

## Hydrogen as a Donor in Zinc Oxide

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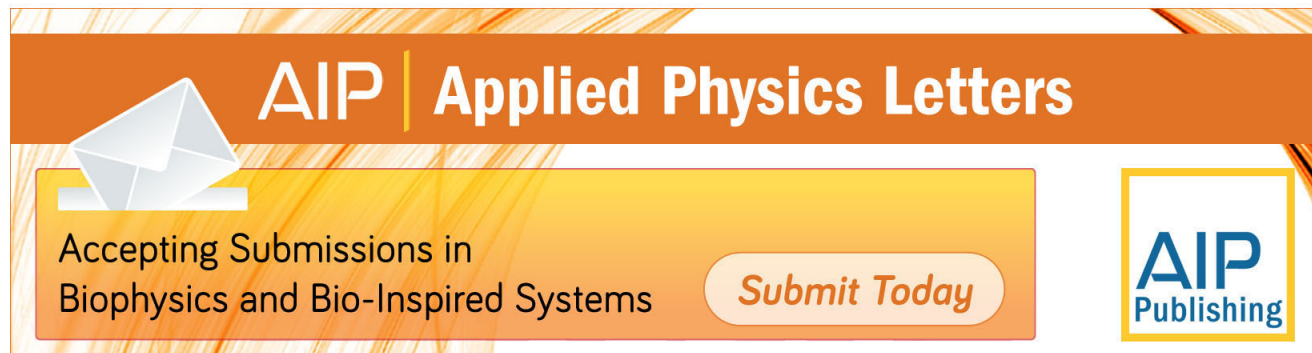
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The anomalously weak intensities of the *P*-branch regions of the *B*-type bands likewise remains unexplained. In the light of the present interpretation, Coriolis interaction has been pretty well ruled out as a cause. The two most probable causes now seem to be electrical anharmonicity and vibrational-rotational in-

teraction. Investigations of the latter effect<sup>19</sup> seem to indicate that these effects are certainly too small to account for the anomaly in the stretching fundamental region when a reasonable value for the change in  $\kappa$  between the two vibrational states is assumed.

<sup>19</sup> H. C. Allen, *J. Chem. Phys.* **22**, 83 (1954).

## Hydrogen as a Donor in Zinc Oxide

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Hydrogen is found to diffuse into and increase the conductivity of single ZnO crystals. The diffusion rates have been obtained, as well as the temperature and pressure dependencies of the quantity of hydrogen in the crystal. This quantity is found to be influenced by the electrons already in the crystal. It is thought likely that hydroxyl groups are formed from the hydrogen and oxide ions. The donor center has an ionization energy of 0.04 ev.

### INTRODUCTION

ZINC oxide is an *n*-type semiconductor with a forbidden gap width of about 3 ev. The precise nature of the donor centers is imperfectly understood although they are thought to be interstitial zinc atoms<sup>1</sup>; certainly chemical analysis shows that there is present a stoichiometric excess of zinc. In the work described here zinc oxide crystals were grown which had a variety of initial conductivities. Provided extreme conditions were avoided (e.g., not heating above about 700°C) these conductivities remained unaltered. However, if the crystals were heated in hydrogen the conductivity increased, but it returned to its original value if the hydrogen was subsequently removed.

Mollwo<sup>2</sup> was the first to study this phenomenon. He found that heating zinc oxide crystals in hydrogen changed the luminescent properties of the crystals and increased their conductivity. He obtained diffusion constants for the process, reported that the conductivity increased with the square root of the hydrogen pressure and obtained a value for the heat of solution of hydrogen in zinc oxide. We have extended this work.

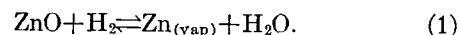
### APPARATUS AND MATERIALS

*Crystals of zinc oxide* were grown using Scharowsky's technique<sup>3</sup> in which zinc vapor reacts with oxygen at about 1200°C in the presence of hydrogen. The crystals were long colorless hexagonal needles 5–20 mm in length and 0.005–0.015 cm in diameter. The room temperature specific conductivity of the crystals ranged from 0.01 ohm<sup>-1</sup> cm<sup>-1</sup> or less up to about 5 ohm<sup>-1</sup> cm<sup>-1</sup>,

the larger crystals usually having the larger conductivity. The conductivity of those crystals of low conductance usually increased markedly with increasing temperature, while the others depended less sharply on temperature. Thus by selection, a crystal suitable for a particular experiment could usually be found.

