JOURNAL OF SOLID STATE CHEMISTRY 8, 297–303 (1973)

An EPR Study of Magnetic Interactions in Solid Solutions Between MgO and Antiferromagnetic Oxides. II. MgO–MnO

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Received September 22, 1972

The solid solutions of MnO in magnesium oxide have been studied by EPR. When the manganese concentration increases, the typical EPR spectrum of the isolated ions is gradually replaced by a single Lorentzian line, which we attribute to clusters of exchange-coupled ions. The principal features of the EPR spectrum are examined as a function of the manganese concentration. In this way, an indication about the importance of the contributions from the isolated and the associated ions to the experimental spectrum as well as about the strength and range of action of the exchange interactions between magnetic ions is obtained.

Introduction

Manganous oxide MnO has a face-centered cubic structure as does magnesium oxide. Unlike NiO, manganous oxide gives solid solutions with MgO only in a limited range of composition (*1*).

Pure manganous oxide is an antiferromagnetic compound, with a Néel temperature $T_N = 122$ K (*2*). Its magnetic structure is the same as that of NiO and is called f.c.c. ordering of the second kind (*3*). In MnO the exchange interactions between n.n. and n.n.n. ions are nearly the same, while in NiO the interactions between n.n.n. ions are by far the strongest (*4*). In pure MnO the exchange interaction constants are both antiferromagnetic and have the values: $J_{\text{n.n.}} = 10$ K and $J_{n.n.n.} = 11$ K (*5*). In dilute solid solutions of Mn^{2+} ions in MgO, the values of J obtained by the analysis of the EPR spectra of the pairs are $J_{\text{n.n.}} \approx J_{\text{n.n.n.}} = 15$ K (*6, 7*).

In solid solutions with magnesium oxide, the Mn^{2+} ions enter substitutional sites and give an EPR spectrum at room temperature. Study of the EPR spectrum of Mn^{2+} ions in solution in MgO has been made till now only on very dilute samples, which show only the spectrum of the isolated ions (*8*), and on samples of concentration of about 1 mole %, which show also a more complicated spectrum due to pairs of manganous ions in n.n. and n.n.n. sites (*6, 7, 9*).

We have extended the study of the EPR spectra of this system towards higher values of the manganese concentration to obtain by this way some indications about the strength and the range of action of the interactions between paramagnetic ions in magnesium oxide.

When the concentration of manganese in solution increases, the EPR spectrum is gradually modified, revealing the development of interactions between neighboring Mn^{2+} ions that produce first a broadening of the isolated-ion spectrum and then a new spectrum without hyperfine structure, which we attribute to associated ions. The study of the changes of the EPR spectrum as a function of the concentration of manganese in solution gives information about the importance of these interactions.

Experimental

The solid solutions of MnO in MgO have been prepared starting from pure MgO and MnO_2, mixing and grinding them with care and then firing the mixture for 24 hr at 1350°C in air. The phase diagram of this system shows that in these conditions a solid solution between MgO and MnO up to a concentration of 25 mole % of

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manganese is obtained. The concentration of manganese in the samples is given as the mole fraction f of MnO in the solid solution.

The EPR spectra have been measured with a Varian V-4502-12 spectrometer working at X-band frequency ($\nu \approx 9.52$ kMHz) with a modulation of 100 kHz. The g values have been obtained by comparison with polycrystalline DPPH.

The relative intensities of the spectra have been obtained by calculating the first moment of the usual first derivative of the absorption curve (*10*). The samples with a manganese concentration higher than $f = 0.02$ caused an unbalance of the microwave bridge that increases with concentration. This effect probably depends on the increase in the electrical conductivity of the MgO induced by the presence of manganese. To obtain reliable intensity values of the EPR spectra of these samples the intensity measured on the spectra was multiplied by a correction factor determined using a standard sample containing DPPH, following the method employed by Setaka (*11*).

