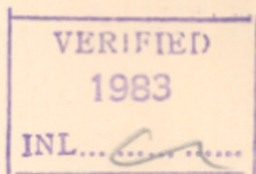


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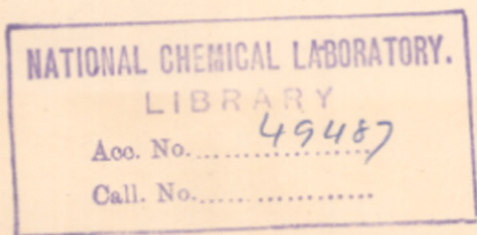


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ELECTRONIC PROPERTIES AND DEFECT  
STRUCTURE OF ZINC OXIDE CRYSTAL  
PREPARED BY ZnS OXIDATION

### A THESIS SUBMITTED TO

### THE UNIVERSITY OF POONA

### FOR THE DEGREE OF

### DOCTOR OF PHILOSOPHY

CHAPTER IV

CHEMISORPTION OF OXYGEN ON ZINC  
OXIDE SINGLE CRYSTAL PREPARED BY  
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ACKNOWLEDGEMENT



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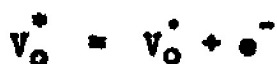
## A B S T R A C T

Single crystals of zinc oxide were prepared by the oxidation of zinc sulfide in controlled oxygen atmosphere at about  $1170^{\circ}\text{C}$ . Oxygen pressure was found to affect the growth appreciably. Various runs were made using the mixtures of oxygen and nitrogen. Exact oxygen pressure was measured with the aid of a galvanic cell containing  $\text{ZrO}_2 + 15\% \text{CaO}$ . Clear needle-like crystals were usually obtained with maximum dimensions of  $10 \times 0.5 \times 0.5 \text{ mm}$  when oxygen pressure was  $\sim 10^{-3}$  atmospheres. Sometimes plate-like crystal and dendritic formation were also observed.

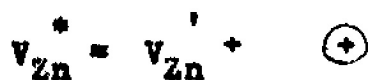
Conductivity measurements were carried out on these needle-like and plate-like crystals. For measurement of conductivity the two ends of the crystal were coated with silver paste and heated to about  $200^{\circ}\text{C}$  for 30 minutes. The crystal with adherent coating of silver obtained as above was pressed between two molybdenum strips screwed to a silica base. To ensure perfect contact molybdenum strips were covered

with a silver foil to which the leads, also of silver wire, were soldered. The whole assembly was introduced in a furnace, the temperature of which was measured by a calibrated chromel-alumel thermocouple. The electrical resistance was measured at 50 cycles A.C. with a Philips Conductivity bridge Model PR 9500.

In the temperature range 25-200°C, ZnO crystals exhibit n-type conductivity with an activation energy of 0.02 ev. The charge carriers (electrons) arise due to the ionization of neutral oxygen vacancies and neutral zinc interstitials:



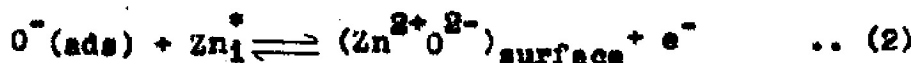
At 200-600°C the conductivity changes to p-type and the activation energy becomes 0.92 ev. This change has been attributed to the ionization of vacant zinc sites.



The resistance decreases after annealing at  $600^{\circ}\text{C}$  presumably due to the increase in the concentration of zinc vacancies. Absorption spectrum shows an absorption edge at  $390\text{ m}\mu$  corresponding to a band gap of  $3.24\text{ ev}$ .

The variation of conductivity with temperature for the plate-like crystals in air was found to be different from that for needle-like crystals. This was attributed to chemisorption of oxygen on plate-like crystals. The study of chemisorption was extended to thin films of  $\text{ZnO}$ . Thin films of  $\text{ZnO}$  were prepared by evaporating zinc in vacuum and then oxidising in air. The surface conductivity was measured on specimen where the two electrodes were applied on the surface of  $\text{ZnO}$  separated by a distance of about  $1\text{ cm}$ . On plotting the resistance against temperature, it is observed that at first the resistance falls slowly upto  $150^{\circ}\text{C}$  and then there is a steep fall in resistance upto  $280^{\circ}\text{C}$ , then again it starts rising and reaches a maximum at about  $400^{\circ}\text{C}$ ; on heating still further it starts

decreasing gradually. We find that the observed behaviour in air is consistent with the following simultaneous equilibria taking place on the surface of zinc oxide.



These reactions move to the right as the temperature is raised. However, the enthalpy of the reaction (2) is larger than that of (1), so that at low temperatures reaction (1) predominates and the release of adsorbed oxygen releases one electron and hence increases the conductivity. At high temperatures reaction (2) predominates and  $O^-(ads)$  starts reacting with neutral zinc interstitial ( $Zn_1^*$ ) atoms. As the  $O^-(ads)$  and  $Zn_1^*$  get used up, the reactions (1 and 3) move to the left to maintain equilibrium. This whole process leads to a decrease in the number of free  $e^-$  and an increase in the resistance.

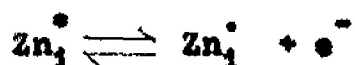


Indium doped ZnO films were prepared by evaporating Zn-In alloy from a tungsten filament in a vacuum of the order of  $10^{-6}$  mm of Hg. Care was taken to evaporate the alloy completely to avoid any change in concentration. The film was homogenised by heating in air at  $800-900^{\circ}\text{C}$  for several hours. It has been observed that at high indium concentration, the sharp maxima and minima of resistance disappears and the resistance remains constant upto  $400^{\circ}\text{C}$ .

The electrical resistance of ZnO thin films has also been measured in hydrogen and nitrogen atmospheres. The resistance follows the following order:

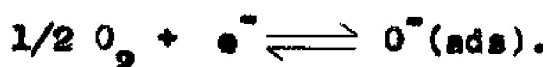
$$R_{\text{ZnO}(\text{H}_2)} < R_{\text{ZnO}(\text{N}_2)} < R_{\text{ZnO}(\text{air})}.$$

The high conductivity in nitrogen has been attributed to the ionisation of zinc interstitials following the equation:



The activation energy for this ionization is small

(0.05 ev) and hence all the zinc interstitials are ionized at room temperature. However, in presence of oxygen, the adsorbed oxygen atoms on the surface act as traps and decrease the concentration of electrons



The resistivity in presence of oxygen is therefore higher than that in presence of nitrogen. In  $H_2$  atmospheres the electron concentration is further increased due to creation of excess zinc interstitials which ionize to give electrons.

Single crystals of zinc oxide were irradiated by  $\gamma$ -rays obtained from a  $Co^{60}$  source at  $25^\circ C$ ,  $100^\circ C$  and  $300^\circ C$  in air. The resistance first increases with irradiation time, reaches a maximum after about five hours, then decreases slightly and finally attains a constant value. At  $100^\circ C$  the maximum in the resistance appears earlier and at  $300^\circ C$  it vanishes completely. This behaviour has been attributed to the change from n-type to p-type

conduction due to adsorption of oxygen.

The effect of ambient atmospheres has also been studied. In nitrogen atmosphere ( $P_{O_2} \simeq 10^{-3}$  atm.), the resistance decreases with irradiation time which supports the above conclusion. When the crystal is irradiated in presence of hydrogen, resistance initially decreases then starts increasing again and finally becomes constant. This has been attributed to the reduction and subsequent precipitation of zinc as a separate phase.

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**CHAPTER I**  
**GENERAL INTRODUCTION**

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## CHAPTER - I

### GENERAL INTRODUCTION

Zinc oxide is finding increasing applications in a number of electronic devices since it is piezoelectric and also as a catalyst for many hydrogenation and other reactions. Though for catalytic reactions, zinc oxide in its powder form is preferable because of the requirement of high surface area, efficient electronic devices could only be made with single crystals. Furthermore, to understand the basic processes operative in a catalytic reaction on a semiconductor it is fruitful to make studies on single crystals. In past various attempts were therefore made to grow single crystals of zinc oxide using various methods, viz; condensation of zinc oxide vapours at elevated temperatures, oxidation of zinc vapours by oxygen or air, by chemical reaction of zinc fluoride with air or by the hydrothermal growth. We succeeded in growing zinc oxide single crystals by a simpler method i.e. by oxidation of polycrystalline ZnS. The electronic properties and the defect structure

of zinc oxide single crystal prepared by this new method was studied by the measurement of electrical conductivity.

Studies on polycrystalline ZnO in the form of compressed discs, or the evaporated films have shown a pronounced effect of oxygen chemisorption on the electrical conductivity of zinc oxide. In fact, electrical measurements have often been used as a complimentary tool in the study of catalysis or chemisorption on surfaces of solids. However, the quantitative interpretation of these results have often been difficult in view of many uncertain parameters in the polycrystalline materials. We therefore synthesised plate type single crystals having large surface to volume ratio and studied their electrical conductivity as a function of oxygen chemisorption at different temperatures.

The effect of radiation on crystalline matter has recently assumed great technical importance. Particularly, in the past few years

the changes in the catalytic activity of a semiconductor brought about by gamma ray irradiation have attracted a great deal of attention. As these changes are generally attributed to the modifications of the defect structure, it is desirable to study the electronic effects due to a controlled amount of imperfections in catalytic semiconductors. We have studied the defect structure of

$\gamma$ -irradiated zinc oxide single crystal, by following the changes in the electrical conductivity. This type of irradiation introduces a large number of defects in a reasonably well controlled manner.



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## CHAPTER II

### PREPARATION OF ZINC OXIDE SINGLE CRYSTALS

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## CHAPTER - II

### PREPARATION OF ZINC OXIDE SINGLE CRYSTALS

#### INTRODUCTION

Zinc oxide occurs in nature in the form of large single crystals commonly known as zincite. Usually these crystals are red in colour due to the presence of large concentration of impurities such as manganese and iron. Such natural crystals are not useful for quantitative investigations.

As zinc oxide sublimes ( $1720^{\circ}\text{C}$ ) before it melts (above  $2000^{\circ}\text{C}$ ) and is practically insoluble at room temperature in any solvent, many conventional methods of the crystal growth are not practicable.

First attempt to prepare single crystals of zinc oxide was made by Fritch<sup>1</sup> in 1935. His method was based upon the sublimation of pressed and heated specimen of zinc oxide. He finished with prismatic needle-shaped crystals, about 5mm long and a few tenths of millimeter thick.

Scharowsky<sup>2</sup> (1953) and Bogner and Mollowo<sup>3</sup> (1958) reported preparation of zinc oxide single crystals by the vapour phase oxidation of zinc. Zinc was evaporated in a quartz boat at 720-760°C. The vapours of zinc were carried by carrier gas ( $H_2 + N_2$ ) to another oven at 1330°C to 1380°C. Oxygen was introduced through another quartz tube. Zinc vapour was oxidised as it emerged into the second oven. Zinc oxide crystals thus grown had the cross section of 0.3-1 m.m. and a length of 1-2 cms. They were colourless and had a shape of regular hexagonal prisms. Sometimes plates of size 1-2 cm. x 0.3-0.5 mm. x 0.5 - 0.15 mm. were also formed. They were found to contain Cu, Mg, Si and Al as impurities.

In 1960 Nielsen and Dearborn<sup>4</sup> reported a method for the preparation of zinc oxide single crystals using  $PbF_2$  as flux. A mixture of 22 gms. of zinc oxide and 200 gms. of  $PbF_2$  was taken in a 100 ml. platinum crucible covered with lid and was heated upto 1150°C for 2-4 hours in an electrical furnace.

The crucible was then cooled at a constant rate of 1 to 10<sup>o</sup>C per hour. Small crystals were obtained by this method. At the surface the shape of the crystals were nearly platy but actually they were drum-like. A change in atmosphere from air to oxygen did not affect the crystal growth. The ratio of the growth in the a direction to that in the c direction varied from 80 at 1180<sup>o</sup>C to nearly unity at 1050<sup>o</sup>C.

In 1961 Ikumaro Kubo<sup>5</sup> reported the growth of zinc oxide single crystal by chemical reactions of zinc fluoride with air. Seven gms. of zinc fluoride powder were charged in a platinum crucible (35 mm. diameter and 40 mm. depth). The bottom of the crucible was maintained at 1050<sup>o</sup>C by a Bunsen burner. Top of the crucible was air cooled. Transparent needle like crystals and dendritic crystals were formed. X-ray diffraction showed the crystals to be hexagonal and growth parallel to the c axis.

Walker<sup>6</sup>(1963) showed that it was possible to obtain zinc oxide single crystals hydrothermally. Crystals as large as 1/16th of an inch in cross section were reported. They were slightly green in colour due to heavy iron contamination, as the crystals were grown in an unplated steel vessel.

Laudise and Ballman<sup>7</sup>(1960) synthesised the single crystals of zinc oxide and zinc sulfide by improving on the method of Walker and obtained single crystals of several grams. Studies were done between temperatures 200-400°C. At temperatures below 200°C rate of growth was quite low. The crystals were hemimorphic, amber in colour and were heavily contaminated with iron, as was confirmed from the conductivity changes.

Recently (1964), Laudise, Kolb and Caporaso<sup>8</sup> have reported the growth of large (10 to 20 gms.) macroscopically sound crystals of zinc oxide by the hydrothermal method. The crystals have been grown at a rate of 10 to 15 mils per day. They found that the addition of  $\text{Li}^+$  was very helpful in suppressing the dendritic formation.

Although the hydrothermal method is the best for growing large sized single crystals, the facility is not readily available in all laboratories. The vapour phase oxidation of zinc compounds appears to be particularly suitable for laboratory research. Growing of zinc oxide single crystals from zinc sulfide was therefore attempted and this has resulted in a very simple and successful method.

## EXPERIMENTAL

Single crystals of zinc oxide were prepared by the oxidation of zinc sulfide powder (99.999% pure) in controlled oxygen atmospheres at  $1170^{\circ}\text{C}$ . Pure zinc sulfide was precipitated by the following method<sup>9</sup>: C.P. zinc oxide was dissolved in dilute HCl c.p., stirred and filtered. This solution of  $\text{ZnCl}_2$  was heated to about  $90^{\circ}\text{C}$  and filtered again. Then bromine water was added to it to oxidise iron, chromium, etc. and  $\text{NH}_3$  was passed to redissolve the precipitate. It was filtered again to remove insoluble hydroxides such as  $\text{Fe}(\text{OH})_3$ . This solution was precipitated fractionally with purified  $\text{H}_2\text{S}$ . ( $\text{H}_2\text{S}$  was purified by passing through the bubblers containing  $\text{Ba}(\text{OH})_2$  and finally distilled water). The liquid was decanted and the precipitate discarded. Finally  $\text{H}_2\text{S}$  was passed to give complete precipitation. This precipitate was washed with hot distilled water and centrifuged. Finally zinc sulfide precipitate was dried at  $120^{\circ}\text{C}$ . Approximately 10-15 grams of zinc sulfide was taken every time in a silica tube

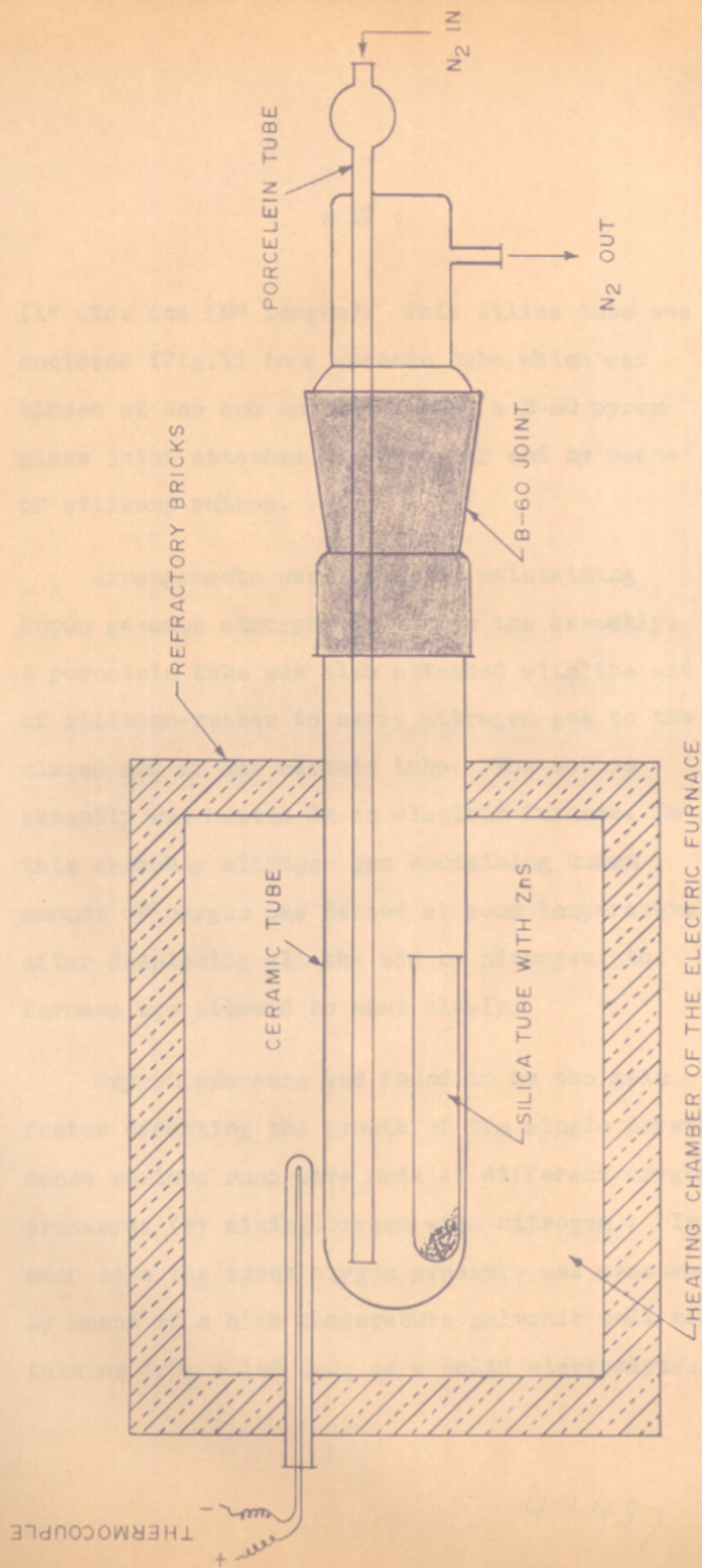


FIG. 1. ARRANGEMENT FOR THE PREPARATION OF ZnO SINGLE CRYSTALS.



(1" dia. and 12" length). This silica tube was enclosed (Fig.1) in a ceramic tube which was closed at one end and was having a B-60 pyrex glass joint attached at the other end by means of silicone-rubber.

Arrangements were made for maintaining known gaseous atmospheres inside the assembly. A porcelain tube was also attached with the aid of silicone-rubber to carry nitrogen gas to the closed end of the ceramic tube. The entire assembly was heated in an electric furnace. In this assembly nitrogen gas containing known amount of oxygen was passed at room temperature. After displacing all the air by nitrogen, the furnace was allowed to heat slowly.

Oxygen pressure was found to be the main factor affecting the growth of the single crystals. Hence various runs were made at different oxygen pressures (by mixing oxygen with nitrogen). In each case the exact oxygen pressure was measured by means of a high temperature galvanic cell containing  $ZrO_2 + 15\% CaO$ , as a solid electrolyte.

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Quantitative measurements in the region 1 to  $10^{-8}$  atmospheres for this cell have been shown to possess a linear relationship between the cell e.m.f. and the logarithm of oxygen pressures at temperatures between 600 to  $750^{\circ}\text{C}^{10}$ . The cell is capable of measuring oxygen pressures in vacuum systems as well as flowing gas mixtures. We heated the cell upto  $700^{\circ}\text{C}$  and the e.m.f. produced was measured by means of a potentiometer. Temperature was measured exactly by means of a calibrated Pt-Pt + 10% Rh thermocouple. The e.m.f. of the cell:

$$\text{Pt, } P_{\text{O}_2}'' \left| \text{ZrO}_2 (15\% \text{ CaO}) \right| P_{\text{O}_2}', \text{ Pt}$$

is given by the relation:  $E = \frac{RT}{nF} \ln \frac{P_{\text{O}_2}'}{P_{\text{O}_2}''}$

where:

$P_{\text{O}_2}''$  - is the fixed oxygen pressure which was always kept constant at 0.20 atmospheres of oxygen; and

$P_{\text{O}_2}'$  - is the unknown partial pressure of oxygen present in nitrogen.

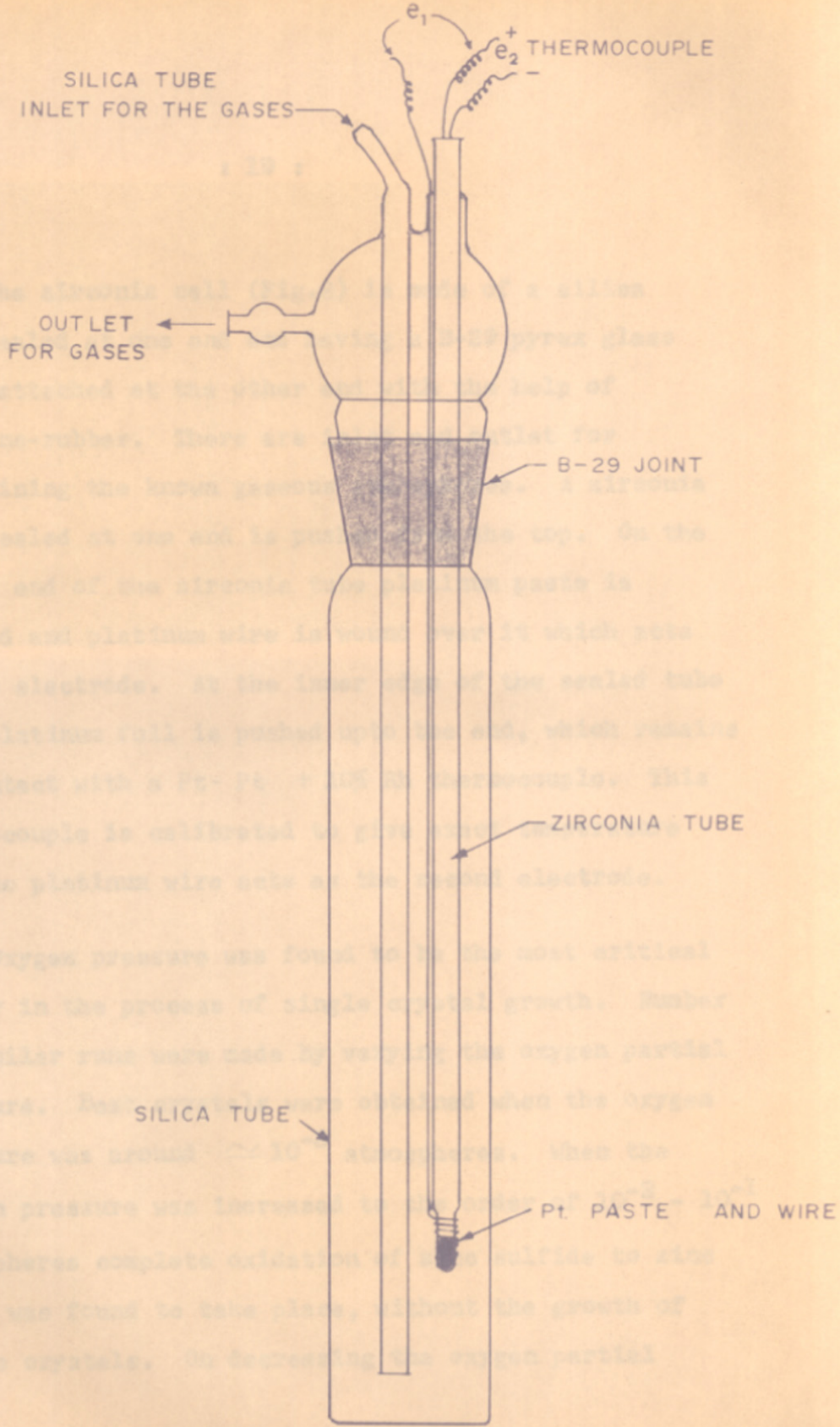


FIG. 2. DIAGRAM OF THE ZIRCONIA TUBE ASSEMBLY FOR MEASURING OXYGEN PRESSURES.

The zirconia cell (Fig.2) is made of a silica tube sealed at one end and having a B-29 pyrex glass joint attached at the other end with the help of silicone-rubber. There are inlet and outlet for maintaining the known gaseous atmospheres. A zirconia tube sealed at one end is pushed from the top. On the sealed end of the zirconia tube platinum paste is applied and platinum wire is wound over it which acts as one electrode. At the inner edge of the sealed tube some platinum foil is pushed upto the end, which remains in contact with a Pt- Pt + 10% Rh thermocouple. This thermocouple is calibrated to give exact temperature and the platinum wire acts as the second electrode.

Oxygen pressure was found to be the most critical factor in the process of single crystal growth. Number of similar runs were made by varying the oxygen partial pressure. Best crystals were obtained when the oxygen pressure was around  $\approx 10^{-3}$  atmospheres. When the oxygen pressure was increased to the order of  $10^{-2}$  -  $10^{-1}$  atmospheres complete oxidation of zinc sulfide to zinc oxide was found to take place, without the growth of single crystals. On decreasing the oxygen partial

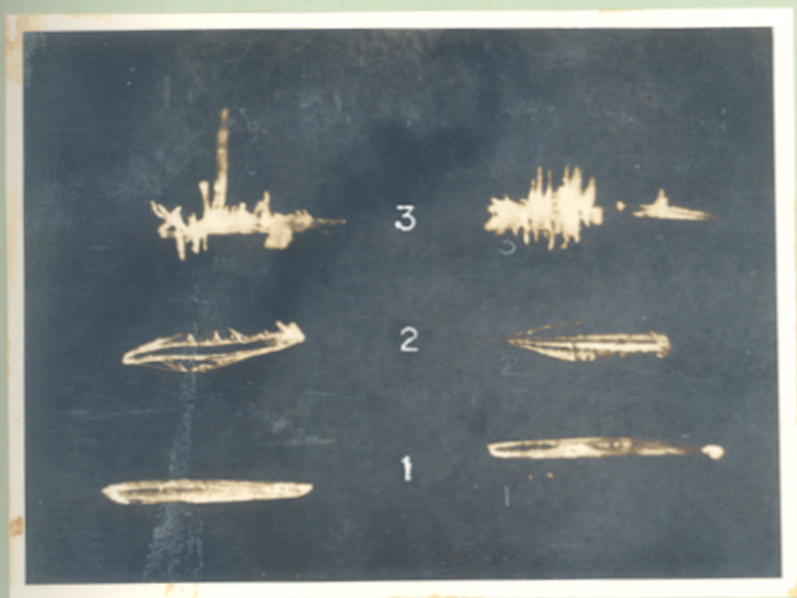


FIG. 3. ZINC OXIDE SINGLE CRYSTALS

1- ROD-TYPE

2- PLATE-TYPE

3- DENDRIC



pressure below  $10^{-3}$  atmospheres, i.e. to about  $10^{-4}$  -  $10^{-5}$  atmospheres, the rate of growth as inferred from the resultant crystal size, decreased. Only small crystallites of zinc oxide were observed.

