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ELECTRON PARAMAGNETIC RESONANCE OF OXYGEN ON ZnO AND ULTRAVIOLET-IRRADIATED MgO

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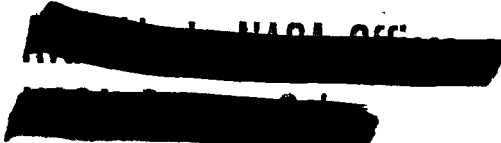National Aeronautics and Space Administration
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ABSTRACT

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A study has been made of the interaction of oxygen with samples of zinc oxide and ultraviolet-irradiated magnesium oxide using electron paramagnetic resonance techniques. Adsorption of oxygen at room temperature results in the rapid formation of a radical species, having $g_{xx} = 2.077$, $g_{yy} = 2.0011$, and $g_{zz} = 2.0073$ for oxygen on irradiated MgO and $g_{xx} = 2.051$, $g_{yy} = 2.0020$, and $g_{zz} = 2.0082$ for oxygen on ZnO. The radical is stable to temperatures of 200° C. The nature of this species is discussed and it is postulated that O_2^- is the entity adsorbed on the surface.

INTRODUCTION

The nature of room temperature oxygen adsorption on metal oxides has been the subject of numerous investigations[1-5]; however, it is not clear whether the chemisorbed[6] species is O_3^-, O_2^-, O^-, a peroxy group that is covalently bonded to the surface as S-O-O·, or some combination of these. Several other possibilities have been ruled out by thermodynamic considerations.[2] Electrical conductivity and electron paramagnetic resonance (e.p.r.) experiments have shown that a charge transfer step is involved when O_2 is adsorbed on an n-type semiconductor such as ZnO.[5,7-9] Oxygen adsorption has also been studied on irradiated nickel oxide,[10] magnesium oxide,[10] and silica gel;[11] but the identity of the adsorbed species is likewise uncertain.

It is interesting to note that all four of the oxygen entities that are mentioned above are paramagnetic, and therefore might well be studied by e.p.r. techniques. The purpose of the present work has been to use this technique to study the paramagnetic oxygen species which are formed on degassed ZnO and ultraviolet-irradiated MgO. The e.p.r. spectra are discussed in the light of other e.p.r. studies and theoretical considerations.

EXPERIMENTAL

Magnesium oxide samples for this study were from the same batch preparations as used in earlier work.[12,13] MgO I was prepared from reagent grade powder and contained about 0.001% Fe while MgO II was prepared from the same reagent grade powder which was impregnated with $FeCl_3$ to a total of 0.006% Fe. The powders were boiled in water for several hours, extruded into pellets with a hypodermic syringe, and dried in air at 100° C. Degassing was carried out by heating the pellets to 800° C in a vacuum (10^{-6} torr) for 16 h. The BET surface area measured on one sample of MgO I after this treatment was 170 m^2/g. After degassing, the M_gO pellets were then irradiated from 16 to 48 h in vacuum using a low pressure mercury vapor lamp with an intensity of 60 $\mu W/cm^2$ at 2537 $\overset{\circ}{A}$. When the irradiation step had been completed, the e.p.r. spectrum was recorded at room temperature, oxygen was admitted to the sample at room temperature, and the e.p.r. spectrum was recorded at -190° C.

The zinc oxide samples were prepared from reagent grade zinc oxide and a high purity zinc oxide pigment (S.P. 500) that was manufactured by the New Jersey Zinc Company. A batch was also made by decomposing zinc carbonate. Most of the data were taken on the S.P. 500 that had been slurried in water, extruded into pellets, calcined 16 h in a stream of O_2, and degassed at 400° C for 2 h in a vacuum. Other samples of ZnO were degassed at 500° or 550° C.

The e.p.r. spectrum was recorded before and after oxygen was admitted to the sample. The oxygen, which was obtained from a commercial source, was an extra dry grade and had a minimum purity of 99.6%. It was used without further purification.

