\phi - \phi'') \neq 0$ at a critical angle ϕ_c there is only normal component and hence the reflected light is completely plane-polarized with its electric vector perpendicular to the plane of incidence. But this is true only for non conducting media. For conducting media R_p never becomes zero but it goes through minimum. For molybdenum sulphide films this angle is equal to 60^o, and is called the principle angle of incidence. For non conducting media $\tan \phi_c = n$. But for conducting media i.e. for absorbing media this relation does not hold good and the modified expression for the critical angle at which minimum occurs is $\sin^2\phi_c \tan^2\phi_c = n^2 + K^2$. The relation between R_p / R_s and angle of incidence is also shown in fig.4.6. Since the amplitude components R_p and R_s for the incident light are considered positive and real, the negative

Sing in the Fresnel equations for reflection indicates that $\delta_s = \pi$ for all angles of incidence, while $\delta_p = \pi$ up to the polarizing angle and is zero beyond. Thus the phase difference $\Delta = \delta_p - \delta_s = 0$ up to the polarizing angle. Simultaneously the ratio of the amplitude components given by R_p / R_s decreases from unity to Zero as the angle of incidence approaches the polarizing angle, after which it rises to unity again. Whereas the value of R_p / R_s never drops to zero but has a rather high minimum.

4.4.2 Optical Constants :

The R_p/R_s method of reflectivity measurements has been employed by Goswami and Rao[2]. The optical constants have been determined from the R_p/R_s values by a graphical method due to Avery[5] because the algebric relations cannot be solved directly for n and k. Using the expressions for the R_p and R_s components by Goswami and Rao (equations 4.8 and 4.9) the curves relating R_p/R_s to n and K for 12 angles of incidence from 25^o to 80^o in the step of 5^o, for q values of n from 1 to 5 in the step of 0.5 and for the 16 values of K from 0 to 3.0 in the step of 0.2 were generated with the help of computer. Such typical curves are shown in figs. 4.7 and 4.8.

For a particular thickness and angle of incidence, the values of R_p/R_s thus determined experimentally were used to obtain the pair of values of n and K from the above said curves. Such pairs of n and K are evaluated for different angles of incidence. The real value of n and K is then determined from the intersection of the curves of K versus n shown in fig.4.9. The value of refractive index (n) is found to be 3.7 and extinction coefficient is 0.82.

The optical constants n and K are also calculated by using the relation

$$K = \alpha \frac{\lambda}{4\pi}$$

and $$\sin^2 \phi_c \tan^2 \phi_c = n^2 + K^2$$

where α is absorption coefficient and ϕ_c is critical angle corresponding to Brewester angle. The values of n and K are found to be 1.12 and 0.63 respectively.

The R_p/R_s method of reflectivity measurements has been used by Agarwal and Patel[6] for the measurement of optical constants of WSe_2 and $Mo_xW_{1-x}Se_2$ single crystals. A.Goswami and B.V.Rao[2] for the cuprous sulphide films. Pawar and Shikalgar[7] succeeded in determining optical constants of chemically deposited CdS:Li thin films.

<u>Dielectric Constants</u> -

The real (ϵ_1) and imaginary (ϵ_2) parts of the complex dielectric constant (ϵ^*) of the molybdenum sulphide thin film are evaluated from the optical parameters n and K using the relations $\epsilon_1 = n^2 - K^2$ and $\epsilon_2 = 2\ nK$.

The values of ϵ_1 and ϵ_2 are 13.2 and 6.06 respectively.