*Conductance measurements* were made in the apparatus shown in Fig. 1. Four 0.002 in. platinum wires were attached to the crystal so that the potential drop down the crystal could be measured as current flowed through it, thus avoiding trouble arising from rectifying contacts. Good contact was made to the end current leads with a little platinum paste baked on at 600°C in air. The potential probe wires were looped around the crystal and contact was made by discharging a condenser through the end pairs of electrodes thereby providing a very small contact area at the probes.

Hydrogen reduces zinc oxide at elevated temperatures, the reaction usually becoming noticeable at about 450°C. In order that appreciable quantities of hydrogen should enter the crystal, it was necessary to heat it to 500–700°C, which would normally have resulted in rapid reduction. To avoid this the crystal was surrounded by a small cap of sintered zinc oxide, and the hydrogen used was saturated at room temperature with water vapor. Thus the hydrogen could reduce the sintered material and so provide an atmosphere containing zinc and water which would suppress the reaction (1).



The added water would further aid this suppression. With these precautions a crystal could be heated for a

<sup>1</sup> T. J. Gray, *J. Am. Ceram. Soc.* **37**, 534 (1954).

<sup>2</sup> E. Mollwo, *Z. Physik* **138**, 478 (1954).

<sup>3</sup> E. Scharowsky, *Z. Physik* **135**, 318 (1953).

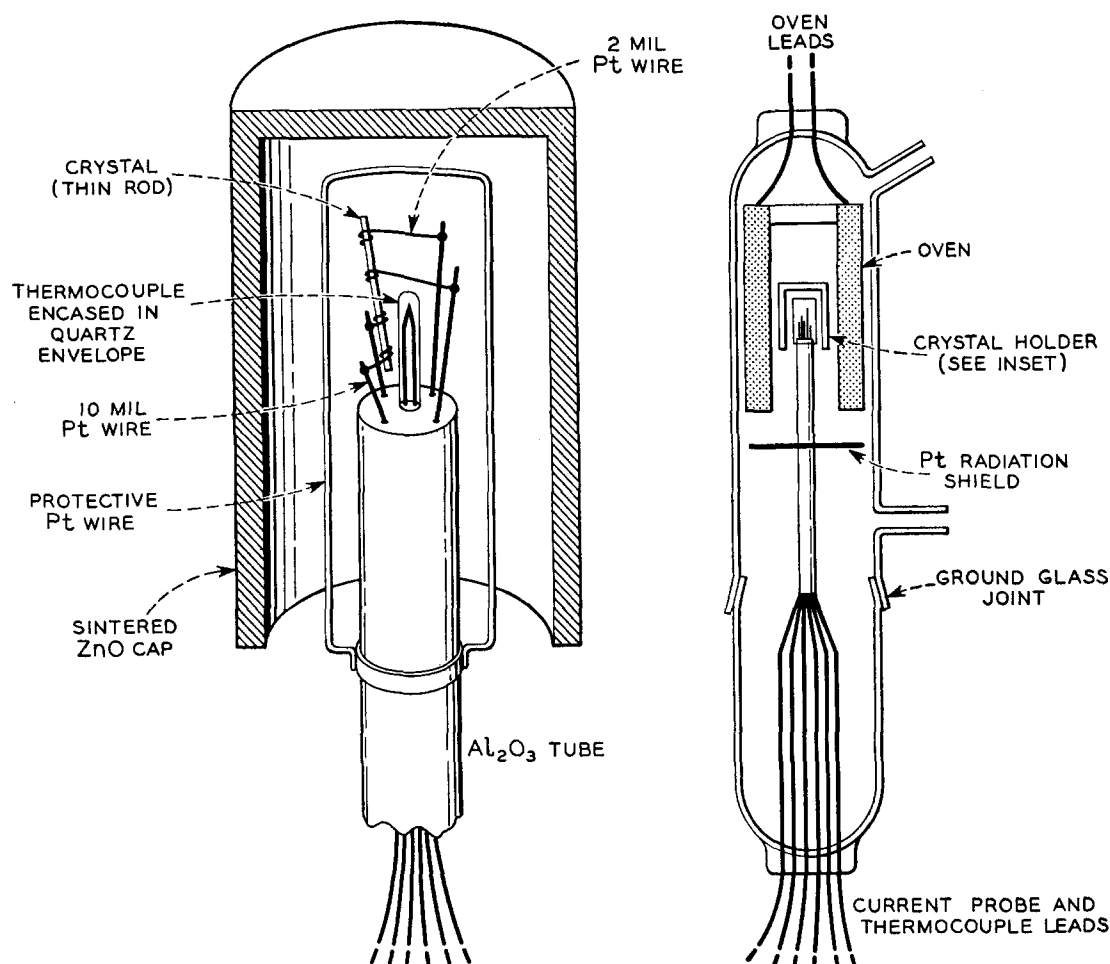


FIG. 1. Apparatus for measuring conductivity of zinc oxide crystals.

