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Electron Spin Resonance Investigation of Electrical Conductivity Parameters of Zinc Oxide during Surface Reactions

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The effect of the electron transfer process between the bulk and surface of ZnO upon oxygen sorption was investigated by measuring the changes of the following ESR parameters: the spin densities of the $g = 1.96$ and $g \sim 2.0$ signals, the intensity of a Mn^{2+} reference sample, and the crystal current of the microwave detector. The approach was also used to investigate the relative density of conduction electrons in mixtures of copper in ZnO. A theory was developed to show that these ESR parameters may be used to describe the density of electrons in the conduction band of ZnO, and the theory was applied to the results of oxygen sorption on ZnO. Evidence is presented which shows that the $g = 1.96$ signal of ZnO should probably be assigned to electrons in the conduction band and not to electrons in donor states. Application of this ESR approach in investigations of heterogeneous catalysis, particularly oxidation reactions, is discussed.

INTRODUCTION

The adsorption of oxygen on ZnO has been investigated in many laboratories as a model for the study of catalytic, semiconductive, and photoconductive properties of solids (*1, 2*). Photoadsorption and photodesorption of oxygen on ZnO have also been studied extensively (*3–7*). Nevertheless, questions still remain concerning the kinds of sorbed oxygen species and their interchangeable character during chemisorption and photoirradiation. In addition, we still do not have a complete understanding of how the electronic properties of a catalyst control and participate in chemical reactions at the surface.

Electron spin resonance (ESR) has provided considerable insight into some of these questions. For example, it has been reported that there are at least two paramagnetic centers resulting from oxygen sorption on ZnO (*8–15*). One gives rise to an anisotropic signal at $g = 1.96$ originating from electrons in the conduction band and/or in donor levels, and the other gives rise to signals near $g \sim 2.0$ originating from sorbed oxygen species (*11–15*). The fact that oxygen sorption causes the concurrent decrease of the spin density of the $g = 1.96$ signal and increase of the $g \sim 2.0$ signals indicates that electron transfer occurs between the bulk and the surface of ZnO (*11–14*). We have also employed ESR to investigate the reaction of carbon monoxide on ZnO with presorbed oxygen, and we have identified two reactions with markedly different rates, one of which occurs with rapid electron transfer between the bulk and the surface (*11*).

The ESR technique has further potential in investigations of such electron transfer processes, and this potential is discussed in the present paper. The experimental approach which we used makes use of the fact that electron transfer between the bulk and the surface of a semiconductor changes the density of electronic carriers. Such changes may produce significant changes in the cavity Q, which can be detected by measuring the concurrent changes in the sensitivity for ESR detection of a reference signal and/or the bias current of the microwave crystal

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detector. In the present study we investigated how the changes of ESR sensitivity and crystal current can be used to understand electron transfer between the bulk and the surface as a result of oxygen chemisorption on ZnO and to further understand how this information fits into the band model picture of ZnO. This approach has been applied in a preliminary way to the study of photoadsorption and photodesorption of oxygen on semiconductors (*6*, *7*). It should also be valuable to extend the approach to study surface chemical reactions which alter the electronic properties of a catalyst and to study means by which the surface reactions can be controlled.

EXPERIMENTAL DETAILS

The adsorption and ESR measurements were carried out with samples of powdered ZnO (0.25 g, New Jersey Co., SP 500) placed in a quartz tube (4 mm i.d.). A sealed capillary containing $MgO:Mn^{2+}$ powder (courtesy of JEOL, Japan) was inserted into the center of the quartz tube as a means of measuring relative ESR sensitivity. The placement of the MgO:Mn reference provided assurance that it experienced the same microwave power as the ZnO and that effects such as concentration of microwave fields by dielectrics and microwave skin penetration were minimized. The $MgO:Mn^{2+}$ in its sealed capillary was chemically isolated from the ZnO and was not affected by the thermal treatments given to the ZnO. The ZnO sample tube was attached to a Pirani gauge and trap (50-ml volume) and to a calibrated volume (104 ml) with stopcocks. The calibrated volume was connected to a vacuum and gas handling system including a McLeod gauge. The Pirani gauge and the trap were cooled in liquid nitrogen. The ESR measurements were made with a JEOL P-10 type spectrometer (X-band) using 10^5 Hz field modulation.

