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The Electron Spin Resonance of the Mn^{2+} Ion on the Surface of Magnesium Oxide

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The behavior of the Mn^{2+} ion on the surface of MgO was studied by using the ESR technique. The powder of MgO, the surface of which was doped with the Mn^{2+} ion, was calcined at different temperatures from 100 to 1000°C in a vacuum, and then the ESR spectra were observed at room temperature. It was noticed that the spectral intensity showed a minimum at about 500°C, that the zero-field splitting parameter, D, increased with the temperature, and that the hyperfine coupling constant, A, decreased enormously at about 700°C. The environments around the Mn^{2+} ion on the surface of MgO were discussed on the basis of these results. When H_2, CO, or O_2 was added after the calcination, the D and A values changed in the temperature range above 500°C. Especially when O_2 was introduced, the D value fell to zero upon treatment at 1000°C. The crystal field around the Mn^{2+} ion and the bonding between the Mn^{2+} ion and its environments were discussed by taking into account the results of the magnetic-susceptibility measurements of the manganese ion on MgO.

Many studies have been done on the ESR of the Mn^{2+} ion doped in the bulk of solids. These have dealt with the phase transition,[1] the defects,[2] the crystal field of solids,[3] *etc.* Several studies have also been done on the ESR of the Mn^{2+} ion on the surfaces of ion-exchange resin[4] and zeolite.[5-7] The character of the bonding between the Mn^{2+} ion and the adsorbent, the kind of adsorption site,[5,6] and the crystal field around the Mn^{2+} ion[7] have been discussed in these studies.

In this paper, the Mn^{2+} ion is selected as a probe for the surface of magnesium oxide in the expectation that information about the Mn^{2+} ion and its environments on the surface will be obtained from the ESR spectrum of the ion. The information, if any is obtained, may also be useful in discussing the surface reactivity of magnesium oxide doped with transition metal ions.[8,9] The ESR spectrum of the Mn^{2+} ion offers several parameters: the spectral intensity, the hyperfine coupling constant, and the zero-field splitting parameter. The intensity of the spectrum, which is proportional to the concentration of the Mn^{2+} ion, can be taken as a measure of the oxidation or reduction of the manganese ion, because the ion takes different valencies. The hyperfine coupling constant, as revealed by van Wieringen[10] and Matsumura,[11] is correlated with the ionic character in the bond between the Mn^{2+} ion and its environments. The zero-field splitting parameter gives information about the crystal field, that is, the symmetry of the environments around the Mn^{2+} ion.

Changes in the valence state and in the environment of the manganese ion on the surface of magnesium oxide, resulting from the thermal treatment and the introduction of various gases, were investigated by the ESR technique and by magnetic-susceptibility measurements.

Experimental

The powder of magnesium oxide was prepared by the calcination of magnesium hydroxide, which had itself been obtained from the methylation of magnesium

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metal, followed by the hydrolysis of the methylate, in an atmosphere of oxygen for 4 hr at 700°C. The magnesium metal (99.9999%) was supplied by the Material Research Corporation (U. S. A.). The calcination temperature is sufficiently high to bring about the complete dehydration of magnesium hydroxide.[12,13] The resulting magnesium oxide gave none of the ESR spectrum of paramagnetic species.

Silica gel was prepared from water glass and sulfuric acid and was calcined at 500°C for 5 hr.[14]

The powders of magnesium oxide and silica gel were immersed into an aqueous solution of manganese nitrate, and the products were dried at 110°C for 24 hr in air. The amount of the adsorbed Mn^{2+} ion is 0.3 wt% of the Mg^{2+} ion. As the surface area of the magnesium oxide is determined to be 69 m^2/g by the B. E. T. method from the nitrogen adsorption, the mean distance between Mn^{2+} ions is estimated to be about 11.4 Å when the Mn^{2+} ions are distributed homogeneously. If the latter situation is granted, the contribution of the dipole-dipole interaction between Mn^{2+} ions is assumed to be negligible in the ESR spectra and the features of the spectra may be treated on the basis of the crystal field around the Mn^{2+} ion.