short time to  $650^\circ$  in 100 atmospheres of hydrogen without serious reduction.\*

However, the zinc vapor was found to alloy with the platinum wires and cause them to crumble away. While this merely necessitated frequent replacement of the crystal wires, it completely vitiated the readings of the platinum-platinum rhodium thermocouple and as a consequence this was enclosed in a quartz envelope as shown in Fig. 1.

An oven, made from platinum/rhodium wire wound on a magnesium oxide former, was used to heat the crystal and ZnO cap. As shown in Fig. 1, the oven could be readily removed to allow replacement of the wires or crystal.

\* In experiments in nonisothermal closed evacuated quartz tubes, containing Zn and ZnO crystals, it was observed that ZnO distilled from the hot regions under conditions where the vapor pressure of ZnO is negligible. We assume that this effect is due to reaction of ZnO with a small quantity of hydrogen trapped during seal off. The water produced reacts with zinc at the cold end of the tube. Hydrogen is regenerated and repeats the process. Such distillation caused etching of the residual crystals, which could be avoided if the quartz tubes instead of being sealed off were pumped through a high impedance.

The whole assembly could be connected to a vacuum system which allowed experiments to be performed in hydrogen at and below atmospheric pressure. For pressures above one atmosphere the crystal holder and oven were together placed in a pressure bomb. The electrical leads were brought out through Stupakoff glass to metal seals soldered into the cap of the bomb. The hydrogen pressure was obtained from cylinders, and was measured on a Heise Bourdon-type gauge. Since the thermocouples were connected through two metal-glass seals, one in the stem base and one in the cap of the bomb, care had to be taken that these connections were free from temperature gradients. For this reason the bomb was surrounded by a jacket through which cooling water circulated and the inside of the bomb was packed with glass wool to minimize convection currents. Nevertheless it is unlikely that all temperature gradients were eliminated, and so less reliance is placed on the precise work required for the evaluation of the common ion effect, which is mentioned below, when this was obtained from the high pressure apparatus, than when it was obtained when the crystal

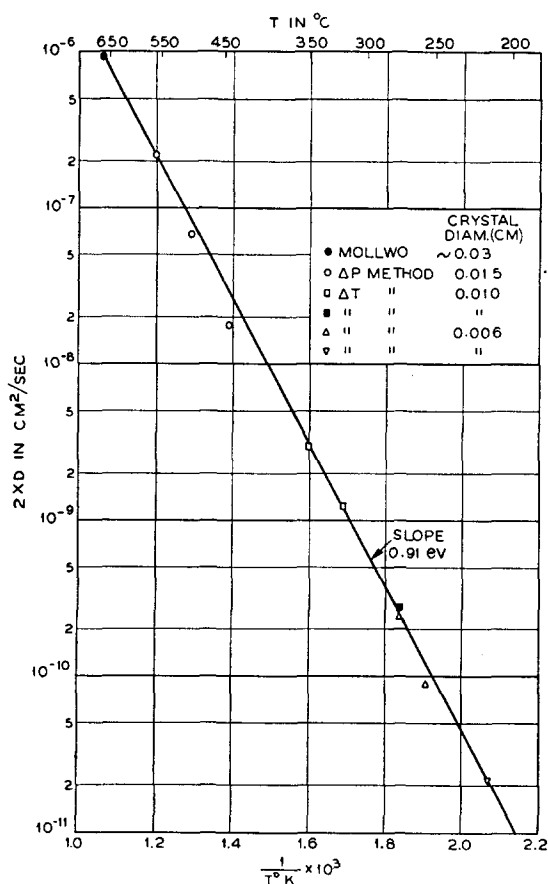


Fig. 2. Diffusion coefficient of hydrogen in zinc oxide as a function of temperature.

holder was in the open with no temperature gradients in the exterior thermocouple connections.

