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Hall Effect Studies of Oxygen Chemisorption on Zinc Oxide

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Dual ac Hall effect measurements of the chemisorption of oxygen on gallium-doped zinc oxide have shown that oxygen is chemisorbed primarily as O_2^- between 100° and about 180°C, and as O^- above about 230°C.

I. INTRODUCTION

We have reported previously (*1*) the application of a dual ac Hall effect measurement for the quantitative study of the role of the conduction band electrons in the chemisorption of oxygen, and in the oxidation of carbon monoxide on indium-doped polycrystalline zinc oxide. It was shown that the chemisorption of oxygen on indium-doped zinc oxide is associated with an electronic charge transfer from zinc oxide to the surface oxygen species, and that O^- is the predominant chemisorbed species in the temperature range between 200° and 350°C. Results on the oxidation of carbon monoxide indicate that the conduction band electrons are intimately involved in the reaction, and that O^- is an important transient species.

We have now extended our study of the chemisorption of oxygen to a lower temperature in order to learn more about the nature and extent of the chemisorption, and about the possible transformation of different forms of chemisorbed oxygen on zinc oxide.

II. EXPERIMENTAL

In studying the chemisorption of oxygen on zinc oxide, it is desirable for samples to have adequate surface area to provide sufficient sensitivity in the measurement of amount chemisorbed and changes in the conduction electron concentration. The amount of oxygen that can be chemisorbed on zinc oxide with charge transfer is of the order of magnitude 1×10^{13} molecules/cm^2. The sample surface area may be increased by using polycrystalline-sintered material, but this introduces macroscopic inhomogeneities into the samples (such as pores, cavities, and narrow connecting necks between the grains) that often provide serious problems in electrical conductivity measurements. The Hall coefficient, however, has the advantage of being little affected by such inhomogeneities and grain boundaries.

Some discussion of the dual ac Hall effect measurement was given previously (*1*). In the dual ac method, the Hall voltage is measured at a frequency different from that of the magnetic field and the electric current. Thus the balancing out of the misalignment voltage of the Hall probes, which is generally much larger than the Hall voltage, is not critical when the amplifier is tuned to reject the current and magnetic field frequencies. This makes the dual ac method quite attractive for the study of the rapid changes in electrical properties that may occur in a catalyst during chemisorption and catalytic processes.

In measuring the Hall voltage, we have used a sample current of 50 cps and a magnetic field of 60 cps to give Hall voltage at 10 cps. The Hall voltage is measured using a lock-in amplifier in conjunction with

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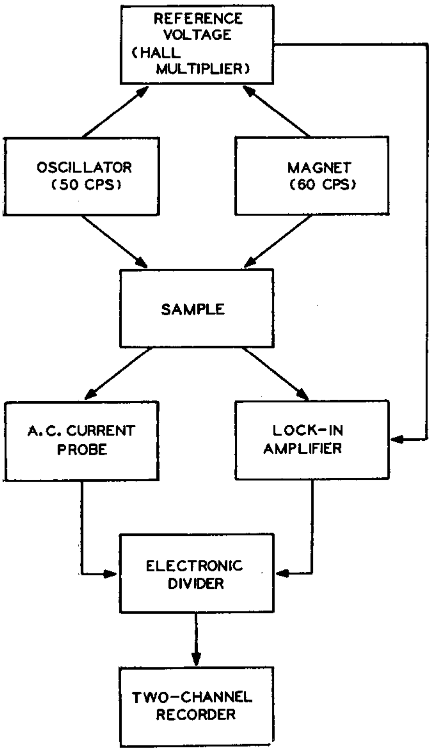

FIG. 1. Block diagram of the dual ac Hall effect apparatus.

a Hall effect multiplier of high Hall output voltage to obtain the reference signal for the lock-in amplifier. Currents are measured with an ac current probe. The current and Hall voltage are fed into a electronic divider to obtain an output that is directly proportional to the carrier concentration. A block diagram of the measuring circuit is given in Fig. 1. The carrier concentration is obtained from the relation*

$$n = 1.18 \times IHd/2qVtw$$

where n is carrier concentration, V is Hall voltage, I is total current, H is magnetic field strength, d is distance between the Hall probes, t is thickness, w is width of the sample, and q is electronic charge. The factor 2 arises from the modulation producing the Hall signal, and 1.18 is the lattice-scattering factor.

The Hall sample was made from powder prepared by impregnating spectroscopically pure zinc oxide with gallium nitrate solution. The sample contained approximately $1.1 \times 10^{18}/\text{cm}^3$ of gallium as determined by spectrographic analysis. The donor concentration estimated from the temperature dependence of the carrier concentration is $1 \times 10^{18}/\text{cm}^3$. Subsequently the sample is sintered at 825°C. The sample has a dimension of $2.6 \times 0.9 \times 0.1$ cm and a surface area of 0.85 m^2/g, as determined by the BET method, using the adsorption isotherm of krypton at liquid nitrogen temperature. Electrodes are 0.001 inch thick strips of platinum foil partially embedded in the sample (as shown in Fig. 2). Pressure is measured with a thermistor gauge calibrated against the McLeod gauge.

