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# Method of Studying the Diffusion Behavior of $Mn^{++}$ in Cubic Oxide by Paramagnetic Resonance Absorption

by

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Electron paramagnetic resonance intensity measurements were used to ascertain the diffusion behavior of  $Mn^{++}$  in  $MgO$  and  $CaO$ .

It was found that an activation energy of transition metal through measuring the temperature at which transition metal begins to diffuse and through measuring Electron Spin Resonance signal intensity shift could be described by the equation  $A \approx C\mu \exp(-E_m/kT) \cdot t$ .

The activation energy for diffusion as determined by this research is 0.55 eV with  $MgO:Mn^{++}$  and 0.79 eV with  $CaO:Mn^{++}$ .

Electron Spin Resonance signal was obtained from the mixture of special grade  $MgO$  or  $CaO$  and acetic manganese solved in ethyl alcohol.

After heat treatment over  $600^\circ C$  the signal shape changes to a very sharp absorption line of 6 peaks, and the peak heights increase with increasing temperature. The signal intensity of each sample was recorded and computing, each level of the diffusion behavior was measured.

## Introduction

The temperature at which  $Mn^{++}$  ion diffuses in Cubic Oxide powder and the activation energy of transferable  $Mn^{++}$  ion inside such mother material of Cubic Oxide can be acquired by measuring Electron Spin Resonance signal change and absorption intensity.

In a study of the system  $Mn^{++}$  ions in  $NaCl$  Watkins<sup>1)</sup> found five different E.S.R. spectra. These spectra were attributed to ; (1)  $Mn^{++}$  ions in an aggregated or precipitated state; (2) Isolated ions which are not near any defect; (3)  $Mn^{++}$  ions with a positive-ion vacancy bound in the nearest cation site; (4)  $Mn^{++}$  ions with a vacancy bound in the next-nearest cation site; and (5)  $Mn^{++}$  ions paired off with a chemical-impurity charge compensator. Special attention are paid to an aggregation of  $Mn^{++}$  ions and to an isolation of it in these spectra in this report.

When  $Mn^{++}$  ions are in an aggregated state, intensity of the main magnetic field is changed a little bit in the sample by the local field which comes from the nuclear magnetic moment of aggregated  $Mn$  nuclei. This change of the strength of magnetic field introduces the broadening of resonance frequency so that the line shape appears as the broad line type.

The E.S.R. spectra of  $Mn^{++}$  ions, which is going to be an isolated ion by diffusion into mother material of oxide crystal at heat treatment, get very sharp absorption line of 6 peaks of hyper fine structure by nuclear magnetic moment.

Utilizing this phenomena, we tried to obtain an activation energy of transition metal through measuring the temperature at which transition metal begins to diffuse and E.S.R. signal intensity shift.

## Theory

The relationship between the number of paramagnetic sites  $N$  and the resonance signal, as given by Ingram<sup>2)</sup>,

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$$\text{is } N = \left( \frac{\beta}{H_i^2 \omega_0^2} \right) T \int A' dH.$$

In this equation  $A'$  is the magnitude of the absorption line,  $H$  is the static magnetic field,  $\omega_0$  is the resonant frequency,  $H_i$  is the magnitude of the microwave magnetic field,  $\beta$  is a constant of proportionality that depends upon the instrumentation.

It has been found experimentally that with careful spectrometer tuning the variation in the term in parentheses can be held to plus or minus a few percent. When working at room temperature, variations in  $T$  are less than this.

Relation between the magnitude of the absorption line and heat treatment time can be expressed by the following equation at each heat treatment temperature.

$$\begin{aligned} A' &= C\mu\tau \exp(-E_m/kT) \{1 - \exp(-t/\tau)\} + A_0' \exp(-t/\tau) \\ A &= \{C\mu\tau \exp(-E_m/kT) - A_0'\} \{1 - \exp(-t/\tau)\} \\ &\approx C\mu \exp(-E_m/kT) \cdot t \quad (A_0'/\tau \approx 0) \\ \therefore E_m &= kT \left\{ C' - \log \left( \frac{dA}{dt} \right) \right\} \end{aligned}$$

$\mu$  is constant of structure crystals,  $\tau$  is the retardation time of diffusion,  $A_0'$  is the signal intensity without heat treatment,  $A$  is the difference between the heat treated signal intensity and the signal intensity without heat treatment,  $E_m$  is activation energy,  $C = A'/N$  and  $C'$  is new constant.

### Experimental Method

To begin with this experiment of the diffusion behavior of  $Mn^{++}$  ions, we solved Acetic Manganese ( $Mn(CH_3COO)_2$ ) 10 mg into a solvent of ethyl alcohol, and then poured this solvent mixing with MgO 10cc of special grade into vacuum pump to vaporize this alcoholic liquor. (Thus the vaporized sample pushed into the depth of 5 cm of E.S.R. sample tube (diameter 0.3 cm), and the quantity of  $Mn^{++}$  ions involved in this sample became about  $10^{16}$  Atoms.)

This sample was heat-treated in air. The sample temperature was measured by chromel-alumel thermocouple. Estimated temperature errors and control accuracies were  $\pm 10^\circ C$ .