#### DIFFUSION MEASUREMENTS

Hydrogen begins to diffuse into a crystal of approximately 0.006 in. diameter at an appreciable rate near 400°C. Such a crystal was chosen which had a specific conductivity, nearly independent of temperature, of about 0.03 (ohm cm)<sup>-1</sup> and a series of experiments was performed with this crystal to determine the diffusion coefficient for hydrogen in zinc oxide.

The movement of the hydrogen was followed by the change of conductivity, it being assumed that the increase of conductivity over the "background" value was proportional to the total amount of hydrogen that had entered the crystal. This presumes that all of the hydrogen is ionized at these temperatures and that the mobility of the conductance electrons is independent of concentration. It was found most convenient to change the hydrogen pressure from 1 atmos to 5 mm of Hg, to follow the hydrogen diffusing out, and from 5 mm to 1 atmos, to follow it diffusing in. These two pressures were chosen because a rapid change could be made from one to the other, with little change in the

temperature of the crystal. The system was in equilibrium before the change of pressure was made, and so by waiting until equilibrium was regained the total change of conductivity could be found. Thus the percent change after various times was calculated. In addition a number of crystals were quenched from 550°C in hydrogen. These were crystals of small diameter and were used to obtain the data at lower temperatures given in Fig. 2. In this case the crystals were heated in air to remove the hydrogen.

A curve was drawn of the function  $Dt/r^2$  vs percent change as calculated from the standard diffusion equations for diffusion into an infinite cylinder.  $D$  is the diffusion constant,  $t$  the time in seconds and  $r$  is the radius of the cylinder in cm. The crystals were in fact hexagonal, but they were assumed to be cylinders with a diameter 10% less than the largest measured diameter. For each particular point in a run knowing the percent change, the time, and the radius of the crystal one obtains from the curve a value for  $D$  which should remain constant throughout the run (though space charge effects could produce smaller rates at the beginning of the run). This value of  $D$  refers of course to diffusion perpendicular to the  $C$  axis.

This calculation of  $D$  takes no account of the increase in rate arising from charge interaction. If the donor centers are completely ionized, if the number of electrons from the hydrogen is greater than the "background" number, and if space charge is limited, which conditions obtain in these experiments, then the diffusion coefficient of the hydrogen ions is half that calculated.<sup>4</sup> This occurs because the electrons are much

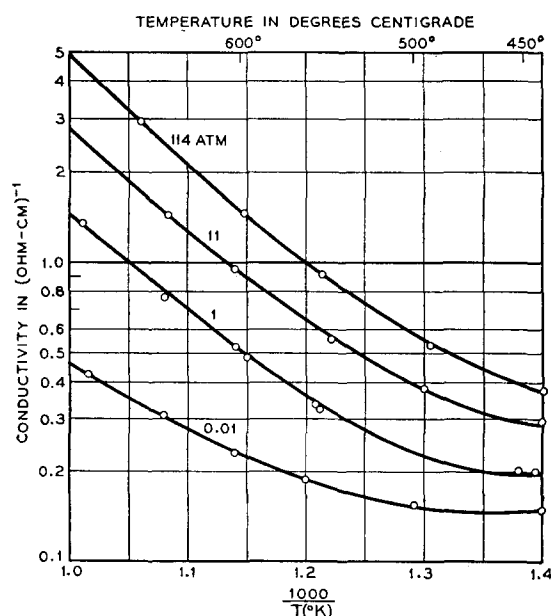


Fig. 3. Specific conductivity of crystal 347 as a function of temperature and hydrogen pressure in atmospheres.

<sup>4</sup> Bardeen, Brattain, and Shockley, J. Chem. Phys. 14, 714 (1946).

more mobile than the protons, so that they diffuse ahead and drag the protons along with them. Mollwo<sup>2</sup> did not consider this effect.

In Table I the detailed results are given for diffusion in and out at one temperature. It can be seen that within the probable experimental error the diffusion constants in and out are the same.

In Fig. 2  $\log 2D$  is plotted against  $1/T$  giving approximately a straight line, the equation of which is

$$2D = 0.063 \exp(-0.91e/kT). \quad (2)$$

Many more diffusion runs on other crystals were performed. In general they fell near the best results just quoted, but, chiefly because the thermocouple was not then enclosed in a quartz tube, there was a good deal of scatter and so the results are not given. Mollwo's diffusion results give an activation energy of 1.12 ev, in fair agreement with our value.