The ZnO was heated at 775°K in vacuum for 30 min prior to adsorption of oxygen at room temperature. A small known amount of oxygen at a pressure measured by the McLeod gauge was introduced into the calibrated volume and subsequently expanded to the sample volume (total volume 154 ml). The pressure change due to the adsorption was followed by the Pirani gauge, providing a measure of the oxygen coverage, N_{O_2} (the number of oxygen molecules sorbed per gram of ZnO. A change in the electrical conductivity of ZnO due to oxygen adsorption alters the cavity Q and produces a change in the crystal current (I_{cc}) of the microwave crystal detector and also in the peak–peak height (I_{Mn}) of the internal reference Mn^{2+} signal.

The crystal current was recorded in the range of 0.4–0.7 mA by a high impedance recorder; above 0.2 mA the rectified current is reported by JEOL to be in the linear region of the crystal diode. In the oxygen absorption study the crystal current was preset at 0.7 mA and changes from this value were recorded for each oxygen addition.

The spin densities of the ESR signals at $g = 1.96$ (denoted by $M^*_{1.96}$) and near $g = 2.0$ ($M^*_{2.0}$) were determined by a first moment calculation. The changes in ESR sensitivity were compensated for by means of the internal reference Mn^{2+} signal (*14*) and by calibration with a solution of 2×10^{-5} *M* DPPH in benzene substituted for the ZnO sample. The precision of the first moment is estimated to be ±10%.

To provide a test sample with an adjustable density of "conduction electrons" we chose finely divided copper powder (thin flakes 10^{-1} to 10^{-2} mm diameter) which was thoroughly mixed with unpretreated ZnO and then placed in a quartz tube (4 mm i.d.) containing the MgO:Mg reference sample. The value of I_{Mn} was measured for each sample; copper contents ranged from 0 to 1.5 wt %.

RESULTS AND DISCUSSION

Oxygen Sorption

It is generally accepted that outgassing ZnO at 500°C in vacuum results in an increase in the electrical conductivity and gives rise to an anisotropic ESR signal at $g = 1.96$ associated with "electrons" in bulk. Subsequent adsorption of oxygen decreases the electrical conductivity and the intensity of the $g = 1.96$ signal. The change in the electrical conductivity results in changes in the cavity Q, the ESR sensitivity (e.g., the intensity of a standard manganese signal), and the crystal current. It has been conven-

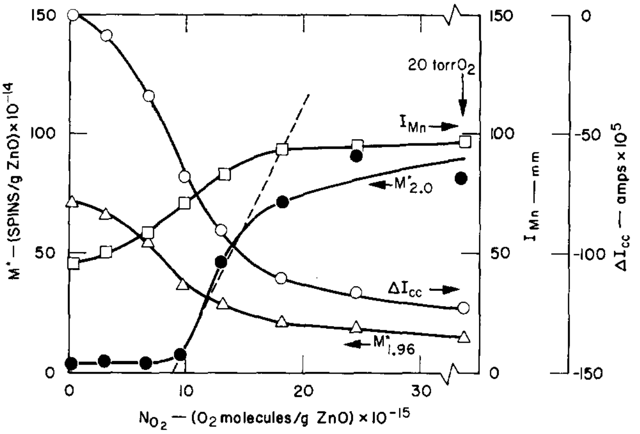

FIG. 1. Effect of oxygen sorption on zinc oxide at 300°K on $M^*_{1.96}$, $M^*_{2.0}$, ΔI_{cc}, and I_{Mn}.

tional to use a reference sample such as Mn^{+2} to monitor ESR sensitivity, and in the present study this technique was used to evaluate the quantitative aspects of electron transfer.

To obtain a better understanding of the interrelationship of the various observable quantities mentioned above, in particular, the relationship between the $g = 1.96$ signal and the conduction band electrons of ZnO, changes of ESR parameters were investigated quantitatively as a function of the amount of oxygen adsorbed. The results are shown in Fig. 1 and in Table 1. The interdependence of the three parameters, which are related to bulk electronic properties, namely, $M^*_{1.96}$, $(1/I_{Mn})$, and I_{cc}, can be seen from the linear plots which are obtained in Fig. 2 by plotting any one of the parameters against another. For the present we will assume that as a result of oxygen adsorption the process of electron transfer from the bulk to the surface is indicated, at least empirically, by a decrease of the three parameters. The basis of these correlations will be discussed in detail in later sections.