Figure Captions

4.1 Reflection spectrometer

4.2 Change in reflectivity of films as a function of angle of incidence for various values of thickness.

4.3 Change in reflectivity as a function of angle of incidence for films prepared at different substrate temperature.

4.4 Variation of parallel component (R_p) with angle of incidence.

4.5 Variation of perpendicular component (R_s) with angle of incidence.

4.6 Relation between R_p/R_s and angle of incidence.

4.7 Curves relating R_p/R_s to n and K at $\phi = 60^o$.

4.8 Curves relating R_p/R_s to n and K at $\phi = 80^o$.

4.9 A curve showing the graphical determination of the values of n and K .

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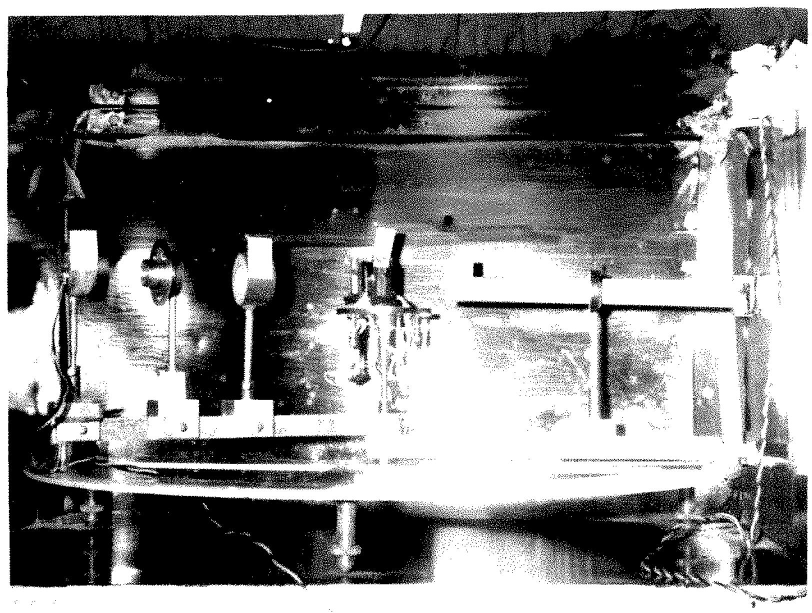

Fig. 4.1 Reflection Spectrometer

1 - Convex lens (L_1)

2 - Narrow slit

3 - Sample holder

4 - Convex lens (L_2)

5 - Polarizer

6 - Photovoltaic cell

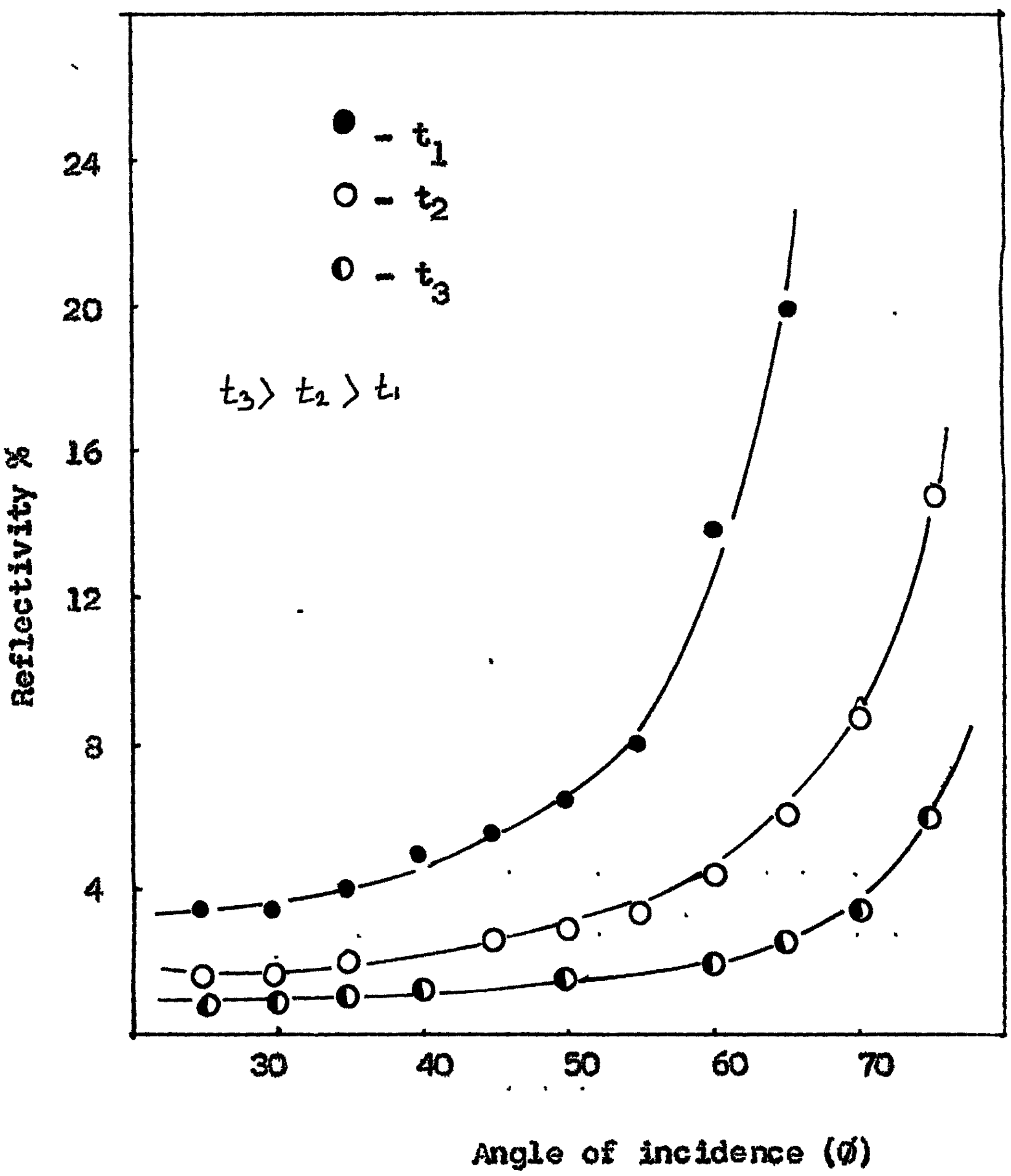
● - t_1
○ - t_2
◐ - t_3
$t_3 > t_2 > t_1$
24
20
16
12
8
4
Reflectivity %
30
40
50
60
70
Angle of incidence (Ø)

