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Electron Spin Resonance of Manganese Ions on Magnesium Oxide

A. J. TENCH
Chemistry Division, A.E.R.E., Harwell, England

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The study of surface properties of oxides using transition metal ions as a probe to investigate the environment of surface ions is potentially a very valuable technique; however, the interpretation of the results can present some difficulties since the location of the paramagetic ions observed is often not known. The reactivity of MgO doped with manganese[1] has been studied previously both by ESR and chemisorption; the results indicate that the Mn^{2+} ion is present in a variety of environments. A recent paper by Yamamura *et al.*[2] reports an ESR study of the behaviour of the Mn^{2+} ion on the surface of MgO. In this note, we wish to suggest an alternative interpretation of the data which indicates that not all the Mn^{2+} is on the surface.

In the latter paper,[2] it is assumed that Mn^{2+} ions initially adsorbed on the surface remain on the surface throughout the various treatments *in vacuo* and in oxygen *etc.*, even when the treatments are carried out at 1000°C. A variation in the A and D values (the hyperfine splitting and zero field splitting values of the Hamiltonian for Mn^{2+}) is attributed to changes of environment at the surface. We suggest that the observed changes in A and D could arise from a changing environment of the Mn^{2+} due to the onset of ionic diffusion processes above 500°C which allow the diffusion of some of the Mn^{2+} ions into substitutional sites in the bulk oxide, where the environment is more nearly octahedral and is characterised by lower D values. The existence of this ionic diffusion phenomena at 600°C has been well characterised,[1] and would be expected, since the ionic sizes of Mg^{2+} and Mn^{2+}, and Mn^{3+} are similar (0.65, 0.80, and 0.66 Å respectively[3]).

Up to 300°C, *in vacuo*, the MgO surface is covered with close to a monolayer of hydroxyl groups[4] and the environment of the manganese ions will not be characteristic of the oxide surface. Heating to 500—600°C reduces the OH^- coverage to less than 10% of a monolayer with the desorption of water. In the paper the authors do not indicate how the ESR spectral intensity was measured but the loss of Mn^{2+} intensity between 300—600°C could arise from the oxidation of Mn^{2+} ions to Mn^{3+} by the water vapour although this appears unlikely, and it seems more probable that Mn^{2+} ions on the bare surface experience a considerable crystal field effect giving rise to large D terms and an apparent loss in Mn^{2+} concentration. Heating the samples at higher temperatures permits the diffusion of manganese ions into the bulk where the environment is more nearly octahedral and the D values will be progressively smaller away from the surface thus giving an apparent increase in concentration of Mn^{2+}. The extremely broad spectrum shown in Fig. 1(b)[2] after treatment at 1000°C for 4 hr *in vacuo* can be interpreted by assuming the broad wings arise from surface Mn^{2+} ions which have a D value of >100 gauss whilst the sharper lines are more characteristic of ions incorporated into the bulk.

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[1] D. Cordischi, R. L. Nelson, and A. J. Tench, *Trans. Faraday Soc.*, **65**, 2740 (1969).

[2] T. Yamumura, A. Hasegawa, Y. Yamata, and M. Miura, This Bulletin, **43**, 3377 (1970).

[3] J. E. Wertz and P. Auzins, *Phys. Rev.*, **106**, 484 (1957).

[4] P. J. Anderson, R. F. Horlock, and J. F. Oliver, *Trans. Faraday Soc.*, **61**, 2754 (1965).

The influence of added gases on the Mn^{2+} spectrum can be explained in a similar manner. For example, previous work[1] has shown that Mn^{2+} ions on a surface can be oxidised very easily with oxygen at comparatively low temperatures and if all the Mn^{2+} was present on the surface as isolated ions, we would expect the intensity to drop to zero after treatment at 300°C. This apparently does not occur and the observed change in D values (Fig. 7)[2] can be explained by a progressive oxidation of the Mn^{2+} ions inwards from the surface and the remaining ions have progressively lower D values. At the same time, some line narrowing would occur due to the reduction in the Van Vleck dipole-dipole interaction[5] as the Mn^{2+} ions are converted to Mn^{3+}. The effect on the hyperfine A values is not so clear, but it seems likely that those Mn^{2+} ions remote from the surface will have an A value close to that reported for single crystals, whereas, those ions near the surface may have a slightly higher value, similar perhaps, to that observed in CaO where the ionic spacing is a little higher. However, this is not regarded as being very significant.

The results reported for Mn^{2+} on silica gel suggest that in this case the Mn^{2+} ion is not incorporated into the silica gel and remains on the surface. When the surrounding hydroxyl groups are removed by thermal treatment *in vacuo* no detailed ESR structure of the Mn^{2+} ion can be resolved and only a broad line is observed due to either the high D values from the surface field or the formation of aggregates of ions. This latter alternative certainly influences the susceptibility studies on MgO, which were carried out using a doping level of 3% manganese ion,[2] and makes any comparison with the ESR studies difficult. It is possible that ion pair formation (with very high D values[6]) also influences the results observed in the ESR study reported by Yamamura[2] where levels of 3000 ppm were used but it is regarded as very unlikely to occur in the earlier studies[1] where doping concentrations of <250 ppm were used.

We think that ESR studies of the Mn^{2+} can be used as a valuable probe of surface properties but the possible diffusion of the ion needs to be considered, and in addition, the concentration of the dopant must be kept low if the formation of ions pairs is to be ignored.

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[5] C. Kittel and E. Abrahams, *Phys. Rev.*, **90**, 238 (1953).

[6] B. A. Coles, J. W. Orton, and J. Owen, *Phys. Rev. Lett.*, **4**, 116 (1960).