It is of interest to discuss some qualitative aspects of the oxygen chemisorption results in Fig. 1. When small amounts of oxygen (up to 10×10^{15} O_2 molecules/g of ZnO) were sorbed on pretreated ZnO, electron transfer from the bulk to the surface occurred while the intensity of the $g = 2.002$ signal remained almost unchanged. How-

TABLE 1
EFFECT OF OXYGEN SORPTION ON ESR PARAMETERS[a]

N_{O_2} (×10^{-15}/g ZnO)	$M^*_{1.96}$ (×10^{-14} spins/g ZnO)	$M^*_{2.0}$	I_{Mn} (mm)	$-\Delta\left(\frac{1}{I_{Mn}}\right)$ (×10^2)	$-\Delta I_{cc}$ (×10^5 A)
0	71	4.0	45.1	0	0
3.1	66	5.0	49.6	0.20	8.5
6.7	56	5.0	57.5	0.48	34
9.7	37	7.0	71.5	0.82	67
13.1	29	47	83.5	1.02	91
18.2	21	72	95.0	1.17	111
24.5	19	93	96.0	1.18	117
20 torr	14	85	99.5	1.22	124

[a] N_{O_2} = amount of oxygen adsorbed at 300°K on ZnO previously heated at 775°K in vacuum for about 1 hr; M^* = absolute spin density of $g = 1.96$ and $g \sim 2.0$ signals corrected for ESR sensitivity changes; I_{Mn} = peak-peak height of derivative signal; $\Delta(1/I_{Mn}) = (1/I_{Mn}) - (1/45.1)$; ΔI_{cc} = change in crystal current.

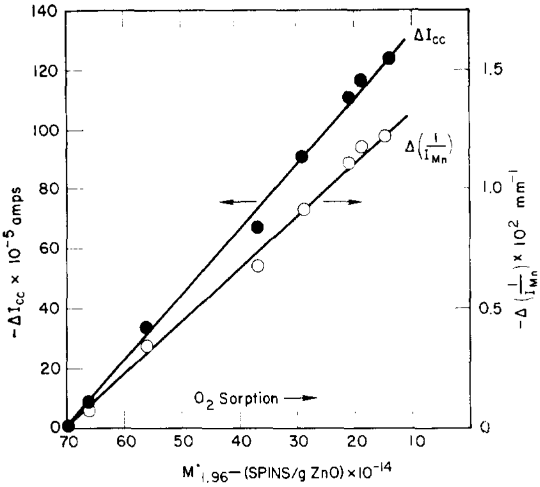

FIG. 2. Relationship between $M^*_{1.96}$, ΔI_{cc}, and $\Delta(1/I_{Mn})$ as a function of oxygen sorption on zinc oxide.

ever, further adsorption of oxygen resulted in the appearance of a signal having three g values, 2.002, 2.008, and 2.049, which will be denoted as the $g \sim 2.0$ triplet signal with spin density $M^*_{2.0}$.

The absence of an ESR signal at low coverages of sorbed oxygen, even though electron transfer to the surface had occurred, suggests that at such low coverages the chemisorbed oxygen species has no detectable resonance (*14*).

At higher coverages between about 10×10^{15} to 15×10^{15} O_2 molecules/g ZnO, the spin density of the triplet signal is proportional to the amount of sorbed oxygen in excess of that sorbed as a "nonresonant" oxygen species (the broken line of Fig. 1), and it is concluded that one sorbed oxygen molecule produces one paramagnetic species of the $g \sim 2.0$ triplet signal. This behavior supports the assignment of the $g \sim 2.0$ triplet signal as a single paramagnetic species of adsorbed oxygen such as O_2^-. Recently, a similar assignment was also suggested by Lunsford and Jayne (*16*). Our assignment is also in harmony with the following observations. First, the result of microwave power saturation experiments showed that the ratio of the three components of the $g \sim 2.0$ triplet signal was almost constant in the range between 5 and 150 mW of microwave power, in agreement with the communication by Fujita and Turkevich (*17*). Second, γ-irradiated single crystals of H_2O_2-$CO(NH_2)_2$ have been shown by Ichikawa *et al.* (*18*) to exhibit three different g values: 2.088_6, 2.008_4, 2.000_9 assigned to the O_2^- ion. Furthermore, a similar $g \sim 2.0$ triplet signal was reported for oxygen sorbed on TiO_2 as well as on ZrO_2 (*7*).