At every oxygen pressure zinc sulfide powder was heated for various durations. Heating for a duration of 48-50 hours was found to be most suitable for crystal growth. On heating for a longer time ( $\sim 120$  hours) no favourable effect was observed on the crystal growth or the crystal size. The heating at  $1170^{\circ}\text{C}$  for 48-50 hours was always followed by a slow controlled cooling. The whole assembly was cooled to a temperature of  $600^{\circ}\text{C}$  in about 24 hours. After this the assembly was cooled rapidly to room temperature. Various conditions for cooling were also tried, but they were not of much help in improving the crystal size.

Figure 3 shows the crystals formed under the oxygen partial pressure of  $10^{-3}$  atmospheres. The crystals were mostly needle shaped, although some

plate type crystals and dendries were also formed. Clear, colourless needle type crystals with maximum dimensions of  $10 \times 0.5 \times 0.5$  mm. were usually obtained at oxygen partial pressure of  $10^{-3}$  atmospheres. A small needle shaped crystal obtained as above was kept as a nucleus for another run. However, no further growth could be detected on the seed. Growth on the silica walls was also absolutely absent. Clusters of zinc oxide single crystals were usually observed around the polycrystalline zinc oxide. Increase in temperature and duration of heating beyond the above mentioned values did not influence the size of the crystals.

To confirm that these crystals were of zinc oxide and not of zinc sulfide, the powdered crystals were subjected to chemical and x-ray diffraction analysis and the ultra violet absorption. (The results of ultra violet absorption will be discussed in the next chapter). A few crystals were powdered and an x-ray powder diffraction pattern was taken. In addition the crystal growth axis was determined by x-ray rotation photographs on a few

crystals. The purity of few crystals was checked by spectral analysis. The confirmation that they are single crystals was done by looking at them through a microscope under polarised light.





FIG. 4. X-RAY DIFFRACTION PATTERN OF THE  
POWDERED ZINC OXIDE CRYSTAL.

## RESULTS

Figure 4 gives the x-ray diffraction pattern of the powdered zinc oxide crystal. The  $d$  values were calculated and compared with those for a standard sample (ASTM). The agreement is good showing that the crystals are of pure zinc oxide. No additional lines were observed.

The rotation photograph taken around the long axis of the crystal shows that the  $c$  axis of the unit cell is parallel to the long axis of the crystal.

The crystal powder was spectroscopically analyzed for various inorganic impurities. The results are tabulated below:

|    |   |                                   |     |
|----|---|-----------------------------------|-----|
| Cu | < | 25                                | ppm |
| Mg | < | 25                                | ppm |
| Si | < | 25                                | ppm |
| Al | ! | Searched for but<br>not detected. |     |
| Fe | ! |                                   |     |

## DISCUSSION

The formation of zinc oxide single crystals from zinc sulfide powder can be explained in two ways. One possibility is the direct oxidation of zinc sulfide to form zinc oxide. But since the original zinc sulfide is in a finely powdered state, it is not likely that this zinc sulfide (solid) will ~~an~~ directly give rise to large zinc oxide single crystals.

The other alternative is the reaction of zinc sulfide vapour with oxygen. First the zinc sulfide (solid) evaporates at higher temperatures to give zinc sulfide vapour. This vapour in presence of oxygen gives rise to zinc oxide vapour, which slowly deposits to give zinc oxide single crystals. We can illustrate the steps in the following way:



Requirement of a critical oxygen pressure for the growth of zinc oxide single crystals suggests that the oxidation of zinc sulfide (vapour) i.e. the reaction (2) is the rate determining step. The rate of reaction (2) in the forward direction is proportional to  $P_{O_2}^{1/2}$  so at low oxygen pressures the rate of formation of ZnO will be very slow and to have crystals of reasonable size, the reaction will have to  $\xrightarrow{go}$  on for a long time. Thus during the course of 36 hours only some small crystallites of ZnO were formed.

While an increase in the oxygen pressure to about  $10^{-2}$  atmospheres increases the rate of formation of zinc oxide (vapour), a situation which is not helpful for single crystal growth. In addition the rate of direct conversion of zinc sulfide(solid) to zinc oxide(solid) also becomes quite fast. Hence it is not possible to expect an appreciable growth of the crystals.

When the formation of zinc oxide takes place via vapour phase and the rate of cooling i.e. the rate of condensation is very fast, dendritic crystals

are formed. Dendritic crystal growth could be appreciably reduced by reducing the ambient oxygen pressure. Exact condition when the plate type crystals are grown could not be established.

Growth of the crystals was always observed on the polycrystalline zinc oxide powder<sup>3</sup> and not on the walls on the silica tube. Hence we can assume zinc oxide powder to be the favourable substrate for the growth of the zinc oxide single crystals.

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### **CHAPTER III**

#### **ELECTRONIC PROPERTIES AND DEFECT STRUCTURE OF ZINC OXIDE CRYSTALS PREPARED BY ZnS OXIDATION**

---

## CHAPTER - III

### ELECTRONIC PROPERTIES AND DEFECT STRUCTURE OF ZINC OXIDE SINGLE CRYSTAL PREPARED BY ZnS OXIDATION

#### INTRODUCTION

A number of studies on the electrical properties of polycrystalline zinc oxide are reported in the literature<sup>1-10</sup>, but their results suffer from the usual uncertainties associated with polycrystalline materials. Studies on single crystals of controlled defect structure are relatively few.

Firtsh(1935)<sup>11</sup> was the first to study the Hall coefficient and electrical conductivity of zinc oxide single crystals grown by the sublimation of the pressed pellets of zinc oxide. He also studied the effect of heat treatment in oxygen and in vacuum. His studies were confined in the range - room temperature to liquid air temperature. He observed an increase in conductivity in case of samples preheated in oxygen and slowly cooled.



Hutson(1957)<sup>12</sup> prepared needle-like transparent single crystals of n-type zinc oxide by the direct oxidation of zinc vapours with oxygen at  $1200^{\circ}\text{C}$ . He measured the Hall coefficient and the electrical conductivity at temperatures between  $55^{\circ}\text{K}$  and  $300^{\circ}\text{K}$ . The variation of the carrier concentration with temperature indicated that the virgin crystals contained more than one donor species. However, when the crystals were doped with H, Li or excess Zn a single donor level was effective. Lithium was found to give rise to some acceptor levels also. The mobility variation with temperature indicated that at low temperatures impurity scattering was predominant and above  $200^{\circ}\text{K}$  the optical mode scattering was important.

Pohl(1959)<sup>13</sup> also studied the electrical properties of zinc oxide single crystals prepared by the oxidation of zinc vapour. The single crystals were doped with excess zinc by heating it in zinc vapour at high temperature and were quenched to room temperature. Initially, at room temperature the conductivity increased with time and finally reached a constant value. When the crystals pre-

treated with zinc vapour were heated in air, a decrease in conductivity was observed but it did not reach the initial value. The first heating in zinc was found to give rise to irreversible changes whereas subsequent heating in air or zinc were reversible and the rate was controlled purely by diffusion processes.

Bogner(1961)<sup>14</sup> studied the electrical conductivity and Hall voltage of single crystals of zinc oxide prepared by the vapour phase oxidation of zinc at  $1380^{\circ}\text{C}$  in oxygen and of those doped with In or Cu. In the case of the crystals doped heavily with indium the reciprocal of Hall coefficient showed a very slight temperature dependence. In the crystals with small donor concentrations, the reciprocal of Hall coefficient falls in the beginning and reaches a maximum as the temperature is raised and then at still higher temperatures increases slowly.

Bogner and Mollowo(1958)<sup>15</sup> gave a method by which zinc oxide crystals of definite composition can be deposited from the vapour phase. Measurements on composition,

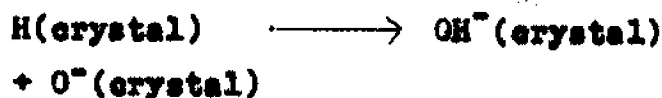
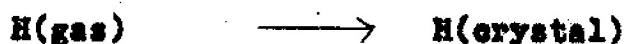
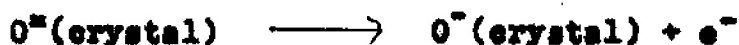
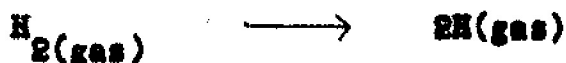
conductivity and I-R adsorption of crystals doped with Cu and In were carried out. In contrast to the expected behaviour they observed a decrease rather than an increase in conductivity on doping with Cu during the growth of the crystals. Conductivity was approximately proportional to the inverse of the square of the copper concentration.

Rupprecht(1958)<sup>16</sup> prepared single crystals of zinc oxide doped with Cu and In by the vapour phase oxidation of zinc as done by Bogner and Mollowo. The electron concentrations were determined from the Hall effect and conductivity studies at temperatures between 650°K to 700°K. A slight decrease in the electron mobility was observed with increasing concentration of electrons.

Mollowo(1954)<sup>17</sup> showed that the conductivity of zinc oxide crystals in hydrogen varied as  $pH_2^{1/2}$ . He considered the increase in conductivity might arise from excess zinc formed at the surface by hydrogen reduction, which diffused into the crystals.

Lander and Thomas(1956)<sup>18</sup> prepared single crystals of zinc oxide by the direct oxidation of zinc vapours at about 1200°C, in the presence of hydrogen using Scharowsky's method. The crystals were colourless hexagonal needles, 5-20 mm. in length and .005 to .015 cm in diameter. The conductivity in hydrogen showed a  $P_{H_2}^{1/4}$  dependence, disagreeing from the Mollowo's results. They concluded that the hydrogen when in excess diffused in the lattice and the solubility varied as  $P_{H_2}^{1/4}$ . This hydrogen might be in the form of interstitial protons and might diffuse from one to another interstitial position. The other suggested alternative was that the protons might combine with oxygen ions to form  $OH^-$  groups. The ionization energy for the donor centre was observed to be .04 ev, whereas the ionisation energy of interstitial hydrogen atom was estimated to be several times larger. They concluded that the only way to explain the experimental results was through the formation of  $OH^-$  ions at the surface

by the combination with oxygen. The formation of  $\text{OH}^-$  centre was explained as follows:



Mohanty and Azaroff(1961)<sup>19</sup> measured the electron density distribution for the undoped crystals, as well as those heated in zinc vapour from the x-ray diffraction data. The observed x-ray diffraction intensities were used to obtain the electron density projection perpendicular to the c-axis. They concluded that the interstitial zinc atoms present in the crystal were 1000 times more than that calculated from the conductivity data. It was therefore inferred that most of the zinc interstitials are unionized.

It is clear from the above survey of the literature that most of the work reported on the conductivity and Hall coefficient was carried out on zinc oxide crystals prepared by the vapour phase oxidation of zinc vapours. It is well-known that the electrical properties in a crystal would very much depend on the past history of the sample, i.e. pretreatment of the oxide and the method of preparation. We have therefore undertaken to study these properties of zinc oxide single crystals prepared by an entirely new method described in the last chapter i.e. oxidation of zinc sulfide vapours.

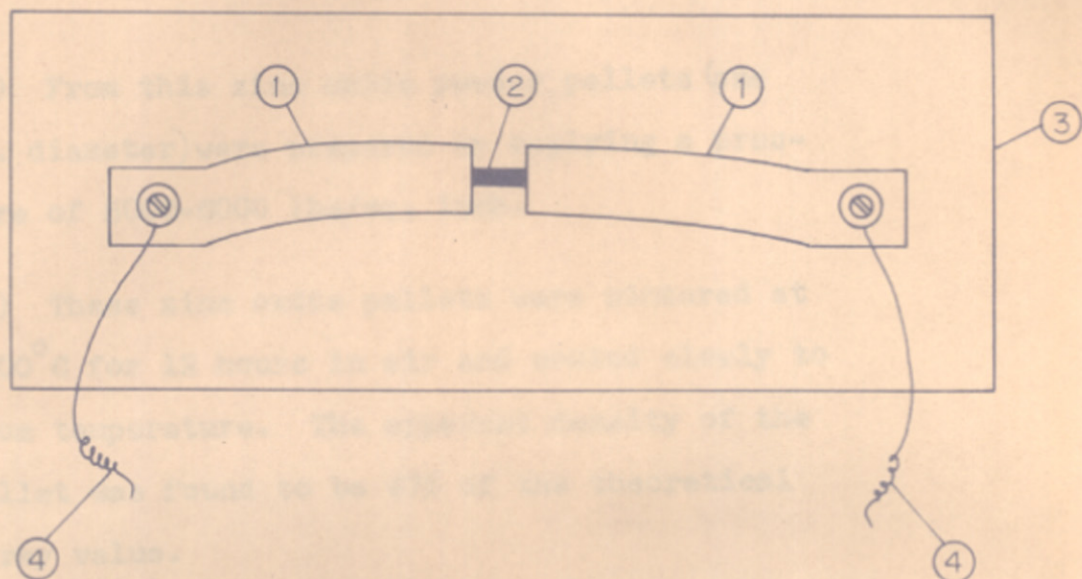
## EXPERIMENTAL

Conductivity measurements were carried out on rod type zinc oxide single crystals. For comparison some ~~zinc oxide~~ additional data on sintered ZnO polycrystalline pellets have also been obtained. The single crystals of zinc oxide were prepared by the method given in Chapter II. Zinc oxide powder pellets were prepared by the following method.

### (1) Precipitation of zinc sulphide:

Pure zinc sulphide was precipitated by dissolving zinc oxide in HCl and passing  $H_2S$  under ammonical conditions (described in Chapter II).

(2) This zinc sulphide powder was filled in a silica boat and was heated in a silica tube furnace to a temperature of  $900-950^{\circ}C$  for about 4-5 hours to convert it completely to zinc oxide. For establishing the complete conversion ~~to~~ zinc sulphide to zinc oxide, x-ray powder pattern was taken using a copper target.



- ① MOLYBDENUM STRIPS COVERED WITH SILVER FOIL
- ② ZnO SINGLE CRYSTAL
- ③ A SILICA BASE
- ④ CONNECTING SILVER WIRES

FIG.5. SAMPLE HOLDER ASSEMBLY FOR ELECTRICAL CONDUCTIVITY MEASUREMENTS.



(3) From this zinc oxide powder, pellets (one cm. diameter) were prepared by applying a pressure of 5000-6000 lbs/sq. inch.

(4) These zinc oxide pellets were sintered at  $1100^{\circ}\text{C}$  for 12 hours in air and cooled slowly to room temperature. The apparent density of the pellet was found to be 67% of the theoretical x-ray value.

For the measurement of conductivity the two ends of the zinc oxide crystal were coated with silver paste and the crystal was heated to about  $200^{\circ}\text{C}$  for 30 minutes. Thus adherent coatings of silver on the two ends of the crystal were obtained and they acted as the two electrodes. In the case of the zinc oxide powder pellets, aquadag was applied on the two circular faces of the pellet.

Fig. 5 shows the sample holder assembly used for the measurement of conductivity of the single

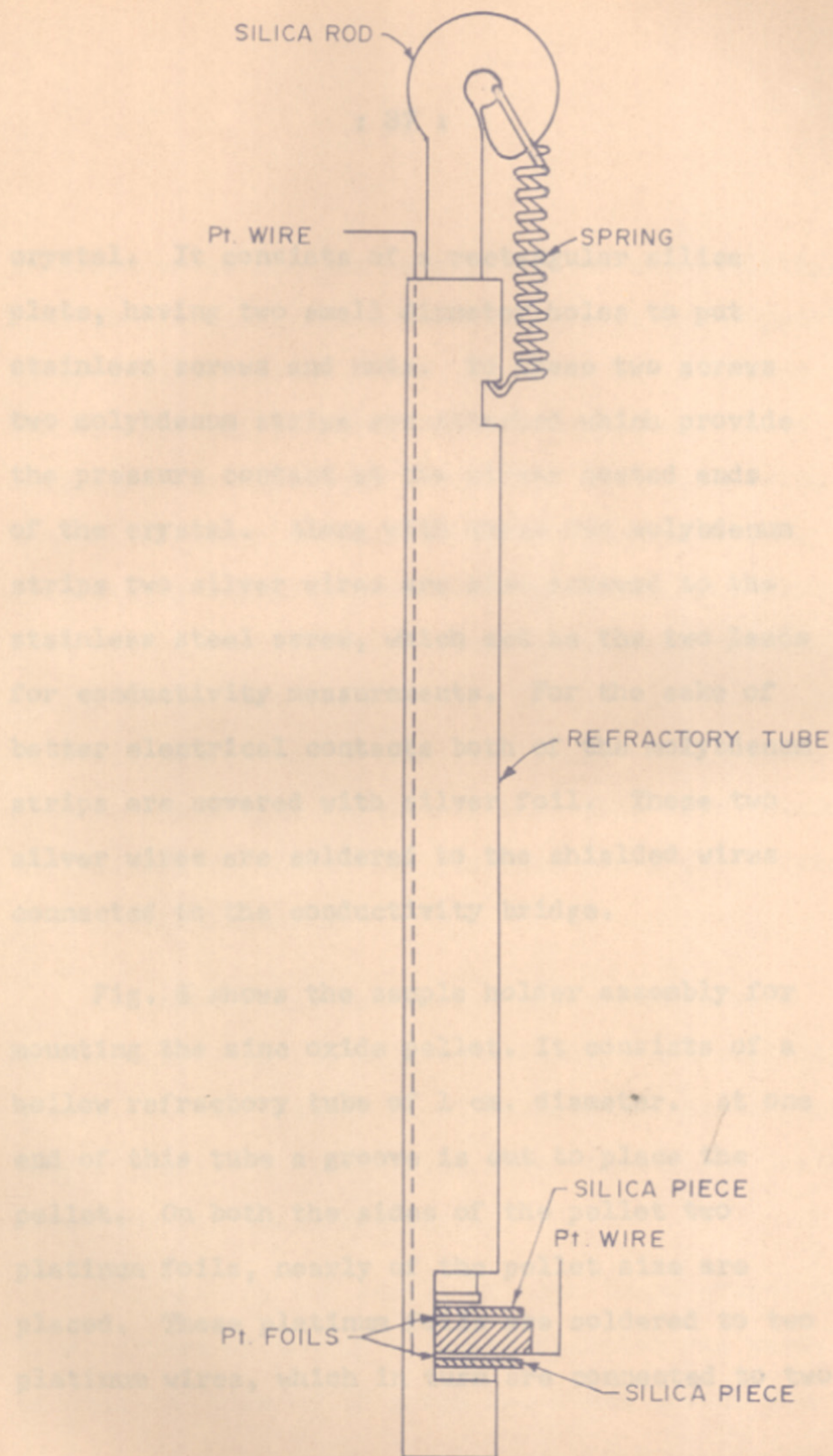


FIG. 6. SAMPLE HOLDER ASSEMBLY FOR PELLETS.

crystal. It consists of a rectangular silica plate, having two small diameter holes to put stainless screws and nuts. To these two screws two molybdenum strips are attached which provide the pressure contact at the silver coated ends of the crystal. Along with these two molybdenum strips two silver wires are also screwed to the stainless steel screw, which act as the two leads for conductivity measurements. For the sake of better electrical contacts both of the molybdenum strips are covered with silver foil. These two silver wires are soldered to the shielded wires connected to the conductivity bridge.

Fig. 6 shows the sample holder assembly for mounting the zinc oxide pellet. It consists of a hollow refractory tube of 1 cm. diameter. At one end of this tube a groove is cut to place the pellet. On both the sides of the pellet two platinum foils, nearly of the pellet size are placed. These platinum foils are soldered to two platinum wires, which in turn are connected to two

shielded wires for the measurement of conductivity. Both the platinum foils on either sides are supported by a silica disc. From the other end a silica rod is inserted to reach the silica plates. This silica rod is flattened at the end in contact with the silica plate and has a loop on the other end. Pressure is applied to reduce the contact resistance with the help of a spring attached between the loop of the silica rod and a groove in the refractory tube. To avoid shortening of the two leads, one platinum wire is taken from inside and the other from outside the refractory tube. The platinum wires are covered with porcelain beads.

The electrical resistance measurements were carried out with the help of a Philips Conductivity bridge (PR 9500 model) at 50 cycles. For resistances higher than 10 M  $\Omega$  a R.I.E. meter (Leeds and Northrup Model No. CAT 5620) was used.

For heating the sample to high temperatures a tube furnace of nearly 2 inches diameter was used. Kanthal 'A' wire of 18 gauge was wound around the tube.

Proper thermal insulation was provided. In this furnace another silica tube sealed at one end was placed inside which the sample holder was located. For measurement of temperature a chromel-alumel thermocouple calibrated against a standard thermocouple was kept near the sample and the e.m.f. was recorded with the help of a potentiometer. For controlling and regulating the temperature at required points, a temperature controller (Fallbügel-regler Medin.H, supplied by Hartmann and Braunn, Frankfurt, W. Germany) was connected to the furnace. Another thermocouple from the furnace was attached to the temperature controller and it was possible to control the temperature at the required value.

To get an idea about the majority current carriers in the single crystal, the direction of the thermoelectric e.m.f. was observed by means of the hot point method, i.e. by heating one end of the crystal and keeping the other end at room temperature. Measurements were performed at two temperatures, one at  $25^{\circ}\text{C}$  and

another at  $300^{\circ}\text{C}$ . These temperatures were selected for some reasons discussed later.

Conductivity measurements were carried out on rod type zinc oxide single crystals:

- (1) Before annealing.
- (2) After annealing.

The change in conductivity as a function of temperature was measured on some crystals between  $25^{\circ}\text{C}$  to  $500^{\circ}\text{C}$ . The same crystals were then subjected to annealing at  $600^{\circ}\text{C}$  for two hours and were quenched to room temperature. Conductivity measurements were carried out on these crystals again.

The conductivity of zinc oxide powder (pellets) was measured in air in the temperature range  $25^{\circ}$ - $500^{\circ}\text{C}$ . The pellet was heated for some time in air and brought back to room temperature. It was then heated in air once more and the changes in resistances were recorded.

The pellets were preheated upto  $600^{\circ}\text{C}$  in hydrogen and then cooled to room temperature. The changes in resistance were then recorded along with temperature.

For ultraviolet absorption two optically transparent quartz plates were placed on the sample holder of the Unicam Spectrometer (Model SP 500). The crystal was fixed with the help of araldite at the center of one of the quartz plates and the other quartz plate acted as a blank. The whole assembly was covered with a thin aluminium foil which had two equal sized holes one just above the crystal and another at the corresponding position at the blank quartz plate. Absorption at wave lengths varying from 300 to 450  $m\mu$  was measured.



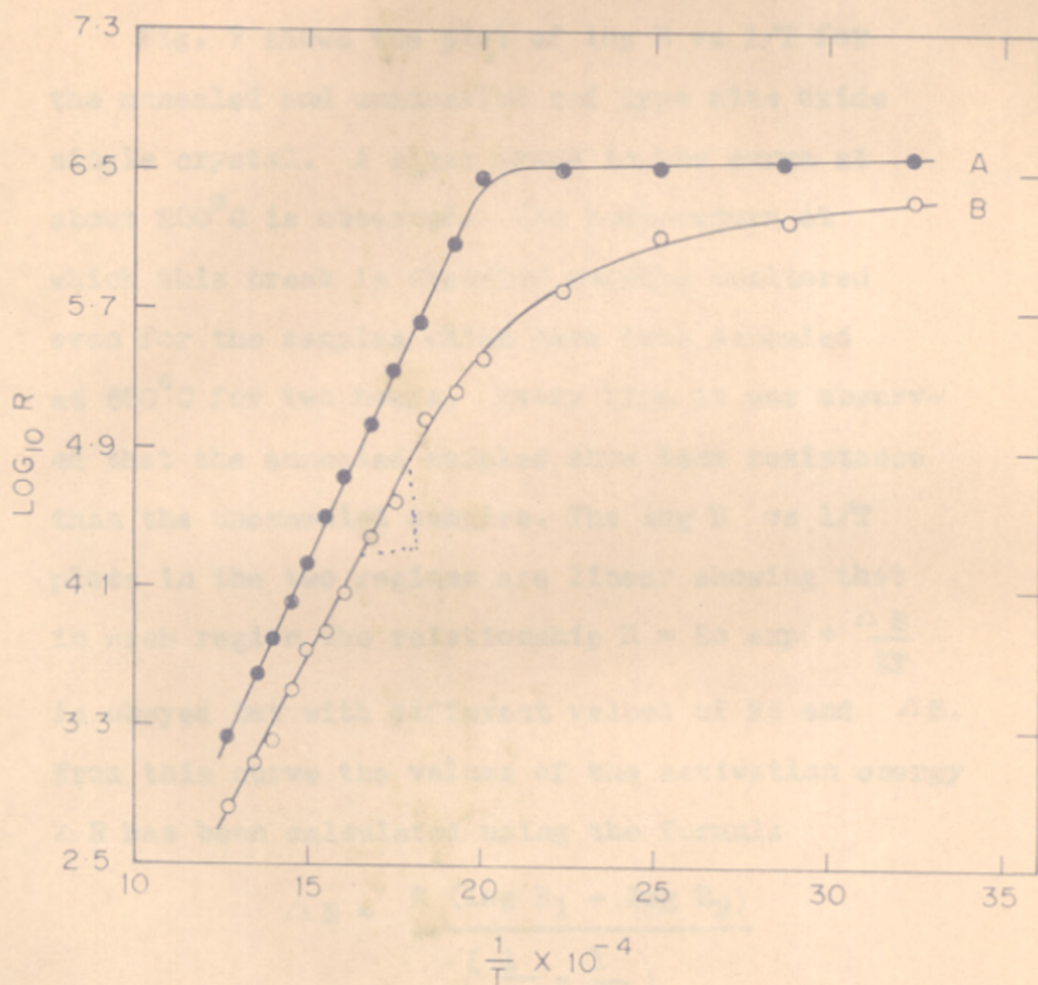


FIG. 7.  $\text{LOG}_{10} R$  Vs  $\frac{1}{T}$  PLOT FOR ROD TYPE  $\text{ZnO}$  SINGLE CRYSTAL IN AIR.

A. BEFORE ANNEALING. B AFTER ANNEALING AT  $600^{\circ}\text{C}$ . FOR 2 HOURS.



## R E S U L T S

Fig. 7 shows the plot of  $\log R$  vs  $1/T$  for the annealed and unannealed rod type zinc oxide single crystal. A clear break in the curve at about  $200^{\circ}\text{C}$  is observed. The temperature at which this break is observed remains unaltered even for the samples which have been annealed at  $600^{\circ}\text{C}$  for two hours. Every time it was observed that the annealed samples show less resistance than the unannealed samples. The  $\log R$  vs  $1/T$  plots in the two regions are linear showing that in each region the relationship  $R = R_0 \exp + \frac{\Delta E}{KT}$  is obeyed but with different values of  $R_0$  and  $\Delta E$ . From this curve the values of the activation energy  $\Delta E$  has been calculated using the formula

$$\Delta E = \frac{R (\log R_1 - \log R_2)}{\left( \frac{1}{T_1} - \frac{1}{T_2} \right)}$$

The values come to be 0.4 Kcal and 21.2 Kcal for the temperature ranges  $25^{\circ}\text{C} - 200^{\circ}\text{C}$  and  $200^{\circ}\text{C} - 600^{\circ}\text{C}$  respectively.