These specimens were calcined at various temperatures from 100 to 1000°C for 4 hr in a vacuum and were exposed to such gases as oxygen, hydrogen, and carbon monoxide at each temperature and at 0.5 atm. Oxygen gas was also introduced under the same conditions as above after the magnesium oxide containing the Mn^{2+} ion on its surface had been calcined at 1000°C.

The specific susceptibilities of the manganese ion on the magnesium oxide (Mn/Mg=0.03 by weight, ten times the concentration in the case of the ESR measurement), treated at room temperature and at 500, 800, and 1000°C for 4 hr in a vacuum (10^{-4}—10^{-5} Torr), were measured to give information as to the valence state of the manganese ion. The specific susceptibility of the manganese oxide prepared by heating manganese nitrate at 110°C for 24 hr was also determined after treatment under the same conditions. The measurements of the specific susceptibility were carried out at room temperature by the Faraday method, using a Cahn RG electrobalance.

Estimation of the *D* Value and the Ionicity.

Since the Mn^{2+} ion has $S=5/2$ and $I=5/2$ and since its ground state is ^6S, the hyperfine and fine structures are expected to occur in the ESR spectrum. However, since the specimen used is in a powder state and has a small zero-field splitting, the observed spectrum of the Mn^{2+} ion on the surface of magnesium oxide consists of six hyperfine structures due to the allowed transition, $\Delta m_I=0$, and the weak lines, observed between hyperfine structures, due to the forbidden transitions, $\Delta m_I=\pm 1$, as may be seen in Fig. 1.

The following two methods have been proposed for the estimation of the zero-field splitting parameter, *D*, or the distortion of the crystal field from cubic symmetry on the basis of the ESR spectrum of the Mn^{2+} ion. One is Allen's method,[15] which utilizes the relation, shown in Fig. 2, between the value of *D* and the ratios of the intensity of the hyperfine line of $m_I=-5/2$ to those of $m_I=-1/2$ and $m_I=-3/2$. An alternative method is to use the intensity ratio of the forbidden lines to the allowed lines; this method has been proposed by Bleaney and Rubins[16] and by de Wijn and van Balderen.[17] Though the value estimated by this method is in considerable agreement with that ob-

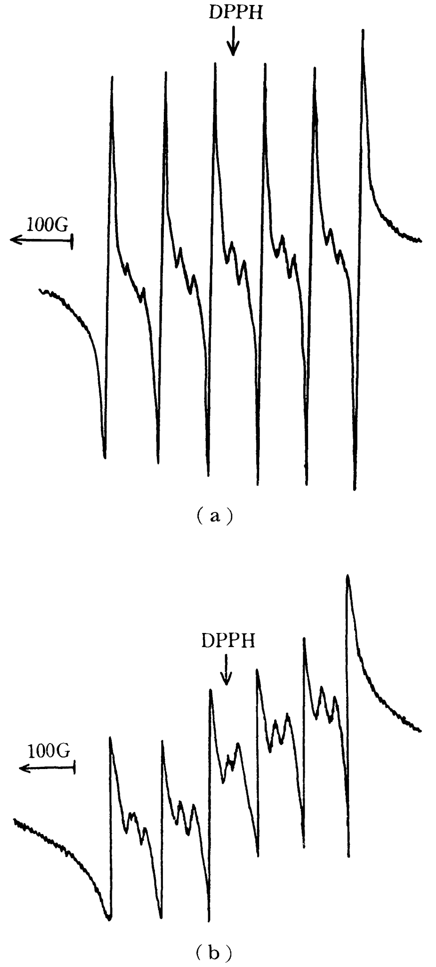

Fig. 1. ESR spectra of Mn^{2+} ion on magnesium oxide, treated (a) at 110°C for 24 hr in air and (b) 1000°C for 4 hr in a vacuum.