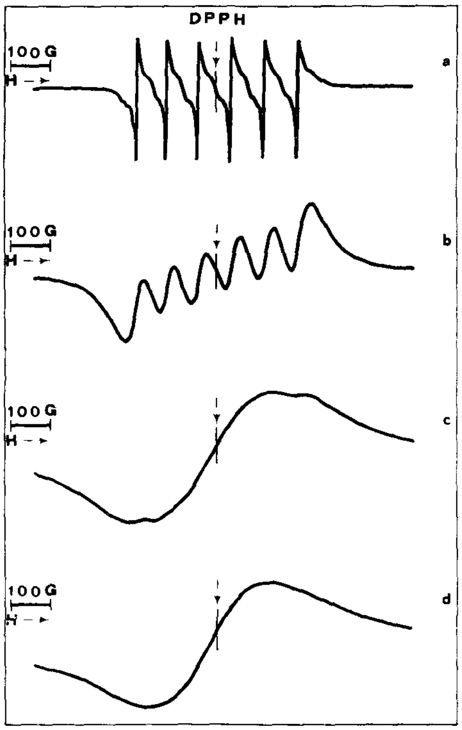

FIG. 1. EPR spectra of solid solutions MgO–MnO for some samples: (a) $f = 0.001$; (b) $f = 0.008$; (c) $f = 0.06$; (d) $f = 0.1$.

Results and Discussion

1. *Assignment of the EPR Spectra*

The EPR spectra of solid solutions MgO–MnO are shown in Fig. 1 for several samples. The spectrum of the low concentration samples is typical of the Mn^{2+} ions in sites of cubic symmetry (Fig. 1a). Powder-sample spectra exhibit six nearly equispaced lines of Lorentzian shape of equal width and height. At higher MnO concentration the six lines broaden and overlap increasingly on each other (Fig. 1b), until the hyperfine structure disappears (Fig. 1c). When the manganese concentration is sufficiently high ($f = 0.1$) the spectrum shows a single absorption of nearly Lorentzian shape (Fig. 1d) which we attribute to clusters of manganese ions coupled by exchange.

The study of the gradual changes in the observed spectrum and the determination of the total manganese concentration at which the isolated-ion spectrum has the maximum intensity is of considerable interest. In fact this allows, as we have already shown (*12*), the range of action of the exchange interactions between Mn^{2+} ions in the magnesium oxide to be determined.

We will now examine the expected form for the spectrum of the isolated and the associated ions in a powder sample in more detail.

a. Isolated ions. The EPR spectrum of Mn^{2+} ions isolated in solution in the magnesium oxide has been studied in single crystals as well as in powders (*8*, *13*). The single-crystal spectrum shows six groups of five lines, due to the presence of five fine structure transitions, each divided in six components by the hyperfine interaction with the nuclear magnetic moment of Mn^{2+}. The absorptions due to the central fine structure transition ($M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$) are the most narrow and strong. The spectrum is not isotropic, in spite of the cubic symmetry of the site occupied by the Mn^{2+} ion, because there is a cubic field splitting term that removes the degeneracy of the ground level and splits it into a twofold and a fourfold degenerate level. The angular dependence of the fine structure transitions in the EPR spectrum is given in first order by (*14*):

$$\begin{aligned} H &\approx H_0 && \text{for the transition } M = \tfrac{1}{2} \leftrightarrow -\tfrac{1}{2} \\ H &\approx H_0 \pm 5pa && \text{for the transition } M = \pm\tfrac{1}{2} \leftrightarrow \pm\tfrac{3}{2} \\ H &\approx H_0 \pm 2pa && \text{for the transition } M = \pm\tfrac{3}{2} \leftrightarrow \pm\tfrac{5}{2}, \end{aligned} \tag{1}$$

where a is the cubic field splitting parameter and $p = 1 - 5\Phi$, with $\Phi = l^2m^2 + l^2n^2 + m^2n^2$. The parameters l, m and n are the direction cosines of the external magnetic field with respect to the cubic axes of the crystal. Only the central transition $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ is isotropic to first order and may be easily observed in powder spectra.