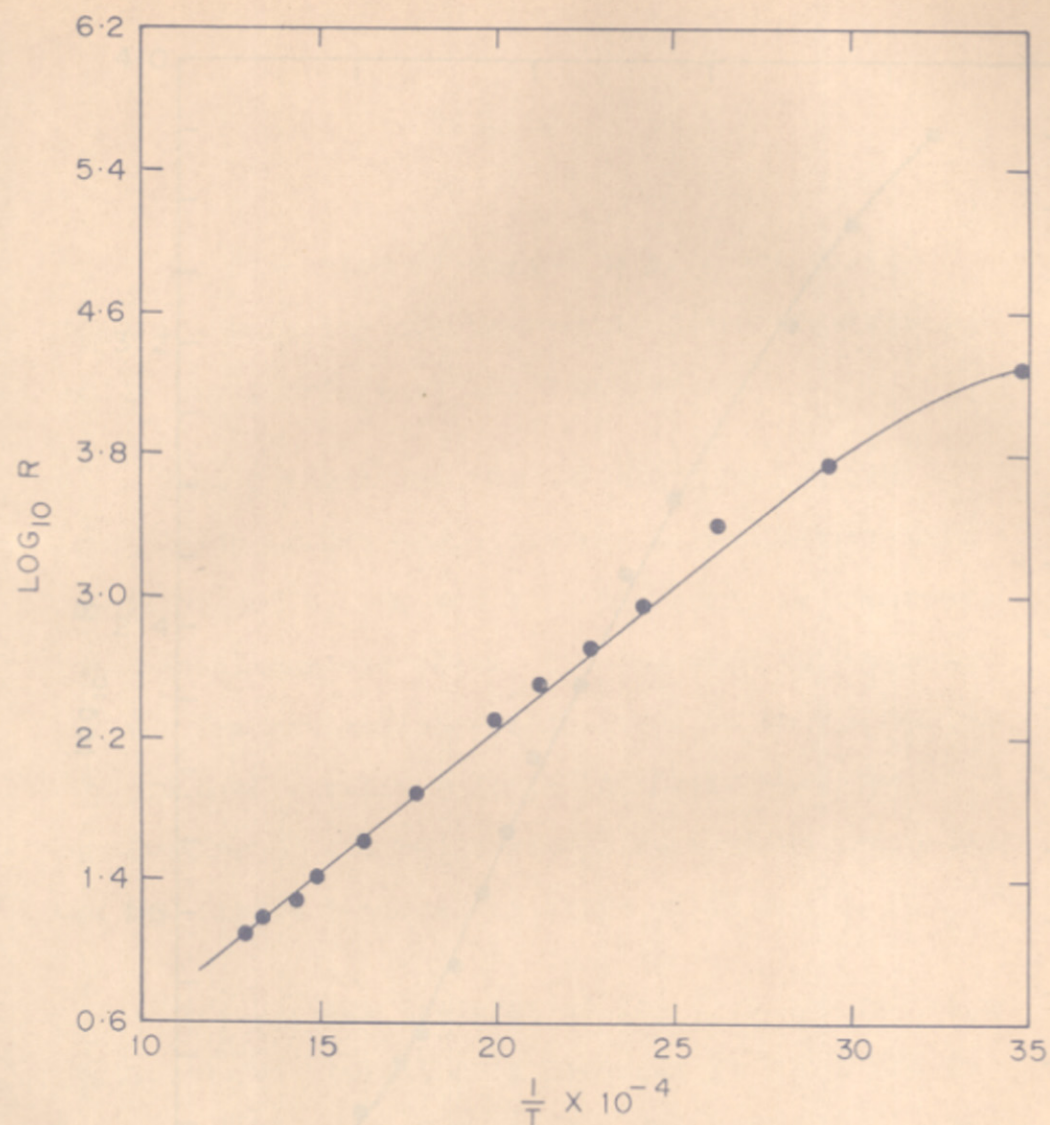


FIG. 8  $\text{LOG}_{10} R$  Vs.  $\frac{1}{T}$  PLOT FOR ZnO PELLET IN AIR

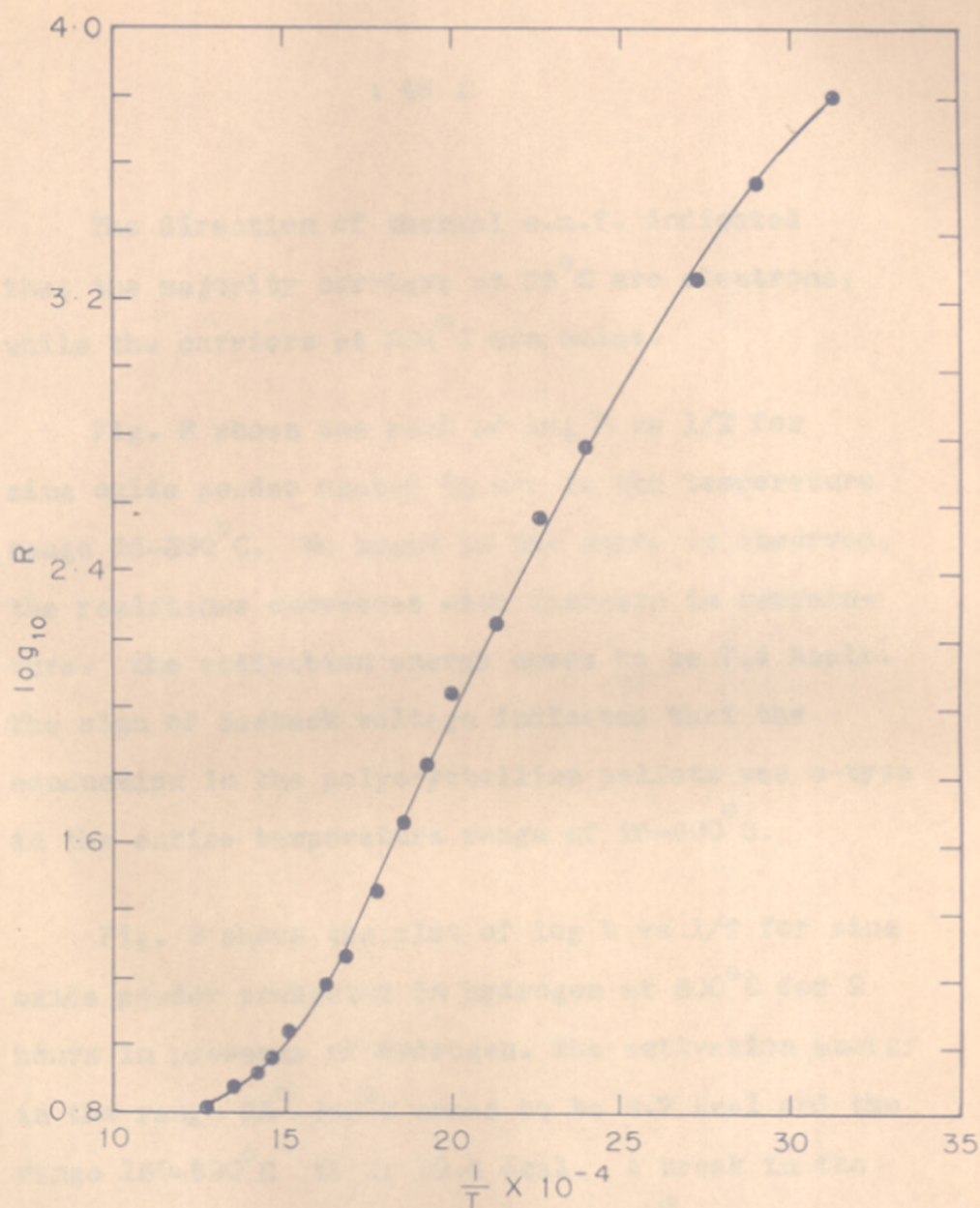


FIG. 9.  $\log R$  Vs  $\frac{1}{T}$  PLOT FOR ZnO PELLETS IN HYDROGEN.

The direction of thermal e.m.f. indicated that the majority carriers at  $25^{\circ}\text{C}$  are electrons, while the carriers at  $300^{\circ}\text{C}$  are holes.

Fig. 8 shows the plot of  $\log R$  vs  $1/T$  for zinc oxide powder heated in air in the temperature range  $25-500^{\circ}\text{C}$ . No break in the curve is observed, the resistance decreases with increase in temperature. The activation energy comes to be 7.4 Kcal. The sign of Seebeck voltage indicated that the conduction in the polycrystalline pellets was n-type in the entire temperature range of  $25-500^{\circ}\text{C}$ .

Fig. 9 shows the plot of  $\log R$  vs  $1/T$  for zinc oxide powder preheated in hydrogen at  $500^{\circ}\text{C}$  for 2 hours in presence of hydrogen. The activation energy in the range  $25^{\circ}-150^{\circ}\text{C}$  comes to be 6.7 Kcal and the range  $150-500^{\circ}\text{C}$  it is 10.4 Kcal. A break in the  $\log R$  vs  $1/T$  curve is obtained at  $150^{\circ}\text{C}$ .



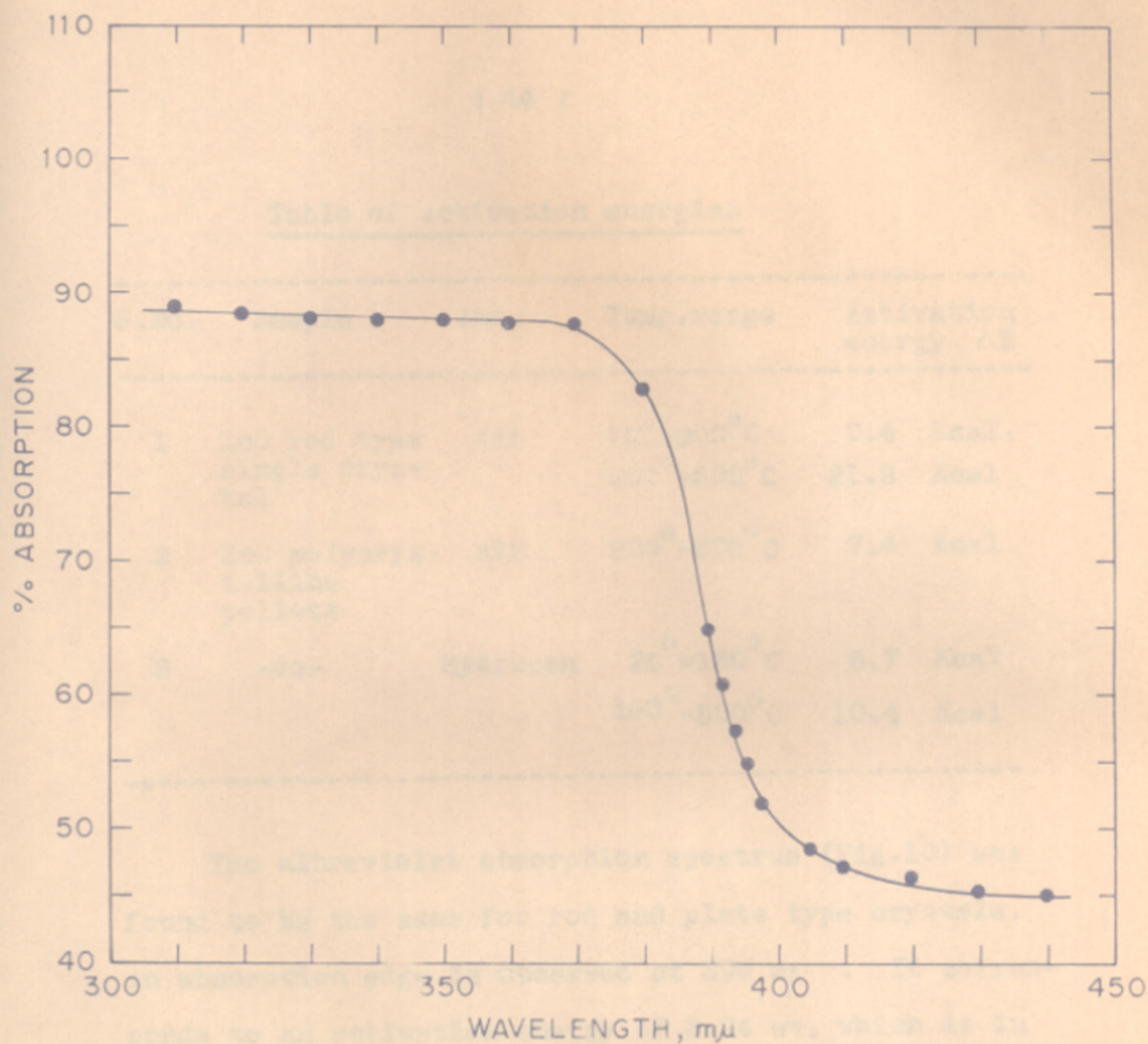


FIG. 10. AN ULTRAVIOLET ABSORPTION SPECTRUM OF A ZINC OXIDE SINGLE CRYSTAL AT ROOM TEMPERATURE

Table of activation energies

| S.No. | Sample                         | Atm.     | Temp.range              | Activation energy $\Delta E$ |
|-------|--------------------------------|----------|-------------------------|------------------------------|
| 1     | ZnO rod type<br>single crystal | Air      | 25°-200°C<br>200°-500°C | 0.4 Kcal.<br>21.2 Kcal       |
| 2     | ZnO polycrystalline<br>pellets | Air      | 200°-500°C              | 7.4 Kcal                     |
| 3     | -do-                           | Hydrogen | 25°-150°C<br>150°-500°C | 6.7 Kcal<br>10.4 Kcal        |

The ultraviolet absorption spectrum (Fig.10) was found to be the same for rod and plate type crystals. An absorption edge is observed at  $390 \text{ m}\mu$ . It corresponds to an activation energy of 3.24 eV, which is in agreement with the earlier reported value of  $3.2 \text{ eV}^{20}$ .

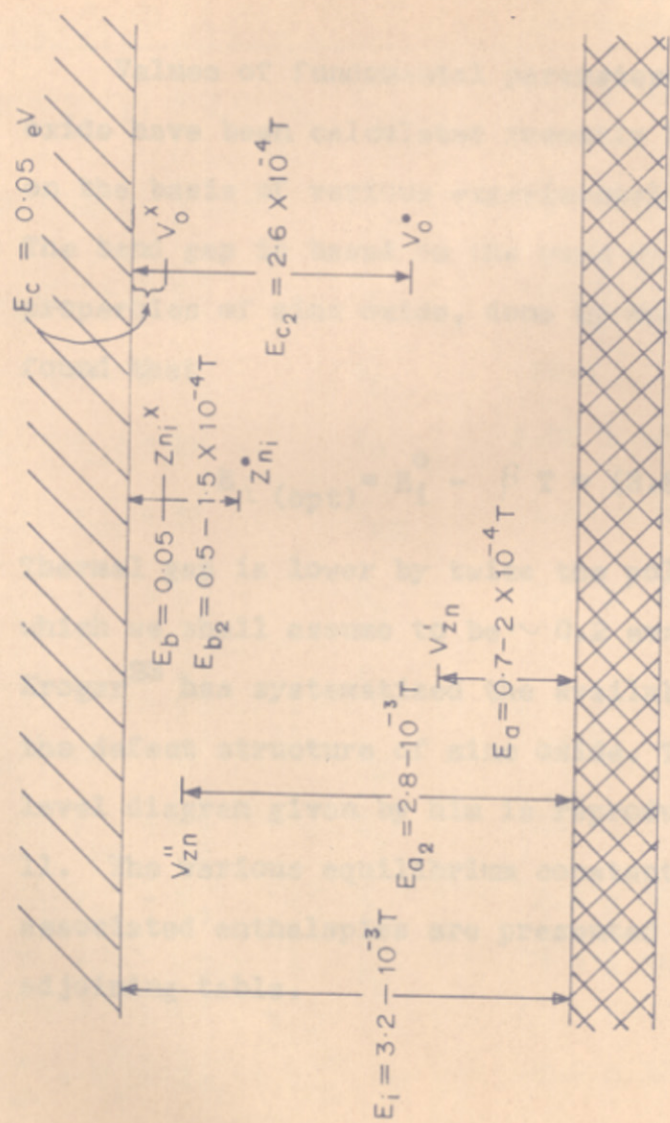


FIG. 11. ELECTRONIC ENERGY LEVELS OF NATIVE IMPERFECTIONS IN ZnO.

## DISCUSSION

Values of fundamental parameters of zinc oxide have been calculated recently by Garrett<sup>21</sup> on the basis of various experimental results. The band gap is based on the work on the optical properties of zinc oxide, done by Mollwo<sup>22</sup>, who found that

$$E_i(\text{opt}) = E_i^0 - \beta T = (3.6 - 10^{-3}T) \text{ ev.}$$

Thermal gap is lower by twice the polaron energy which we shall assume to be  $\sim 0.2$  evm. Recently, Kroger<sup>23</sup> has systematized the available data on the defect structure of zinc oxide. The energy level diagram given by him is reproduced in Fig. 11. The various equilibrium constants and the associated enthalpies are presented in the adjoining table.



(Table reproduced from "The Chemistry of Imperfect Crystals")  
F.A. Kroger, p.701). Table

Parameters of equilibrium constants for ZnO near  
T = 1350°K

| Reaction                                                                                                         | Constant                    | K <sup>O*</sup><br>(atom fraction, atm) | H <sup>+</sup> or E <sup>O*</sup><br>(eV) | E <sup>O</sup> |
|------------------------------------------------------------------------------------------------------------------|-----------------------------|-----------------------------------------|-------------------------------------------|----------------|
| $\text{ZnO} \rightleftharpoons \text{Zn(g)} + \frac{1}{2} \text{O}_2(\text{g})$                                  | K <sub>ZnO</sub>            | $1.5 \times 10^{10}$                    | 4.89                                      |                |
| $\text{ZnO} \rightleftharpoons \text{Zn(g)} + \text{O(g)}$                                                       | K <sub>Zn,O</sub>           | $7.5 \times 10^{12}$                    | 7.49                                      |                |
| $\text{O}_{2(\text{g})} \rightleftharpoons 2 \text{O(g)}$                                                        | K <sub>D</sub>              | $2.5 \times 10^5$                       | 5.2                                       |                |
| $\text{O} \rightleftharpoons \text{e}' + \text{h}^\bullet$                                                       | K <sub>i</sub>              | 29.4                                    | 3.44                                      | 3.1            |
| $\text{V}_{\text{Zn}}^* \rightleftharpoons \text{V}_{\text{Zn}}' + \text{h}^\bullet$                             | K <sub>2</sub>              | $5.25 \times 10^{-1}$                   | 0.97                                      | 0.8            |
| $\text{V}_{\text{Zn}}' \rightleftharpoons \text{V}_{\text{Zn}}'' + \text{h}^\bullet$                             | K <sub>22</sub>             | $1.44 \times 10^3$                      | 2.97                                      | 2.8            |
| $\text{V}_{\text{O}}^* \rightleftharpoons \text{V}_{\text{O}}^\bullet + \text{e}'$                               | K <sub>c</sub>              | $2.1 \times 10^{-2}$                    | 0.22                                      | 0.05           |
| $\text{V}_{\text{O}} \rightleftharpoons \text{V}_{\text{O}}^\bullet + \text{e}'$                                 | K <sub>o2</sub>             |                                         |                                           | 2.0            |
| $\text{Zn}_i^* \rightleftharpoons \text{Zn}_i' + \text{e}'$                                                      | K <sub>D</sub>              | $10^{-2}$                               | 0.22                                      | 0.05           |
| $\text{O} \rightleftharpoons \text{V}_{\text{Zn}}' + \text{V}_{\text{O}}^\bullet$                                | K <sub>s/</sub>             | $10^5$                                  | 4.04                                      |                |
| $\text{O} \rightleftharpoons \text{V}_{\text{Zn}}^* + \text{V}_{\text{O}}^*$                                     | K <sub>s</sub>              | $2.8 \times 10^8$                       | 6.29                                      |                |
| $\text{Zn}_{\text{Zn}}^* + \text{V}_i^* \rightleftharpoons \text{Zn}_i' + \text{V}_{\text{Zn}}'$                 | K <sub>F/</sub>             | $7.9 \times 10^{-2}$                    | 4.36                                      |                |
| $\text{Zn}_{\text{Zn}}^* + \text{V}_i^* \rightleftharpoons \text{Zn}_i^* + \text{V}_{\text{Zn}}^*$               | K <sub>F</sub>              | $8.2 \times 10^2$                       | 6.67                                      |                |
| $\frac{1}{2} \text{O}_{2(\text{g})} \rightleftharpoons \text{O}_{\bullet}^* + \text{V}_{\text{Zn}}^*$            | K <sub>O<sub>2</sub>V</sub> | 3.06                                    | 2.0                                       |                |
| $\text{O(g)} \rightleftharpoons \text{O}_{\bullet}^* + \text{V}_{\text{Zn}}^*$                                   | K <sub>OV</sub>             | $6.1 \times 10^{-3}$                    | -0.6                                      |                |
| $\text{Zn(g)} \rightleftharpoons \text{Zn}_{\text{Zn}}^* + \text{V}_{\text{O}}^*$                                | K <sub>ZnV</sub>            | $6.1 \times 10^{-3} (?)$                | -0.6 (?)                                  |                |
| $\text{Zn}_{\text{Zn}}^* \rightleftharpoons \text{Zn(g)} + \text{V}_{\text{Zn}}^*$                               | K <sub>Zn</sub>             | $4.6 \times 10^{10}$                    | 6.89                                      |                |
| $\text{O}_{\bullet}^* \rightleftharpoons \text{O(g)} + \text{V}_{\text{O}}^*$                                    | K <sub>o</sub>              | $4.6 \times 10^{10} (?)$                | 6.89 (?)                                  |                |
| $\text{In}_{\text{Zn}} + \text{V}_{\text{Zn}}'' \rightleftharpoons (\text{In}_{\text{Zn}} \text{V}_{\text{Zn}})$ | K <sub>p</sub>              | 4 (?)                                   | -0.6                                      |                |

On comparing the various activation energy values obtained by us, with those reported by Kroger<sup>23</sup>, it is concluded that the following ionizations are possibly responsible for the creation of charge carriers which take part in the electrical conduction in our zinc oxide crystal in the temperature range of present investigation:



$V_O^{\bullet}$  and  $Zn_1^{\bullet}$  give rise to donor levels. The ionization energy of both these donor states is reported to be 0.05 ev.<sup>23</sup> The n-type behaviour (confirmed by the sign of thermoelectric e.m.f.) and the low activation energy (0.02 ev) found in the temperature range 25°C to 200°C clearly suggests that the ionization of these donor states is predominant in the temperature range 25°C to 200°C. It is difficult to distinguish between these two from the data available at present. It is quite likely that both the reactions may proceed to the same extent simultaneously.

The electrical conductivity  $\sigma$  is related to the number of carriers  $n$  and their mobility  $\mu$  by the following equation:

$$\sigma = n \cdot e \cdot \mu$$

where  $e$  is the electronic charge. The mobility of electrons in the conduction band of ZnO has been experimentally determined by several workers<sup>12</sup>. Although its value may not be exactly the same in our sample, we may use it for a rough evaluation of the order of magnitude of  $n$ . Using the value  $\mu = 100 \text{ cm}^2/\text{sec} \times \text{volt}$  we get  $n = 6 \times 10^{12}/\text{c.c.}$  At room temperature about half of the donors ( $V_O^\bullet$  or  $Zn_i^\bullet$ ) will be ionised because the activation energy is only 0.02 ev. So the total number of donors is estimated to be of the order of  $10^{13}/\text{c.c.}$  This is much smaller than that in the single crystals grown by the vapour phase oxidation of zinc.

The activation energy (0.92 ev) and the sign of thermoelectric e.m.f. around  $300^\circ\text{C}$  corresponds to the reaction (3). This indicates that vacant

zinc sites are created at high temperatures ( $> 300^{\circ}\text{C}$ ) and their number becomes larger than  $10^{13}/\text{c.c.}$  so that when they ionise to give rise to holes, the conductivity changes from n-type to p-type.

The decrease in resistance after annealing the sample at  $600^{\circ}\text{C}$  for about two hours shows that the total number of current carriers increases. This indicates that the number of vacant zinc sites increases on prolonged heating at  $600^{\circ}\text{C}$ . On slow cooling the conductivity is reversible indicating that zinc vacancies are destroyed.

As mentioned earlier  $\log R$  vs  $1/T$  plot for zinc oxide pellets in air comes out to be linear with an activation energy of  $7.6 \text{ Kcal} \approx 32 \text{ ev.}$  in the temperature range  $25-500^{\circ}\text{C}$ . This  $\Delta E$  is different from the two values observed in the case of single crystal. Furthermore the conduction is n-type in the entire temperature range and no break in the conductivity curve appears.

We consider these differences as significant enough to point out that the conduction processes in the single crystal and the polycrystalline pellets are entirely different. An obvious explanation is that the surface conductivity has a predominant role to play in the sintered polycrystalline material. The observed activation energy for the polycrystalline material is thus due to the donor states on the surface. The possible donor is  $\text{Zn}_1^\bullet$  which ionizes as follows:



Activation energy reported for this process is 0.4 ev and the one observed by us is 0.32 ev. The decrease may be due to a large density of surface defects and consequent broadening of the donor states due to their mutual interaction. The broadening of the impurity levels decreases the gap between the level and the bottom of the conduction band and hence decreases the activation energy.

In the case of conductivity measurements in hydrogen zinc oxide is partially reduced to form  $(Zn_i^0)$  neutral zinc interstitials. First activation energy corresponds to the removal of one electron. The two activation energies in the two different temperature ranges indicate that there are two different mechanisms of conduction taking place. The exact mechanisms could not be put forward on only conductivity data. But the low activation energy in both the temperature ranges shows that the electrons are easily available for conduction and this can happen only when they are taken from neutral zinc interstitials.

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## **CHAPTER IV**

**CHEMISORPTION OF OXYGEN ON ZINC OXIDE SINGLE  
CRYSTAL PREPARED BY ZnS OXIDATION**

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## CHAPTER - IV

CHEMISORPTION OF OXYGEN ON ZINC OXIDE  
SINGLE CRYSTAL PREPARED BY ZnS OXIDATION

## INTRODUCTION

Some studies in regard to effect of oxygen chemisorption on the electrical conductivity of zinc oxide samples have already been reported in the literature.

Morrison(1955)<sup>1</sup> studied the change of conductivity of ZnO as a function of temperature (upto 800°C) in oxygen.

He concluded that at low temperatures ( < 20°C) the bulk conductivity is not influenced by adsorption and electronic changes on the surface because the equilibrium between the surface and the bulk is not established at such low temperatures. On the other hand at temperatures above 500°C such equilibrium is established and the conductivity is dependent on oxygen adsorption. As the oxygen ions become adsorbed on the surface they trap conduction electrons from the interior and the conductance decreases. The conductivity varies with oxygen pressure  $p_{O_2}$  approximately according to the equation:

$$\sigma = A p_{O_2}^{-1/4}$$

In the intermediate temperature 20 -500°C the results

are also explained and depend to a large extent on the past history of the sample.