Fig. 4.2

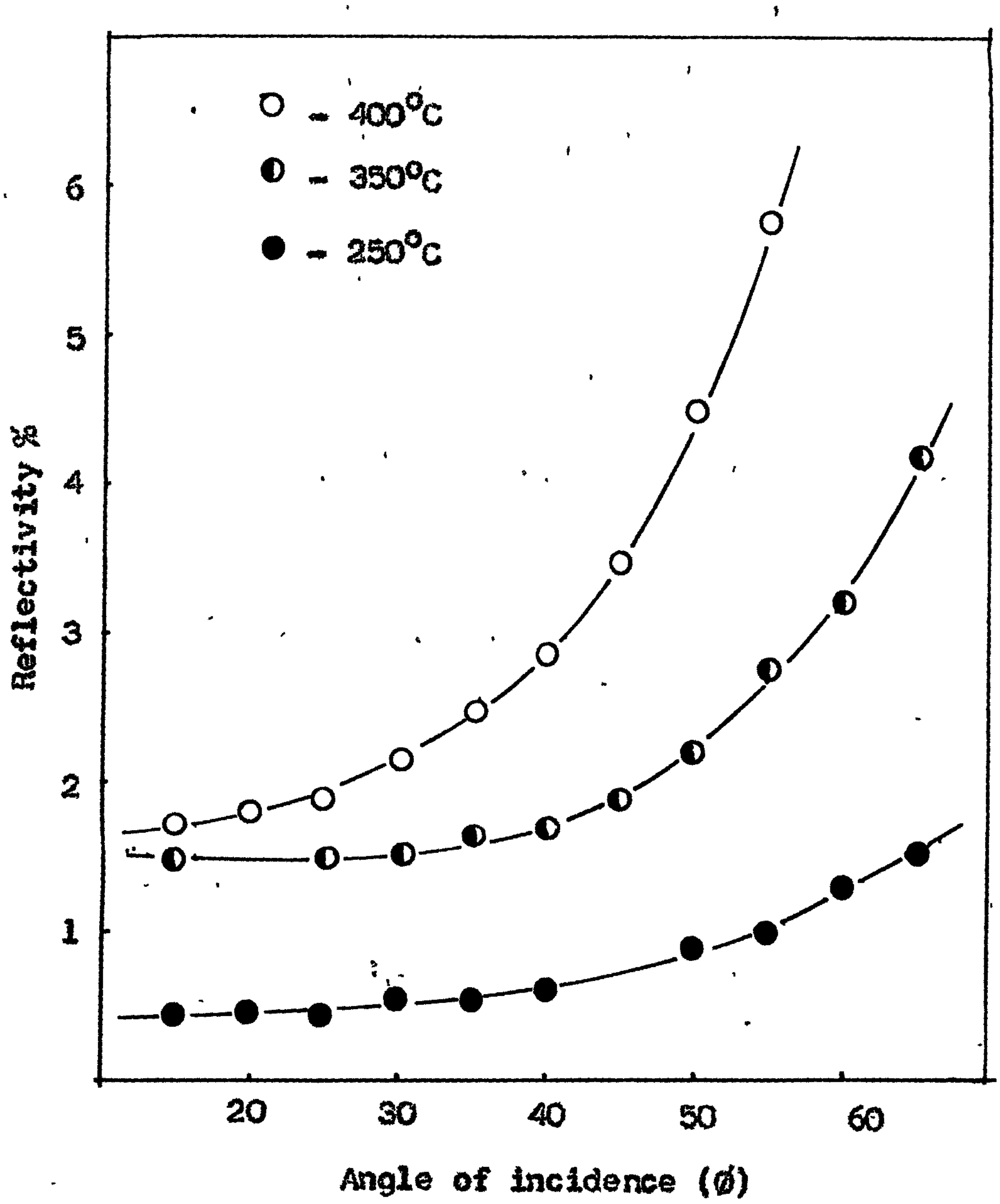
O - 400°C
◐ - 350°C
● - 250°C
Reflectivity %
1
2
3
4
5
6
20
30
40
50
60
Angle of incidence (Ø)