When the manganese concentration is lower than $f = 0.002$, some additional weak absorptions appear in the spectrum, one on either side of each of the six main lines for a total of twelve (Fig. 1a). They are not the forbidden $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$, $\Delta m = \pm 1$ transitions that have been observed for very low manganese concentrations (*15, 16*), because the number of these forbidden transitions is ten also in powders (*15*). Instead we think that they are due to the other fine structure transitions that show up for high concentrations of manganese in spite of their anisotropy. In the spectrum of powders the strongest absorptions correspond to the orientations of the external magnetic field for which the resonance field is maximum or minimum (*17*). The angular dependence of the resonance field of the different transitions is given by the Eq. (1), and therefore the orientations of the magnetic field along which H has extremes are the directions of the cubic axes of the crystal ($\Phi = 0$, $p = 1$) and those with $l^2 = m^2 = n^2 = \frac{1}{3}$ ($\Phi = \frac{1}{3}$, $p = -\frac{2}{3}$). For the latter orientations the distance between the absorptions due to a given hyperfine component of a transition $M = \pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$ from the corresponding hyperfine component of the central $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition is given by $\pm\frac{5}{3}a = \pm 33.27$ G ($a = 19.96$ G) to the first order (*8*), while for a transition $M = \pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$ the same distance is $\mp\frac{4}{3}a = \mp 26.61$ G. The experimental value of the distance is about 33 G, in good agreement with the value predicted for the transitions $M = \pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$.

A further support to this assignment is the fact that the distance between the two maxima symmetrically placed on either side of each principal line is not constant but increases on going from the lowest field line ($m = -\frac{5}{2}$) to the highest field line ($m = \frac{5}{2}$). This effect arises from second-order terms in the angular dependence of the lines. The distance between the transitions $M = +\frac{3}{2}, m \leftrightarrow +\frac{1}{2}, m$ and $M = -\frac{3}{2}, m \leftrightarrow -\frac{1}{2}, m$ is given by (*8*):

$$\Delta H = 5pa - (A^2/H_0)\,2m \qquad (2)$$

(where A and a are in gauss) and, recalling that for the orientations chosen $p = -\frac{2}{3}$, one gets:

$$\Delta H = -\tfrac{10}{3}a - (A^2/H_0)\,2m \qquad (3)$$

Since a is positive ΔH is maximum when $m = \frac{5}{2}$ and minimum when $m = -\frac{5}{2}$, as observed. Moreover, the values of ΔH obtained from the Eq. (3) are in good agreement with the measured ones.

The maxima of the transitions $M = \pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$ are not clearly observed in the spectra, probably because these transitions are wider and weaker than the preceding ones.

When the manganese concentration is further increased the principal lines broaden and overlap more and more until the hyperfine structure of the spectrum disappears (when $f > 0.04$).

Figure 2 shows a plot of the peak-to-peak linewidth ΔH measured at room temperature an hyperfine component of the isolated ions spectrum as a function of the manganese concentration. The linewidth cannot be measured accurately when $f > 0.01$ because of the increasing overlap of the six main lines, so that these values have been neglected. The observed behavior agrees well with the theory of the dipolar broadening of the EPR spectrum of isolated ions, which predicts a linear dependence of ΔH on f when $f < 0.01$ (*18*).

b. Pairs of ions. As we recalled in the previous paper (*12*), when two paramagnetic ions in a diamagnetic matrix are close enough to produce an exchange interaction stronger than the Zeeman interaction $g\beta H$, the system behaves as a unit and gives an EPR spectrum different from that of the isolated ions. In particular, for pairs of Mn^{2+} ions with a spin $s = \frac{5}{2}$ a manifold of six energy levels is formed, each of them being specified by the energy value $\frac{1}{2}JS(S+1)$ with respect to the level $S = 0$, where S is the spin of the pair and takes all the values $S = 0, 1, 2, 3, 4, 5$. The level $S = 0$ is diamagnetic: the EPR spectrum of the other levels is described by the spin Hamiltonian (*19*):

$$\begin{aligned}\mathscr{H} &= g\beta H\cdot S + \tfrac{1}{2}J\{S(S+1) - 2s(s+1)\} \\ &\quad + D_S\{S_z^2 - \tfrac{1}{3}S(S+1)\} + E_S\{(S_x^2 - S_y^2)\} \\ &\quad + \tfrac{1}{2}AS\cdot(I_i + I_j)\end{aligned} \qquad (4)$$

where the first four terms have the meaning already recalled (*12*) while the last one refers to the hyperfine interaction with the nuclei of the two Mn^{2+} ions. The axial and rhombic parameters of the fine structure of the pair D_S and E_S have the form already seen (*12*), while the