A conventional e.p.r. spectrometer which had a TE 102 mode cavity with a resonance frequency of 9.1 Gc/sec (X-band) was used in this work. Spectra were recorded at $20°$ or $-190°$ C. The magnetic field was measured with a nuclear magnetic resonance gauss meter. The g values were obtained by comparison with the value for the Cr^{+3} impurity in MgO (g = 1.9797). This isotropic Cr^{+3} impurity line was present in the MgO powder and was superimposed on the ZnO spectra by attaching a small single crystal of MgO onto the outside of the sample tube. The number of spins associated with a particular line was determined by numerically integrating the derivative spectrum and comparing with a standard. The standard was a small single crystal (110 μg for the MgO data, 13 μg for the ZnO data) of freshly recrystallized $CuSO_4 \cdot 5H_2O$ that was attached to the side of the sample tube with a commercial varnish. The vertical sensitivity variation of the cavity was experimentally determined so that the metal oxide line sample could be compared with the standard point sample. With the standard secured on the sample tube, both the sample and the standard were at the same temperature and in the same intensity of microwave field. An estimated error of ±20% in the number of spins per gram of sample was the result of errors in the weight of the standard, the numerical integrations, and the linear density of the sample.

Oxygen gas adsorption experiments were carried out by expansion from one known volume to another in a system equipped with a calibrated dc thermocouple gage. The final pressure of the system was usually less than 10^{-2} torr

and the adsorption was measured at room temperature. An error of $\pm$ 10 % was estimated for results from this measurement.

RESULTS

Oxygen on MgO

As described in two earlier papers,[12,14] ultraviolet or gamma irradiation of MgO produces paramagnetic surface defects (S' and S centers, respectively), which are believed to be electrons trapped at lattice vacancies. Upon exposure to oxygen at relatively low pressures (~20 μ) the room temperature e.p.r. spectrum of these defects rapidly disappeared. Samples of MgO that were first irradiated with ultraviolet light and exposed to oxygen showed a new spectrum when they were cooled to -190° C. This derivative spectrum is displayed in Fig. 1 with the indicated g values listed in table I. The intensity of the spectrum was less for MgO I than for MgO II, in accord with the relative intensities of the S' centers.[12]

Exposure to oxygen at room temperature and a pressure of 20 torr appreciably reduced the amplitude of the oxygen spectrum because of spin-spin interactions between the chemisorbed oxygen and physically adsorbed oxygen.[7] The oxygen spectrum shown in Fig. 1 could be reproduced by evacuating the sample at room temperature. Heating the sample to progressively higher temperatures in vacuum showed that the oxygen radicals[15] decreased in number fairly rapidly near 250° C. The weak line at g = 2.009 was destroyed much more rapidly than the main oxygen spectrum and is probably the spectrum of a different species. The remaining spectrum for the radical was almost entirely destroyed by heating the sample in vacuum to 300° C for 16 h. Ultraviolet irradiation, however, caused the S' center to reappear, and upon exposure

to oxygen the oxygen radical was again formed.

The results of the adsorption measurements along with the number of S' spins and oxygen spins are listed in table II. It may be observed that the number of oxygen radicals was 40% of the number of S' centers, but the number of oxygen molecules adsorbed on the sample equals the number of S' centers. To establish that irradiation actually enhanced the amount adsorbed, the oxygen adsorption (8.6 μliter O_2/g) was first carried out on a degassed, irradiated sample; then the sample was degassed for 4 h but not irradiated and the oxygen adsorption repeated (2.2 μliter O_2/g); finally, the sample was degassed for 2 h, irradiated, and the oxygen was adsorbed (5.3 μliter O_2/g). The initial pressure was the same for these three measurements. The evidence seems conclusive that the ultraviolet irradiation did enhance the amount of oxygen that was adsorbed.