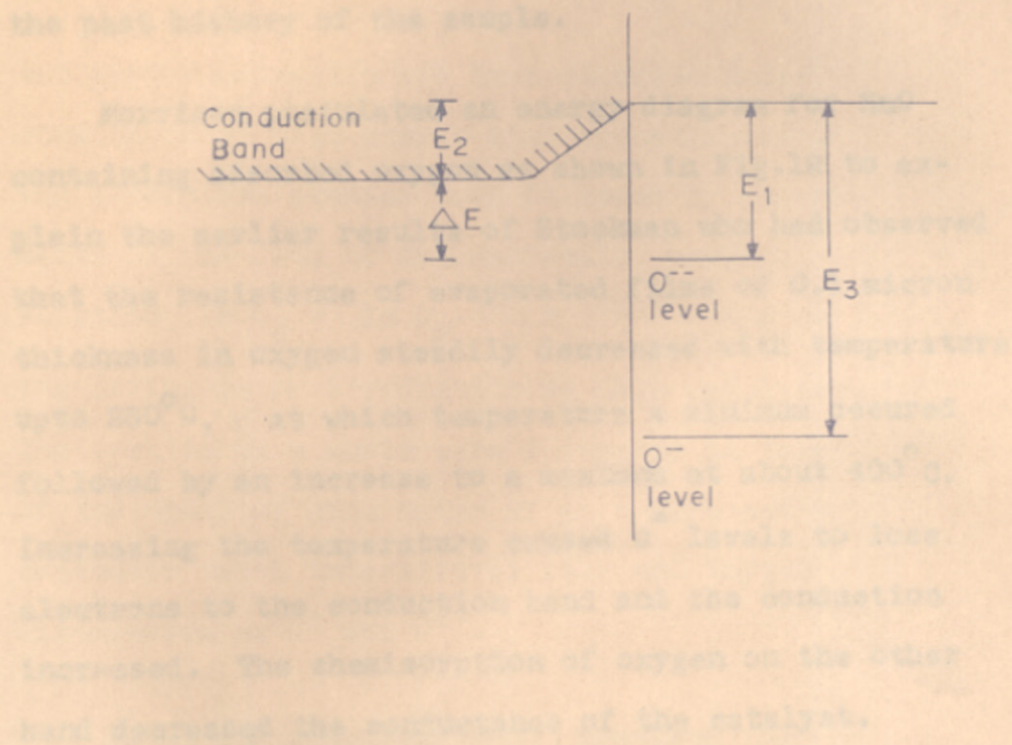


FIG. 12. POSTULATED ENERGY-LEVEL DIAGRAM FOR ZINC OXIDE, SHOWING OXYGEN LEVELS.

are more complicated and depend to a large extent on the past history of the sample.

Morrison postulated an energy diagram for ZnO containing adsorbed oxygen as shown in Fig.12 to explain the earlier results of Stockman who had observed that the resistance of evaporated films of 0.1 micron thickness in oxygen steadily decreased with temperature upto  $250^{\circ}\text{C}$ , at which temperature a minimum occurred followed by an increase to a maximum at about  $400^{\circ}\text{C}$ . Increasing the temperature caused  $\text{O}^{\cdot-}$  levels to lose electrons to the conduction band and the conduction increased. The chemisorption of oxygen on the other hand decreased the conductance of the catalyst.

Barry and Stone(1960)<sup>2</sup> studied the kinetics of adsorption of oxygen over zinc oxide over the temperature range from  $25^{\circ}\text{C}$  to  $390^{\circ}\text{C}$ , which provided the evidence of two types of chemisorption, one prevalent below  $200^{\circ}\text{C}$  and the other above  $300^{\circ}\text{C}$ . The mode of preparation and pretreatment of oxide were found to exert a strong influence on the adsorption behaviour. Photo-desorption of oxygen was confirmed to be the normal behaviour for ZnO,

but photo-adsorption had been observed under conditions of high excess zinc concentration. The adsorption studies were followed by experiments on the rate of intramolecular oxygen reaction  $18 \text{ O}_2 + 18 \text{ O}_2 \rightleftharpoons 2 \text{ }^{18}\text{O}^{16}\text{O}$ , and on the influence of irradiation on this catalysis. The results as a whole were discussed in terms of the model of zinc oxide as an n-type semiconductor with interstitial zinc and oxygen chemisorbed as  $\text{O}^-$  and  $\text{O}^{2-}$ .

Bevan and Anderson(1950)<sup>3</sup> measured the electronic conductivity of zinc oxide in the range 500-1000<sup>o</sup>C, in air and observed that it varies widely according to the mode of preparation. At low oxygen pressures the conductivity was observed to be quasi-metallic and fairly reproducible for different samples, irrespective of their origin. It is suggested that the differences between samples arise largely from the variation in the relative importance of the

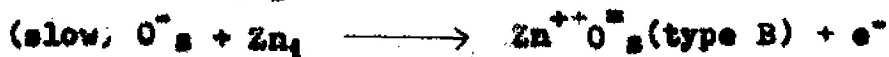
conduction and the bulk phase conduction processes. Conductivity in oxygen at low pressures ( $> .01 - .1$  mm of Hg) varied with oxygen pressure in a reversible way, according to the law  $K = A p_{O_2}^{-1/4}$ . This type of dependence gives support to an impurity conduction arising from  $O^2 = 1/2 O_2 + 2e^-$  reaction occurring at surface. At low oxygen pressures, however, the conductivity became independent of oxygen pressure. The bulk phase conductivity of ZnO is probably high, but electrons are trapped by chemisorption of oxygen on the surface.

Barry and Klier(1961)<sup>4</sup> measured the electrical conductivity of powdered zinc oxide with simultaneous measurements of adsorption and desorption of gases. These measurements yielded information on the charge transfer during the reversible and irreversible adsorption.

Kokes(1962)<sup>5</sup> calculated the amounts of oxygen chemisorbed on ZnO prepared by the following ways:

(I) decomposition of zinc oxalate, (II) decomposition of zinc carbonate, (III) oxidation of metallic zinc. Results indicated the existence of two types of oxygen chemisorption, one appearing at room temperature and the other appearing at 200°C or above. ZnO doped, as well as undoped showed an electron resonance signal that reflected the concentration of free electrons. The effect of low and high temperature adsorption has been examined. Interpretation of these results leads to the conclusion that at low temperature oxygen is chemisorbed as  $O^-$  ions (type A) and at high temperatures as  $O^{--}$  (type B).  $O^-$  ions were supposed to be formed by reaction with conduction electrons and  $O^{--}$  were stabilized by the migration of donors to the surface.

Glenza and Kokas(1962)<sup>6</sup> suggested that the oxygen adsorption at high temperatures was a two step consecutive process involving an unstable surface species as an intermediate. They explained that type B adsorption always occurred via the following consecutive steps:



They suggested that only type A adsorption should affect the conductivity; type B should have a negligible effect.

Gleiza and Kokes(1965)<sup>7</sup> did the measurements of the adsorption of oxygen at low pressures (  $< 10\mu$  ) on sintered zinc oxide pellets and the conductivity change have been observed as a function of temperature, amount of oxygen adsorbed, pretreatment and doping. The results were consistent with the suggestion made earlier that the stable form of chemisorbed oxygen at  $-80$  to  $150^{\circ}\text{C}$  (type A) was different from the stable form of chemisorbed oxygen above  $300^{\circ}\text{C}$  (type B). Details of the results suggest (a) A was an intermediate in the formation of B; (b) A was formed by reaction with conduction electrons; (c) B was formed by reaction of A with ionized donors.

Krusmeyer and Thomas(1958)<sup>8</sup> showed theoretically that the interaction of oxygen with an initially bare n-type surface first created a



"depletion layer" on the surface, which caused a decrease in the surface concentration of majority carriers. In this region, an increase in the oxygen pressures would further depress the concentration of quasi-free electrons, and the conductivity therefore would be correspondingly lowered. When the upwards bending of the semiconductor bands near the surface caused by chemisorbed oxygen was such that the upper limit of the valence band had come sufficiently close to the Fermi level, electrons could be transferred to the acceptor oxygen molecules directly from the valence band. At this stage, quasi-free holes would start to contribute to the surface conduction and an "inversion layer" with p character would be formed. An increase in oxygen pressure would increase the hole concentration on the surface and the conductivity would be correspondingly increased.

Cimino, et.al. (1963)<sup>9</sup> showed that the weak chemisorption of oxygen observed in the temperature range 20-130°C on powder samples of ZnO either

pure or doped with  $\text{Li}^+$  or  $\text{Ga}^{3+}$ , could exert a positive influence on the electrical conductivity of  $\text{ZnO}$ . The dependence of the conductivity on the oxygen pressure, as well as the sign of Seebeck voltage, pointed to the presence of p-type inversion layers on the surface. Treatment of the samples in high vacuum at  $450^\circ\text{C}$  removed the p-type surface layers and the normal n-type behaviour could thereafter be observed.

Medved(1961)<sup>10</sup> studied the decay kinetics of the photoconductivity of  $\text{ZnO}$  as a function of intensity of illumination and ambient oxygen pressure.

Watanabe and Wada(1965)<sup>11</sup> observed that the presence of adsorbed oxygen decreased the electronic conductivity of  $\text{ZnO}$  powder. The rate of desorption of oxygen increased with temperature. The data yielded an activation energy of 1.0 to 1.1 eV for oxygen desorption. It was shown that this was the binding energy for the chemically adsorbed oxygen.

Electrical conductivity of evaporated films of zinc oxide in oxygen was measured by Stockmann<sup>12</sup> (1960) at temperatures 20 to 800°C. He found that in oxygen the conductivity increased with temperature upto 250°C at which temperature a maximum occurred and was followed by a decrease to a minimum at 400°C. At high temperatures the conductivity was independent of the previous history of the sample and only depended on the temperature and the oxygen pressure. At low temperatures on the other hand, the conductivity was dependent on the sample history, being higher greater the zinc in ZnO lattice. At intermediate temperatures the conductivity decreased irreversibly with time with a rate of change which was greater for a zinc excess produced by reduction than for a zinc excess remaining when zinc oxide was formed.

The conductivity of thin films were also measured by Tischer(1954)<sup>13</sup> at high temperatures. The curves were found to be reversible with temperature in the range 20 to 175°C, but one obtained irreversible

changes if the samples were heated to  $\sim 250-300^{\circ}\text{C}$ . A very rapid rise in the conductance was found in the temperature range 300 to  $500^{\circ}\text{C}$ .

More recently Arghiropoulos and Teichner(1964)<sup>14</sup> studied the influence of adsorption of oxygen on the electrical conductivity of polycrystalline zinc oxide. The electrical conductivity  $\sigma$  was found to be proportional to  $p_{\text{O}_2}^{-1/n}$  where  $n \sim 2$  at  $150^{\circ}\text{C}$  and 4 at  $600^{\circ}\text{C}$ . The plot of  $\log \sigma$  vs  $1/T$  showed the maximum at  $300^{\circ}\text{C}$  and minimum at  $450^{\circ}\text{C}$  in the case of fresh zinc oxide samples, but these extrema disappeared if the sample was heated to  $900^{\circ}\text{C}$  in vacuum and cooled to room temperatures.

Myasnikov(1957)<sup>15</sup> coated a quartz tube with a  $10\mu$  thick zinc oxide film. He observed that the electrical conductivity of this film was smaller in oxygen than in vacuum, but the difference was less the higher was the frequency of the electrical current.

$\sigma$  was found to decrease as the oxygen pressure increased from .001 to 1 mm Hg according to the equation

$$\left(\frac{\sigma}{\sigma_0}\right)^2 = \frac{K}{p} \quad \dots (1)$$

where  $\sigma_0 = \sigma$  in vacuum.  $K$  was  $55 \times 10^{-5}$  at  $620^\circ\text{C}$  and  $1.3 \times 10^{-5}$  at  $250^\circ\text{C}$ . At  $-80^\circ\text{C}$  oxygen had no effect on  $\sigma$ . Except for first .05 sec. the decrease of  $\sigma$  after oxygen admission to the film agreed with equation

$$\frac{\sigma_0}{\sigma} = K_1 t + \text{const} \quad \dots (2)$$

where  $t$  = time, and  $K_1$  was 6 to 35  $\text{sec.}^{-1}$ , increasing with  $p$ . The rise of  $\sigma$  during desorption was represented by

$$\ln \left[ 1 - \left( \frac{\sigma}{\sigma_0} \right) \right] = -K_2 t + \text{Const.} \quad \dots (3)$$

$K_2$  was  $.0024 \text{ sec.}^{-1}$  at  $412^\circ$ , independent of  $p$ .  $\ln K_1$  and  $\ln K_2$  were inversely proportional to absolute temperature. Equation (1) is obtained if it is assumed that the sorbed amount of O is proportional to  $p$  and concentration of  $\text{Zn}^+\text{O}_2^-$  complex formed in the sorption is approximately equal to the concentration of  $\text{Zn}^+$  ions in  $\text{ZnO}$  before sorption. Equations 2 and 3 are also accounted for in the same manner. Activation energy for adsorption is 8000 cal. and for desorption is 2300 cal. The heat of reaction

from equilibrium experiments was 10,000 to 12,000 cals. The chemisorption of oxygen on zinc oxide is caused by electrostatic forces.

## EXPERIMENTAL

Various zinc oxide samples having different surface to volume ratios were prepared to study the effect of oxygen chemisorption.

### (1) Zinc oxide plate type single crystals<sup>16</sup>

The preparation of this has already been described in Chapter I.

### (2) Thin films of zinc oxide

Thin films of zinc oxide were prepared in the following way: Fused silica slides were used as substrate for the deposition of films. They were thoroughly cleaned with chromic acid and detergents and then rinsed with distilled water and dried. These slides were then kept at the bottom of a vacuum chamber. At the top of these slides a tungsten filament was adjusted. Small pieces of pure zinc metal were kept in this filament. The chamber was connected to a mercury diffusion pump. After getting a vacuum of  $5 \times 10^{-6}$  mm of Hg, the tungsten filament was heated electrically to evaporate the metal completely. A shining metal deposit was always obtained on the silica slides. These films were then kept in a furnace in air

and were heated to  $450-500^{\circ}\text{C}$  for about 20-24 hours to get a zinc oxide film. Aqua dag was

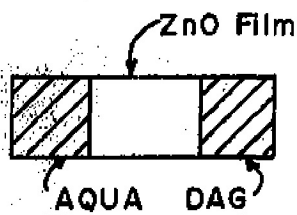


FIG. 13. DIAGRAM OF  $\text{ZnO}$  THIN FILM SHOWING SURFACE CONDUCTION (TYPE A).

was applied at the ends to measure the surface conduction (thin film A). These samples gave the largest surface area to volume ratio.

### (3) Sandwiched films of zinc oxide

On a pyrex glass slide, a strip of gold was evaporated by the similar technique as we did for zinc. This acted as one electrode

Au(I) . Over this another circular film of zinc was evaporated and oxidised to  $\text{ZnO}$ . This film was further sandwiched by another Au film to give another electrode Au(II) . The resistance was measured across the film (thin film B).



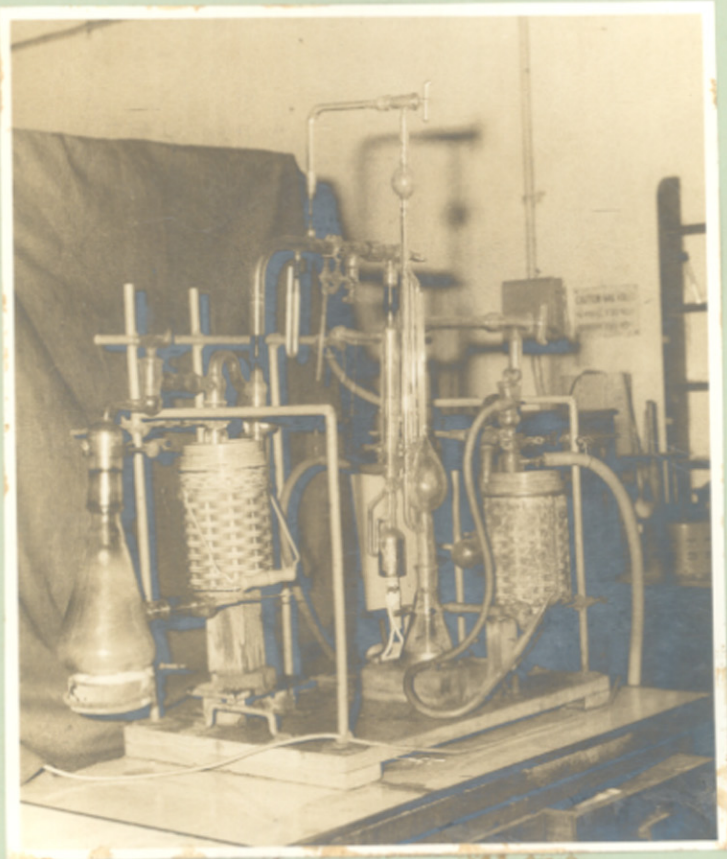


FIG. 15. VACUUM EVAPORATION UNIT FOR  
THE DEPOSITION OF THIN FILMS.

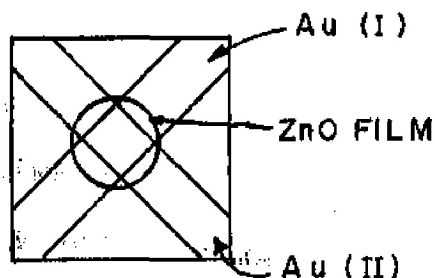


FIG. 14. DIAGRAM OF ZnO THIN FILM SANDWICHED BETWEEN TWO GOLD ELECTRODES, BULK CONDUCTION (TYPE B)

### Description of vacuum evaporation unit

An apparatus designed and constructed at our Laboratory (Fig. 15) was used. The vacuum obtained was of the order of  $5 \times 10^{-6}$  mm of Hg. A rotary oil pump (Masynth, capable of giving vacuum of  $10^{-8}$  mm of Hg) was connected to a electrically heated mercury diffusion pump through a stop cock, a phosphorous pentaoxide trap and an ice cold trap. This mercury diffusion pump in turn was connected to a manometer and a McLeod gauge and a stop cock to release vacuum. This was further connected to an ice cold trap, which was connected by B-40 joint to a vacuum chamber through a stop cock. It was possible to disconnect the vacuum chamber from the B-40 joint to place the substrate plates. Another B-24 (male-female) joint was supplied in the vacuum chamber. Through this joint two tungsten wires were connected to a porcelain plug. To this plug

the tungsten filament carrying the substance to be evaporated was always connected. This was heated with the aid of a variac connected to ammeter in series to control the current being passed.

#### Preparation of zinc oxide (indium doped) films

A known amount of BDH(AR) zinc metal (99.99% pure) was taken along with a weighed amount of indium metal (99.98%, Fluka). Both of these metals were taken in a 10 cm long pyrex tube (sealed at one end) and was connected to the vacuum unit described earlier. When a vacuum of the order of  $5 \times 10^{-6}$  mm of Hg was achieved, the pyrex tube was sealed at the other end also, with the aid of bunsen burner. This tube was then heated to  $450-500^{\circ}\text{C}$  in a furnace for about 12 hours, for melting the zinc and indium metals and making a homogeneous alloy of the two. This alloy was evaporated in vacuum from a tungsten filament to give thin films of Zn-In. Utmost care was taken to deposit the metal completely. This would ensure that the composition of the deposited film would not be very different from that of the starting alloy. These Zn-In thin films were oxidised by heating slowly in air in a furnace at about  $400^{\circ}\text{C}$ . First the films turned black at about  $200^{\circ}\text{C}$  and later on heating for a longer time at higher temperatures they turned into transparent white films.

As it is likely that the film might be heterogenous in composition due to the different rates of evaporation of zinc and indium metals, they were heated upto  $600-700^{\circ}\text{C}$  in air for six hours to make the film homogenous. The two ends of the films were coated with aqua dag to measure the surface conductance. Before doing the actual measurements, the films were heated to  $100^{\circ}\text{C}-150^{\circ}\text{C}$  to remove the traces of moisture and make better contact with aqua dag.

Five different samples were prepared to see the effect of indium concentration on conductivity by varying the indium concentration(0, 0.3, 0.8, 1.0, 2.6% In by weight).

It must be noted that the composition of the film may not be exactly as that given above and these studies would only indicate the effect of increasing concentration of indium in a qualitative way.

For electrical measurements the sample holder assembly was the same as described in Chapter III. The slide having the film with an adherent coating of aqua dag was pressed between two molybdenum strips screwed to a silica base.

Fig. 10.1  
 Figure 10.1  
 Measurements were  
 made at  $100-150^{\circ}\text{C}$ .

The resistance measurement was carried out as described earlier. For measurements in atmospheres different from air (i.e. hydrogen and nitrogen and vacuum) a silica tube sealed at one end was taken. To the other end a B-34 female joint was attached. To B-34 male joint another silica tube was attached to carry the required gas upto the bottom of the bigger tube. Two pairs of glass to metal joints were also attached to the B-34 male joint, to give contact with the inner leads for the measurement of resistance and the temperature. Inside the tube two platinum wires were attached one to "metal to glass" joint and a chromel-alumel thermocouple was attached to the other. Silica plate sample holder assembly was connected to the two platinum wires. For increasing the temperature slowly and keeping it constant at the required values, a controller was used. This was connected to the heating furnace and it was possible to cut off the current at the required places automatically.

Conductivity measurements on zinc oxide plate type single crystals were carried out in hydrogen atmosphere also. The crystal after being mounted on the sample holder was heated to  $600^{\circ}\text{C}$  in hydrogen for two hours. After this the crystal was cooled to room temperature in hydrogen atmosphere and the conductivity measurements were carried out in the temperature range  $25-500^{\circ}\text{C}$ .



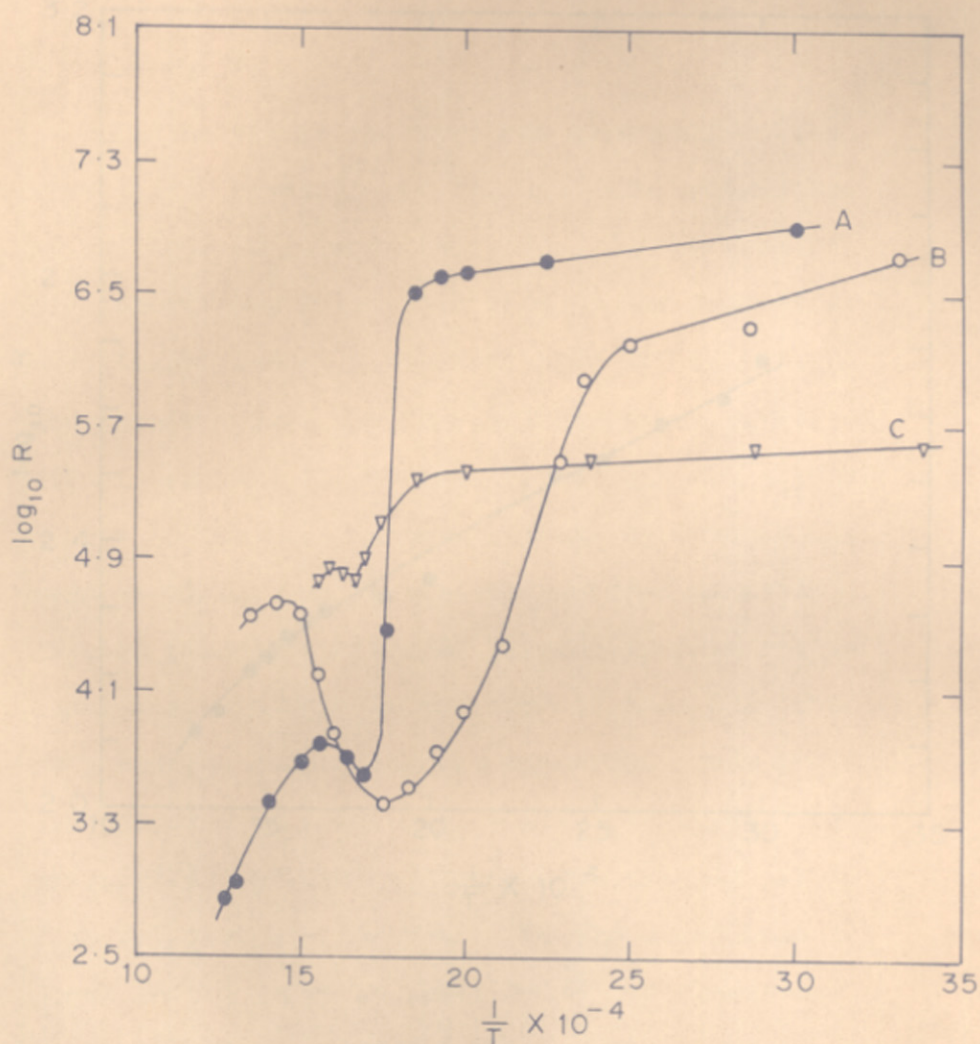


FIG. 16  $\log_{10} R$  Vs  $\frac{1}{T}$  PLOT IN AIR FOR  
 A-ZnO SINGLE CRYSTAL (PLATE TYPE)  
 B-ZnO THIN FILM (SURFACE CONDUCTION)  
 C-ZnO THIN FILM (BULK CONDUCTION)

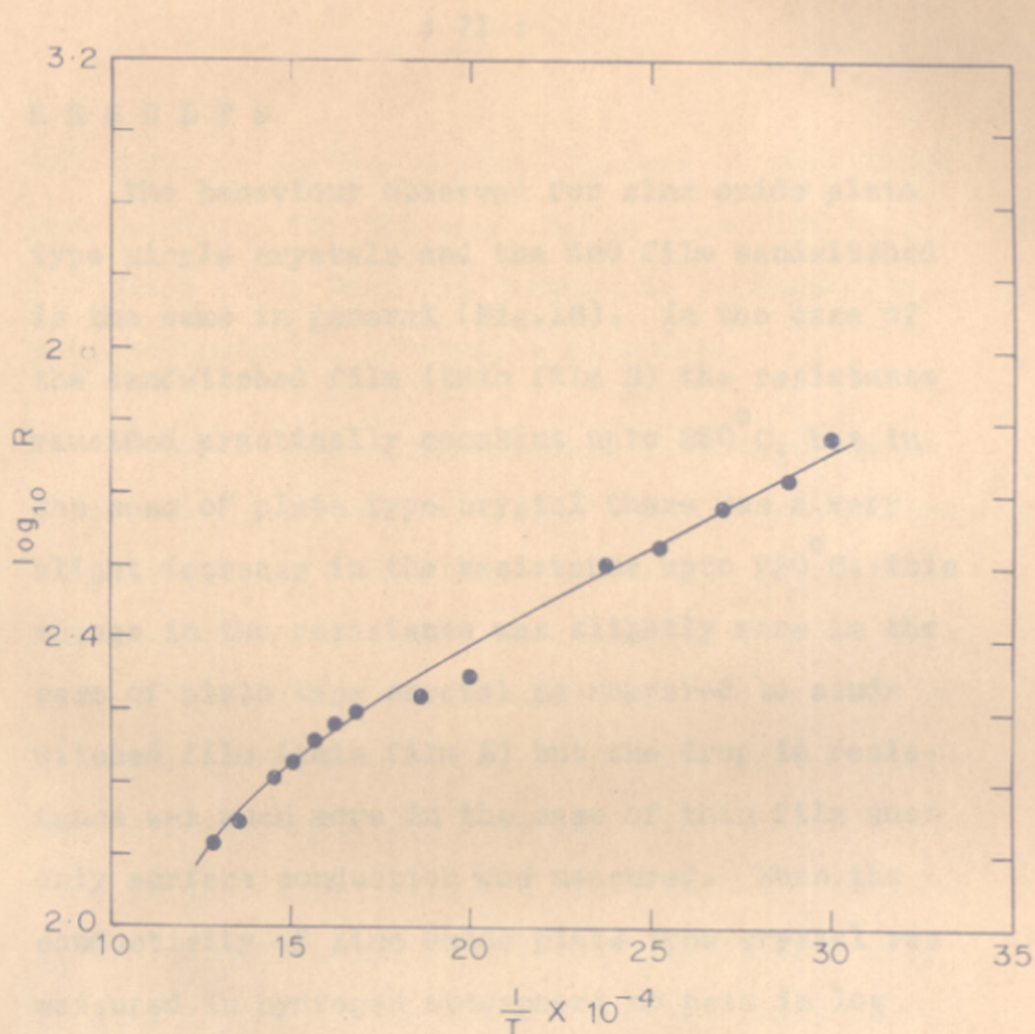


FIG. 17.  $\log R$  Vs  $\frac{1}{T}$  PLOT FOR ZnO PLATE TYPE CRYSTAL IN HYDROGEN.