#### SOLUBILITY OF $H_2$ IN $ZnO$

In order to determine the equilibrium concentration of hydrogen in zinc oxide as a function of temperature and pressure, a crystal with a low background conductivity as nearly as possible independent of temperature, was chosen, and its equilibrium conductivity measured in various hydrogen pressures at various temperatures. It was impractical to follow the hydrogen below about 450°C both because the quantity was usually small compared to the background, and because the diffusion times became too long. The results of such an experiment on crystal 34<sub>7</sub> are plotted in Fig. 3. By subtracting out the background conductivity the conductivity due to the hydrogen is obtained, and this is plotted in Fig. 4. The line for 16 atmos given by

TABLE I. Diffusion of  $H_2$  in  $ZnO$  at 500°C;  $r = 7.5 \times 10^{-3}$  cm.

Time sec	Specific conductivity $\sigma_0$	$\Delta\sigma$	% change	$2Dt/r^2$	$2D$
H <sub>2</sub> at 1 atmos to 5 mm (out)					
0	0.159				
8	0.141	0.018	19%	0.008	$5.6 \times 10^{-8}$
20	0.132	0.027	28	0.017	4.8
45	0.113	0.046	48	0.058	7.2
70	0.104	0.055	57	0.086	6.9
100	0.095	0.064	67	0.128	7.1
160	0.087	0.072	75	0.156	5.4
240	0.077	0.082	85	0.280	6.5
360	0.071	0.088			Best value
630	0.066	0.093			
$\infty$	0.063	0.096	100		$6.5 \times 10^{-8}$
H <sub>2</sub> at 5 mm to 1 atmos (in)					
0	0.064				
13	0.0867	0.023	24	0.0125	$5.4 \times 10^{-8}$
30	0.098	0.034	35.5	0.0290	5.4
50	0.1105	0.046	48	0.0580	6.5
70	0.123	0.059	61	0.100	7.9
105	0.133	0.069	72	0.156	8.3
160	0.141	0.077	80	0.220	7.7
255	0.154	0.090	93		Best value
$\infty$	0.159	0.095	100		$6.85 \times 10^{-8}$

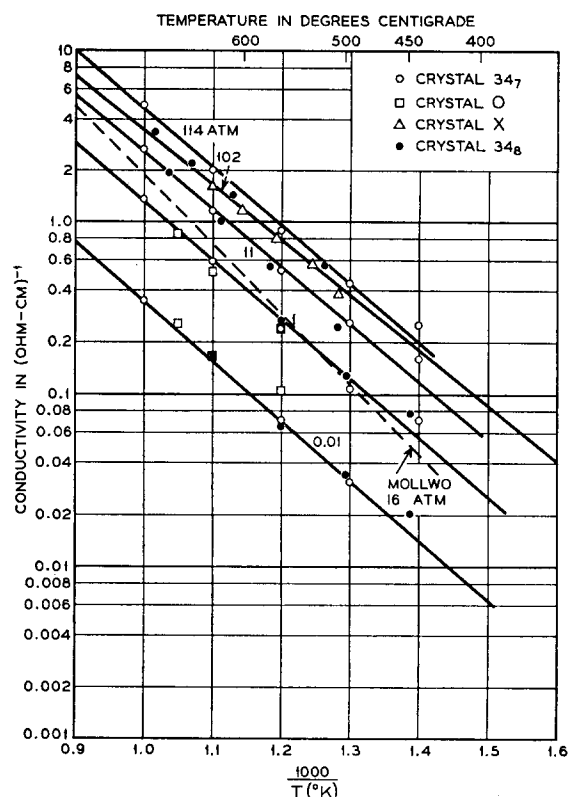


FIG. 4. The contribution to the specific conductivity of various zinc oxide crystals made by hydrogen at different pressures and temperatures.

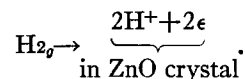
Mollwo is also included in this figure and is in fair agreement with our results.

Preliminary results obtained by A. R. Hutson of these laboratories show that in the range 150 to 300°K the electron mobility varies at  $T^{-\frac{1}{2}}$  and at 25°C has a value of 200 cm<sup>2</sup>/v sec. These results together with the assumption that all the donors are ionized, enable us to connect the hydrogen solubility with the conductivity, by the equation,

$$n = 9.6 \times 10^{12} \sigma T^{\frac{1}{2}},$$

where  $n$  is the number of hydrogen A/cc,  $\sigma$  the specific conductivity and the temperature is expressed on the Kelvin scale. This equation is used to calculate the solubility of hydrogen in A/cc, which is plotted in Fig. 5.