The sample was quenched by pulling it out of the furnace after a given time of the heat treatment. Followingly, equal quantities of further several samples with heat treatment at different temperature were poured into E.S.R. tubes.

The klystron frequency and attenuation controls were kept constant. However, the slide screw tuner were adjusted for each run. The signal amplifier gain was varied as necessary to give nearly maximum recorder response for each sample.

The diffusion behavior was computed by measuring the signal intensity of each sample.

During the process of making samples, if  $Mn(CH_3COO)_2$  is mixed with an oxide powder, after solving into water, it becomes hydroxide and causes structural shifts of mother crystal in most case. Therefore it is always necessary to check crystal structures of heat treated-samples with X ray diffractometer.

In MgO, when it is treated with water it becomes  $Mg(OH)_2$  until  $300^\circ C$  and the crystal structure changes to Cadmium Iodide Structure, but on the other hand if ethyl alcohol is used for the treatment of  $Mn(CH_3COO)_2$ , the crystal structure of MgO is confirmed by X ray there is no change during the heat treatment from the room temperature to  $1300^\circ C$ .

### Results

If the E.S.R. signal of a sample without heat treatment was measured at room temperature,  $g$  values ( $g = 2.0086$ ) and it becomes a signal of a broad line curve of Lorentzian type  $\left( \frac{\Delta H}{\Delta H_{msl}} = 1.78 \right)$

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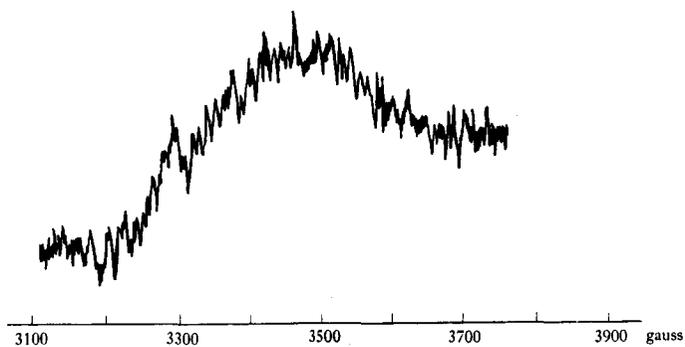


Fig. 1. Resonance curve of Lorentzian type of  $MgO : Mn^{++}$  for heat treatment at  $400^{\circ}C$  100 minutes.

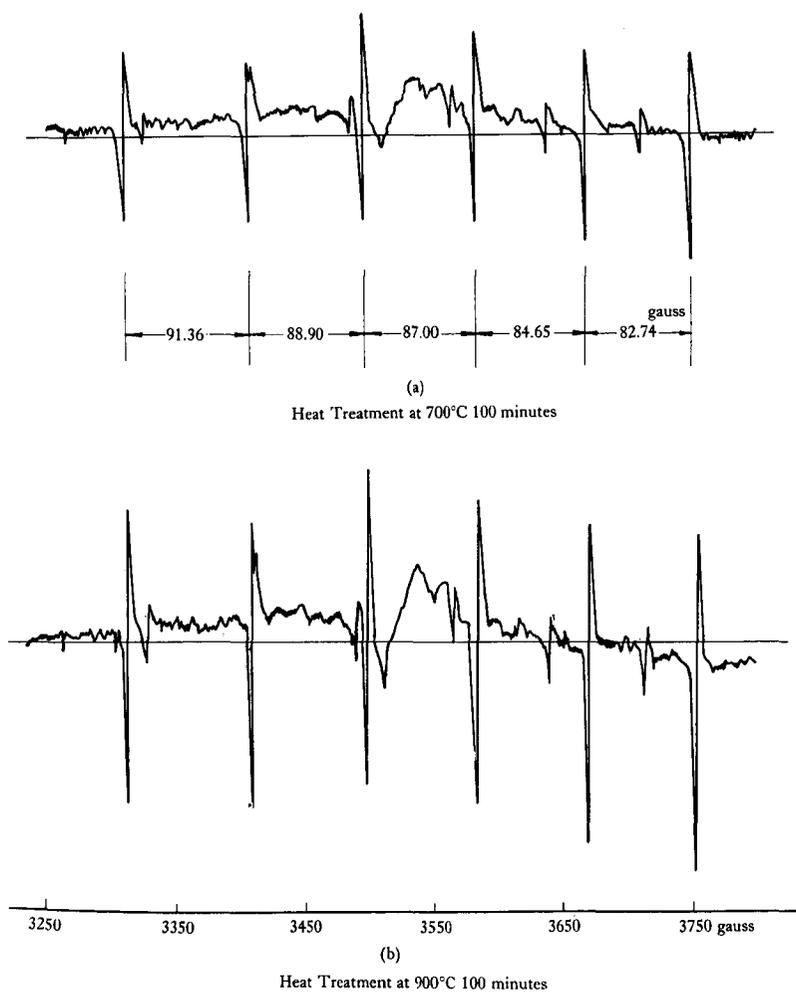


Fig. 2. E.S.R. Resonance signal of isolated  $MgO : Mn^{++}$  (X-band spectrometer  $\nu=9414.5MC/S$ ).