## R E S U L T S

The behaviour observed for zinc oxide plate type single crystals and the ZnO film sandwiched is the same in general (Fig.16). In the case of the sandwiched film (thin film B) the resistance remained practically constant upto  $250^{\circ}\text{C}$ , but in the case of plate type crystal there was a very slight decrease in the resistance upto  $250^{\circ}\text{C}$ . This change in the resistance was slightly more in the case of plate type crystal as compared to sandwiched film (thin film B) but the drop in resistance was much more in the case of thin film when only surface conduction was measured. When the conductivity of zinc oxide plate type crystal was measured in hydrogen atmosphere no peak in  $\log R$  vs  $1/T$  plot was observed. On the other hand a break in the curve at about  $300^{\circ}\text{C}$  was observed. The activation energy for the temperature range  $25-300^{\circ}\text{C}$  was 1.2 Kcal. and for  $300-500^{\circ}\text{C}$  was 2.2 Kcal. (Fig.17).

In the case of those thin films where only surface conduction was measured (thin film A) a steady drop in resistance was observed upto  $100^{\circ}\text{C}$ , after this temperature a steep fall in resistance is observed and we get a minima in the  $\log R$  vs



1/T curve at  $250^{\circ}\text{C}$ . Minimum changes of resistance were observed for the sandwiched thin film (Fig. 16) which shows that the extrema in conductivity are attributable to surface phenomena.

From  $250^{\circ}$ - $350^{\circ}\text{C}$  an increase of resistance is observed, in the case of plate type crystal and the sandwiched film. The order of the increase in resistance for the plate type crystal is much more as compared to the sandwiched film. A maximum of the resistance is observed at  $350^{\circ}\text{C}$ . An increase in resistance upto  $400^{\circ}\text{C}$  is also observed in the case of thin film (type A). A maximum is observed at  $400^{\circ}\text{C}$ . The order of the increase in this case is much larger as compared to the two cases considered earlier.

After this it has been found that the resistance starts decreasing in all the cases. This decrease continues upto maximum temperature studied i.e.  $500^{\circ}\text{C}$ . All these samples had greater surface to volume ratio as compared to rod type crystals. It can be seen as the ratio keeps on increasing the changes in resistance are more. They are maximum for the thin film of type A and the minimum for the sandwiched film (type B).

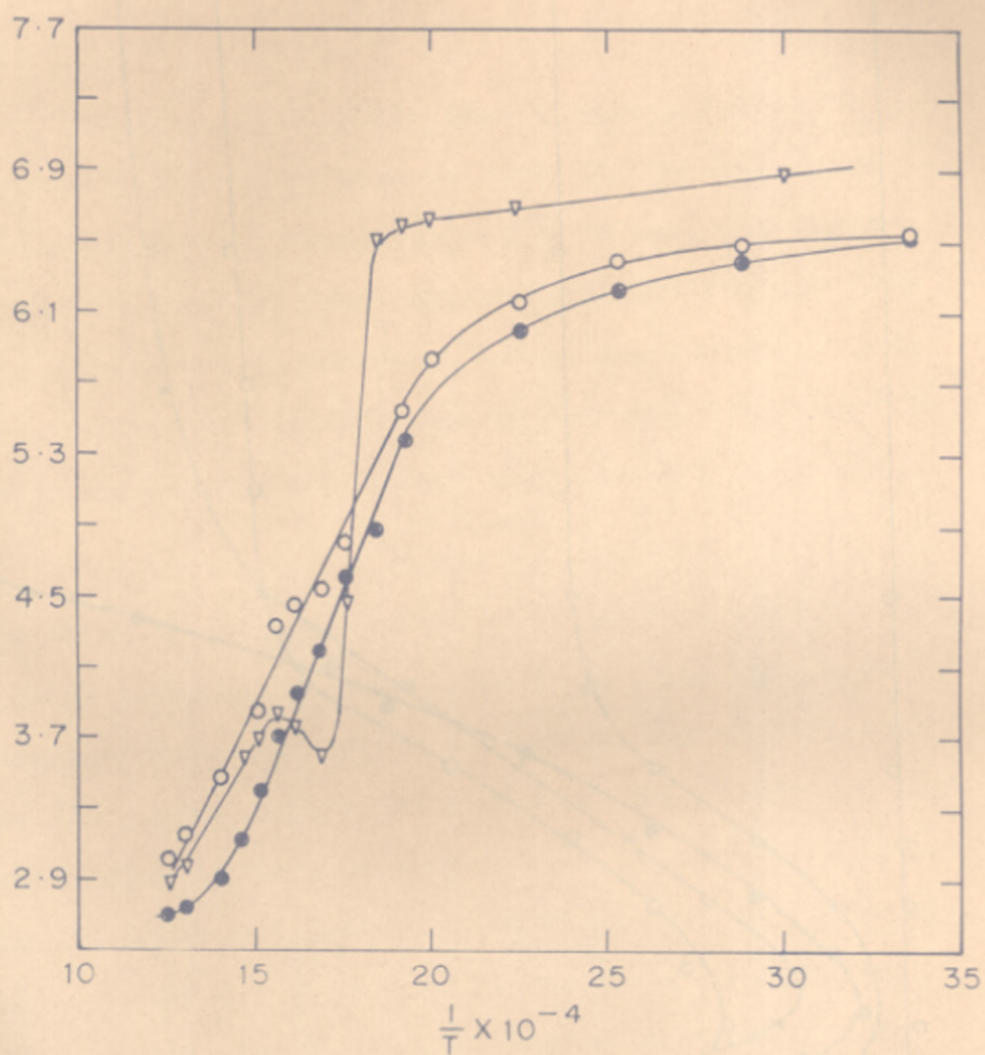
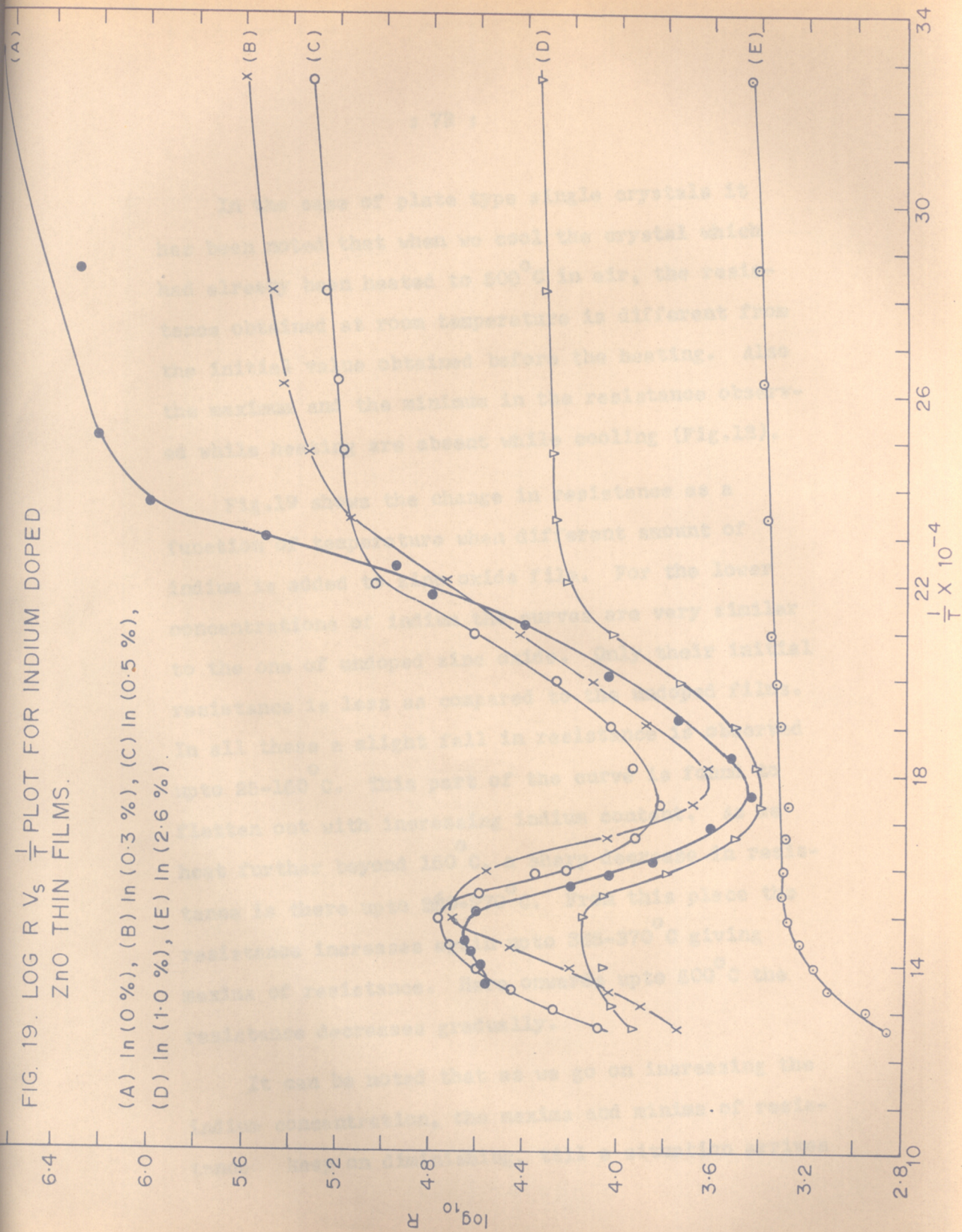


FIG. 18. LOG R Vs  $\frac{1}{T}$  PLOT FOR SUCCESSIVE HEATING AND COOLING OF ZnO PLATE TYPE CRYSTAL IN AIR.



FIG. 19.  $\log R V_s \frac{1}{T}$  PLOT FOR INDIUM DOPED  
ZnO THIN FILMS.

(A) In (0%), (B) In (0.3%), (C) In (0.5%),  
(D) In (1.0%), (E) In (2.6%).



In the case of plate type single crystals it has been noted that when we cool the crystal which had already been heated to  $500^{\circ}\text{C}$  in air, the resistance obtained at room temperature is different from the initial value obtained before the heating. Also the maximum and the minimum in the resistance observed while heating are absent while cooling (Fig.18).

Fig.19 shows the change in resistance as a function of temperature when different amount of indium is added to zinc oxide film. For the lower concentrations of indium the curves are very similar to the one of undoped zinc oxide. Only their initial resistance is less as compared to the undoped films. In all these a slight fall in resistance is observed upto  $25-150^{\circ}\text{C}$ . This part of the curve is found to flatten out with increasing indium content. As we heat further beyond  $150^{\circ}\text{C}$ , a sharp decrease in resistance is there upto  $260-270^{\circ}\text{C}$ . From this place the resistance increases again upto  $365-370^{\circ}\text{C}$  giving maxima of resistance. Here onwards upto  $500^{\circ}\text{C}$  the resistance decreases gradually.

It can be noted that as we go on increasing the indium concentration, the maxima and minima of resistance keep on diminishing, till a situation arrives



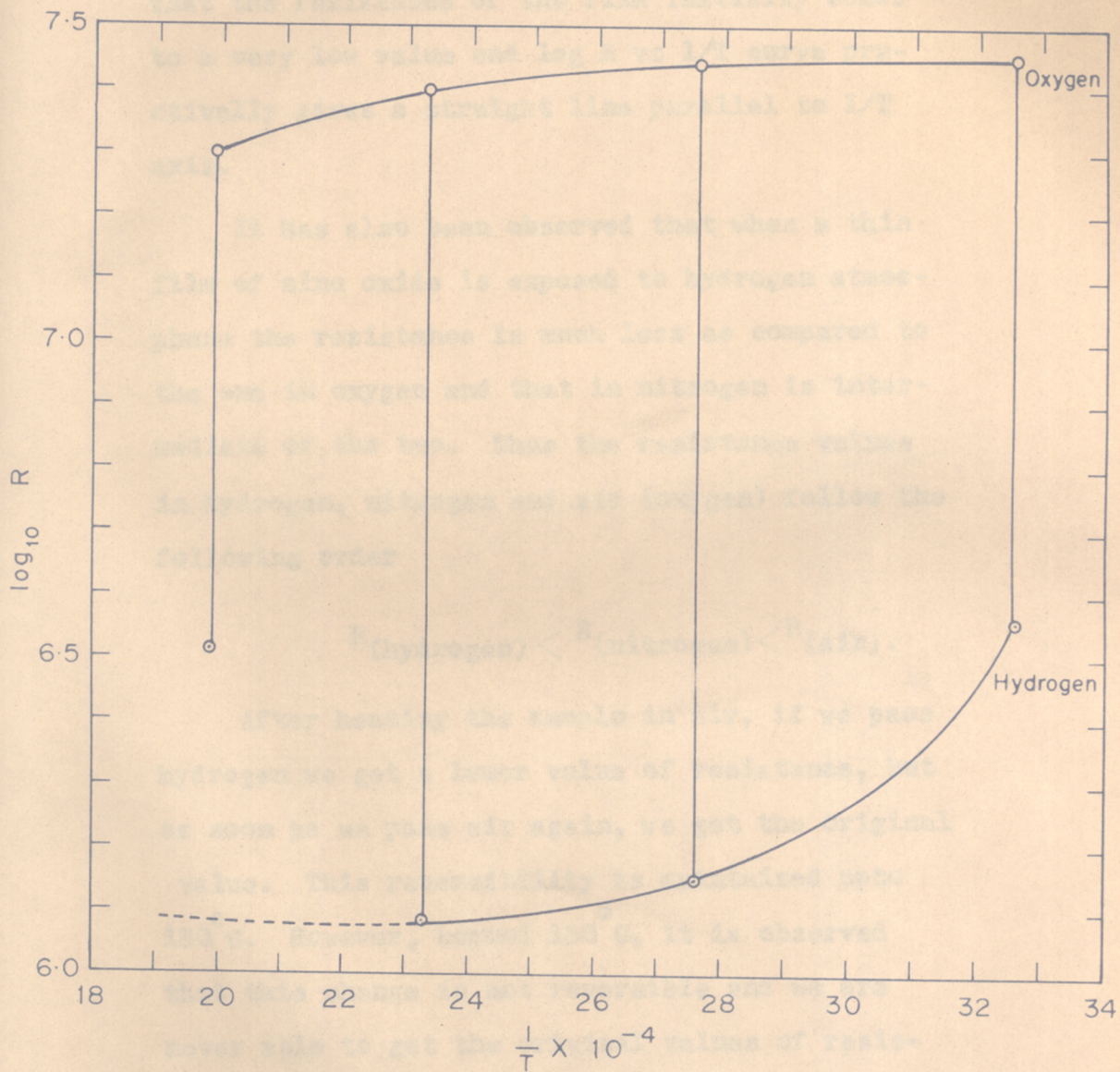


FIG. 20. CHANGES IN RESISTANCE FOR ZnO THIN FILM ON BEING EXPOSED TO HYDROGEN AT VARIOUS TEMPERATURES.

that the resistance of the film initially comes to a very low value and  $\log R$  vs  $1/T$  curve practically gives a straight line parallel to  $1/T$  axis.

It has also been observed that when a thin film of zinc oxide is exposed to hydrogen atmosphere the resistance is much less as compared to the one in oxygen and that in nitrogen is intermediate of the two. Thus the resistance values in hydrogen, nitrogen and air (oxygen) follow the following order

$$R(\text{hydrogen}) < R(\text{nitrogen}) < R(\text{air}).$$

After heating the sample in air, if we pass hydrogen we get a lower value of resistance, but as soon as we pass air again, we get the original value. This reversibility is maintained upto  $150^{\circ}\text{C}$ . However, beyond  $150^{\circ}\text{C}$ , it is observed that this change is not reversible and we are never able to get the original values of resistance in air (Fig.20) once the sample has been heated in hydrogen. The thin films which have already been preheated in hydrogen (upto  $500^{\circ}\text{C}$ ) and nitrogen (upto  $300^{\circ}\text{C}$ ) did not show much



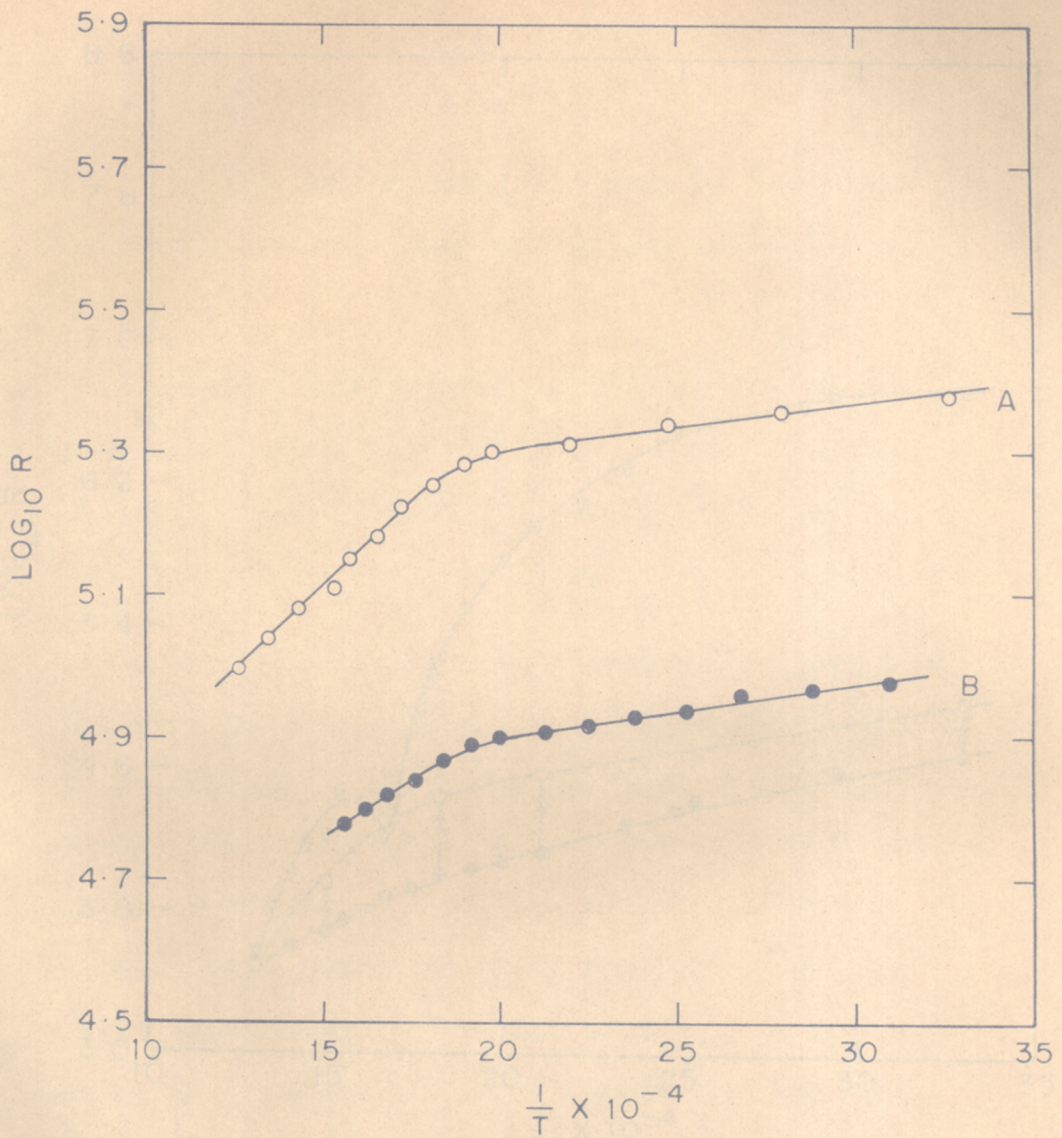


FIG. 21.  $\text{LOG}_{10} R$  Vs.  $\frac{1}{T}$  PLOT FOR ZnO THIN FILM

A - IN NITROGEN  
B - IN HYDROGEN



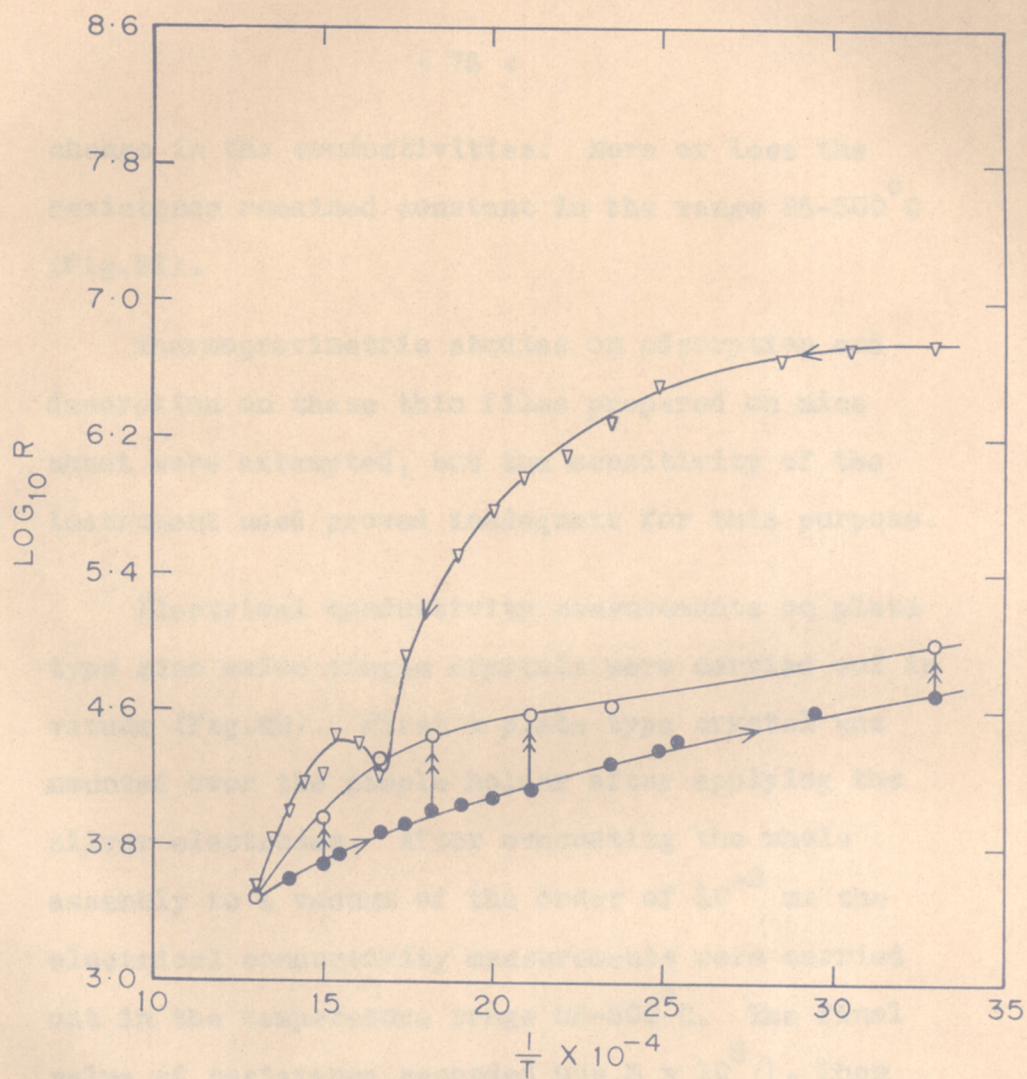


FIG.22.  $\text{LOG}_{10} R$  Vs.  $\frac{1}{T}$  PLOT FOR ZnO PLATE TYPE CRYSTAL IN VACUUM AND CHANGES IN RESISTANCE ON EXPOSING TO AIR AT VARIOUS TEMPERATURES.



change in the conductivities. More or less the resistance remained constant in the range 25-500° C (Fig.21).

Thermogravimetric studies on adsorption and desorption on these thin films prepared on mica sheet were attempted, but the sensitivity of the instrument used proved inadequate for this purpose.

Electrical conductivity measurements on plate type zinc oxide single crystals were carried out in vacuum (Fig.22). First a plate type crystal was mounted over the sample holder after applying the silver electrodes. After evacuating the whole assembly to a vacuum of the order of  $10^{-3}$  mm the electrical conductivity measurements were carried out in the temperature range 25-500° C. The final value of resistance recorded was  $3 \times 10^3 \Omega$ . Then the crystal was cooled back to room temperature in vacuum. The resistance recorded at room temperature was much less as compared to the initial resistance of the crystal. At this stage, at room temperature the vacuum was released. Increase in resistance was recorded as a function of time till the resistance practically became constant. The

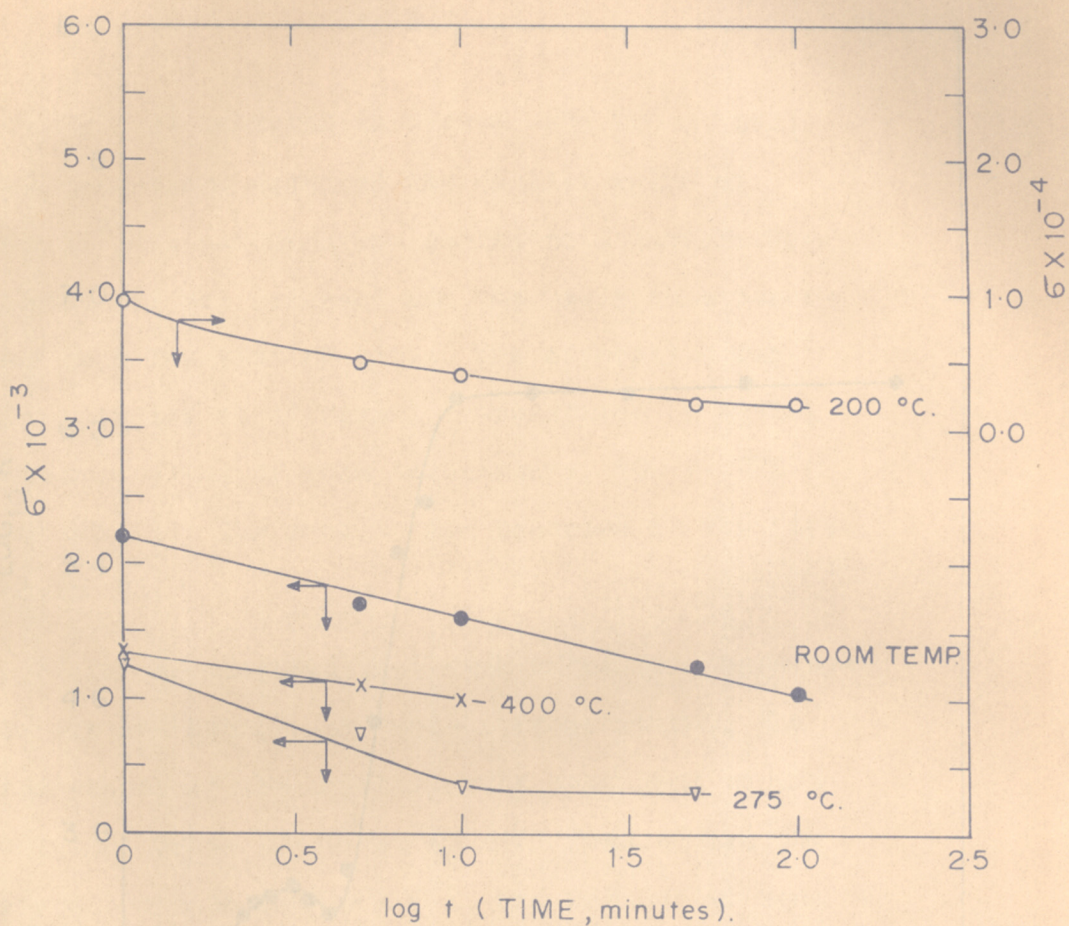


FIG. 23. CHANGES IN CONDUCTIVITY WITH TIME ON A ZnO PLATE TYPE CRYSTAL ON OXYGEN ADSORPTION AT VARIOUS TEMPERATURES.