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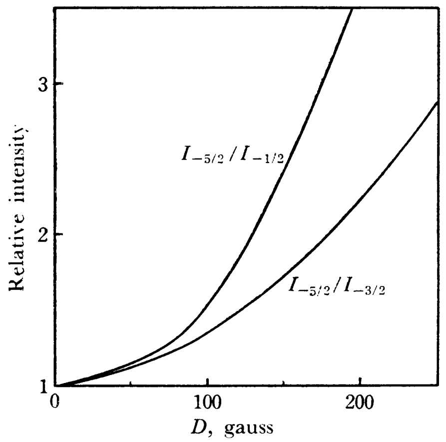

Fig. 2. The relations between relative intensity and D value proposed by Allen.[15]

tained by Allen's method, this method is not adopted in the present study since the estimation of the intensities of the forbidden lines is accompanied by a rather large error.

An almost linear relation between the coupling constant of the hyperfine structure, A, and the ionicity of the bonds between the Mn^{2+} ion and the environments has been proposed by Matsumura. It is shown in Fig. 3,[11] where the ionicity has been calculated from the electronegativities of the Mn^{2+} ion and the surrounding negative ions and the number of the latter ions, after Pauling.[18] The ionicity of the bonds was, therefore, estimated in terms of this relation.

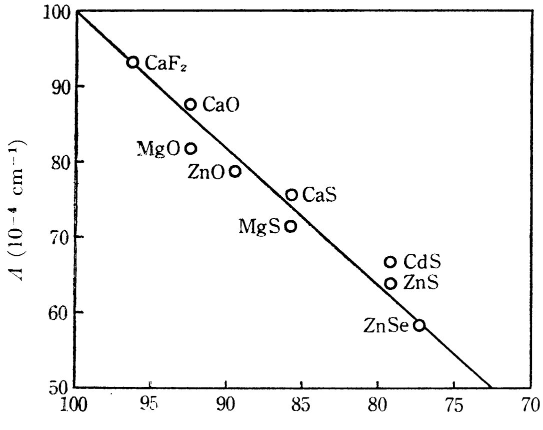

Fig. 3. The relation between A value and ionicity proposed by Matsumura.[11]

Results and Discussion

ESR Spectra of the Mn^{2+} Ion on the Surface of MgO in Air at Room Temperature. After the magnesium oxide containing the Mn^{2+} ion on its surface had been dried at 110°C for 24 hr in air, the ESR spectrum was measured at room temperature (Fig. 1). The zero-field splitting parameter, D, was evaluated to be 46 gauss from the relative intensities of their spectral lines by using the relations shown in Fig. 2. The ionicity was estimated to be 90% from the observed value of the hyperfine coupling constant, A, (89.4 gauss) and Fig. 3. The value of g was also determined to be 2.0022.

Effect of the Calcination Temperature in a Vacuum on the ESR Spectrum of the Mn^{2+} Ion on MgO. The intensity of the ESR spectrum of the Mn^{2+} ion on magnesium oxide changed with the calcination temperature, as is shown in Fig. 4, while the g value hardly changed at all from 2.0022. The intensity should be proportional to the concentration of the Mn^{2+} ion, since the Mn^{3+} ion does not participate in the ESR spectrum because of the strong spin-lattice interaction and since the spectrum of the Mn^{4+} ion, with $g=1.9980$ and $A=76$ gauss, is considerably different from those obtained here.[19-21] Accordingly, the concentration of the Mn^{2+} ion falls remarkably with a rise in the temperature, reaches a minimum at about 500°C,