From the plots of the log of the solubility against  $1/T$  for a given pressure we may obtain the heat of the reaction



It is found to be about 3.2 ev (heat is absorbed).

In Fig. 6 the logarithm of the conductivity due to the hydrogen at two different temperatures, is plotted against the logarithm of the square root of the hydrogen

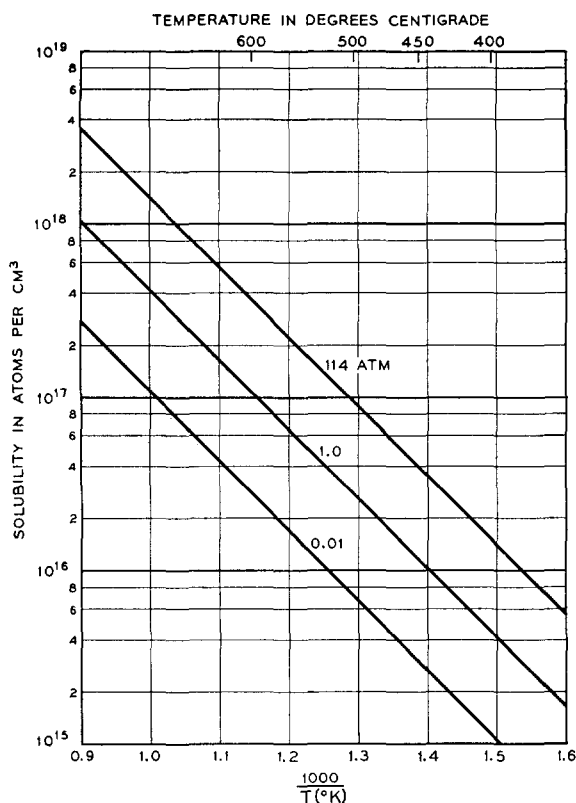


FIG. 5. Solubility of hydrogen in zinc oxide as a function of temperature and hydrogen pressure.

pressure. Two straight lines result with slopes 0.53 and 0.51. These values are very close to 0.50, which is the slope to be expected if the hydrogen conductivity varies as  $P_{H_2}^{1/2}$ .

These relations are true however only when the number of electrons supplied by the hydrogen is considerably greater than the number already free in the crystal. To follow the behavior when this is not the case is not easy because small differences between the observed and background conductivities are involved. First of all the conductivity of the crystal is measured

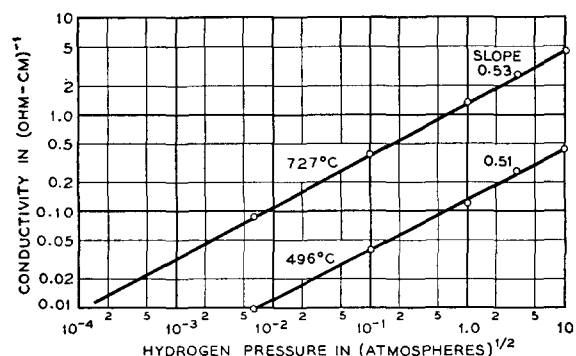


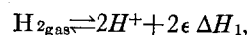
FIG. 6. Conductivity due to hydrogen at two temperatures, as a function of pressure. The slopes show that the conductivity varies as  $P_{H_2}^{1/2}$ .

over the required temperature range in oxygen (see Fig. 7). Then hydrogen is admitted to the desired pressure at about 200°C whereupon the conductivity usually increases at once by 3–5%. As the temperature is so low hydrogen could not diffuse into the crystal, and we conclude that the hydrogen has caused the conductivity increase by affecting the surface in some way. The conductivity is followed to higher temperatures and the curve follows closely the oxygen curve though is displaced from it. In the region of 400°C the curve starts to rise sharply as appreciable amounts of hydrogen enter the crystal. The conductivity produced by the hydrogen is again obtained by subtracting out the background conductivity which is taken to be the extrapolation of the curve in the hydrogen atmosphere at low temperatures, drawn parallel to the oxygen curve.