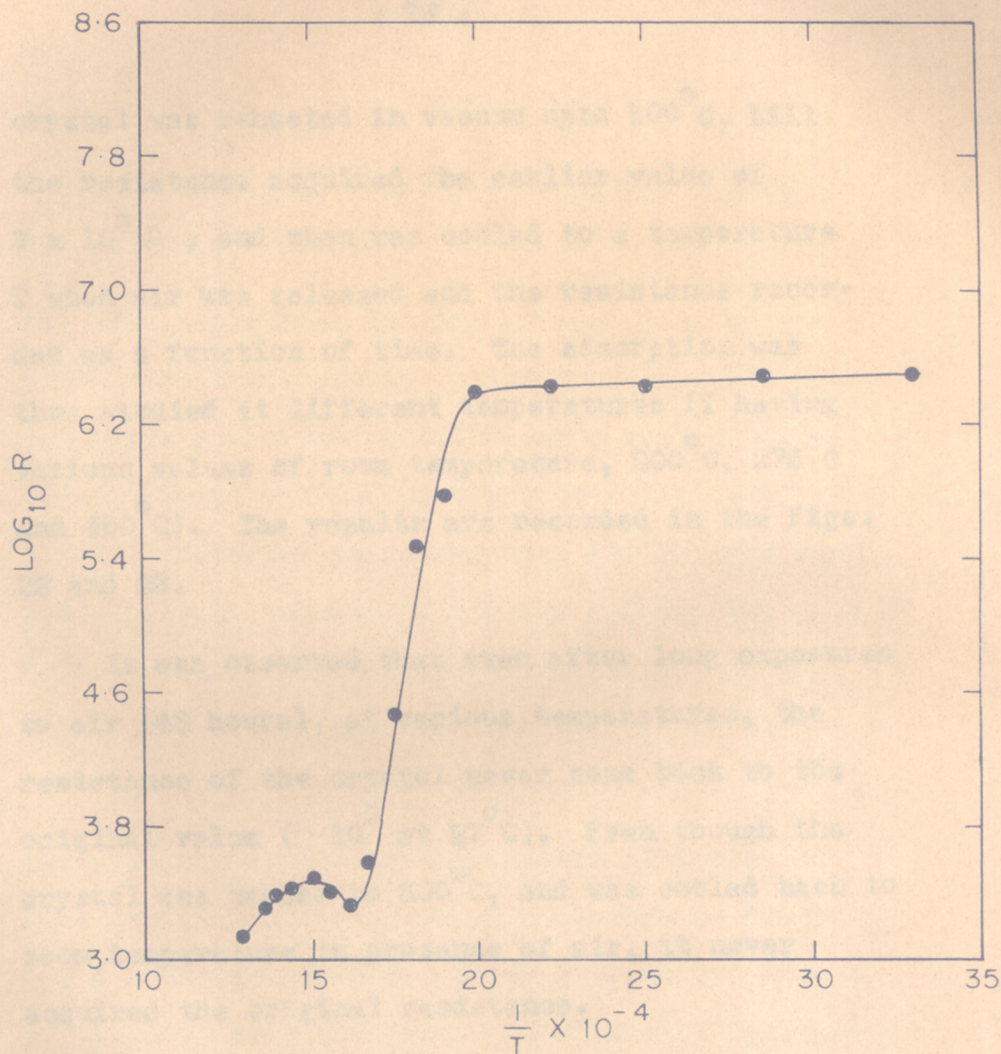


FIG. 24.  $\text{LOG}_{10} R$  Vs.  $\frac{1}{T}$  PLOT FOR THE  $\text{ZnO}$  PLATE TYPE CRYSTAL FOR A FRESH EXPOSED SURFACE.

crystal was reheated in vacuum upto  $500^{\circ}\text{C}$ , till the resistance acquired the earlier value of  $3 \times 10^3 \Omega$ , and then was cooled to a temperature  $T$  when air was released and the resistance recorded as a function of time. The adsorption was thus studied at different temperatures ( $T$  having various values of room temperature,  $200^{\circ}\text{C}$ ,  $275^{\circ}\text{C}$  and  $400^{\circ}\text{C}$ ). The results are recorded in the Figs. 22 and 23.

It was observed that even after long exposures to air (48 hours), at various temperatures, the resistance of the crystal never came back to the original value ( $\sim 10^6$  at  $27^{\circ}\text{C}$ ). Even though the crystal was heated to  $500^{\circ}\text{C}$ , and was cooled back to room temperature in presence of air, it never acquired the original resistance.

However when the top surface of the crystal was removed by rubbing on an emery paper, etching, washing and drying and a fresh surface was exposed, the original behaviour was reproduced (resistance of the order of  $10^6 \Omega$ ). Conductivity measurements were carried out again on this crystal and the results are given in Fig. 24.

## DISCUSSION

The important properties observed can be summarized as follows:

- (1) The resistance vs temperature plot for the fresh zinc oxide sample (plate type crystal) in air shows a minimum at  $325^{\circ}\text{C}$  and a maximum at  $370^{\circ}\text{C}$ . These extrema were not observed on a crystal preheated in vacuum upto  $500^{\circ}\text{C}$ , even when the sample is exposed to air for a long time. It however reappears when the upper surface of the crystal is etched and measurements are carried out on a freshly exposed surface.
- (2) The resistance vs temperature plot for the zinc oxide thin films, shows a minimum at  $300^{\circ}\text{C}$  and a maximum at  $390^{\circ}\text{C}$ . These extrema are absent in the low resistance zinc oxide thin films heavily doped with indium.
- (3) The resistance depends on the ambient atmospheres and follows the order

$$R_{(\text{O}_2)} > R_{(\text{N}_2)} > R_{(\text{H}_2)}$$

The resistance values are found to be reversible in the temperature range  $25-150^{\circ}\text{C}$ . These results are not in agreement with those reported by

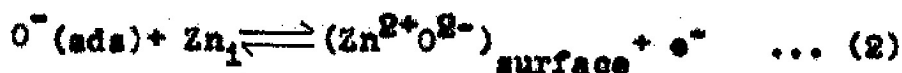
Cimino, Molinari and Gramarossa<sup>9</sup>, who have found that the surface conductivity of zinc oxide is enhanced by the adsorption of oxygen.

These minima and maxima in the conductivity plots for fresh zinc oxide samples have been explained by Arghiroopoulos and Tiechner<sup>14</sup> as arising due to the interplay of two opposing factors:

- (I) the liberation of electrons due to thermal ionisation of zinc interstitials migrating from the bulk to the surface under the influence of the strong electric field present at the surface, and
- (II) electron consumption due to chemisorption.

However, it is difficult to see how the migration of the neutral zinc is enhanced by the proposed field at the surface.

We find that the observed behaviour is more consistent with the following simultaneous equilibria taking place on the surface of the zinc oxide. The interpretation is on lines <sup>to</sup> similar that given by Barry and Stone:



These reactions move to the right as the temperature is raised. However, enthalpy of reaction (2) is larger than that of (1), which brings out clearly that at low temperatures reaction (1) will predominate over reaction (2), and the release of adsorbed oxygen releases one electron and hence increases the conductivity of the sample.

But at high temperatures reaction (2) predominates over the reaction (1) and the  $O^-(ads)$  starts reacting with the neutral zinc interstitial atoms ( $Zn_i^*$ ). As the  $O^-(ads)$  and  $Zn_i$  gets used up, the reactions (1) and (3) move to the left to maintain the equilibrium. This whole process leads to a decrease in the total number of free electrons( $e^-$ ) and hence results in an increase of resistance. This whole idea can be developed mathematically in the following way



Let the equilibrium constants for the three reactions given above be  $K_1$ ,  $K_2$  and  $K_3$  respectively and the corresponding enthalpy changes be  $E_1$ ,  $E_2$  and  $E_3$  respectively.

So at equilibrium at any temperature we are having  $Zn_1^*$ ,  $Zn_1^+$ ,  $e^-$ ,  $O^-(ads)$  and  $O_2(gas)$ . We denote the concentrations of these by  $x$ ,  $y$ ,  $z$ ,  $n$  and  $p_{O_2}$  respectively. Considering the equilibrium for the reaction 1, 2 and 3 and applying the law of mass action, we get the following set of equations:

From equation 1: we get

$$\frac{p_{O_2}^{1/2} \cdot n}{x} = K_1 \quad \dots (4)$$

where  $K_1$  is given by:

$$K_1 = K_1^0 \exp \left( -E_1/RT \right) \quad \dots (5)$$

From equation 2: we get

$$\frac{n}{x \cdot z} = K_2 \quad \dots (6)$$

where  $K_2$  is expressed as:

$$K_2 = K_2^0 \exp \left( -E_2/RT \right) \quad \dots (7)$$

and from equation 3: we get

$$\frac{n \cdot y}{x} = K_3 \quad \dots (8)$$

where  $K_3$  is given by:

$$K_3 = K_3^0 \exp \left( -E_3/RT \right) \quad \dots (9)$$

Furthermore, if we assume that interstitial zinc (ionized and unionized) is the only defect present in the crystal, we can express the neutrality condition as follows:

$$y = n + z \quad \dots (10)$$

On solving the four simultaneous equations (4, 6, 8 and 10), we get the concentration of free electrons ( $n$ ) at any temperature as:

$$n^2 = \frac{K_1^2 K_3}{K_2 p_{O_2} \left( \frac{K_1}{p_{O_2}^{1/2}} + 1 \right)} \quad \dots (11)$$

As we know, at low temperatures amount of adsorbed oxygen is much more as compared to the number of free electrons: i.e.  $z \gg n$ . We get from equation 4:

$$\frac{K_1}{p_{O_2}^{1/2}} \ll 1 \quad \dots (12)$$

or

$$n^2 = \frac{K_1^2 K_3}{K_2 p_{O_2}} \quad \dots (13)$$

Hence we get,

$$n^2 = A \exp \left( - \frac{2E_1 + E_3 - E_2}{KT} \right) \quad \dots (14)$$

Similarly while considering the equilibrium at high temperatures, we can assume that the number of free electrons predominate over the amount of adsorbed oxygen:

$$\text{i.e. } n \gg x$$

Applying the condition to the equation (4) we get the equation:

$$\frac{K_1}{P_{O_2}^{1/2}} \gg 1 \quad \dots (15)$$

or

$$n^2 = \frac{K_1 K_3}{K_2 P_{O_2}^{1/2}} \quad \dots (16)$$

Hence we get:

$$n^2 = B \exp \left( - \frac{E_1 + E_3 - E_2}{RT} \right) \quad \dots (17)$$

Equations (14) and (17) fit in very nicely with the experimental results if  $(2E_1 + E_3 - E_2)$  is +ive and  $(E_1 + E_3 - E_2)$  is -ive, i.e.: if  $2E_1 > E_2 > E_1$  and  $E_3$  is very small.

At low temperatures (equation 14)  $n$  would rise with temperature as  $(2E_1 + E_3 - E_2)$  is positive whereas at high temperatures (equation 17)  $n$  would fall with temperature because  $(E_1 + E_3 - E_2)$  is negative. As  $n$

falls the surface resistance increases and a stage comes when the surface resistance becomes comparable to the bulk resistance and from this stage the latter also starts taking part in the conduction. In the bulk the number of thermally generated carrier increases with increasing temperature and the resistance decreases with temperature as has been actually observed in the experiment in the temperature range  $370-500^{\circ}\text{C}$ .

When the sample is cooled to room temperature in vacuum the original path (Fig.22) is not retraced because the surface loses oxygen and becomes more conducting than the bulk and so on cooling in vacuum the conduction takes place mostly on the surface. Hence a deviation is observed in the heating and cooling curves right from the high temperature end itself. On the other hand when we cool the sample in air it merely follows the path (A Fig.18) as is actually expected, bulk still takes part in the conduction along with surface. It may also be added that oxygen adsorption on lowering the temperature takes place on the new zinc oxide surface which has been freed from the interstitial zinc during the heating of the specimen from  $25$  to  $500^{\circ}\text{C}$ . So when the sample is heated a second time in air these extrema are not observed, because beneath

the adsorbed oxygen layer we have got a layer of stoichiometric zinc oxide and the interstitial zinc atoms required for the mechanism discussed above are not available.

It is also observed that at room temperature the resistance in hydrogen is much less as compared to oxygen and increases as we switch over to nitrogen and oxygen. The low energy of activation and the high resistivity in hydrogen at room temperature can be explained by considering the ionization of zinc interstitials:



which gives out electrons which can be held responsible for the decrease in resistance.

When we change the atmosphere from hydrogen to oxygen, there is an increase in the resistance of the thin film which can be explained by correlating it to the chemisorption of oxygen. This results in the trapping of electrons upto  $150^\circ\text{C}$ . The process is found to be of the reversible nature upto  $150^\circ\text{C}$ , i.e. the resistance comes back to the original value even after repeated changes of the ambient atmosphere. It can be represented in the form of a chemical equation as:



which explains the view that the adsorbed oxygen reacts with the conduction electrons and decreases their number and hence the resistance of the sample becomes high. While in the case of hydrogen a partial reduction of the surface takes place raising the number of interstitial zinc ions and the conduction electrons, so the resistance of the film becomes low.

When the thin films of zinc oxide are doped with indium, they become more and more n-type as we go on increasing the indium concentration that is the number of free electrons for conduction increases with increasing indium concentration and so the resistance of the film is observed to decrease with indium addition. Finally for very heavily indium doped zinc oxide film, the concentration of free electrons is so high that the relative change in the number of electrons due to adsorption and desorption of oxygen is small and hence the changes in the conductivity are not noticeable.

On measuring the conductivity of plate type crystal in hydrogen, the activation energies observed are very low, which means that electrons are easily available for conduction, which is possible only when the number of zinc interstitials ( $Zn_i$ ) are quite large.





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CHAPTER V

EFFECT OF GAMMA IRRADIATION ON ZINC OXIDE

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## CHAPTER - V

## EFFECT OF GAMMA IRRADIATION ON ZINC OXIDE

## INTRODUCTION

The study of radiation damage in semiconductors, first initiated by Lark-Horovitz and his collaborators, has become a subject of great practical interest. There are two types of effects associated with radiation damage i.e. (I) electronic effects, (II) lattice effects. Examples of the former are changes in the electronic conductivity, paramagnetic contribution to the susceptibility, scattering of conduction electrons, etc. Lattice defects arise from the local disturbance in the lattice and alter the density, deformation behaviour, self and impurity diffusion, thermal conductivity and on certain occasions the crystal structure. Lattice damage consists of vacant lattice sites, interstitial atoms and clusters of both.

Although radiation damage by neutrons and charged particles are quite extensively studied there are only a few studies on the effect of  $\gamma$ -rays on the electronic properties of semiconductors.  $\gamma$ -rays are able to displace atoms through the Compton electrons and photoelectrons pro-

duced when the energetic photons interact with the atoms of the solid.

In what follows we give a brief account of the work that has already been done in this branch.

Fan and Lark-Horovitz<sup>1</sup> (1958) found that on  $\gamma$ -ray irradiation n-type indium antimonide was converted to p-type one, indicating that the radiation induced defects were acceptors.

Whitsett<sup>2</sup> in 1958 measured the Hall coefficient and resistivity of n- and p-type crystals of InSb immersed in liquid air during the  $\gamma$ -irradiation for 48 hours and annealing for 500 hour. Irradiation of n-type samples removed  $7 \times 10^{-12}$  conduction electrons/cm<sup>3</sup> hour. No annealing was observed at 77°K. For p-type it introduced  $2.8 \times 10^2$  holes/cm<sup>3</sup> hour. Annealing afterwards followed a bimolecular recombination law.

Matsura and Inuishi<sup>3</sup> (1961), carried out irradiation of (I) crucible grown, (II) vacuum floating zone grown n-type silicon, by  $\gamma$ -rays from a  $^{60}\text{Co}$  source. First sample had an oxygen content of  $> 10^{18}$  atoms/cm<sup>3</sup>, while second had very small oxygen content. The low temperature electron bombardment studies revealed that interstitials and vacancies become unstable in

silicon lattice well below room temperature and are annihilated at sinks or trapped at impurity atoms. The defect remaining in oxygen contaminated sample at room temperature was an oxygen-vacancy complex. This acted as an acceptor located as 0.17 ev below the conduction band. In the oxygen free samples the defect was a donor-vacancy complex, which acted as an acceptor at 0.4 ev to 0.5 ev below the conduction band.

Cleland, Crawford and Holmes<sup>4</sup> (1956) irradiated the high purity n- and p-type germanium by  $\gamma$ -rays from 900 Curie  $\text{Co}^{60}$  source. The extrinsic electron concentration in the n-type specimen was found to decrease on irradiation. Extended exposures converted n-type Ge to p-type indicating the presence of an acceptor level at  $\sim 0.26$  ev above the valence band. Exposure of p-type Ge caused a decrease in extrinsic hole concentration with a rate much less than that for n-type.

Pigg and Crawford<sup>5</sup> (1964) studied the annealing of changes in the electrical properties of antimony doped germanium, caused by  $\text{Co}^{60}$  gamma irradiation at 77°K. A new energy level at 0.09 ev below the conduction band was observed after annealing at 370°K.

The level has been tentatively attributed to oxygen-vacancy complexes.

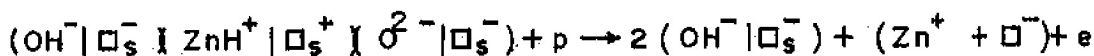
Taylor and Wethington Jr.<sup>6</sup> (1954) observed that the catalytic activity of zinc oxide was lowered on irradiating with  $\gamma$ -rays. This was attributed to some electronic changes in the catalyst produced by irradiations or to the poisoning by radiation polymerized reactants not removed by pumping prior to irradiation.

Taylor and Kohn<sup>7</sup> (1957), irradiated the alumina catalyst in vacuum by  $\gamma$ -rays from a  $\text{Co}^{60}$  source. Catalyst prepared at  $400^{\circ}\text{C}$  showed a seven fold increase in catalytic activity, when irradiated at  $-78^{\circ}$  for 30 minutes. The enhancement disappeared on standing for 2-4 days at room temperature and could be restored by further irradiation.

Berry and Klier<sup>8</sup> (1961) measured the electrical conductivity of powdered zinc oxide samples together with the adsorption and desorption of gases. These measurements yielded information on the charge transfer during the reversible and irreversible adsorption. The irradiation of  $\text{ZnO}$  with adsorbed hydrogen at  $0^{\circ}\text{C}$  resulted in an increase in conductivity which was many times greater than that of pure zinc oxide and was almost irreversible. It was concluded that



positive holes were getting trapped at adsorbed hydrogen which caused more hydrogen to be adsorbed as  $\text{OH}^-$  ions. The overall process was represented as follows:



The observed increase in conductivity of ZnO with adsorbed isobutene at  $0^\circ$  and  $-78^\circ\text{C}$  strongly suggested the formation of positive ions in the surface.

It was supposed that oxygen was rapidly adsorbed as -ive ions which removed electrons from the conduction band and decreased the conductivity. In the end either ZnO was exhausted of free electrons or a boundary layer potential was set up which prevented any further electron transfer. On this basis  $\gamma$  -irradiation did not affect the first part of the adsorbed oxygen but it desorbed the weakly adsorbed oxygen. They supposed that the radiation induced holes were unable to discharge the adsorbed oxygen ions or more probably that the competitive readorption process was too rapid for the desorption to occur.

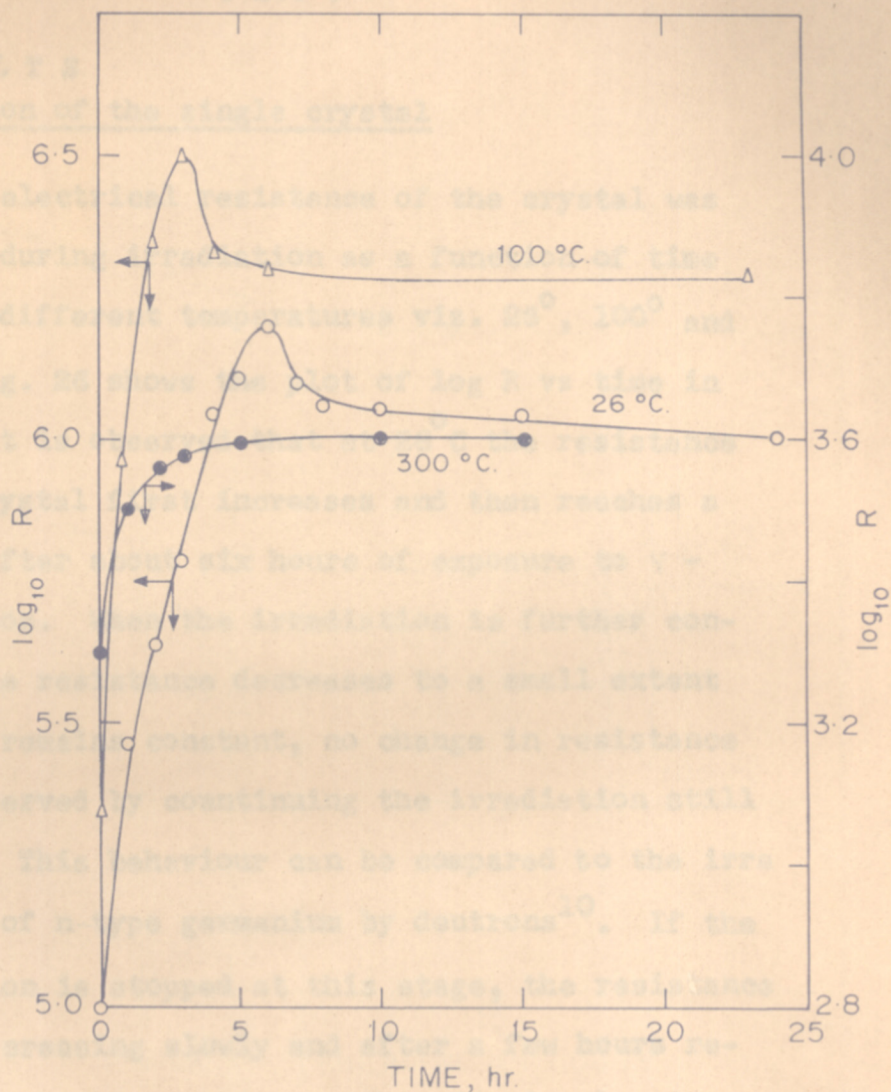


FIG. 26. CHANGES IN THE RESISTANCE OF ZnO CRYSTAL WITH TIME WHEN THE CRYSTAL IS CONTINUOUSLY IRRADIATED, AT THREE DIFFERENT TEMPERATURES.

From the work of Barry and Klier and Taylor et.al. it is noticed that  $\gamma$  -rays can bring about profound changes in the catalytic activity of semi-conductors. As these changes are generally attributed to the modifications of the defect structure, we have studied the effect of  $\gamma$  -irradiation on the defect structure of ZnO, a well-known hydrogenation catalyst by following the changes in its electronic conductivity.

## EXPERIMENTAL

Gamma irradiation studies were carried out on the following types of samples:

- (1) ZnO single crystal (rod type).
- (2) ZnO powder (in the form of pressed pellets).
- (3) ZnO thin films.

The preparation of single crystals have been described in Chapter II, the preparation of ZnO powder pellets is given in the Chapter III and the preparation of ZnO thin films are given in Chapter IV.

All the samples were irradiated by  $\gamma$ -rays from gamma-cell 220, a thousand Curie cobalt 60 irradiation unit, supplied by the Atomic Energy of Canada Ltd. It is designed for use in an unshielded room. Basically the unit consists of an annular shaped source, a lead shield around the source and a long cylindrical drawer free to move vertically through the centre of the source. The drawer carries samples (materials to be irradiated) from outside the shield to the source. The two positions of the drawer are termed as the "loading position" and the "irradiating position". Irradiation of samples upto six inches in diameter and eight inches in height can

be undertaken with complete safety for operating personnel. Liquids, gases, electrical and mechanical connections could be introduced to the sample chamber through a straight access tube in the drawer top. An electric digital timer automatically terminates an irradiation after a maximum interval of 999.9 hours. The drawer is raised or lowered by a chain or sprocket system driven by an electric motor. The digital timer starts only when the drawer reaches the irradiating position. It automatically terminates an irradiation by returning the drawer to the loading position at the end of pre-set time. The sample chamber is a hollow thin walled aluminium cylinder. A lift out door is attached to it along with a snap action. Locking ring at top. A  $1\frac{3}{8}$  inch diameter hole in the roof of the chamber provides entry to the access tube in the drawer top.

Silica plate sample holder attached with molybdenum springs (described in Chapter III) was used for the mounting of single crystals and thin films and for the measurement of conductivity changes, along with  $\gamma$  irradiation and annealing. For ZnO pellets, zirconia tube sample holder with pressure contact (described in Chapter III) was used.

For irradiating the samples at temperatures higher than room temperature a furnace was designed to give a uniform temperature upto 600<sup>o</sup> C. A cylindrical hollow tube of silica of approximately 2" in diameter and 4" long was wound with Kanthal 'A' tape and was well-insulated.

For the measurement of temperature a calibrated chromel-alumel thermocouple attached to millivoltmeter (0-80 mv) was used. The thermocouple end was kept in a sealed silica tube and was kept in the vicinity of sample to get the exact temperature of the sample. For

irradiating in different atmospheres e.g. nitrogen and hydrogen, a set up was designed to maintain a controlled gaseous atmosphere. A pyrex vessel of 2.5 inches diameter was sealed at one end making a flat bottom and at the other end it was attached to a B-60 female joint. To the B-60 male joint two pyrex glass tubes were attached (one of them was long enough to go to the bottom of the vessel) to facilitate the entry and the exit of the gas. Two metal to glass joints were also provided. Every joint had two wires attached to it on both the sides. To one of these joints a pair of platinum wires were soldered for attaching the sample holder assembly. To the other joint chromel-alumel thermocouple was attached to measure the temperature.