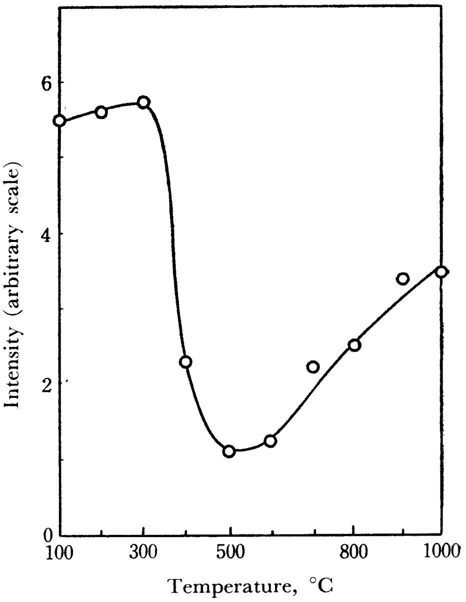

Fig. 4. The variation in ESR spectral intensity of Mn^{2+} ion by the treatment at different temperatures.

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[18] L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York (1940), p. 69.

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and then increases to some extent with a further rise in the temperature. On the other hand, the calcination up to 1000°C brings about a small decrease in the surface area of the magnesium oxide, from 69 to 60 m^2/g.

Specific Susceptibility. The specific susceptibilities of magnesium oxide containing the Mn^{2+} ion on the surface and of manganese oxide prepared from manganese nitrate were measured after the samples had been calcined at 500, 800, and 1000°C. The results are shown in Table 1.

TABLE 1. SPECIFIC SUSCEPTIBILITY OF MANGANESE OXIDE TREATED AT VARIOUS TEMPERATURES IN A VACUUM

	χ*			
	Room temp.	500°C	800°C	1000°C
Manganese on MgO	120.88	87.50	134.66	151.51
Manganese oxide	30.03	80.46	55.03	50.81

* unit of χ: 10^{-6} cgs emu

TABLE 2. SPECIFIC SUSCEPTIBILITY OF VARIOUS MANGANESE OXIDES

	χ*	Ref.
MnO	75.9	22
Mn_3O_4	55.8	22
Mn_2O_3	69.0	22
MnO_2	38.4	22
^{55}Mn	9.9	22
8MnO-5MgO	91.63	23
2MnO-11 MgO	126.87	23

* Unit of χ: 10^{-6} cgs emu

The value of the former is considerably decreased by the calcination at 500°C and then increased by the treatment in the higher-temperature range; the values at 800 and 1000°C are rather higher than that at room temperature. On the other hand, the value of the latter exhibits a remarkable increase at 500°C and then decreases with a further rise in the temperature. For comparison with these results, the values of various manganese oxides and of manganese oxide in magnesium oxide (*m*MnO-*n*MgO) are presented in Table 2.[22,23]

The electronic configurations of various manganese ions are as follows:

$Mn^{1+} \cdots (3d)^5(4s)$ $\quad$ $Mn^{3+} \cdots (3d)^4$

$Mn^{2+} \cdots (3d)^5$ $\quad$ $Mn^{4+} \cdots (3d)^3$

The specific susceptibility, therefore, should decrease with the increase in the valence of the manganese ion.

The data in Tables 1 and 2 and the results shown in Fig. 4 lead us to the following speculation: the manganese ions on magnesium oxide are mainly bivalent at room temperature, but some of them are oxidized to a higher valence state, namely Mn_2O_3, by calcination at 500°C in a vacuum, and these oxidized ions are in turn reduced to bivalence or, further, to univalence when treated at 800 and 1000°C. On the other hand, as may be seen from these tables, the manganese ion in manganese oxide may be Mn^{4+} at room temperature, and it may then be reduced to Mn^{2+} by heating at 500°C in a vacuum. This discrepancy may be attributed to the influence of the ground.

Variations in *D* and *A* Values. The values of *D* and *A* of the Mn^{2+} ion on magnesium oxide were estimated to be as is shown in Figs. 5 and 6 after calcination at 100, 300, 500, 800, and 1000°C in a vacuum, followed by the addition of hydrogen, carbon monoxide, or oxygen at each temperature.