<center>Oxygen on ZnO</center>

The spectrum of the radical produced when oxygen was adsorbed on degassed zinc oxide is shown in Fig. 2. A portion of this spectrum was published earlier by Kokes,[7] but in his paper the low field part was omitted. In agreement with the earlier work,[7] it was found that the number of oxygen spins did not increase linearly with the amount of oxygen adsorbed for residual gas pressures less than 0.5 μ. For higher residual gas pressures the number of oxygen radicals and the number of molecules adsorbed are listed in table II. The ratio of oxygen radicals to oxygen molecules adsorbed is slightly greater than one.

A spectrum comparable to that shown in Fig. 2 was observed when oxygen was adsorbed on all of the ZnO samples studied. If the ZnO was degassed at

500° C rather than at 400° C, the slow adsorption process became appreciable and the oxygen radical spectrum decreased in intensity upon standing at room temperature.

After a sample was exposed to oxygen and the characteristic spectrum observed, the zinc oxide was evacuated at 200° C for 30 min. While most of the spectrum decreased uniformly to about 5% of its original intensity, the line at $g = 2.013$ remained the same. This line undoubtedly represents a different species. Upon exposure to oxygen at room temperature the oxygen radical spectrum returned to only 15% of its original intensity.

DISCUSSION OF RESULTS

Identification of the E.P.R. Spectra

The identity of the species that contributes to the spectra of Fig. 1 and 2 (excluding the minor lines at $g = 2.009$ and $g = 2.013$) will be discussed first in terms of the e.p.r. parameters. The g tensors are the most distinguishing features of the spectra presented here since there is no hyperfine splitting with the oxygen-16 molecule. It seems clear that the low field portion of the oxygen spectrum for both metal oxides is a part of the whole spectrum. This point is demonstrated when the area above the base line for the derivative spectra is compared with the area below the base line. The two areas should be equal. With the good signal-to-noise ratio that was observed, these areas could be determined accurately and it is apparent that the low field portion of the spectra must be included. Hence, the g tensor has three unique symmetry axes. This can only be true for an atomic radical in orthorhombic symmetry, for a diatomic molecule in an external electric field that has a component perpendicular to the internuclear axis, or for a

polyatomic molecule. The latter case exists when CO_2 is adsorbed on irradiated MgO.[12]

The spectrum attributed to the O^- species has been observed in gamma-irradiated aqueous alkali-metal hydroxide glasses[16] and x-irradiated calcium fluorophosphate.[17] Each of these materials gives rise to a crystal field of axial symmetry. Qualitatively, the parameters can be explained by postulating a splitting of the 2p level such that p_z lies well above p_x and p_y. If this splitting is sufficiently large, g_{zz} should be approximately 2.0023 and $g_{xx} = g_{yy} \gg 2.0023$.[16] The experimental O^- g values are $g_{zz} = 2.002$ and $g_{xx} = g_{yy} = 2.070$ in the hydroxide glasses, and $g_{zz} = 2.0012$ and $g_{xx} = g_{yy} = 2.0516$ in the fluorophosphate. An orthorhombic field would also split the p_x and p_y levels; however, it seems improbable that the splitting would be such that $g_{yy} \simeq g_{zz} \simeq 2.002$, as is the case for the spectra shown in Figs. 1 and 2.

A similar situation exists for the O_3^- molecule ion. The spectrum of this ion has been observed in gamma-irradiated $KClO_3$[18] ($g_{zz} = 2.0025$, $g_{xx} = 2.0113$, and $g_{yy} = 2.0174$) and in NaO_3[19] ($g_{xx} = g_{yy} = 2.015$ and $g_{zz} = 2.003$). Here, too, the splitting is such that $g_{xx} \simeq g_{yy} \gg g_{zz}$, which is opposite to the case for the oxygen radical on MgO and ZnO.