At coverages above 2×10^{16} O_2 molecules/g ZnO, the spin density of the $g \sim 2.0$ triplet signal did not increase with sorption of oxygen. This result suggests that coverage of the species giving rise to the $g \sim 2.0$ triplet signal is limited, as it must be if it is a charged species (*12*), and that the additional sorption at the highest coverages occurs principally as neutral species. Such an explanation is consistent with the fact that very little additional electron transfer occurred at the higher coverages, even when the ZnO was exposed to 20 torr oxygen (Fig. 1).

Mixtures of ZnO and Powdered Copper

In order to investigate how the ESR sensitivity depends upon the electrical conductivity of a sample, a series of measurements was made on mixtures of finely divided copper–metal powder added to powdered ZnO. The $MgO:Mn^{2+}$ reference sample provided a resonance signal whose intensity, I_{Mn}, was proportional to the cavity Q. The ZnO served merely as a diluent, and the mixtures may be approximated to an imperfect dielectric since the metal particles were very small and not in contact. The skin depth of microwaves (10^{10} Hz) in copper is 6.6×10^{-4} mm (*19a*), which is smaller than the average diameter of the copper flakes but about the order of their thickness. Although microwave power penetration is not complete, it is reasonable to expect that the average power loss per particle of copper is independent of copper concentration at sufficiently low concentrations.

The results tabulated in Table 2 show that the intensity of the manganous line decreased with increasing copper concentration. In Fig. 3 the parameter $\Delta(1/I_{Mn})$ is linearly proportional to the weight percentage of copper which is assumed to be proportional to the overall conductivity of the sample.

TABLE 2

EFFECT OF COPPER POWDER IN ZnO POWDER ON THE RESONANCE OF Mn^{2+} IN A CAPILLARY IN THE ZnO[a]

Cu in ZnO (wt %)	I_{Mn} (mm)	$\Delta\left(\frac{1}{I_{Mn}}\right)$ ($\times 10^2$)
0	130	0
0.2	108	0.16
0.5	78	0.51
1.0	63	0.82
1.5	46	1.4

[a] I_{Mn} = peak–peak height of derivative signal; $\Delta(1/I_{Mn}) = (1/I_{Mn}) - (1/130)$.

THEORETICAL CONSIDERATIONS

Some aspects of the experimental results are discussed by showing that the ESR technique, by means of the electron transfer parameters mentioned above, can provide quantitative information on the relative concentration of conduction band electrons. This information will be applied to the band model picture of ZnO in order to provide a basis for understanding the origin of the $g = 1.96$ signal.

In this section we develop the basis for evaluating the relative density of conduction band electrons, n_c, and the change in this density resulting from processes such as oxygen chemisorption. The development considers microwave fundamentals in order to show how a change of conduction electron density alters the cavity Q, and how such a change in Q can be inferred from an experimentally measured change of the intensity of an ESR signal or from the change of reflected microwave power from the sample cavity.

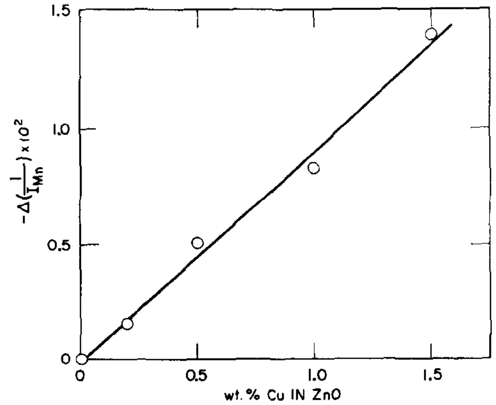

FIG. 3. The dependence of $\Delta(1/I_{Mn})$ on the weight percentage of copper powder in zinc oxide.