The *D* value increases with the temperature, particularly abruptly from 500°C. When hydrogen is added after the calcination, the value also increases with the calcination temperature above 500°C, but the value is low as compared with that in the absence of hydrogen. The introduction of carbon monoxide causes the value to reach a maximum near 500°C. In the case of oxygen, it changes slightly from room temperature to 500°C, but thereafter it falls to almost zero at 1000°C.

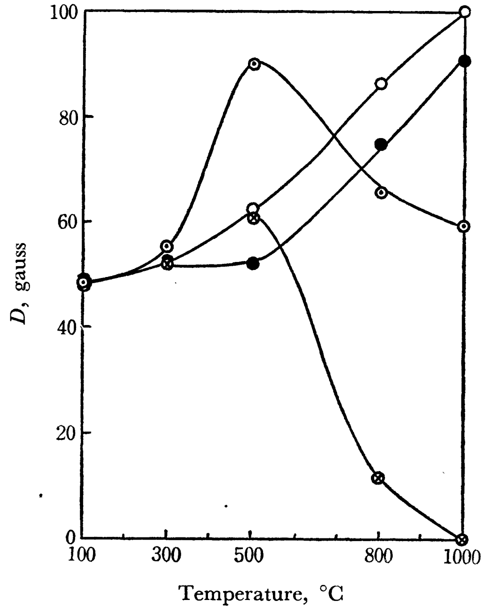

Fig. 5. The variations in *D* value by the addition of gases at different temperatures; ○: in a vacuum, ●: H_2, ⊙: CO, and ⊗: O_2.

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[22] International Critical Tables, **6**, 355, 357.

[23] H. Bizette and B. Tasai, *Compt. Rend.*, **217**, 444 (1943).

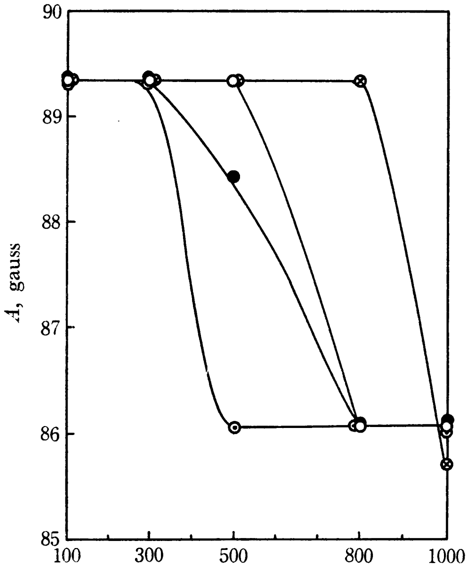

Fig. 6. The variations in A value by the addition of gases at different temperatures. Symbols in this figure have the same meaning as those in Fig. 5.

Upon calcination in a vacuum, the value of A decreases remarkably above 500°C and remains constant, 86.2 gauss, at temperatures higher than 800°C. The bonding between the Mn^{2+} ion and its surroundings, accordingly, has a high degree of covalent character in the temperature range above 500°C. When hydrogen is added, the A value is steadily reduced by the treatments from 300 to 800°C, and then it remains constant, 86.2 gauss. By the addition of carbon monoxide, however, the A value already reaches to 86.2 gauss at 500°C and remains unchanged when treated at higher temperatures. When oxygen was introduced, the A value hardly changes till 800°C, but it reaches its lowest value, 85.7 gauss, at 1000°C.

Two effects are entangled with each other in the results of these experiments; one is due to the calcination, and the other, to the introduction of gas at different temperatures. Therefore, we attempted to remove the former effect by precalcining the magnesium oxide with the Mn^{2+} ion at 1000°C for 4 hr in a vacuum. The zero-field splitting parameter, D, was estimated when oxygen was added at different temperatures from 100 to 1000°C, as is shown in Fig. 7. The value falls abruptly to zero upon treatment at a temperature above 500°C. From the results, it is conceivable the oxygen is coordinated to the Mn^{2+} ion and that the crystal field around the ion is less distorted and becomes almost cubic-symmetrical at 1000°C. Such a cubic symmetry may be attributed to the cubic bulk structure of magnesium oxide.