Such an experiment is illustrated in Fig. 7 in which the conductivity in oxygen and in one atmosphere of hydrogen is plotted on a linear scale vs  $1/T$ . A similar curve was obtained for hydrogen at 1/100 atmos. The conductivity due to hydrogen, roughly proportional to the concentration of hydrogen, is plotted vs  $1/T$  in Fig. 8. It is seen that below the base conductivity of about 0.4 the slopes of the lines are 1.35 and 1.14 ev with a mean value of 1.26, which is almost exactly twice the slope (0.62 see below) obtained in the high concentration region. Furthermore the straight lines are separated approximately by a factor of 10 indicating a pressure dependence of  $P_{H_2}^{1/2}$  instead of  $P_{H_2}$  as observed in the high concentration region. It was not possible to continue these particular curves to the higher regions because the necessary temperature would result in reduction of the crystal. However at 100 atmos of  $H_2$  the concentration of hydrogen was greater than the background and the slope was about 0.62 ev. The slowness of the diffusion and various complicating factors precluded following with the necessary precision the high pressure runs to low concentrations, however the indications were that the behavior was similar to the low pressure work.

These results may be interpreted as follows. Thermo-electric power measurements (A. R. Hutson) show that even when the crystals have high conductivity the Fermi level is still well below the conduction band, so that the system is nondegenerate and we may use the familiar mass action relations in which we will assume that the concentrations are proportional to the activities. The treatment is closely analogous to the "common ion" effect, the "common ion" now being the electron.

Since the donor hydrogen atoms are all ionized, we may write the reaction



where  $\Delta H_1$  is the heat of the reaction, and

$$K_1 = \frac{[H^+]^2 [e^-]^2}{P_{H_2}}. \quad (3)$$

When the electrons from the hydrogen are present in excess of these permanently in the crystal, we have

$$[H^+] = [\epsilon]. \quad (4)$$

Under these conditions

$$[\epsilon]^4 = K_1 P_{H_2}.$$

The specific conductivity  $\sigma_0$  we take to be proportional to  $[\epsilon]$ , (neglecting the mobility correction). Thus,

$$\sigma_0 \propto P_{H_2}^{1/4} \cdot K_1^{1/4} \quad (5)$$

as is observed.

From the Van't Hoff equation,

$$\frac{d \ln K_1}{dT} = \frac{\Delta H_1}{RT^2}. \quad (6)$$

Thus for a given pressure, the slope of  $\ln \sigma_0$  vs  $1/T$  gives us  $\Delta H_1/4R$ . If however there is only a small amount of hydrogen present then:

$[\epsilon] \approx C$ , a constant, the concentration of electrons supplied by the completely ionized and immobile impurities already in the crystal. From 3,

$$[H^+] = \frac{K_1^{1/4}}{C^{1/4}} P_{H_2}^{1/4}.$$

Thus the concentration of hydrogen should vary as  $P_{H_2}^{1/4}$ , and further  $\ln[H^+]$  vs  $1/T$  at a fixed pressure should give a straight line with a slope of  $\Delta H_1/2R$ , twice what it was before. We have seen that these predictions are approximately fulfilled, at least for the low pressure experiments.

#### IONIZATION ENERGY OF THE HYDROGEN DONOR CENTER

Low temperature Hall and conductance measurements to be reported in detail by A. R. Hutson, show that the ionization energy of the donor center is about 0.04 eV.

#### NATURE OF THE DONOR CENTERS

Mollwo reported that the hydrogen conductivity varied as  $P_{H_2}^{1/4}$ . Unless he was working in the region in which the hydrogen contribution to the conductivity was small compared to the background conductivity, which did not appear to be the case, this result disagrees with our  $P_{H_2}^{1/4}$  dependence. Mollwo only performed experiments at 1 and 20 atmos while we covered a much wider range, yet it is hard to see why there should be such a discrepancy. Certainly a simple picture as presented above predicts the  $P_{H_2}^{1/4}$  relation. Mollwo also considered it possible that the increase in conductivity might arise from excess zinc made at the surface by hydrogen reduction, diffusing into the crystal. However, we found that the solubility was independent of the partial pressure of water in hydrogen, which would not

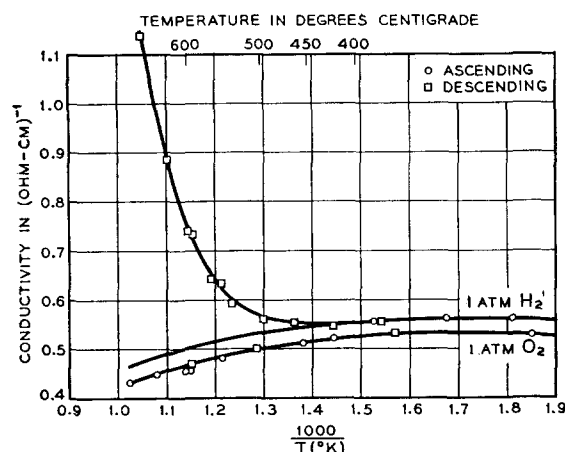


FIG. 7. Curves used to evaluate "common ion" effect.

be so if zinc were entering the crystal. We conclude that hydrogen does in fact enter the lattice, and when in excess its solubility varies as  $P_{H_2}^{1/4}$ .