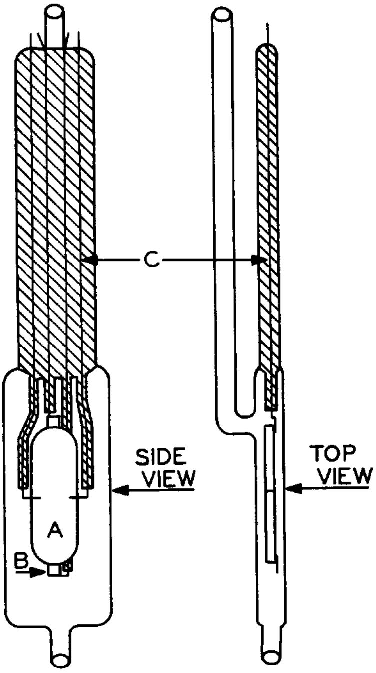

FIG. 2. Sample holder: a, sample; b, electrode; c, lead wires embedded in glass.

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* In case a space-charge region forms near the surface and the average carrier concentration of that region varies because of changes in ambient conditions (while bulk concentration remains the same), the variations in the Hall coefficient of the sample can be shown [Petritz, R. L., *Phys. Rev.* **110,** 1254 (1958)] to reflect the changes in the carrier concentration of the surface region.

III. RESULTS

The chemisorption of oxygen was studied on gallium-doped zinc oxide between the temperatures of 100° and 250°C. The sample was outgassed at 450°C prior to each adsorption measurement. Approximately the same amount of oxygen was introduced to the sample at different temperatures, and the decrease in the number of conduction electrons was observed. The results are summarized in Table 1. The second and third columns of the table give the decrease in the number of conduction electrons and the number of oxygen molecules chemisorbed 10 min after oxygen is admitted to the sample. The ratio of the decrease in number of conduction electrons to the number of oxygen molecules chemisorbed is given in the fourth column. The ratio is 1 up to 180°C, increases with increasing temperature, and becomes 2 at 230°.

TABLE 1
CHEMISORPTION OF OXYGEN ON ZINC OXIDE BETWEEN 100° AND 250°C

Temperature	Decrease in no. of electrons	Number of oxygen molecules chemisorbed	$\Delta e/O_2$
100°	4.9×10^{15}	5.0×10^{15}	1.0
150°	4.9	5.1	1.0
170°	5.1	4.8	1.1
180°	5.1	5.1	1.0
190°	6.8	5.5	1.2
200°	7.8	5.1	1.5
210°	8.6	5.2	1.7
220°	7.8	4.7	1.7
230°	10.6	5.3	2.0
240°	8.9	4.4	2.0
250°	9.8	4.7	2.1

In order to observe the actual transformation of the chemisorbed species, oxygen was added to the sample at 160° and the temperature was raised subsequently to 260°C. The decrease in the number of conduction electrons at 160°C, with 5.4×10^{15} oxygen molecules added, was 6.0×10^{15}, giving rise to a ratio of one conduction electron to every oxygen molecule chemisorbed—in accordance with Table 1. By raising the temperature to 260°C with the chemisorbed oxygen on the sample, an additional decrease in the number of conduction electrons of 5.0×10^{15} was observed, taking into account the increase in the number of conduction electrons due to thermal generation. Thus the net total decrease in the number of conduction electrons due to adsorption of 5.4×10^{15} oxygen molecules at 160°C and subsequent heating to 260°C amounted to 10.6×10^{15}, which gives a value of 2 for the ratio of the decrease in conduction electrons to the number of oxygen molecules chemisorbed.

IV. DISCUSSION

There have been various suggestions as to the nature of chemisorbed oxygen species on zinc oxide *(2, 3)*. Barry and Stone *(2)* suggested that the form predominating at room temperature is O^-, and that above 300°C it is O^{2-}. From the changes in the ESR signal due to adsorbed oxygen on zinc oxide, Horiguchi, Setake, Sancier, and Kwan have reached the tentative conclusion that oxygen is transformed according to *(4)*

$$O_2 \rightarrow O_2^- \rightarrow 2O^- \rightarrow 2O^{2-}$$

We have shown previously *(1)* that the chemisorption of oxygen on indium-doped zinc oxide is associated with an electronic charge transfer from zinc oxide to the surface oxygen species, and that O^- is a predominant chemisorbed species in the temperature range between 200° and 350°C.

Present results show that the ratio of the decrease in the number of electrons to the number of oxygen molecules chemisorbed is about 1 for the temperature range 100–180°C. This indicates that oxygen is chemisorbed on zinc oxide primarily as O_2^- for this temperature range. The increase in the ratio starting around 190°C indicates the appearance of O^- species; above about 230°C, the oxygen is chemisorbed primarily as O^-, as indicated by the ratio of 2. The fact that the ratio of the decrease in the number of conduction electrons to the oxygen molecules chemisorbed changes from 1 at 160°C to 2 on heating to 260°C indicates that O_2^- is transformed into the high-temperature chemisorbed species O^-.

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