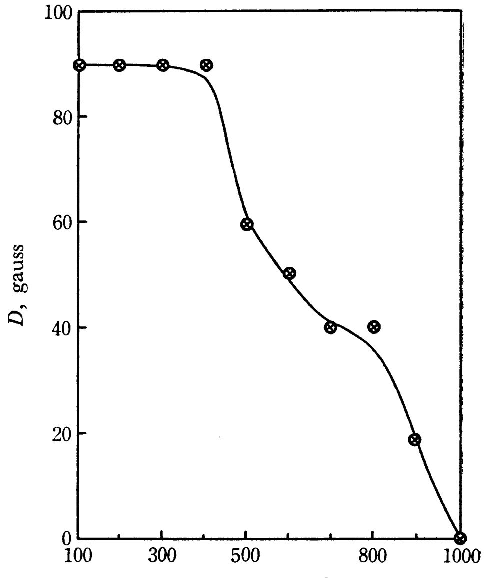

Fig. 7. The variations in D value by the addition of O_2 at different temperatures for the specimen precalcined at 1000°C.

The Mn^{2+} Ion on the Surface of Silica Gel. The ESR spectrum of the Mn^{2+} ion on the surface of silica gel was also investigated. The values of D, A, and ionicity are, respectively, 72 gauss, 98 gauss, and 95%, these values being obtained from the spectrum (Fig. 8) of the sample dried at 110°C for 24 hr in air. By a comparison of these values with those on magnesium oxide under the same conditions, it may be concluded that, on the surface of silica gel, the bonding between the Mn^{2+} ion

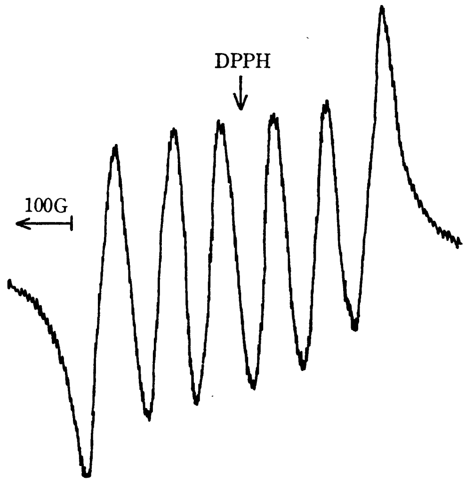

Fig. 8. ESR spectrum of Mn^{2+} ion on silica gel treated at 110°C for 24 hr in air.

and its environments has a higher degree of ionic character and that the crystal field around the Mn^{2+} ion is more distorted from the cubic symmetry than on the surface of magnesium oxide. The calcination of the sample in the same way as in the case of magnesium oxide brings about a complete disappearance of the six hyperfine structures of the Mn^{2+} ion above 300°C. This may be attributed to the fact that the signal becomes broad and smeared out with a rise in the temperature because of an increase in the D value. Even when hydrogen, carbon monoxide, and oxygen were introduced, the six hyperfine structures did not come out again.