Fig. 4.3

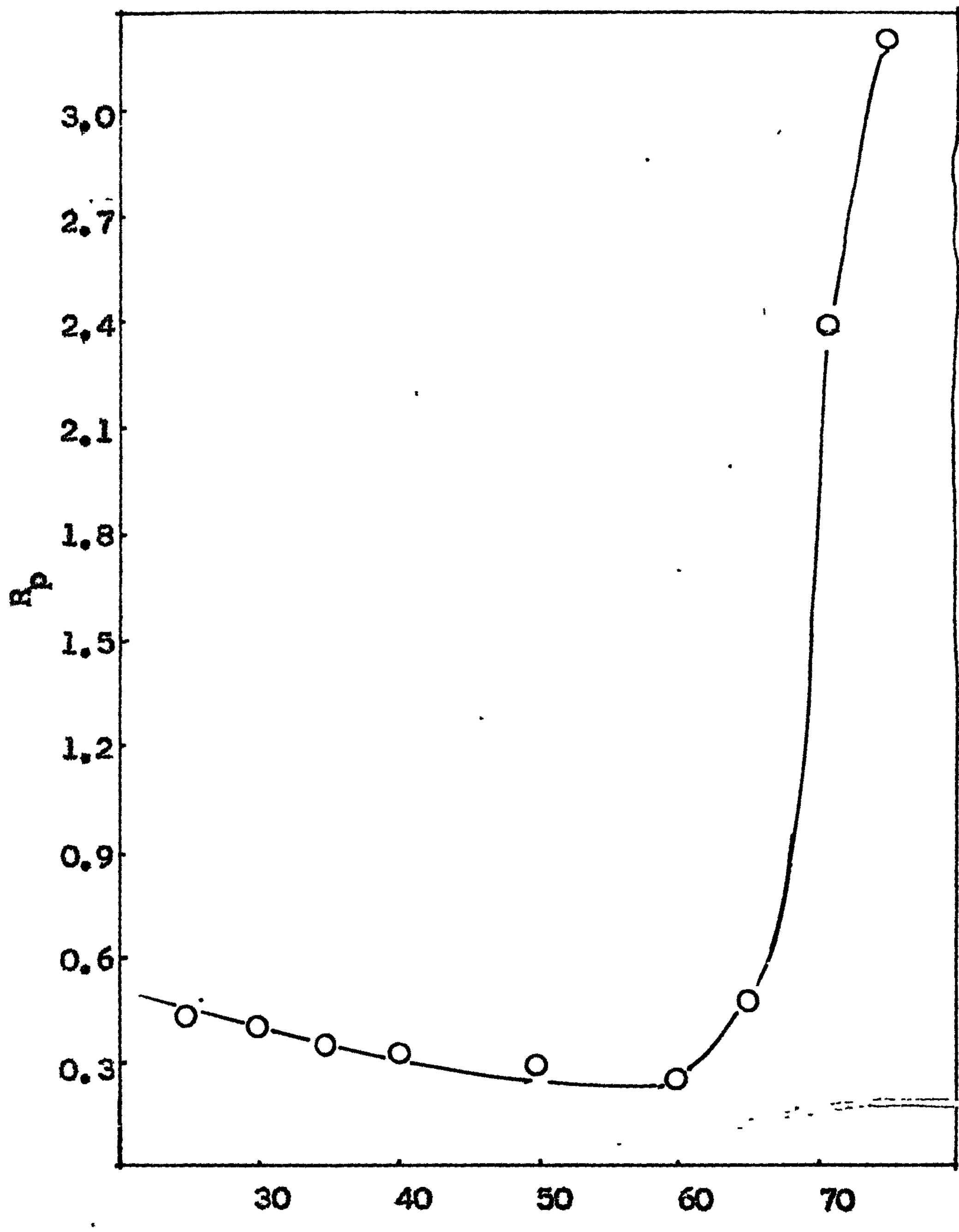

Fig. 4,4