Kanzig and Cohen have given the following theoretical g values for the O_2^- molecule ion:[20]

$$g_{xx} = g_e + 2\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} l \qquad (1)$$

$$g_{yy} = g_e\left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\lambda}{E}\left[-\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\Delta}{(\lambda^2 + \Delta^2)^{1/2}} + 1\right] \qquad (2)$$

$$g_{zz} = g_e\left(\frac{\Delta^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\lambda}{E}\left[\left(\frac{\lambda^2}{\lambda^2 + \Delta^2}\right)^{1/2} - \frac{\Delta}{(\lambda^2 + \Delta^2)^{1/2}} - 1\right] \qquad (3)$$

where y is chosen along a pπ function, and x is the internuclear axis. Here λ is an effective spin-orbit splitting of the molecule ion in the field at the surface; Δ and E are defined in Fig. 3. Further, l represents a correction to the angular momentum about x caused by the surface field; l is unity for the free molecule ion. The free ion would be in a $^2\Pi$ state.[19] If the symmetry about the molecular axis is partially removed, one of the $2p\pi_g$ orbitals will have a higher energy than the other.[19] The expected g values, to first order, will then depend on the ratio of the splitting of these two levels to the spin-orbit coupling coefficient. Zero splitting of the levels would give $g_{xx} = 4$ and $g_{yy} = g_{zz} = 0$; and for infinite splitting, with complete orbital quenching, $g_{xx} = g_{yy} = g_{zz} = 2$. The energy levels for an O_2^- molecule ion chemisorbed on a metal oxide surface would be expected to produce some intermediate g values.

From the experimental g values for the oxygen radical and Eqs. (1) to (3), the parameters λ/Δ, λ/E, and l were calculated. In table III these values are compared with the values for O_2^- in KCl[20] and in NaO_2.[19] Apparently the low symmetry at the surface of the metal oxides and the strong field gradients cause considerably more splitting of the $2p\pi_g$ levels while only slightly altering the $2p\pi_g$-$2p\sigma_g$ splitting. The increased correction

to the angular momentum, l, seems to indicate that the molecule is more restricted on the ZnO than on MgO or in KCl.

The possibility that the oxygen spectra can be attributed to a peroxide group (S-O-O·) has been suggested by Kokes.[7] Ingold and Morton have recently reviewed the g values for various oxy and peroxy radicals.[21] It is clear that the g tensors for the oxy and peroxy radicals are neither in agreement with the tensors for the spectra of oxygen on MgO or ZnO, nor can they be generated from Eqs. (1) to (3), with one exception. The exception was a radical that was formed in irradiated methanol and ethanol.[22] In addition, there is evidence[12] that the electrons trapped in MgO surface defects are in a metastable state with a rather high potential energy. Furthermore, the electron affinity of O_2 is about 1 eV.[2] It seems reasonable that the oxygen molecule upon adsorption would form an ionic-type bond, expecially since CO_2, which has a relatively low electron affinity, is able to capture these electrons.[11] The electron, however, may be less localized for the adsorbed oxygen on ZnO.

As a result of these considerations it is concluded that the radical observed on the surface of the metal oxide is O_2^-. The spectra are recorded near liquid nitrogen temperatures because of the short relaxation time of the species at room temperature. Thus it is not possible to determine from the e.p.r. data alone whether the endothermic reaction

$$O_2^- = O + O^- - 4.1 \text{ eV} \tag{4}$$

occurs on warming to room temperature. Winter[2] gives an energy of dissociation of 4.1 eV for this reaction, which indicates that the equilibrium would remain shifted far to the left, particularly on MgO where the number

of free electrons is limited. On ZnO, where the free electrons become more available on warming, the reaction

$$O + e^- = O^- + 2.1 \text{ eV} \tag{5}$$

must be considered and the possibility for dissociation of the O_2^- ion is somewhat more favorable.