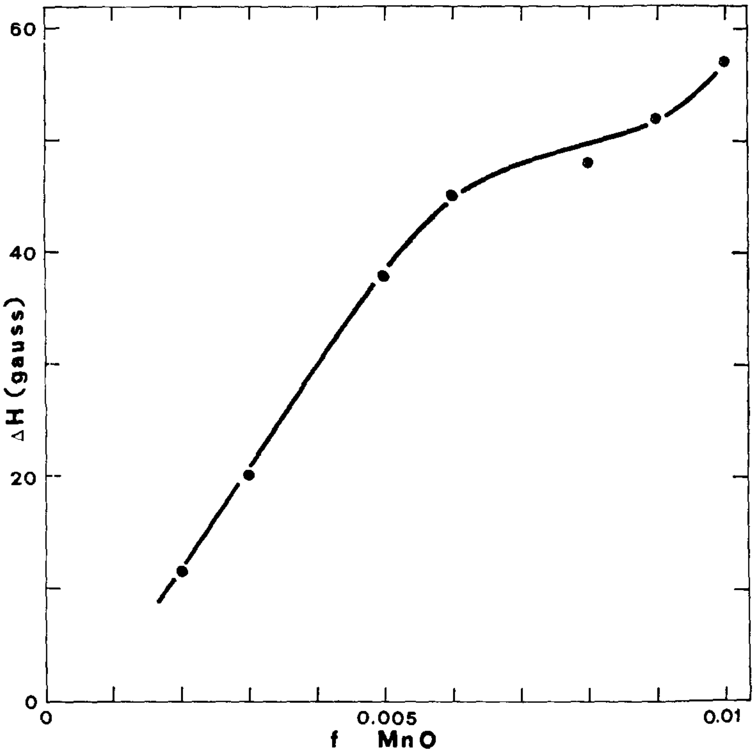

FIG. 2. Dependence of the room-temperature linewidth ΔH of the isolated ions spectrum on the manganese concentration.

parameters α_S and β_S in this case have the values (*19*):

$$\alpha_0 = -\frac{35}{6} \quad \alpha_1 = \frac{37}{10} \quad \alpha_2 = \frac{41}{42}$$

$$\alpha_3 = \frac{47}{90} \quad \alpha_4 = \frac{5}{14} \quad \alpha_5 = \frac{5}{18}$$

$$\beta_0 = \frac{38}{3} \quad \beta_1 = \frac{-32}{5} \quad \beta_2 = \frac{-20}{21}$$

$$\beta_3 = \frac{-2}{45} \quad \beta_4 = \frac{2}{7} \quad \beta_5 = \frac{4}{9}.$$

The n.n. and n.n.n. pairs of Mn^{2+} ions in MgO have already been studied by EPR, and their values of D and E are known (*6*): they can be used to predict the powder spectra of these pairs. For the more distant pairs we make the same approximation used for Ni^{2+} pairs in MgO (*12*). Thus we neglect the terms D_E and E_e of the pairs and we assume the isolated-ion terms D_c and E_c to be zero, as they should be in a perfectly cubic environment. Then the only term of zero splitting of the pairs we have to consider is $D_S = 3\alpha_S D_d$, where $D_d = -g^2\beta^2/r^3$ is the dipolar contribution to D_S and is easily computed when the distance of the two ions r is known.

On the grounds of the values known or computed for D_S and E_S for the different pairs, one can predict the positions of the strongest absorptions in the powder spectrum by using the second-order perturbation formulae given by Bleaney (*20*) for the pairs more distant than the n.n. and the n.n.n., where the condition $D_S \ll g\beta H$ is fulfilled.