This hydrogen may remain as interstitial protons and diffuse from one interstitial position to the next. Alternatively the protons may unite with the oxygen ions to form  $OH^-$  groups. (There appears to be no possibility of forming  $O-H-O$  hydrogen bonds as the minimum  $O-O$  distance in  $ZnO$  is about 3.3 Å and the maximum  $O-H-O$  distance ever observed is only about 2.8 Å.)

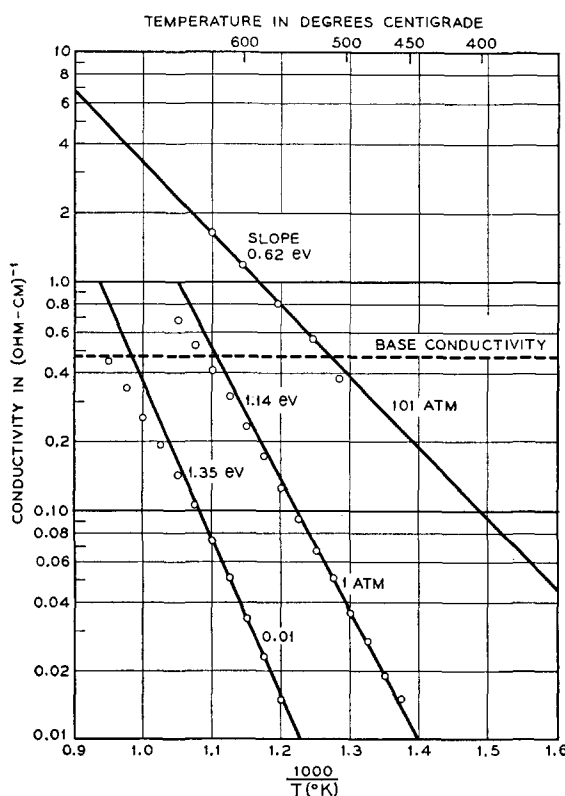
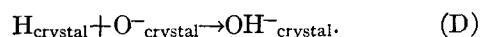
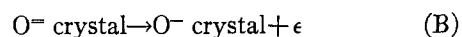


FIG. 8. Conductivity due to hydrogen in the "common ion" region.

It is of interest to compare the behavior of hydrogen in zinc oxide and in germanium. Hydrogen, in considerable quantity, is soluble in germanium single crystals<sup>5</sup> yet apparently does not affect the electrical properties of the crystal. H. Reiss<sup>6</sup> has interpreted this by pointing out that the germanium lattice has in it interstitial holes so large (about 2.5 Å in diameter) that in order to ionize a hydrogen atom occupying one of these holes, energy is required more nearly equal to that required to ionize an isolated hydrogen atom, not one embedded in a medium of high dielectric constant (16 for germanium). In consequence, although the hydrogen is present, it does not ionize and so is not detected electrically. Similar considerations hold for zinc oxide where the dielectric constant is 12 and the interstitial hole diameter is roughly 1.9 Å. The reduced hole size might make the effect somewhat smaller than for germanium but the ionization energy would be expected to be much larger than the observed value of 0.04 eV. This disagreement indicates that the hydrogen does

not simply occupy an interstitial hole. It seems natural to suppose that it unites with an oxygen ion, the OH<sup>-</sup> center spreading the odd electron over a large volume so that it is effectively in a medium of high dielectric constant and easily ionized.

One may consider various steps in the formation of the centers as follows:



In this series the energy required for reaction (B) may be identified with the energy required to form a hole electron pair, that is the forbidden gap width. This suggests that it might be of considerable interest to study the same phenomenon in other oxides and determine whether there is any correlation between the heat of the reaction and the width of the particular forbidden gap.

<sup>5</sup> O. H. Johnson, Chem. Revs. **51**, 431 (1952).

<sup>6</sup> H. Reiss, Phys. Rev. **100**, 1806(A) (1955).