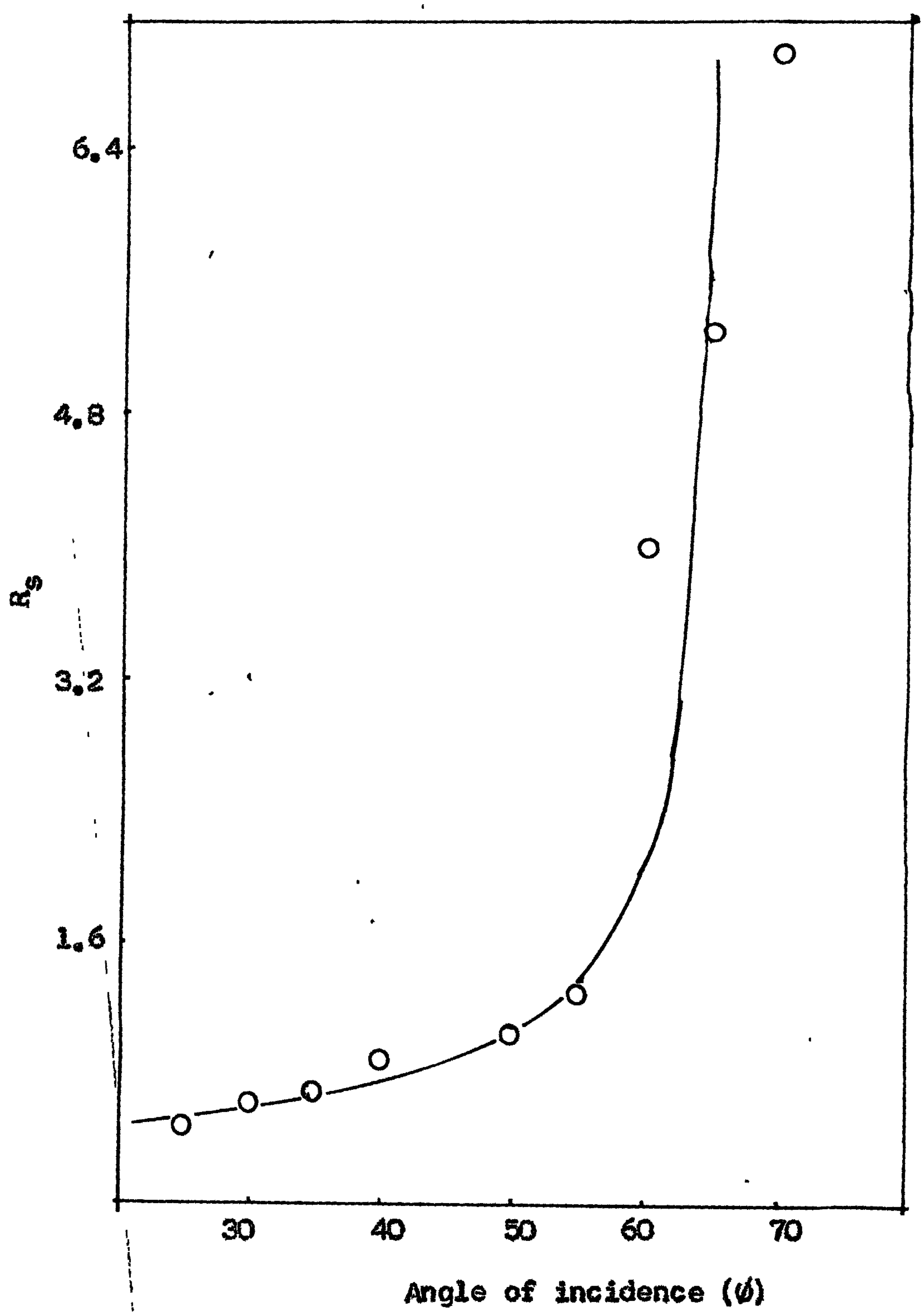

Fig.4.5