The results of this calculation show that the strongest absorptions of the pair spectra are far apart from the central singlet observed, so that they cannot give a significant contribution to it. Moreover, the pair spectrum is probably too anisotropic to be observed in powder samples, taking into account the low concentration of each kind of pair. It may be recalled also that the pair spectrum has a hyperfine structure of eleven equally spaced lines, with a spacing equal to $A/2$, where A is the hyperfine interaction constant of a single ion (*6*). Such a structure has never been observed in our spectra.

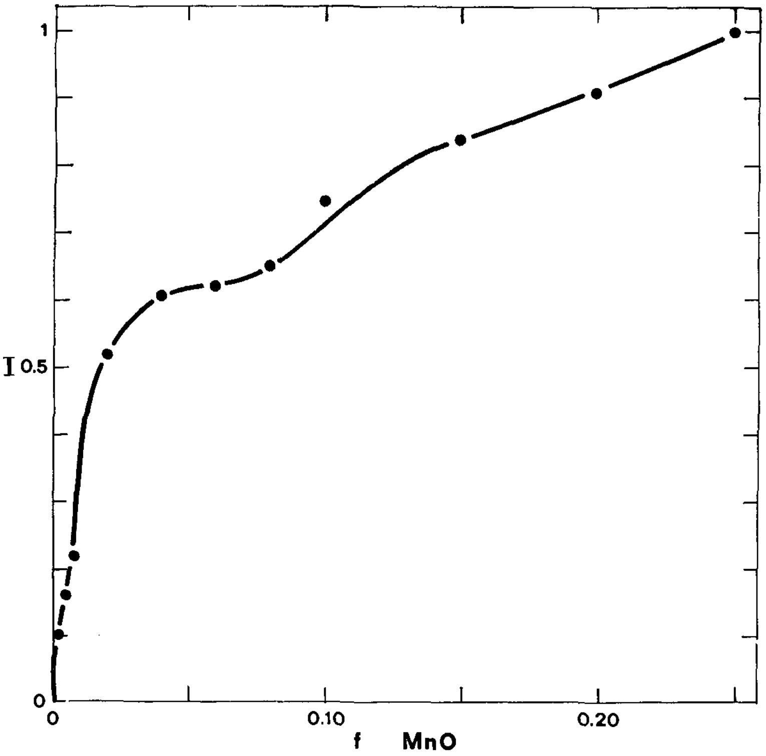

FIG. 3. Relative intensity of the EPR spectrum measured at room temperature in function of the manganese concentration.

c. Clusters of ions. The preceding discussion has shown that the EPR spectra observed in powder samples of solid solutions MgO–MnO do not contain appreciable contributions from the pairs of Mn^{2+} ions. The single Lorentzian absorption observed for high concentrations of manganese must then be attributed to clusters of Mn^{2+} ions close to each other and coupled by strong exchange interactions. It is possible to predict that such a system will produce an EPR spectrum composed of a single isotropic signal with a g value close to that of the isolated ions in the same matrix on the grounds of their total spin Hamiltonian (*21*). Pure MnO itself gives this kind of spectrum above its Néel temperature (*22*).

The experimental spectra show clearly the presence of the spectrum of the isolated ions through its peculiar hyperfine structure up to the concentration $f = 0.03$. At higher MnO concentrations the hyperfine structure disappears, but the spectrum appears to be doubled (Fig. 1c), the wider corresponding to the total linewidth of the isolated ions spectrum and the narrower being due to the associated ions. Only when f is equal or higher than 0.1 the spectrum is composed of the single Lorentzian line of the associated ions (Fig. 1d).

It is interesting to find the contribution of the isolated ions to the experimental spectrum in the intermediate region where there is an appreciable contribution both from the isolated and the associated ions. In fact this allows one to obtain an approximate value of the number m of cationic sites around a given Mn^{2+} ion which must be free from other manganese ions so that the former can be isolated (*12*).