Rectification of Microwave Signals

During ESR operation the microwave bridge is deliberately unbalanced so that the incident microwave power P_0 or voltage V_0 provides a bias for the crystal diode detector. The resulting rectified current, the crystal current I_{cc}, is principally in the square-law region, viz.,

$$I_{cc} \sim V_0^2 \sim P_0. \quad (1)$$

When the spectrometer scans through a resonance, the ESR signal is contained in a rf modulation of the microwave power, e.g., at 10^5 Hz. At resonance, this modulation of the microwave power incident on the crystal detector may be expressed as ΔP_r. The corresponding change in microwave voltage is ΔV_r, and the corresponding rectified current I_r is in the linear region of the detector because of the bias of the crystal detector, that is,

$$I_r \sim \Delta V_r \sim \Delta P_r^{1/2}. \quad (2)$$

We use this information below to show how changes in the electrical conductivity of ZnO affect the magnitude of the ESR signal and the crystal current.

Cavity Losses and ESR Signal Intensity

The intensity of an ESR signal, e.g., that of the $MgO:Mn^{2+}$ reference sample in ZnO, depends upon the cavity Q which in turn is partly determined by the electrical conductivity of the ZnO. An expression of the signal intensity will be developed by considering how the change of the electrical conductivity of a sample changes the cavity Q.

The sensitivity of detection of an ESR signal is given by

$$\frac{\Delta V_r}{V_0} = \pi \sqrt{2}\chi''\eta Q_0, \quad (3)$$

where χ'' is the imaginary part of the complex magnetic susceptibility, η is the filling factor, and Q_0 is a Q factor reflecting all losses (*20*). The value of Q_0 is related to

$$\frac{1}{Q_0} = \frac{1}{Q'_0} + \frac{1}{Q_\epsilon}, \qquad (4)$$

where Q'_0 is the Q of the unloaded cavity (including ohmic losses in the walls and losses due to the cavity coupling hole) and Q_ϵ arises from the dielectric loss of the sample (*19b*).

It will be assumed that a semiconductor powder such as ZnO may be treated as an imperfect dielectric. It has been shown (*21*) that the imaginary part of the complex dielectric constant ϵ'' is related to the electrical conductivity σ by

$$\epsilon'' = \frac{\sigma}{\omega\epsilon_0}, \qquad (5)$$

where ω is the frequency and ϵ_0 is the dielectric constant of free space. The dielectric loss term, ϵ'', is related to Q_ϵ by

$$\frac{1}{Q_\epsilon} = \frac{\pi^3 r^4 \epsilon''}{2V_c d}, \qquad (6)$$

where r, d, and V_c are dimensional factors of the sample and cavity (*19c*). Comparison of Eqs. (5) and (6) shows that σ is proportional to $1/Q_\epsilon$, and it follows that

$$\Delta\left(\frac{1}{Q_\epsilon}\right) \sim \Delta\sigma. \qquad (7)$$

Since the ESR signal intensity is proportional to cavity Q by Eqs. (2) and (3), e.g., $I_{\mathrm{Mn}} \sim Q_0$, Eq. (7) may be rewritten as:

$$\Delta\left(\frac{1}{I_{\mathrm{Mn}}}\right) \sim \Delta\sigma \sim \Delta n_c, \qquad (8)$$

which also assumes that the electrical conductivity is proportional to the density of conduction band electrons. In the above expressions σ for a powder like ZnO is not a homogeneous electrical conductivity but a value averaged over the sample. We shall presently apply Eq. (8) to the results of oxygen chemisorption on ZnO.

Cavity Losses and Crystal Current

The change in cavity Q, e.g., caused by oxygen chemisorption on ZnO, can also be related to the change in crystal current, ΔI_{cc}. This relationship is derived from the definition of cavity Q

$$Q = 2\pi\left(\frac{P_s}{P_L}\right), \qquad (9)$$

and from Eq. (4) by formulating the dielectric power dissipation ΔP resulting from oxygen adsorption:

$$\frac{1}{Q_\epsilon} = \frac{1}{Q_0} - \frac{1}{Q'_0} = \frac{P_L + \Delta P}{2\pi P_s} - \frac{P_L}{2\pi P_s} \qquad (10)$$

where P_L (and ΔP) is the power dissipated per cycle, and P_s, the power stored in the cavity which is assumed to remain essentially constant.