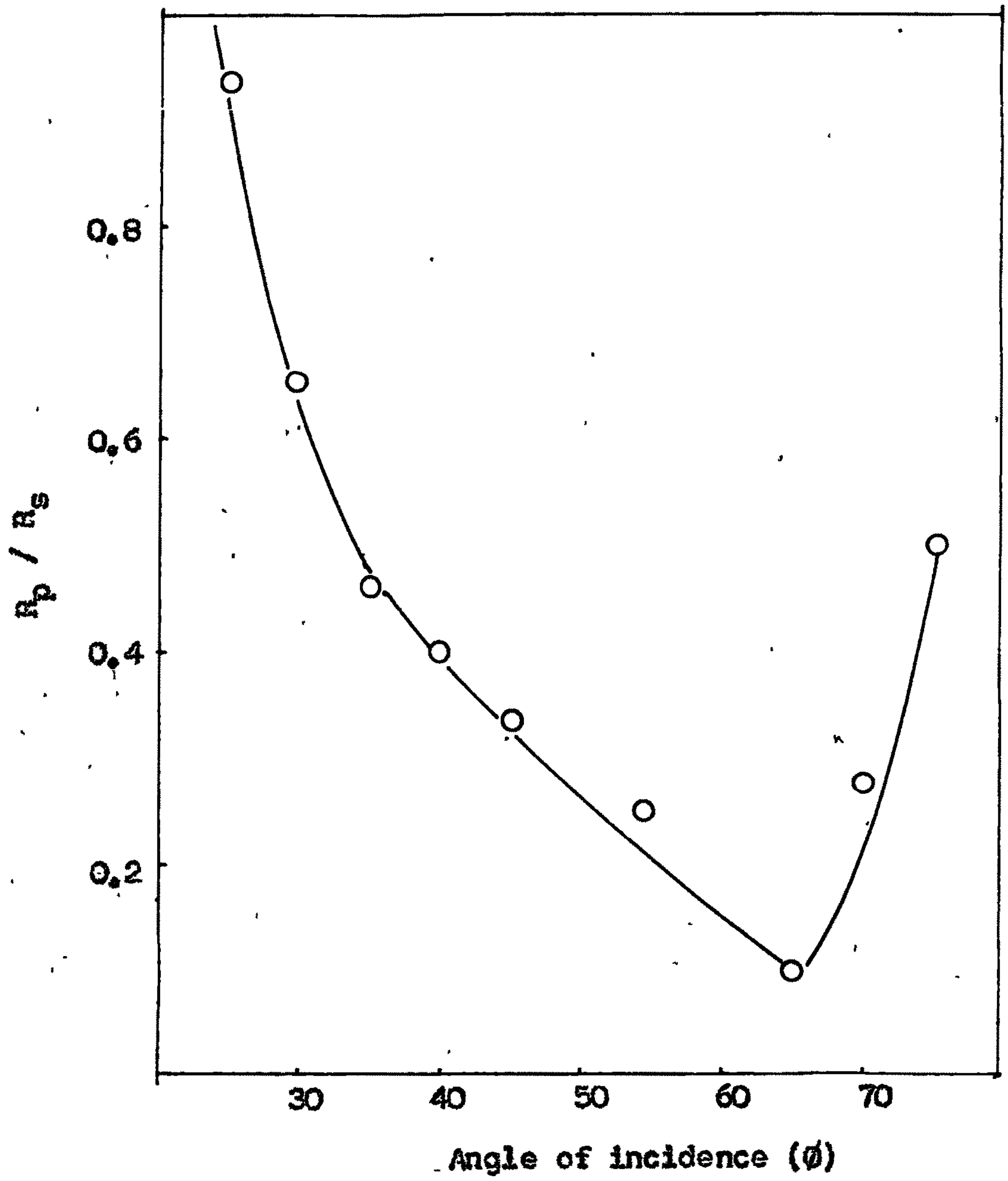

Fig. 4.6

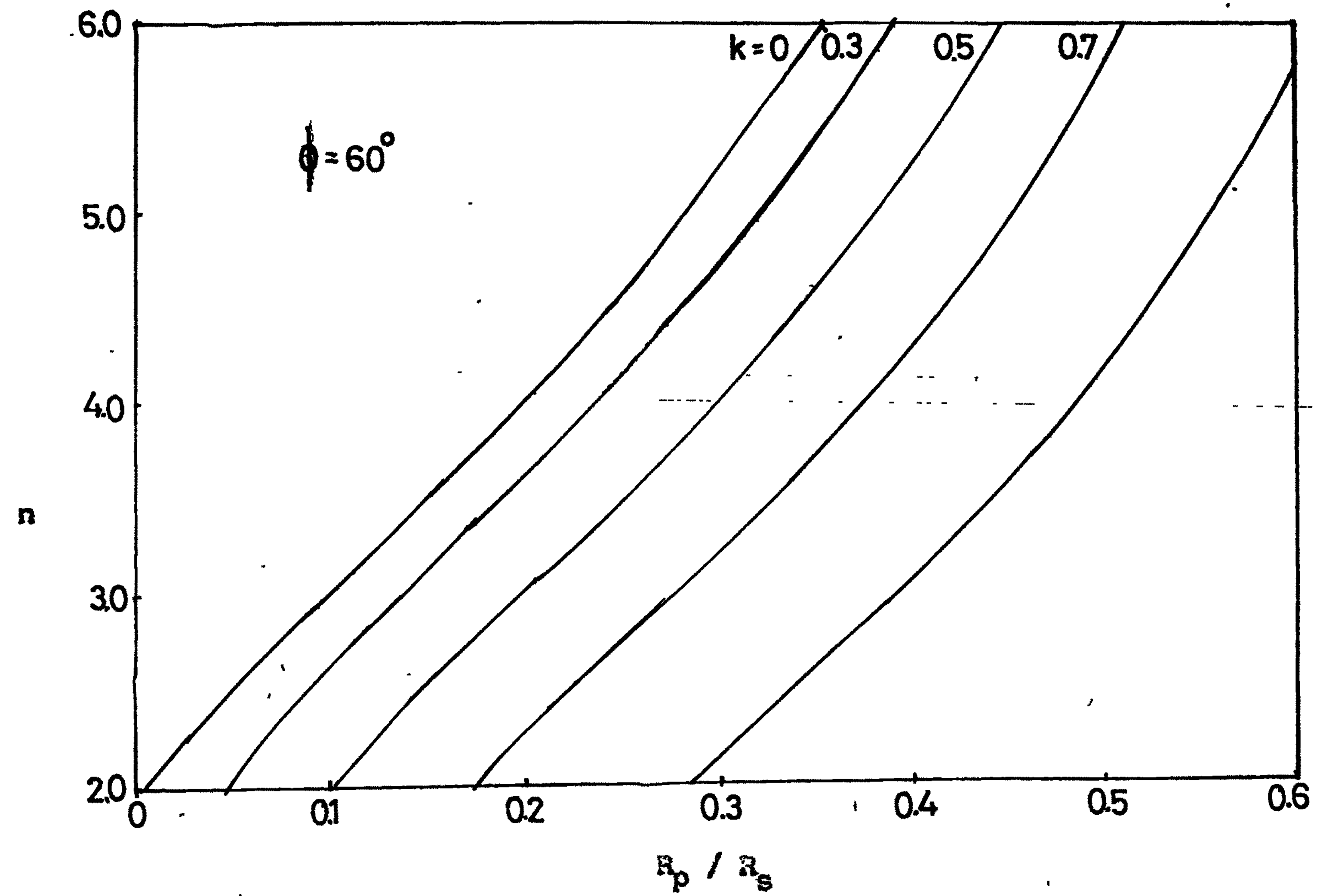