The plot of the total intensity of the EPR spectrum measured at room temperature as a function of the manganese concentration, reported in Fig. 3, gives an indication about this point. The curve shows a region of nearly constant intensity (from $f = 0.03$ to $f = 0.08$). As for the solid solutions between MgO and NiO (*12*) we assume that this effect is due to a decrease of the isolated ions concentration as the total concentration increases, and to the lack of the contribution to the spectrum from the ions in pairs. If we take the beginning of this region as the point where the isolated ions concentration is maximum, as we did before (*12*), we get a value of 32 for m, using the equation $f = 1/(1+m)$, which gives the value of f corresponding to the maximum of the isolated ions concentration for a given m (*12*). In the MgO lattice there are 18 cationic sites around a given cation including up to the next nearest neighbors at a distance of 4.21 Å, and 42 including the third nearest neighbors at a distance of 5.16 Å, using the length of the cubic cell of the pure MgO ($a = 4.212$ Å) (*23*).

Allowing for the uncertainty in selecting the correct experimental value of the mole fraction f corresponding to the maximum of the concentration of the isolated ions, we can conclude that an acceptable value of m is 42. This means that the exchange interaction between manganese ions in the MgO is greater than the microwave quantum used ($h\nu \approx 0.3173$ cm^{-1}) only for distances shorter than 5.16 Å. The range of action of the exchange forces between manganese ions in MgO is therefore much more reduced than for nickel ions (*12*), in agreement with the lower values of the corresponding exchange interaction constants (*4*, *5*).

Figure 4 shows a plot of the room-temperature linewidth ΔH of the associated ions spectrum against f.

The narrowing observed as the manganese concentration increases is to be attributed to the effect of the exchange interactions (*24*). A detailed analysis of this effect is not possible owing to the complexity of this system. We point out, however, that the exchange narrowing seems to be more effective than for the solid solutions MgO–NiO, where a broadening is observed first, and the narrowing begins only when $f > 0.6$ (*12*). This is in agreement with the theoretical prediction that the exchange narrowing is likely to be stronger when the dipole moments are mainly due to the electron spin, as it happens for S state ions (*25*). In a recent study of the EPR spectra of a manganese-substituted spinel a dependence of the linewidth on the manganese concentration similar to that reported here has been found (*26*). Though the exchange interactions between tetrahedral sites in spinels are rather weak (*27*),

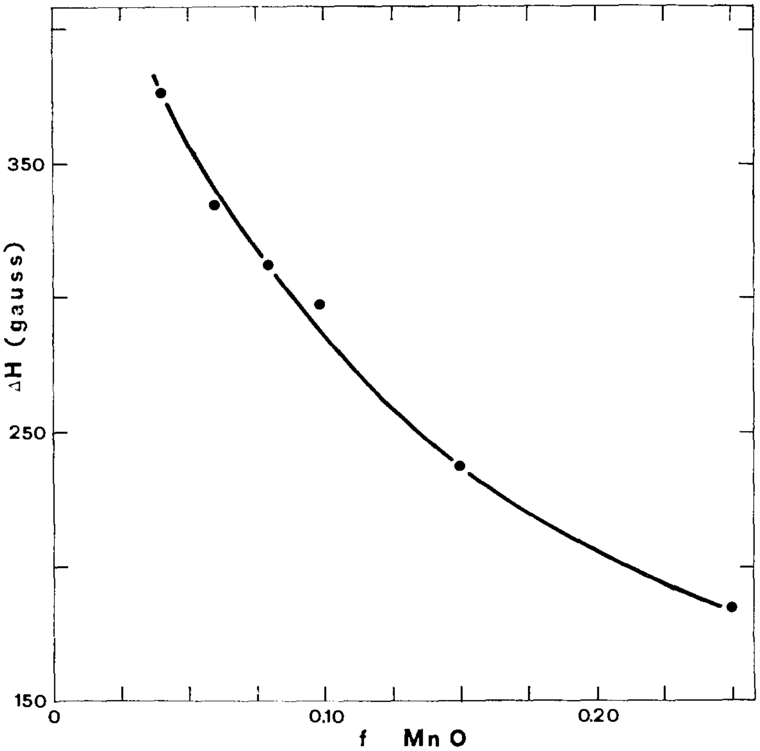

FIG. 4. Dependence of the room-temperature linewidth ΔH of the associated ions spectrum on the manganese concentration.

the narrowing starts from low concentrations, and is attributed to the effect of the exchange.

Acknowledgment

The authors wish to thank Prof. V. Lorenzelli for helpful discussions on many aspects of this work.

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