Adsorption Studies

The gas adsorption and e.p.r. results for O_2 on MgO show that each adsorbed oxygen molecule interacts with an S' center electron, but only about 40% of these interactions result in an O_2^- molecule ion which contributes to the spectrum. The remaining 60% of the adsorbed O_2^- molecule ions may diffuse to surface paramagnetic impurity ions such as Fe^{+3} where spin-spin interactions broaden the individual lines that make up the spectrum. This broadening is, of course, accompanied by a decrease in the amplitude of the spectrum. While the error in the numbers of table II is relatively large, the semiquantitative considerations presented here are believed to be significant.

On ZnO, where a comparatively large number of free electrons have access to the surface, it appears that much of the oxygen adsorbs as O^- for residual pressures less than 0.5 μ (~0.2 μliter/g). This was first observed by Kokes[6] and is also shown in this experiment since the ratio of the O_2^- spin concentration to the concentration of oxygen molecules is much less than one at the low pressures. As more oxygen is adsorbed (~2 μliter/g), the ratio becomes slightly greater than one. If every oxygen molecule adsorbed as O_2^-, this ratio would be exactly one. The deviation of the experimental value from unity is within the estimated error. It is not possible to determine from these results how much of the original O^- is converted to O_2^- as more

gas is adsorbed. But if the assignment of the spectrum to the O_2^- molecule ion is correct, then 90% or more of the oxygen adsorbs as O_2^- for residual gas pressures from 1 to 20 μ. This was experimentally verified only for the initial adsorption step on samples degassed at 400° C.

Heating the ZnO sample to 200° C in vacuum apparently causes some irreversible effects since only a small fraction of the O_2^- radical reformed upon exposure to oxygen. At the elevated temperatures it is possible that some of the O_2^- is converted to $O^=$ before it can desorb.

CONCLUSIONS

1. Experimental evidence shows that oxygen adsorbs on degassed zinc oxide and ultraviolet-irradiated magnesium oxide as a species with an unpaired electron.

2. The e.p.r. spectra indicate that the oxygen adsorbs as the O_2^- molecule ion at a residual gas pressure greater than 1 μ.

FOOTNOTES

1. Stone, F. S.: Advan. in Catalysis 9,270 (1957).

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3. Hirota, K.; and Chono, M.: J. Catalysis 3, 196 (1964).

4. Barry, T. I.; and Stone, F. S.: Proc. Roy. Soc. (London) A255, 124
   (1960).

5. Kokes, R. J.: J. Phys. Chem. 66, 99 (1962).

6. Chemisorption is here defined as a type of adsorption that involves an
   exchange or a sharing of electrons between the adsorbate molecule and
   the adsorbent.

7. Kokes, R. J.: Proceedings of the Third International Congress on Cataly-
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11. Kohn, H. W.: J. Chem. Phys. 33, 1588 (1960).

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    on Magnesium Oxide with Electron Paramagnetic Resonance Techniques).

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15. Ingram's definition of a radical is used here: A radical is a molecule,
    or part of a molecule, in which the normal chemical binding has been
    modified so that an unpaired electron is left associated with the sys-
    tem. See, for example, Ingram, D. J. E., "Free Radicals as Studied by
    Electron Spin Resonance", Butterworths Scientific Publications, London,
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19. Bennett, J. E.; Ingram, D. J. E.; and Schonland, D.: Proc. Phys. Soc. $\underline{A69}$, 556 (1956).

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21. Ingold, K. U.; and Morton, J. R.: J. American Chem. Soc. $\underline{86}$, 3400 (1964).

22. Sullivan, P. J.; and Koski, W. S.: J. American Chem. Soc. $\underline{85}$, 384 (1963); $\underline{86}$, 159 (1964).

