The Identification of O_2^- adsorbed on Magnesium Oxide

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THE adsorption of oxygen on metal oxides has been often investigated,[1] but the identities of the adsorbed oxygen species are not well defined. Many species such as O_3^-, O_2^-, O^-, and covalently bonded oxygen have been suggested on various oxides,[2] but no unambiguous identification has been possible. Electrical conductivity and e.s.r. measurements[3] have shown that in some cases a charge-transfer step is involved when oxygen is adsorbed on the surface and for ZnO and MgO the presence of O_2^- has been suggested. The identification is not very clear since no hyperfine interaction is resolved and the asymmetry of the g factor in diatomic ions is determined by the local crystal field, *i.e.* at the surface. Here is described the results of experiments with the isotopic labelling (^{17}O isotope, spin 5/2) of oxygen to allow a positive identification of O_2^- on the surface of magnesium oxide.

Samples of MgO with a large concentration ($\sim$1%) of electron excess surface centres, analogous to F centres, were formed by the γ-irradiation or photolysis of the high surface-area oxide in presence of hydrogen.[4] These centres (S and S_H) are paramagnetic and react irreversibly with oxygen at 20°; the blue colour is destroyed and a new e.s.r. signal is obtained. The spectrum after addition of $^{16}O_2$ is not simple and can best be interpreted in terms of one species in several well defined, but different, sites of varying thermal stability; this is not unexpected since more than one type of surface centre is known to be present initially. The spectrum of the adsorbed oxygen must be described by several anisotropic g tensors and typical values are $g_1 = 2{\cdot}0777$, $g_2 = 2{\cdot}0089$, and $g_3 = 2{\cdot}0018$.

A similar experiment was repeated with oxygen enriched to 58 atom % of ^{17}O and a spectrum with a rich hyperfine structure was obtained (Figure).

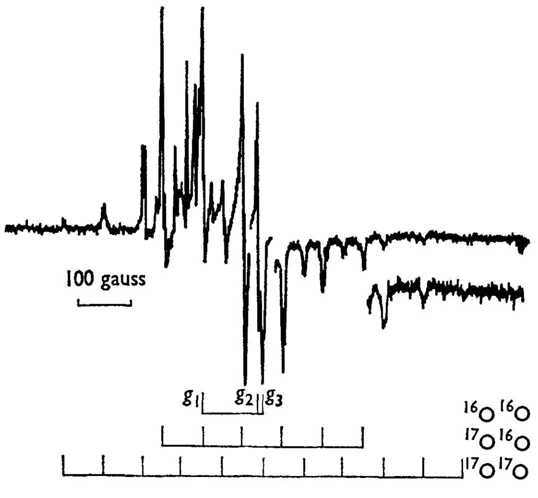

FIGURE. *The first derivative e.s.r. spectrum of* O_2 *on the surface of high surface-area* MgO. *The field increases from left to right and the gain has been reduced by times 5 for the central line; a small portion of the high-field spectrum is overmodulated to show the outermost lines. For clarity no attempt has been made in this diagram to insert levels for the lines around* g_1.

Unirradiated samples treated at the same time, in the same way, gave no e.s.r. signal and clearly the structure observed in the Figure arises from an adsorbed oxygen species. A mass spectrometric analysis of the oxygen used indicates a composition of 18·4% $^{16}O^{16}O$, 48·5% of $^{17}O^{16}O$, and 33·2% of $^{17}O^{17}O$. The height of the central line (g_2,g_3) is $\sim$20% of that expected from a reaction with $^{16}O_2$ and this agrees well with the expected proportion of $^{16}O_2$ in the $^{17}O_2$; giving strong evidence that the species is diatomic and not monatomic. A calculation of the various possible interactions suggests that a very complex hyperfine pattern is to be expected; but, fortunately, both oxygen atoms in the diatomic species appear to have a very similar hyperfine interaction and on this assumption $^{17}O^{16}O$ with $I = 5/2$ will give six lines and $^{17}O^{17}O$ will give eleven lines for each principal value of the hyperfine tensor. The Figure shows that the lines centred around g_2 and g_3 form two sets and can be assigned to species $^{17}O^{16}O$ and $^{17}O^{17}O$ with a measured hyperfine splitting at 9·3 GHz of 77 ± 2 gauss; a further set of lines appears about g_1, with a splitting of 15 ± 2 gauss. The data cannot be easily fitted by assuming an axial hyperfine tensor and a completely asymmetric tensor of the form $A_{xx} = 77 \pm 2$, $A_{yy} = 0 \pm 4$ and $A_{zz} = 15 \pm 2$ gauss is thought to be suitable, where A_{xx}, A_{yy}, and A_{zz} are uncorrected measured values. Spectra obtained at 35·2 GHz support this assignment and confirm the existence of several sites for the oxygen species. It is clear that at 9·3 GHz the influence of second-order hyperfine terms will be significant and these have not been taken into account in the present treatment. A doubling of many of the lines in the Figure arises from a small interaction with a nearby proton.

The hyperfine tensor described above is similar to that obtained very recently by Kanzig[5] for O_2^- in single crystals of KCl and the evidence above shows clearly that we must have a diatomic oxygen species, which both from the method of preparation and from theoretical arguments[6] appears to be O_2^-. The resolution obtained is very good and the directions of the principal values of the g and A tensors must be very similar. The g_1 direction lies along the internuclear axis[7] and A_{zz} will have a similar direction because of the symmetry of the spectra; the largest hyperfine interaction A_{xx} will lie along the $2p\pi_g$ orbital containing the unpaired electron; A_{yy} and g_2 are in the remaining mutually perpendicular direction. Some idea of the unpaired electron spin distribution can be obtained by assuming an axial form for the dipolar term and using the caculated atomic value of 51·4 gauss for B_0,[8] an approximate value for the spin density ρ_p in the $2p\pi_g$ orbital is given by $2B_{\text{obs}}/B_0$. This gives a value $\rho_p = 0{\cdot}9$ indicating that the unpaired electron is largely localised in the $2p\pi_g$ orbitals

Since no significant interaction with $^{25}Mg^{2+}$ ions in the surface is obtained either for $^{16}O_2$ or $^{17}O_2$, the O_2^- ion must be oriented to give a minimum interaction of the $2p\pi_g$ orbitals with the metal ions.

The electron affinity of oxygen[9] is 0·46 ev and the reaction of oxygen with an electron trapped at the surface to give O_2^- is to be expected. The O_2^- ions formed in this way are quite stable at room temperature and do not exchange detectably with the oxide ions of the lattice in several months. In contrast, similar O_2^- ions formed by the irradiation of MgO in the presence of oxygen, exchange completely with the lattice oxide ions.[2b] It is likely that the e.s.r. signal observed on ZnO after oxygen admission[3b] is also due to O_2^-. Similar work is at present in progress on several metal oxides.

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