Fig. 4.7

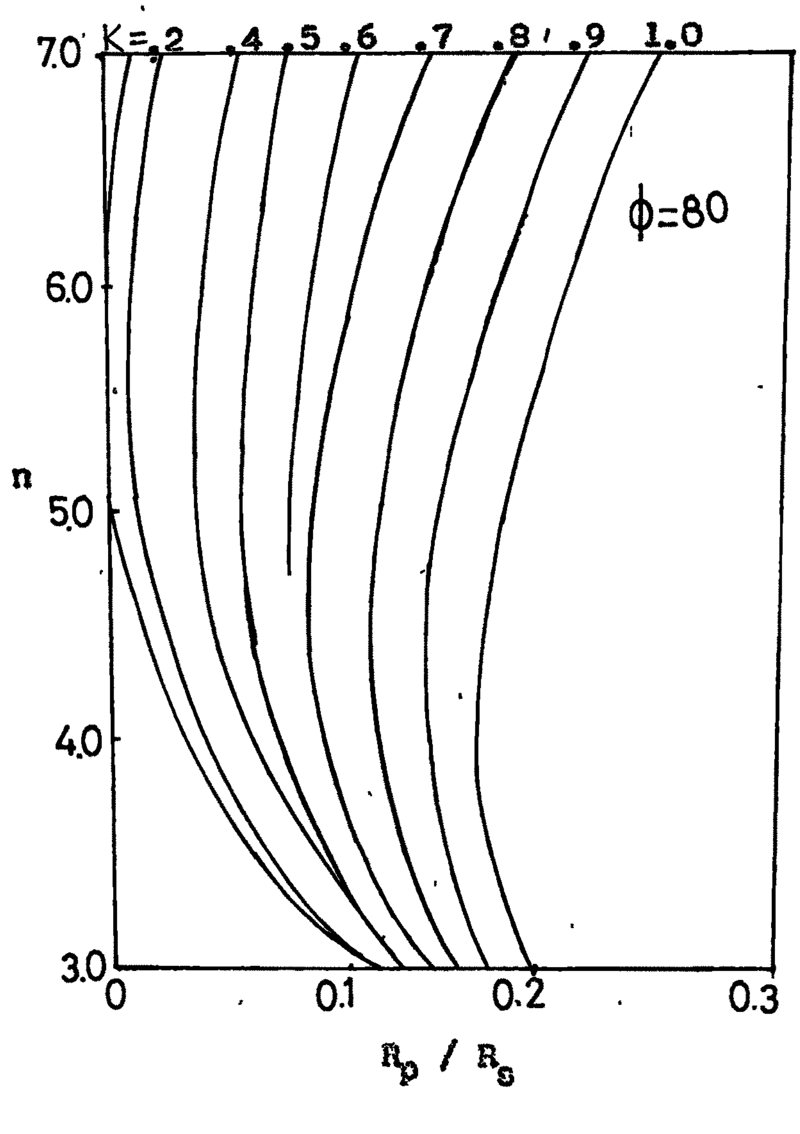