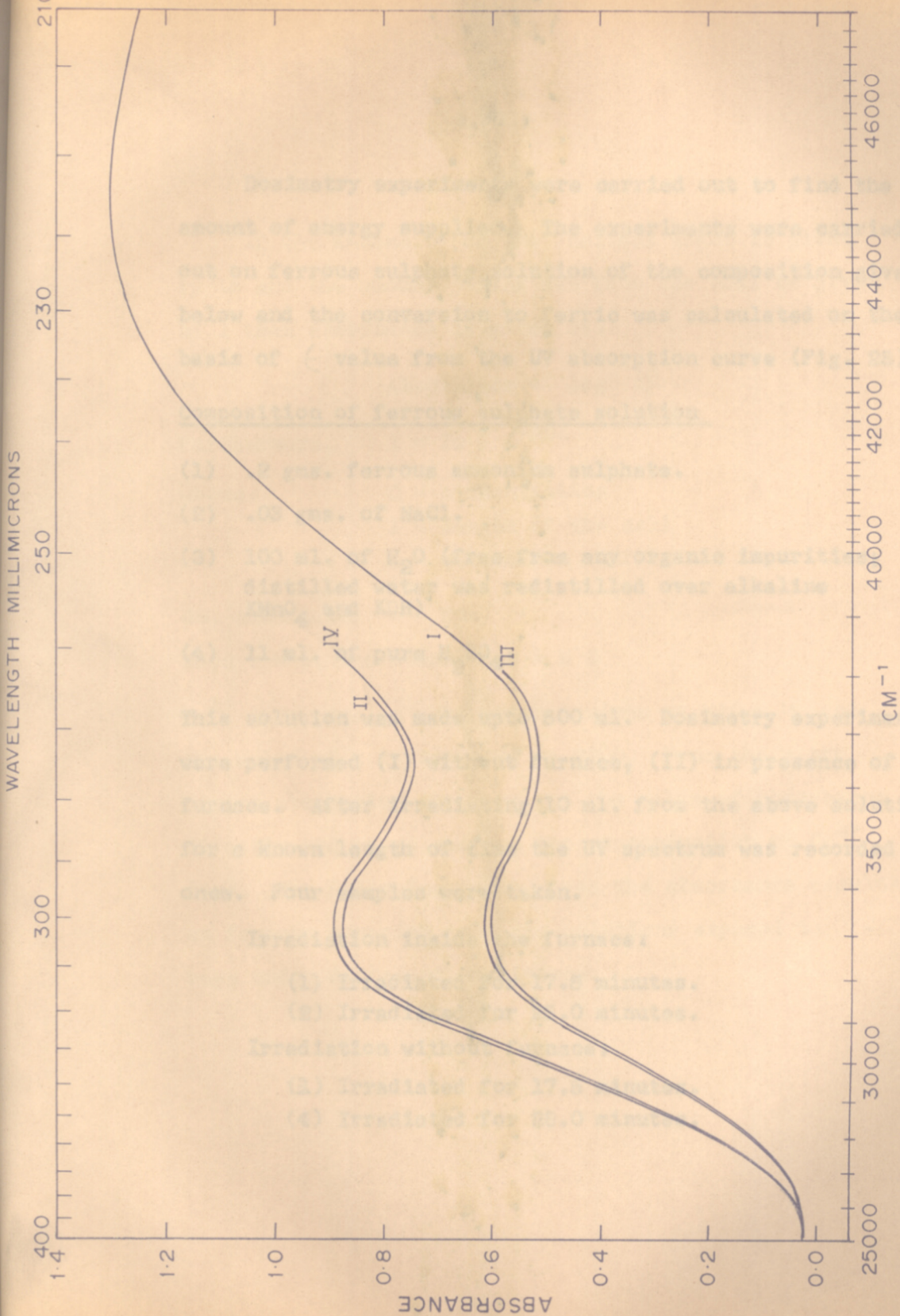


FIG. 25 ULTRA VIOLET ABSORPTION FOR  $\gamma$ -RAY DOSIMETRY EXPERIMENTS.



Dosimetry experiments were carried out to find the amount of energy supplied. The experiments were carried out on ferrous sulphate solution of the composition given below and the conversion to ferric was calculated on the basis of  $\epsilon$  value from the UV absorption curve (Fig. 25).

Composition of ferrous sulphate solution

- (1) .2 gms. ferrous ammonium sulphate.
- (2) .03 gms. of NaCl.
- (3) 100 ml. of  $H_2O$  (free from any organic impurities; distilled water was redistilled over alkaline  $KMnO_4$  and KOH)
- (4) 11 ml. of pure  $H_2SO_4$ .

This solution was made upto 500 ml. Dosimetry experiments were performed (I) without furnace, (II) in presence of furnace. After irradiating 10 ml. from the above solution for a known length of time the UV spectrum was recorded at once. Four samples were taken.

**Irradiation inside the furnace:**

- (1) Irradiated for 17.5 minutes.
- (2) Irradiated for 25.0 minutes.

**Irradiation without furnace:**

- (3) Irradiated for 17.5 minutes.
- (4) Irradiated for 25.0 minutes.

If the intensity of the incident light is given by  $I_0$  and the amount coming out from the cell be given by  $I$  then absorbance is given as:

$$\text{Absorbance} = \log \frac{I_0}{I}$$

Furthermore,  $I = I_0 e^{-ECl}$

where:  $C$  - concentration  
 $l$  - length of the cell  
 $E$  - extinction coefficient

So, Absorbance =  $ECl$

When  $l = 1$ , the absorbance =  $EC$

$Fe^{3+}$  ions give an absorption maximum at  $390 \text{ m}\mu$  and the value of  $E$  is known to be 2200. From the ultra violet absorption curve we get the value of absorbance directly and so we can get the concentration of  $Fe^{3+}$  ions. The following table gives the absorbance results on ferrous ammonium sulphate solutions exposed to  $\gamma$ -rays under different conditions.

Table

| S.No. | Position of sample                                    | Time of irradiation | Absorbance | Concentration of $Fe^{3+}$ ions | Energy absorbed per cc per minute |
|-------|-------------------------------------------------------|---------------------|------------|---------------------------------|-----------------------------------|
| I     | Ferrous-ammonium sulphate solution without furnace    | 17.5 min.           | .61        | $1.66 \times 10^{17}$           | $6.093 \times 10^{16}$            |
| II    | -do-                                                  | 25.0 min.           | .88        | $2.40 \times 10^{17}$           | $6.163 \times 10^{16}$            |
| III   | Ferrous-ammonium sulphate solution inside the furnace | 17.5 min.           | .60        | $1.63 \times 10^{17}$           | $5.904 \times 10^{16}$            |
| IV    | -do-                                                  | 25.0 min.           | .87        | $2.37 \times 10^{17}$           | $6.023 \times 10^{16}$            |

From these results concentrations of the  $\text{Fe}^{3+}$  ions have been calculated and the results are given in the column Vth of the table.

Furthermore, G value for  $\text{Fe}^{3+}$  ion is  $15.6^9$ , i.e. 15.6 molecules of  $\text{Fe}^{3+}$  are formed if 100 ev are absorbed. Hence, the energy absorbed per c.c. per minute could be easily calculated and the values are given in column Vith of the table.

Since the density of the  $\text{FeSO}_4$  solution used is nearly = 1, this figure represents also the energy absorbed per gram of any substance.

#### Irradiation of single crystal

At the two ends of the ZnO single crystal silver paste was applied to act as the two electrodes. After the application of Ag paste the sample was heated to  $250^\circ\text{C}$  for 15-30 minutes to make the silver layer conducting. The crystal was mounted on the silica plate sample holder between the two molybdenum springs and the whole assembly was pushed inside the sample chamber. The two leads for measuring the resistance were taken out and connected to PR 9500 Philips conductivity bridge. Time was recorded by the automatic recorder attached to  $\text{CO}^{60}$  unit. Irradiation in air was continued till the resistance becomes constant. After

that, annealing of the crystal in air was also carried out and the resistance was recorded as a function of annealing time. Similarly ~~in~~ experiments were carried out by irradiating in an atmosphere of hydrogen and of purified nitrogen. Nitrogen was purified by passing the gas over heated activated copper filings and pyrogallol solution.

Irradiation of single crystal as well as annealing were carried out at various different temperature viz.  $25^{\circ}\text{C}$ ,  $100^{\circ}\text{C}$  and  $300^{\circ}\text{C}$  in presence of air. Resistance was recorded as a function of the annealing temperature and the annealing time.

The crystal was cooled suddenly in presence of irradiation to find out the activation energy for conduction in the single crystal.

#### Irradiation of zinc oxide powder (pellet)

Zinc oxide pellets having aqua dag electrodes on the two faces were kept in the zirconia tube sample holder assembly. The assembly was placed vertically in the irradiation chamber. Following experiments were carried out:

- (1) Irradiation at room temperature in air.
- (2) Irradiation at higher temperature in air.
- (3) Irradiation in nitrogen.
- (4) Irradiation in hydrogen.

Annealing studies for all the above samples were carried out in the manner described above.

#### Irradiation of zinc oxide thin films

In case of thin films, two types of arrangements were used for the electrodes. In one both the electrodes were on the upper surface of the thin film so that we were effectively measuring the conductance on the surface. In the other the ZnO film was sandwiched between the two electrodes so that the conductance across the film was measured. The sample holder assembly used for the irradiation of single crystal was also used to irradiate the thin films. For the assemblies of the former type, irradiation was carried out at room temperature ( $28^{\circ}\text{C}$ ) and at  $225^{\circ}\text{C}$  in air. Irradiation in nitrogen and hydrogen were carried out at room temperature. To find out the energy of activation for the conduction, the resistance of the thin film was measured from  $225^{\circ}\text{C}$  to  $30^{\circ}\text{C}$  in presence of irradiation. For the assembly of the second type the changes in resistance during irradiation were measured only at room temperature.

## R E S U L T S

Irradiation of the single crystal

The electrical resistance of the crystal was measured during irradiation as a function of time at three different temperatures viz.  $25^{\circ}$ ,  $100^{\circ}$  and  $300^{\circ}$  C. Fig. 26 shows the plot of  $\log R$  vs time in hours. It is observed that at  $25^{\circ}$  C the resistance of the crystal first increases and then reaches a maximum after about six hours of exposure to  $\gamma$  - irradiation. When the irradiation is further continued the resistance decreases to a small extent and then remains constant, no change in resistance being observed by continuing the irradiation still further. This behaviour can be compared to the irradiation of n-type germanium by neutrons<sup>10</sup>. If the irradiation is stopped at this stage, the resistance starts decreasing slowly and after a few hours remains practically constant. This final value is always higher than the value observed before the crystal was first irradiated. When the same crystal is irradiated a second time the general nature of the plot of  $\log R$  vs time remains unaltered except for the fact that a broadening in the resistance peak is observed. If we repeat the irradiation and annealing cycle 2-3 times successively the peak completely disappears (Fig. 29). The sharp initial increase in



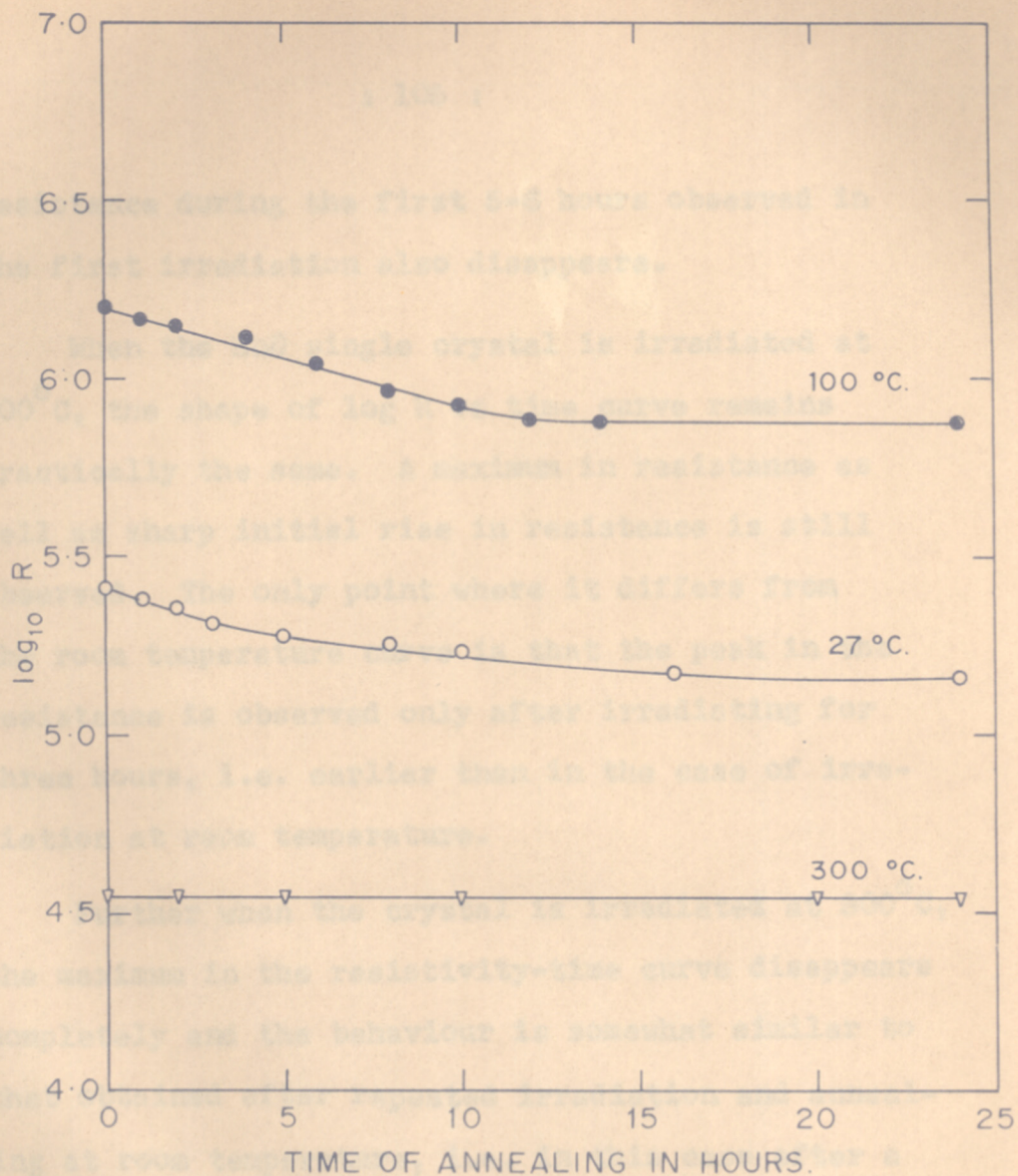


FIG. 27  $\log_{10} R$  Vs ANNEALING TIME CURVE AT VARIOUS TEMPERATURES FOR ZnO SINGLE CRYSTAL.

resistance during the first 5-6 hours observed in the first irradiation also disappears.

When the ZnO single crystal is irradiated at  $100^{\circ}\text{C}$ , the shape of  $\log R$  vs time curve remains practically the same. A maximum in resistance as well as sharp initial rise in resistance is still observed. The only point where it differs from the room temperature curve is that the peak in the resistance is observed only after irradiating for three hours, i.e. earlier than in the case of irradiation at room temperature.

Further when the crystal is irradiated at  $300^{\circ}\text{C}$ , the maximum in the resistivity-time curve disappears completely and the behaviour is somewhat similar to that obtained after repeated irradiation and annealing at room temperature, i.e. in this case after a initial sharp rise in resistance the shape of the curve becomes parallel to the irradiation-time axis (resistance remains constant).

Fig. 27 shows the plot of resistance against time of annealing. All the crystals were previously irradiated for 24 hours at various temperatures. The resistivity values are not comparable because at every temperature an entirely new crystal was used.



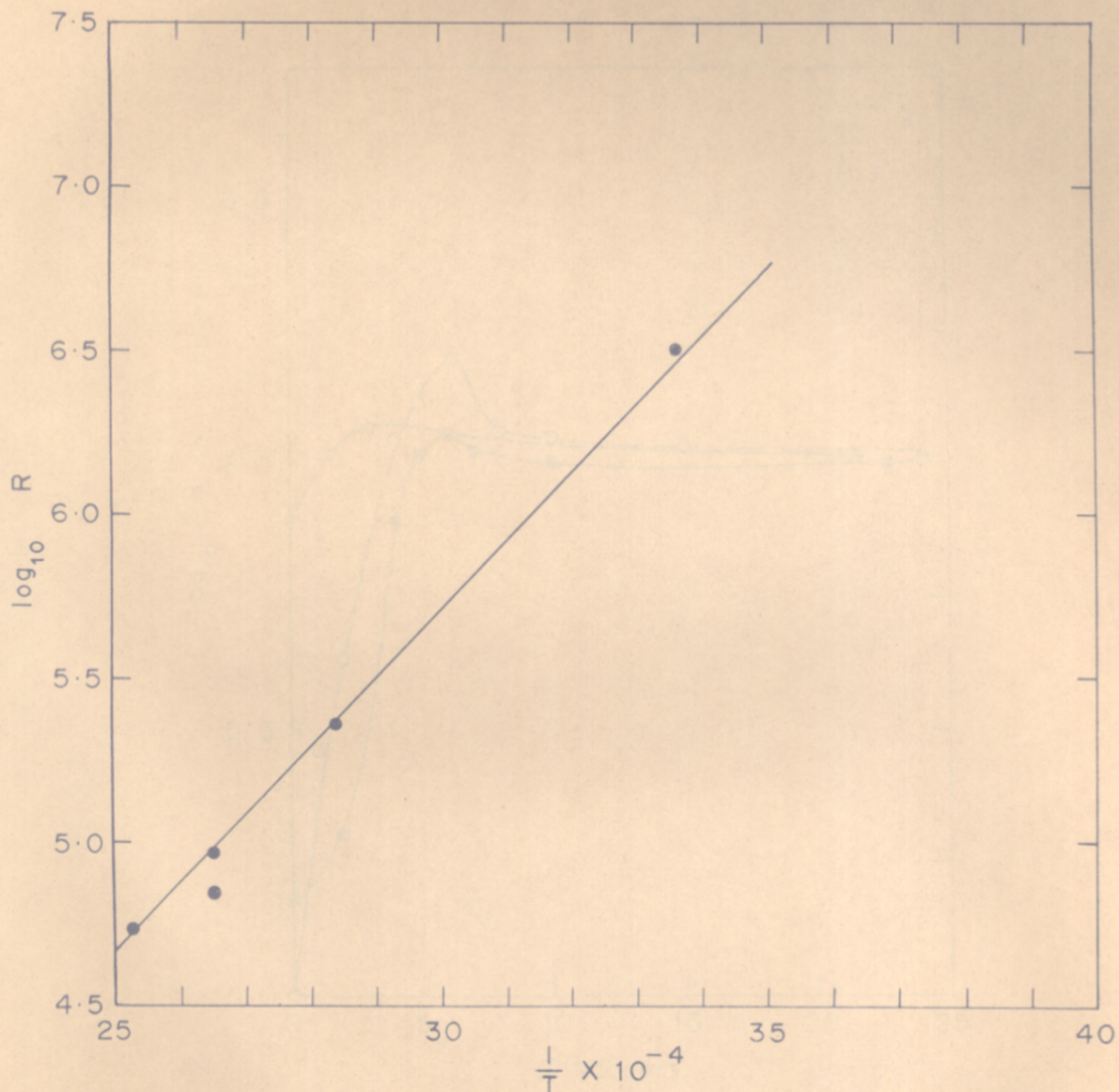


FIG. 28  $\log_{10} R$  Vs  $\frac{1}{T}$  FOR ZnO SINGLE CRYSTAL IN PRESENCE OF IRRADIATION

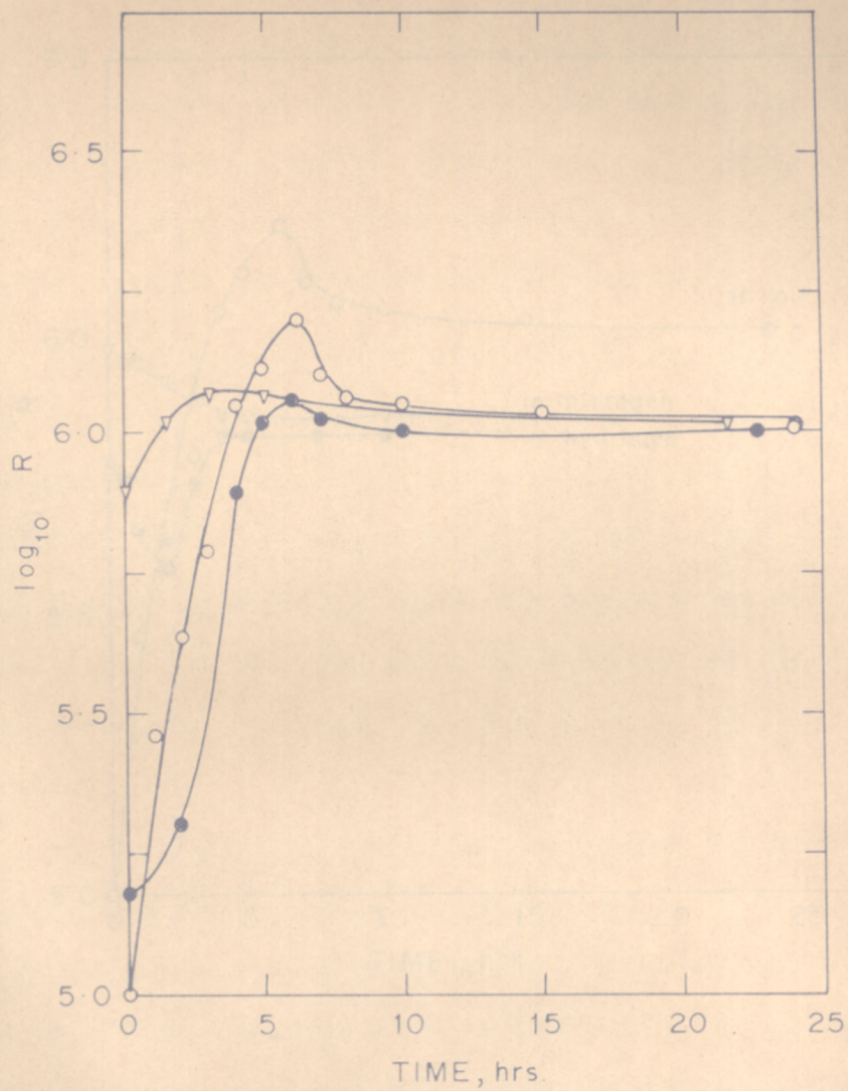


FIG. 29. CHANGES IN THE RESISTANCE AS A FUNCTION OF TIME FOR SUCCESSIVE IRRADIATIONS ON  $\text{ZnO}$  CRYSTAL.



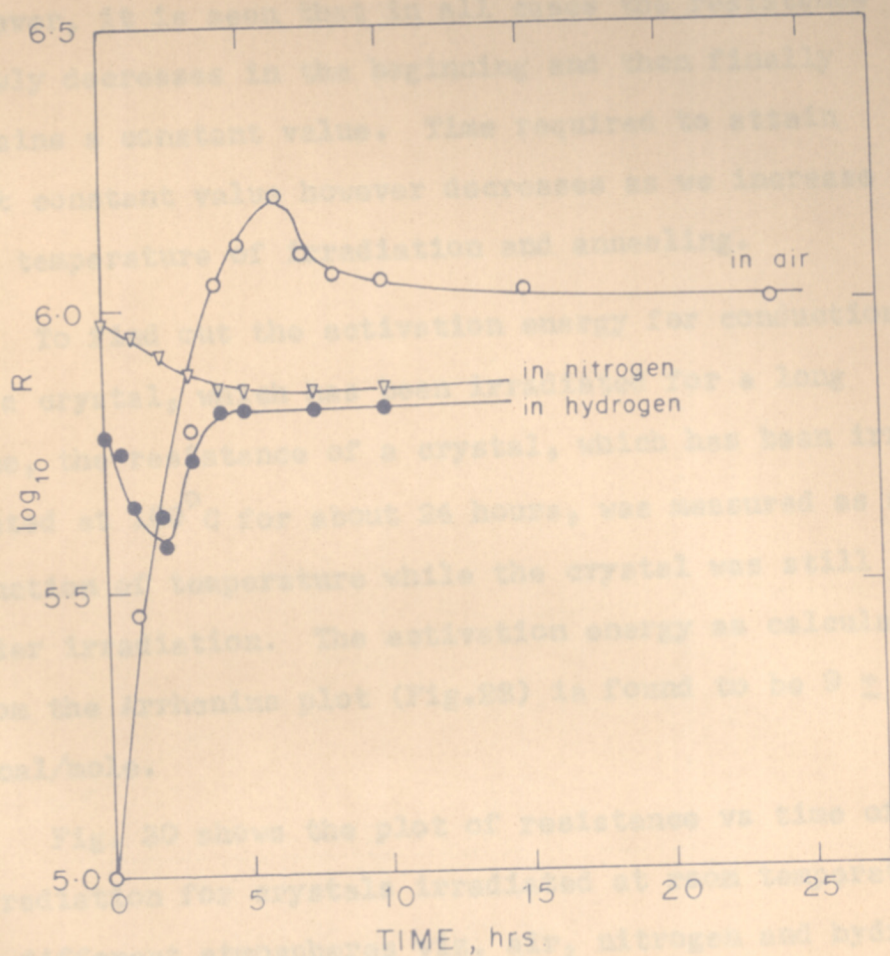


FIG.30 IRRADIATION OF ZnO SINGLE CRYSTAL IN VARIOUS ATMOSPHERES AT ROOM TEMPERATURE.

However, it is seen that in all cases the resistance slowly decreases in the beginning and then finally attains a constant value. Time required to attain that constant value however decreases as we increase the temperature of irradiation and annealing.

To find out the activation energy for conduction in a crystal, which has been irradiated for a long time, the resistance of a crystal, which has been irradiated at  $100^{\circ}\text{C}$  for about 24 hours, was measured as a function of temperature while the crystal was still under irradiation. The activation energy as calculated from the Arrhenius plot (Fig.28) is found to be  $9 \pm 1$  K cal/mole.

Fig. 30 shows the plot of resistance vs time of irradiation for crystals irradiated at room temperature in different atmospheres viz. air, nitrogen and hydrogen. The behaviour observed in nitrogen and hydrogen atmospheres is entirely different from the one when the crystal is irradiated in air. The maximum in the resistance is completely absent.

On irradiating in nitrogen (oxygen content  $\approx 10^{-3}$  parts), the resistance decreases along with irradiation for 4-5 hours. After this the resistance becomes constant (Fig.30).