The relationship between the crystal current and ΔP will depend upon the magnitude of ΔP and P_0. For practical purposes it may be assumed that the response will be in the square-law region, e.g., Eq. (1). Therefore, comparison of Eqs. (1) and (10) leads to

$$\Delta I_{cc} \sim \Delta\left(\frac{1}{Q}\right). \qquad (11)$$

Equation (11) was confirmed for oxygen sorption on ZnO in an experiment similar to that shown in Fig. 1, but for which the cavity Q was determined approximately from the oscilloscope presentation of the klystron mode with the cavity absorption. For oxygen sorption over a given range the change of cavity Q was approximately inversely proportional to the change of the crystal current. These measurements were performed by one of the authors in another laboratory on equipment already described (*11, 14*).

The desired relationship between the change in crystal current and the change in the density of conduction band electrons is obtained by comparison of Eqs. (7), (8), and (11)

$$\Delta I_{cc} \sim \Delta n_c. \qquad (12)$$

We can conclude that Δn_c may be approximated by measurements of either ΔI_{cc} or $\Delta(1/I_{\mathrm{Mn}})$, Eqs. (8) and (12), respectively.

Application of the Theory to Experimental Results

Agreement between theory and experiment is demonstrated by the results obtained by adding copper to ZnO. The linear dependence of the parameter $\Delta(1/I_{\mathrm{Mn}})$ on conductivity predicted by Eq. (8) is in fact shown by the results in Fig. 3. Further assurance that the approximations in the theory are valid is provided by the linear interrelationships among the three electron transfer parameters (Fig. 2). However, for a quantitative evaluation of the conduction electron densities, the parameters $\Delta(1/I_{\mathrm{Mn}})$ and ΔI_{cc} should be used with caution especially when the electrical conductivity of a sample may be influenced by factors such as microwave skin depth or intergranular conductivity.

The probable nature of the paramagnetic center giving rise to the $g = 1.96$ signal was explored. For this purpose the density of conduction band electrons was expressed quantitatively in terms of the spin density of the $g = 1.96$ signal and by using the band model of a semiconductor. Support for the interpretation of the resonance center was provided by the relative behavior of the three electron transfer parameters.

The ESR signal at $g = 1.96$ has been variously attributed to electrons localized in donor states, e.g., interstitial zinc $\mathrm{Zn_i}^+$, or to electrons in the conduction band and/or a shallow donor band [cf. Ref. (*14*)]. Further information on the nature of this paramagnetic center may be obtained by consideration of the band model of an n-type semiconductor and by application of the experimental results of oxygen chemisorption on ZnO. The evidence to be presented favors attributing the $g = 1.96$ signal to electrons in the conduction band.

In order to determine whether the $g =$ 1.96 signal is to be attributed to electrons in donor states or in the conduction band, the relationship between the population of these states was considered. For ZnO the density of electrons in the conduction band n_{c} and in the donor level n_{d} is expressed by

$$\frac{{n_{\mathrm{c}}}^2}{n_{\mathrm{d}}} = N_{\mathrm{c}}\left[\left(\frac{m^{(N)}}{m}\right)^{3/2} D^{-1}\right]\exp - \frac{E_{\mathrm{D}}}{kT}, \qquad (13)$$

where N_{c} is the effective density of states in the conduction band and is estimated to be 3×10^{19} cm^{-3} at 300°K, E_{D} is the energy difference between the donor level and the bottom of the conduction band (about 0.050 eV), and the term in brackets, which contains constants (electronic mass m, density-of-states effective mass $m^{(N)}$, and spin degeneracy of donor states D), is evaluated to be 0.18 (*22*).

If initially it is assumed that the $g = 1.96$ signal arises from electrons on donor states, the spin density of the $g = 1.96$ signal should give the density of occupied donor states, that is,

$$M^*_{1.96} = n_{\mathrm{D}}. \qquad (14)$$

The maximum value of n_{D} will be the maximum value of $M^*_{1.96}$ in Table 1, i.e., before oxygen chemisorption, so that $n_{\mathrm{D}} = 7.1 \times 10^{15}$ g^{-1} $\times$ 5.5 g cm^{-3} $= 3.9 \times 10^{16}$ cm^{-3}. By substitution into Eq. (13), the corresponding density of electrons in the conduction band at 300°K is $n_{\mathrm{c}} = 1.7 \times 10^{17}$ cm^{-3}.