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TABLE I. - TABLE OF g VALUES

Material	g_{xx}	g_{yy}	g_{zz}
Oxygen on untraviolet irradiated MgO	2.077 ± 0.001	2.0011 ± 0.0003	2.0073 ± 0.0003
Oxygen on ZnO	2.051 ± 0.001	2.0020 ± 0.0003	2.0082 ± 0.0003
O_2^- from NaO_2[16]	2.175 ± 0.005	2.000 ± 0.005	2.000 ± 0.005
O_2^- in KCl[17]	2.4359	1.9512	1.9551

TABLE II. - COMPARISON OF RADICAL CONCENTRATION WITH O_2 ADSORBED

	$\dfrac{S' \text{ centers}}{g \text{ MgO}}$, $\times 10^{-16}$	$\dfrac{O_2 \text{ molecules}}{g \text{ metal oxide}}$, $\times 10^{-16}$	$\dfrac{\text{Oxygen radicals}}{g \text{ metal oxide}}$ $\times 10^{-16}$
Ultraviolet-irradiated MgO II	21	23	8.4
ZnO (S.P. 500) No. 1	--	3.2	4.6
No. 2	--	4.1	4.5
No. 3	--	3.0	3.9

TABLE III. – VALUES FOR λ/Δ, λ/E, AND l

CALCULATED FROM EXPERIMENTAL g VALUES

AND EQS. (1), (2), AND (3)

Material	λ/Δ	λ/E	l
Oxygen on ultraviolet irradiated MgO	0.035	0.0032	1.04
O_2^- on ZnO	.017	.0032	1.22
O_2^- in KCl[17]	.23	.0025	1.04
O_2^- from NaO_2[16]	.086[a]	------	----

[a]Calculated after assuming $l = 1.04$.
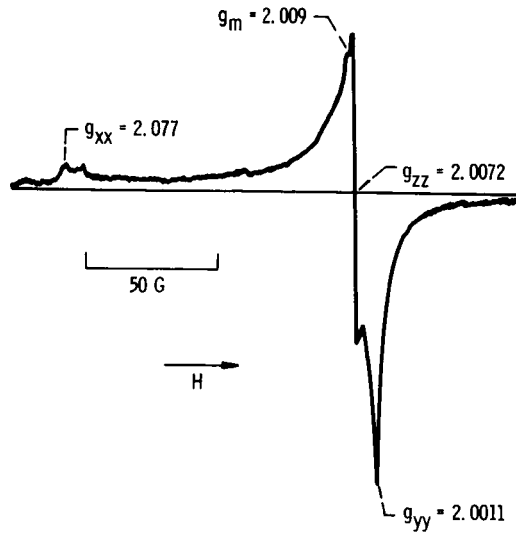
Fig. 1. - Derivative spectrum of oxygen adsorbed on
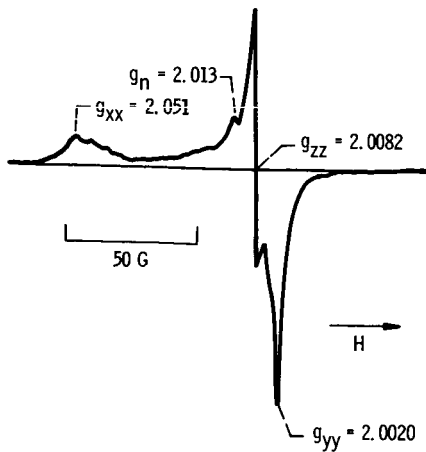ultraviolet-irradiated MgO. Spectrum is recorded at
-190° C.

Fig. 2. - Derivative spectrum of oxygen adsorbed
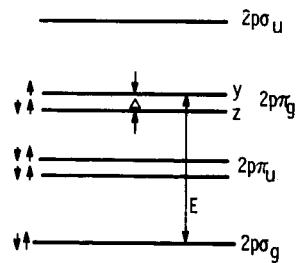on degassed ZnO. Spectrum is recorded at
-190° C.

Fig. 3. - Occupation of electronic
levels of O_2^- in ground state.
(After Kanzig and Cohen[20].)