Fig. 4.8

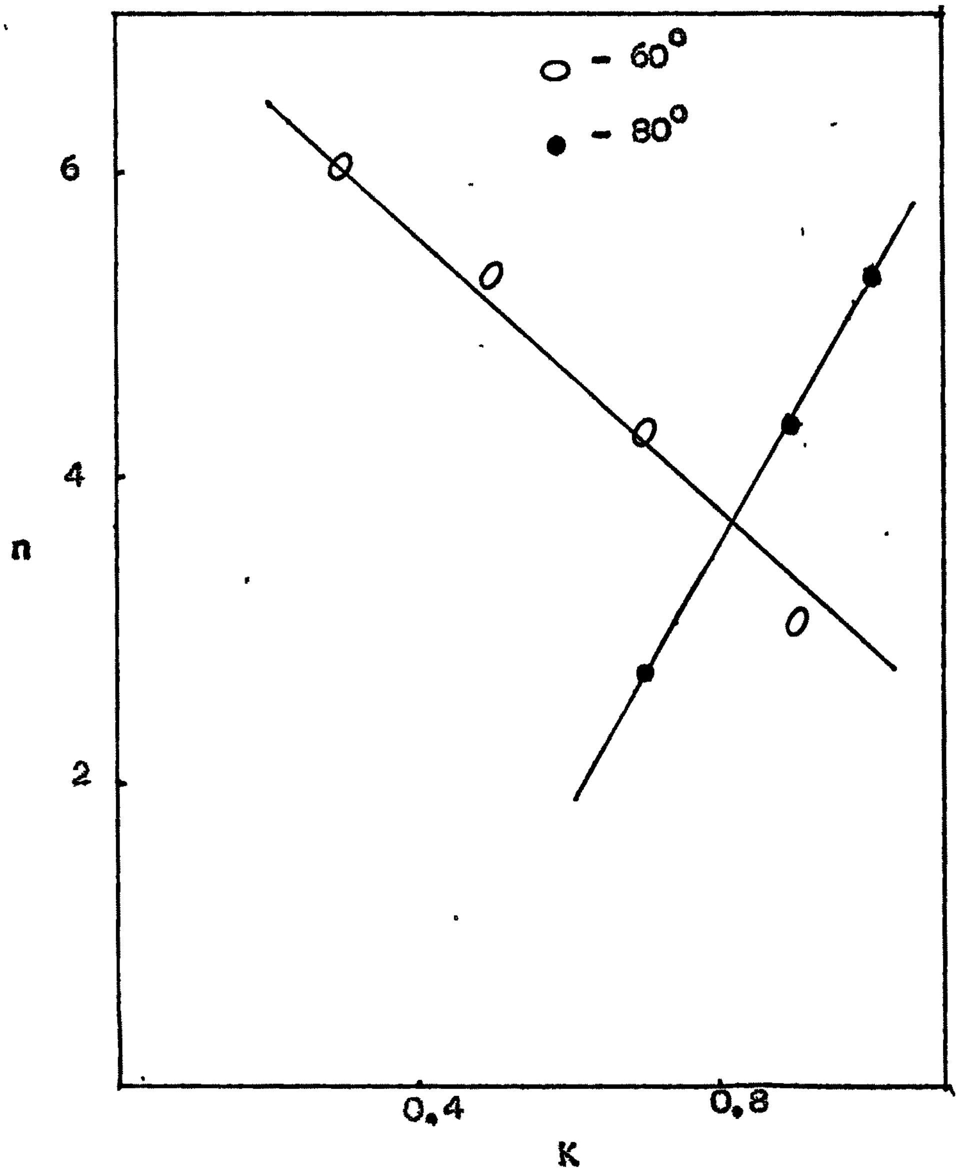

Fig. 4.9