Behavior of the Mn^{2+} Ion on MgO. We will discuss the behavior of the adsorbed manganese ion on the basis of the results of the ESR and susceptibility measurements. When the sample is treated up to 300°C, the coupling constant, A, is comparatively large, which means that the bonding between the Mn^{2+} ion and the environments has a high degree of ionic character, and the zero-field splitting parameter, D, is relatively small. The Mn^{2+} ion, therefore, combines weakly with magnesium oxide and surface hydroxyl groups. Upon treatment at 500°C, however, the distortion of the crystal field increases and the A value decreases; that is, the bonding of Mn^{2+} has a low degree of ionic character. Furthermore, both the ESR spectral intensity shown in Fig. 4 and the susceptibility measurement shown in Table 1 show that the concentration of the Mn^{2+} ion reaches a minimum. This may be interpreted as follows: the Mn^{2+} ion combines with oxygen as a result of the removal of the surface hydroxyl groups by a condensation dehydration, and some Mn^{2+} ions assume a higher valence state, Mn^{3+}. With the treatments at higher temperatures, the distortion of the crystal field increases and the bonding of the Mn^{2+} ion comes to take a much lower ionic character, thus reflecting the strong covalent bonding with oxygen. The increase in both the intensity of the ESR spectrum and the specific susceptibility above 500°C is caused by the elimination of oxygen, accompanied by the reduction of Mn^{3+} to Mn^{2+} or, partially, that of Mn^{2+} to Mn^{1+}. The possibility of the existence of Mn^{1+} may be speculated from the higher value of the susceptibility and the lower intensity of the ESR spectrum at 1000°C than those at room temperature. The presence of the Mn^{2+} ion may also mean that there is little oxygen on the surface of magnesium oxide at 1000°C.

It is somewhat doubtful that the information with regard to the surface of magnesium oxide obtained from the ESR spectra of Mn^{2+} ion can be directly applied to a discussion of its clean surface. Nevertheless, the cationic site, namely, the Mg^{2+} ion, on the surface of magnesium oxide doped with transition metal ions may be in a situation analogous to that of the Mn^{2+} ion observed in the present study, since the adsorption capacity of magnesium oxide increases remarkably upon the addition of a trace of transition metal ions to the bulk of magnesium oxide.[8,9]

The addition of hydrogen after the calcination in a vacuum leads to an increase in the distortion of the crystal field above 500°C, as is shown in Fig. 5. The value of A falls steadily above 300°C, as is shown in Fig. 6. This may be interpreted as follows: a part of the added hydrogen combines with the oxygen adjacent to the Mn^{2+} ion to form water, and then the Mn^{2+} ion enters into combination with the water molecules and the oxygen atoms of magnesium oxide in such a manner that the distortion of the crystal field around the Mn^{2+} ion is relatively small and the bonding bears a high degree of covalent character.

When carbon monoxide is introduced into the system, the A value decreases and the D value reaches a maximum at 500°C. The carbon monoxodie, having a greater reduction ability than hydrogen, easily draws out the oxygen coordinated weakly to the Mn^{2+} ion, and the ion, in turn, combines strongly with the oxygen on the surface of magnesium oxide and is subject to a large distortion of the crystal field from cubic symmetry. Such a distortion may be reduced by a coordination of carbon monoxide or carbon dioxide to the Mn^{2+} ion resulting from treatment at a higher temperature.

On the addition of oxygen, the A value shows no change below 800°C, but it abruptly decreases at 1000°C, while the D value decreases gradually above 500°C and becomes almost zero at 1000°C. It may, therefore, be suggested that oxygen atoms around the ion is slightly distorted from the cubic symmetry below 800°C, and that the bonding is strengthened by the thermal treatment, with the result that the oxygen atoms surrounding the Mn^{2+} ion have a cubic symmetry in the same manner as in the bulk of magnesium oxide.

On the other hand, none of the effects of gases are observed in the case of silica gel; this may indicate that the effect of the gas conceals itself behind the strong influence of the silica-gel surface. As to the manganese ion on the surface of magnesium oxide, the information obtained through the ESR spectrum may also be characterized by the cationic lattice point, Mg^{2+}, activated by the addition of the Mn^{2+} ion. It may, therefore, be mentioned that the manganese ion plays a significant role as a probe for the surface of magnesium oxide and, at the same time, contributes to the surface reactivity of the magnesium oxide in reaction to gases.