However, by assuming that interstitial zinc is the only donor, the maximum carrier concentration will be determined by the solubility in ZnO of zinc which is controlled by the pretreatment temperature. For example, at 775°K the solubility is 2×10^{16} cm^{-3} (*23*), which is a factor of 10 lower than the above calculated value of n_{c}. Therefore, the assumption that the $g = 1.96$ signal is a measure of the electrons in the donor levels appears not to be justified. On the contrary, the agreement between the solubility and the maximum value of $M^*_{1.96}$, within a factor of about 2, strongly suggests that the $g = 1.96$ signal is to be associated with electrons in the conduction band. Evidence that the $g = 1.96$ signal is not associated with paramagnetic surface levels is also suggested by the absence of dipolar broadening of the signal at high pressures of oxygen.

Assignment of the $g = 1.96$ signal to electrons in the conduction band is further supported by the linear relations in Fig. 2 between $M^*_{1.96}$ and the two parameters, ΔI_{cc} and $\Delta(1/I_{\mathrm{Mn}})$, which have been shown to be associated with the density of conduction electrons.

Further confirmation of the assignment is obtained from an investigation of the temperature dependence of $M^*_{1.96}$ (*24*). When account is taken of the temperature dependences of the magnetic susceptibility corrected according to a Curie law and of changes of the ZnO, the results show that the density of electrons associated with the $g = 1.96$ signal decreases reversibly as the temperature is decreased from 300 to 100°K. An opposite temperature effect would be expected if the $g = 1.96$ signal were associated with electrons in donors. In apparent conflict with the above temperature dependence, two other investigators (*12*, *25*) reported that the $g = 1.96$ signal increased with temperature decrease. However, in these two investigations no account was made for the temperature dependence of the magnetic susceptibility or the ESR sensitivity. When the results of the peak–peak intensities (*25*) were corrected (*26*) in an order of magnitude calculation for the effect of temperature on the ESR line width of the $g = 1.96$ signal, magnetic susceptibility, and the skin depth, it was tentatively concluded that the electron density associated with the $g = 1.96$ signal was essentially temperature independent.

Application to Heterogeneous Catalysis

The concept that the ESR technique can be extended to measure changes of electrical conductivity of a solid suggests applications may be made to heterogeneous catalysis. Of special interest will be measurements on semiconductors where catalysis involves electron transfer between adsorbed species and the conduction band of the catalyst. Simultaneous measurements under catalytic conditions of the electrical conductivity parameters and the ESR signals will then help to determine the electronic role of the catalyst. If an ESR signal is observed, one can determine which paramagnetic center, if any, is involved in the electron transfer. If an ESR signal is not observed, due to the high temperatures of catalytic reactions which reduce the ESR signal intensities beyond detection, we may still expect that measurements of the electrical conductivity parameters may provide information on the electronic state of the catalyst. Furthermore, such measurements may provide at least qualitative information on whether during catalysis metal ions on the support are reduced to the metallic state or supported metals are oxidized.

We have employed the extended ESR technique in a preliminary study of a model heterogeneous oxidation reaction, the oxidation of carbon monoxide on ZnO at room temperature. When CO is sorbed on ZnO with presorbed oxygen it is reported that the electrical conductivity of the ZnO increases as a result of the surface reaction in which electrons are transferred from surface states to the ZnO bulk (*9*, *11*). Our measurements of the electrical conductivity parameters, I_{cc}, I_{Mn}, and $M^*_{1.96}$, all show that such CO sorption causes the electrical conductivity to increase. However, the advantages of measuring the I_{cc} and I_{Mn} parameters are that the changes occur rapidly (within seconds) and are linear with electrical conductivity; usually the I_{cc} parameter provides greater sensitivity than I_{Mn} for the detection of changes of electrical conductivity. On the other hand, measuring electron transfer from the 1.96-signal requires scanning of the signal (requiring several minutes) because the signal line width increases with electron density in the solid (*11*). Quantitative studies of the CO oxidation, which will be reported separately, suggest that upon CO sorption the number of electrons transferred per adsorbed oxygen molecule depends upon the oxygen coverage. That is, the coverage of the presorbed oxygen on ZnO determines the character of the chemisorbed oxygen species which may be expected to control the mechanism of a surface oxidation reaction involving chemisorbed oxygen.

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