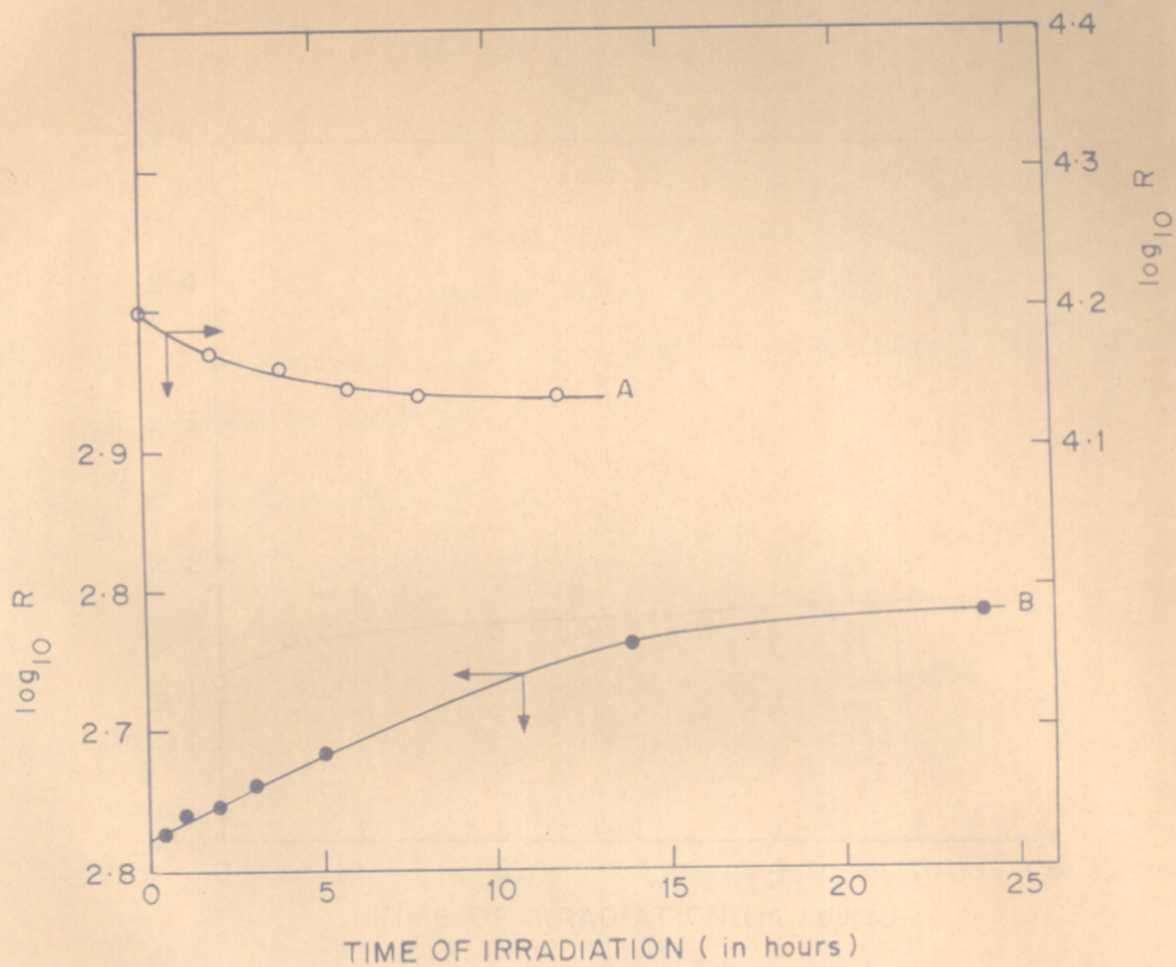


FIG. 31 IRRADIATION OF ZnO PELLETS

A. IN HYDROGEN AT ROOM TEMPERATURE.

B. IN AIR AT 325°C.



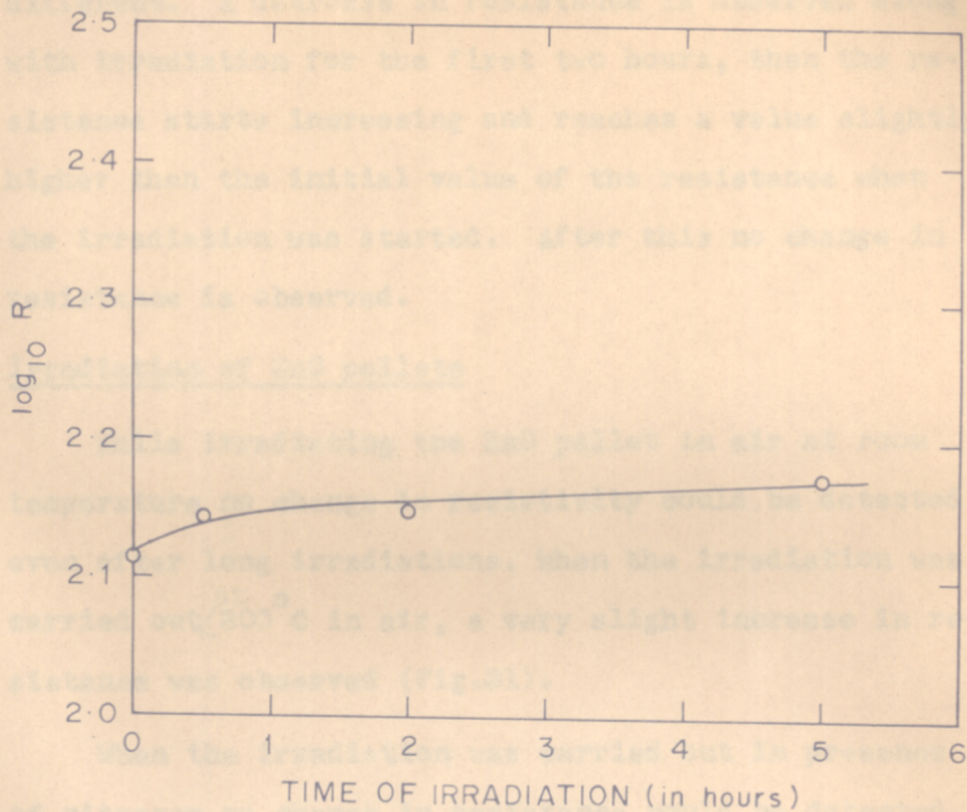


FIG.32 IRRADIATION OF ZnO SANDWICHED FILM (SHOWING BULK CONDUCTION)

The behaviour in the case of hydrogen is still different. A decrease in resistance is observed along with irradiation for the first two hours, then the resistance starts increasing and reaches a value slightly higher than the initial value of the resistance when the irradiation was started. After this no change in resistance is observed.

#### Irradiation of ZnO pellets

While irradiating the ZnO pellet in air at room temperature no change in resistivity could be detected even after long irradiations. When the irradiation was carried out <sup>at</sup> 300°C in air, a very slight increase in resistance was observed (Fig.31).

When the irradiation was carried out in presence of nitrogen no change in resistance could be detected.

On irradiating in presence of hydrogen at room temperature, the resistance was observed to decrease very slightly, for the first few hours and then it remained constant (Fig.31).

#### Irradiation of ZnO thin films

When the sandwiched type ZnO film (type B sandwiched between two Au electrodes) was irradiated, a small increase in resistance was observed for the first 8-10 hours, after which no change in resistance was observed (Fig.32).



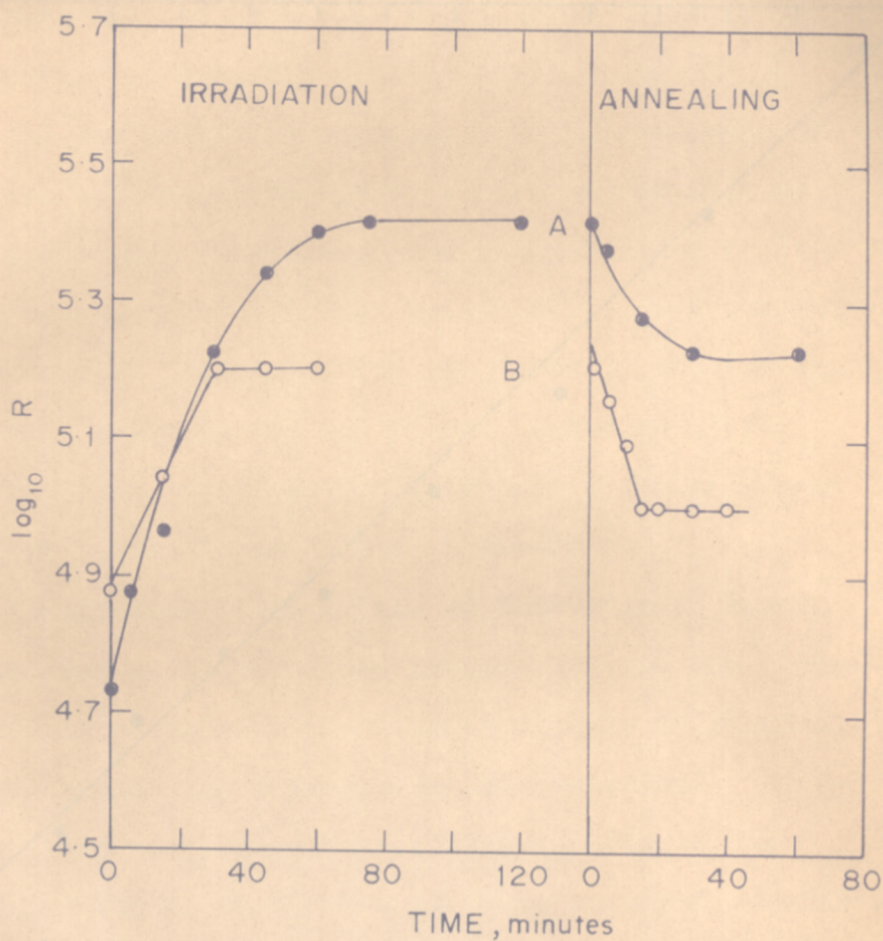


FIG. 33. IRRADIATION AND ANNEALING OF ZnO THIN FILM IN AIR.

A. AT ROOM TEMPERATURE

B. AT 228°C.

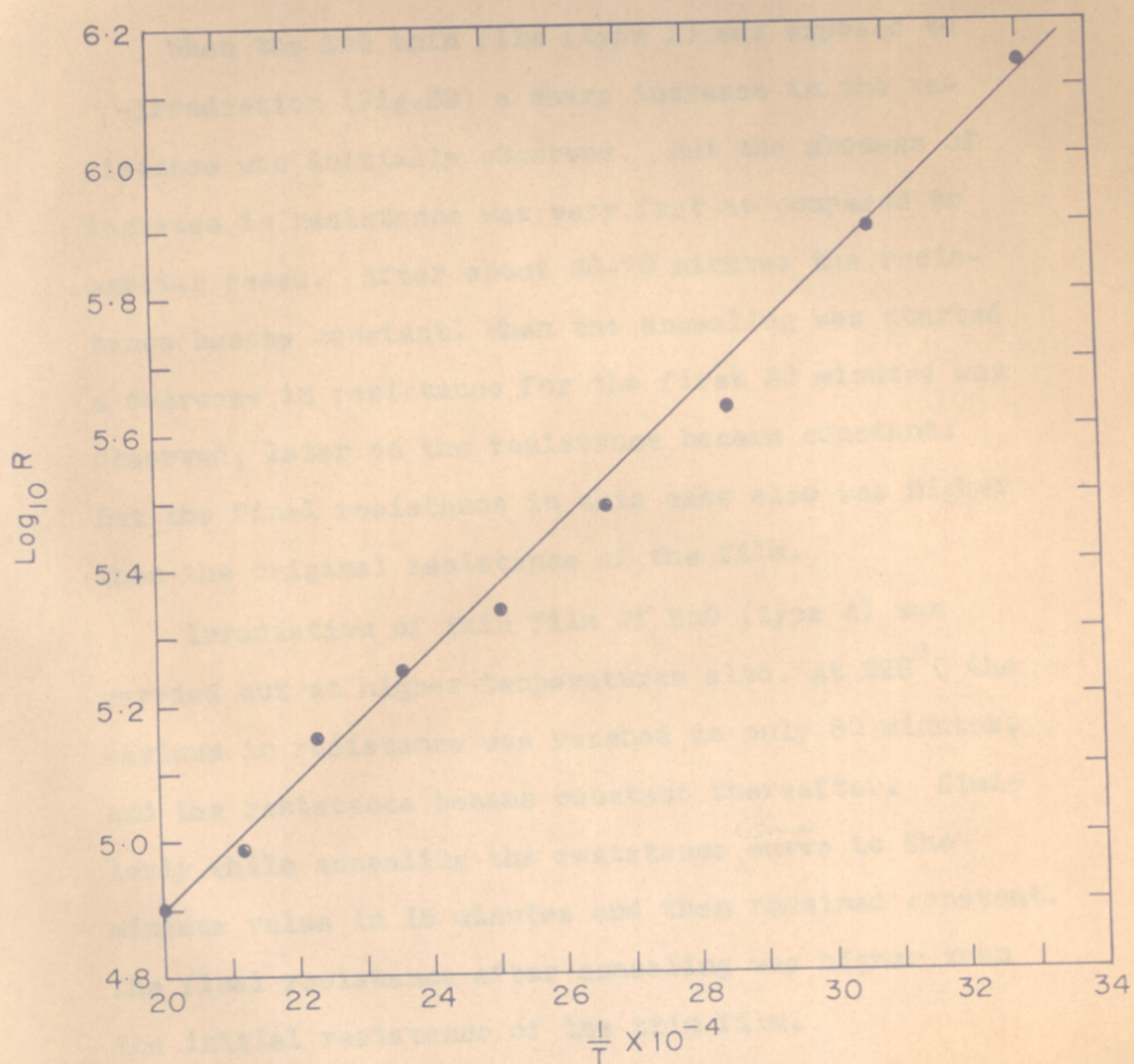


FIG. 34.  $\text{LOG}_{10} R$  Vs.  $\frac{1}{T}$  FOR ZINC OXIDE THIN FILM IN AIR  
IN PRESENCE OF IRRADIATION.



When the ZnO thin film (type A) was exposed to  $\gamma$ -irradiation (Fig.33) a sharp increase in the resistance was initially observed. But the process of increase in resistance was very fast as compared to earlier cases. After about 60-70 minutes the resistance became constant. When the annealing was started a decrease in resistance for the first 30 minutes was observed, later on the resistance became constant. But the final resistance in this case also was higher than the original resistance of the film.

Irradiation of thin film of ZnO (type A) was carried out at higher temperatures also. At  $228^{\circ}\text{C}$  the maximum in resistance was reached in only 30 minutes, and the resistance became constant thereafter. Similarly while annealing the resistance <sup>came</sup> ~~curve~~ to the minimum value in 15 minutes and then remained constant. The final resistance after annealing was higher than the initial resistance of the thin film.

To find out the activation energy for the conduction in the thin film, the film was cooled from  $228^{\circ}\text{C}$  in presence of irradiation after being irradiated for a long time. Fig.34 shows the plot of  $\log R$  vs temperature in presence of irradiation. The activation energy as calculated from the Arrhenius plot is found to be 4.2 K cal.

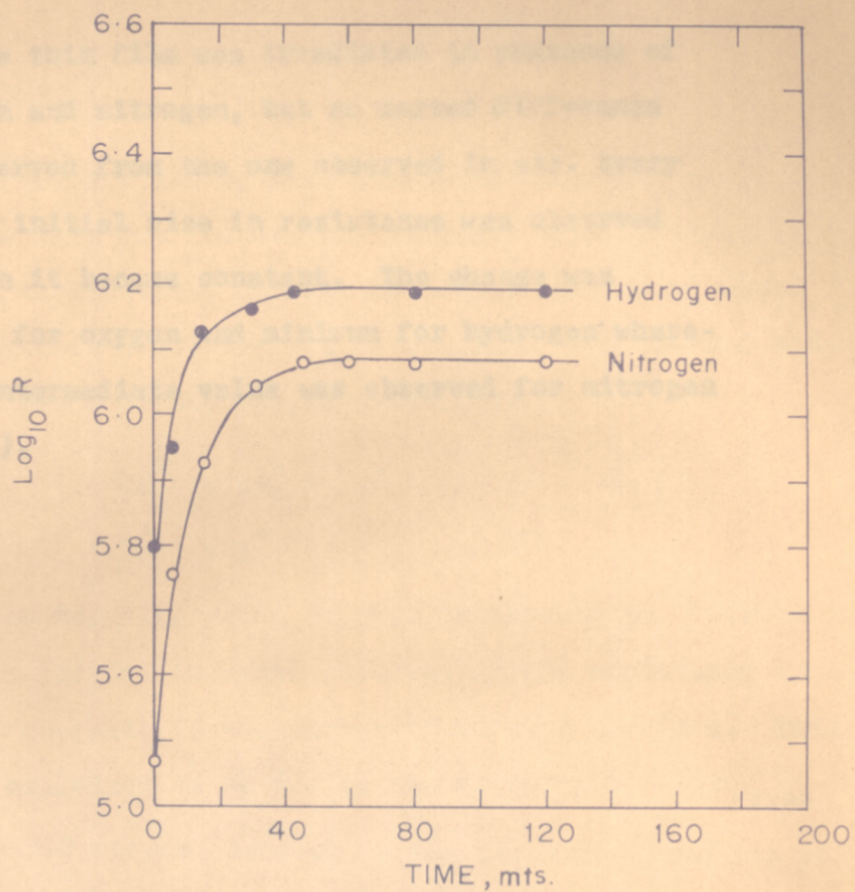


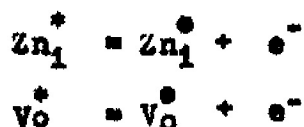
FIG-35. IRRADIATION OF ZnO THIN FILM IN NITROGEN AND HYDROGEN

The thin film was irradiated in presence of hydrogen and nitrogen, but no marked difference was observed from the one observed in air. Every time an initial rise in resistance was observed and then it became constant. The change was maximum for oxygen and minimum for hydrogen whereas an intermediate value was observed for nitrogen (Fig.35).



## DISCUSSION

In Chapter III we have concluded that zinc oxide crystals have got Frenkel and Schottky type of disorder. At room temperature, current is mainly carried by electrons. These electrons can be obtained from neutral zinc interstitials or the oxygen vacancies.

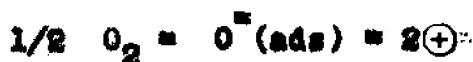


When the zinc oxide crystal is exposed to  $\gamma$ -irradiation, an initial increase observed in the resistance indicates a decrease in the number of current carriers. This can be explained to be due to the trapping of electrons by adsorbed oxygen, leading to the possible formation of  $\text{O}^-(\text{ads})$ ,  $\text{O}^{--}(\text{ads})$  or  $\text{O}^{--}(\text{lattice})$ . The actual mechanism can be explained by postulating a reaction between the gaseous oxygen, oxygen vacancies and the electrons obtained by the ionization of zinc interstitials through an intermediate stage of adsorbed oxygen. The total reaction may be represented by the equation:



Resistance will keep on increasing till all the electrons available for trapping are exhausted. When this

stage is reached the further uptake of oxygen will start releasing the holes according to the equation:



The conductivity is given by:

$$\sigma = (n_e \mu_e + n_h \mu_h) e.$$

where  $n_e$  and  $n_h$  are the number of electrons and holes respectively,  $\mu_e$  and  $\mu_h$  are their respective mobilities and  $e$  is the electronic charge. To illustrate the trend in the resistance changes on progressive decrease of  $n_e$  let us assume that:

$$\mu_e = \mu_h$$

then

$$\sigma \propto (n_e + n_h)$$

As  $n_e, n_h = K$  (constant),  $(n_e + n_h)$  must decrease as the value of  $n_e$  decreases and will be minimum when:

$$n_e = n_h = \sqrt{K}$$

$(n_e + n_h)$  will again start rising for a further decrease in the value of  $n_e$ . This means as long as the number of electrons will predominate the number of holes the resistance will keep on increasing, that is what happens when we start irradiating the crystal, the concentration of electrons decreases and the resistance keeps on increasing. When the electrons are exhausted to an extent that their number becomes less than that of the holes the con-

ductivity becomes p-type, and now as the number of holes increases the resistance decreases. We have seen in this case that further adsorption of oxygen increases the number of holes and hence the conductivity keeps on increasing till the sample is unable to take any further oxygen. After this stage the conductivity remains nearly constant.

When the irradiation is carried out at higher temperatures the rate of oxygen chemisorption will increase and hence the change over from n-to p-type conductivity will be observed earlier. Furthermore, as at higher temperature the total chemisorbed oxygen is expected to be smaller, the ultimate resistance would be higher as is actually observed. Following our earlier conclusions we have assumed the crystal to be a p-type conductor at  $300^{\circ}\text{C}$ , the resistance after irradiation should decrease as the number of holes would increase and then the resistance should finally remain constant. However, a slight increase in the resistance has been actually observed before it finally becomes constant.

This means that the oxygen is actually desorbed by  $\gamma$ -irradiation at  $300^{\circ}\text{C}$ . This would decrease the number of holes and hence the resistance would increase. The stage after which the resistance remains constant

represents an equilibrium between adsorption and desorption of oxygen on zinc oxide.

It is quite clear from the above discussion that the crystal becomes a p-type conductor at the end of 24 hours of irradiation, which is due to the liberation of holes by the adsorbed oxygen. The activation energy which has been found to be  $9 \pm 1$  K cal/mole is thus the activation energy required to release a hole from the adsorbed oxygen. This amount will depend upon whether the ionized species are  $O_2^-$ ,  $O^-$  or  $O^{2-}$ . The presence of all these species have been suggested by Barry and Stone<sup>11</sup>.

As explained above if the changes in resistance are due to the adsorption of oxygen, the reverse, i.e. desorption should be observed when the crystal is annealed. Therefore we expected a peak in the resistivity vs time of annealing curve, when the crystal changes from p-type conduction to n-type conduction. However, we observed only a slow decrease in resistance. It can be tentatively suggested that initial desorption is too fast to be detected by measurement of changes in resistance. But it seems reasonable to assume that the crystal becomes an n-type conductor again, because by  $\gamma$ -irradiating the same crystal, we are able to

retrace the behaviour of the original crystal.

The final resistance observed after the irradiation is found to be always higher than that of the un-irradiated crystal\*. The broadening and the shifting of the peak towards shorter times after successive irradiations supports this view.

(\* this means that some percentage of oxygen is always permanently adsorbed on the sample).

#### Irradiation in nitrogen

It follows from the equation:



that the trapping of electrons would be dependent on oxygen pressure. It is also known that the number of molecules adsorbed is dependent upon ambient oxygen pressure<sup>12</sup>. Hence the changes in the resistance are expected to decrease as we decrease the oxygen pressure while irradiating. The observed changes in resistance when the crystal is irradiated in presence of nitrogen (Fig. 30) are consistent with the above expectation. Oxygen content in nitrogen was measured to be as low as  $10^{-3}\%$ . At such low oxygen pressures one can in fact expect slight desorption rather than adsorption. Desorption is accompanied by the release of electrons hence the conductivity slightly increases. It has been

observed that the resistance remains constant after about five hours of irradiation which means that oxygen cannot be desorbed beyond this limit.

### Irradiation in hydrogen

When the crystal is irradiated in hydrogen atmosphere, a decrease in resistance is observed initially, but after about 4 hours of irradiation the resistance increases again and finally becomes constant. The initial decrease in resistance can be explained in the same way as described above for the irradiation in nitrogen atmosphere, i.e. the desorption of oxygen may be taking place. Here in addition to the desorption, oxygen may also be removed from the lattice and releasing the electrons to the conduction band. Therefore, in this case the initial decrease in the resistance is sharper than that observed during the irradiation in nitrogen atmosphere. After this stage it is expected that the resistance should remain constant. However, it is observed that the resistance increases and comes back practically to the original value. It is therefore suggested that the reduction continues further and the zinc ions from the lattice sites or from interstitials trap electrons and separate out as a second phase in



zinc oxide crystal. Separation of free zinc from zinc oxide crystal has actually been observed by Thomas and Lander<sup>13</sup>.

### Irradiation of ZnO pellets

When the zinc oxide pellet is exposed to  $\gamma$  - irradiations at 300°C a slight increase in the resistance is observed. This can be explained due to slight adsorption of oxygen, i.e. the trapping of electrons from the conduction band. As the pellet was already heated to high temperatures, there should be less number of zinc interstitials ( $Zn_i$ ), i.e. it is already saturated with adsorbed oxygen. So there is a lot of oxygen which has been adsorbed irreversibly at 300°C and hence the amount of oxygen adsorbed due to irradiation is very small. The effect is much less marked in case of pellets as compared to thin films, because of the surface to volume ratio is small in this case.

When the zinc oxide pellet is irradiated in presence of hydrogen, zinc oxide is reduced i.e. there is an increase in the concentration of zinc interstitials ( $Zn_i$ ) by removing chemisorbed oxygen and hence electrons are released for conduction. As oxygen chemisorption at higher temperatures is irreversible, the

loosely bound oxygen which can be removed by hydrogen is very little and hence only a small change in conductivity is observed.

### Irradiation of zinc oxide thin film

#### Irradiation in air and nitrogen

Behaviour in the initial stages is similar to that of the crystal. When the zinc oxide film is exposed to  $\gamma$ -irradiation, an initial increase in resistance is observed which indicates a decrease in the number of current carriers. This can be explained by assuming the trapping of electrons by adsorbed oxygen.

Resistance keeps on increasing till all the electrons available for trapping are exhausted and then it remains constant. In this case no peak is observed in resistance vs irradiation time curve presumably because the change over from n-to p-type takes place very quickly. The process of initial increase in resistance is also very fast as compared to the single crystal, probably because of the bigger surface area available. It takes only 75 minutes for the resistance to become constant.

On annealing the resistance falls gradually presumably due to desorption of oxygen. The final resistance observed after annealing is higher than the initial resis-

tance of the film which indicates that part of the oxygen is irreversibly adsorbed on the sample at room temperature.

As the film is irradiated at higher temperatures ( $228^{\circ}\text{C}$ ) the inflexion point in resistance vs time plot ( $t$ ) moves towards small value of  $t$ . In this case also the annealing is fast and as before the resistance after annealing is found to be higher than the initial resistance of the film. This represents that the process is faster at higher temperatures and all oxygen is taken up in much shorter time while annealing desorption is also comparatively faster.

The activation energy curve gives the amount of energy required to remove an electron from the zinc interstitials.

In the case of irradiation of sandwiched film of zinc oxide the changes in conductivity are negligibly small as the available surface area is small and only a negligible amount of oxygen is adsorbed.

#### Irradiation in presence of hydrogen

Here the behaviour appears similar to that of the single crystal irradiated in hydrogen. The only difference is that the initial minimum is not observed. This is possibly

due to the fact that the first reading was taken after 5 minutes and the minimum might have appeared before that in view of the fact that the changes in thin films are faster as compared to single crystals.

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R E F E R E N C E S

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## ACKNOWLEDGEMENT

I express my thanks to Dr. A. P. B. Sinha for his valuable suggestions and discussions during the pursuit of this work.

I am also grateful to Dr. V. B. Tare for the help he rendered during the course of this investigation.

I thank Dr. H. B. Mathur and Dr. M. P. Reddy for making the Co-60 gamma radiation source available for this work and rendering all assistance in that connection.

Finally, I am grateful to the Council of Scientific and Industrial Research, New Delhi, for awarding me a fellowship and to the Director, National Chemical Laboratory, Poona, for kindly affording all the necessary facilities during the period of investigation.

Prafulla Chandra

Poona-8,  
July, 1966.