(Fig. 1). This signal is independent of time of heat treatment from 5 minutes to 100 hours in the region from room temperature to 500°C. This shows that the relaxation time is shortened by the interaction of each  $Mn^{++}$  ion and  $Mn^{++}$  ion is not isolated.

After heat treatment over 600°C, intensity of the E.S.R. signal of 6 center lines increase with temperature and the signal shape changes to a very sharp absorption line (Fig. 2). This signal has  $g$  value of 2.0011. This shows that  $Mn^{++}$  ion is going to be an isolated ion by diffusion of  $Mn^{++}$  ion into mother material of MgO.

The difference between the heat-treated signal intensity and the signal intensity without heat treatment is defined as the difference-magnitude of the absorption line.

The time spent in which relation between the difference-magnitude of the absorption reaches a level of magnitude depends on individual temperature heat treatment (Fig. 3), and the difference-magnitude was proportional to the heat-treatment time of about 100 minutes (Fig. 4).

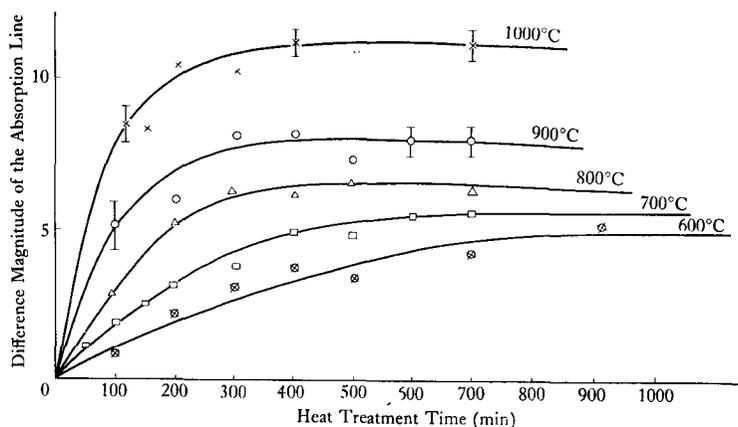


Fig. 3. Heat treatment time at each temperature dependence of the magnitude of the absorption line.

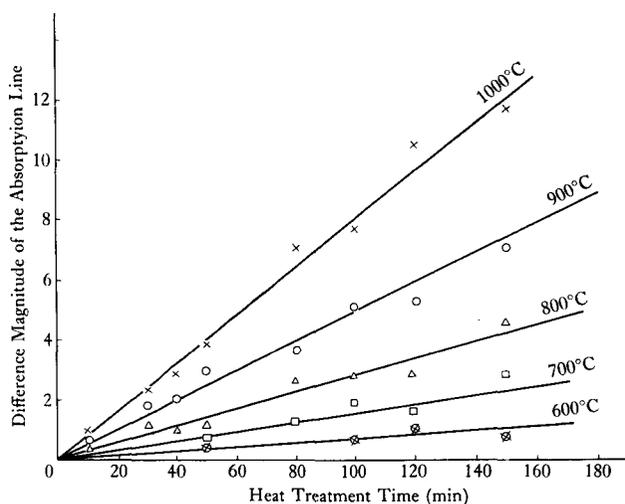


Fig. 4. Magnitude of the absorption line vs heat treatment time until about 150 minutes at each temperature.

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Semi-logarithmic plot of logarithm of the gradient of these lines at  $t=0$  and absolute temperature of heat treatment consists in the following equation

$$\log \left( \frac{dA}{dt} \right) = C' - \frac{E_m}{k} \cdot \frac{1}{T}$$

Activation energy of the diffusion  $Mn^{++}$  in  $MgO$  can be obtained from this equation, and is found to be  $0.55 \pm 0.045$  eV by our experiment. Activation energy for the diffusion of  $Mn^{++}$  ion in  $CaO$  is also obtained as  $0.79 \pm 0.045$  eV. Further experiment are now going on  $SrO$  and  $BaO$ .

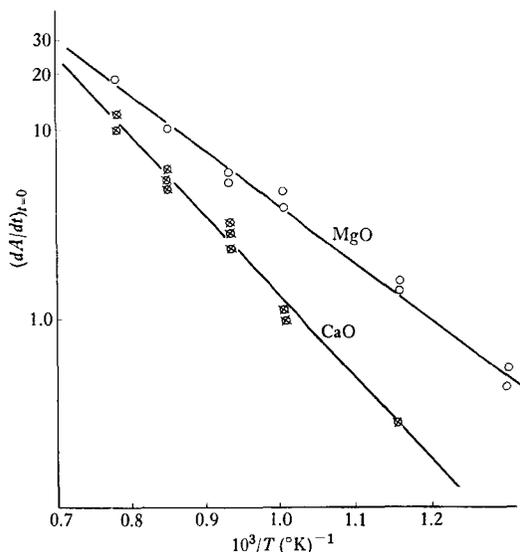


Fig. 5.  $\log \left( \frac{dA}{dt} \right)_{t=0}$  vs  $1/T$  Plots for  $MgO$  and  $CaO$ .

### Discussion

The activation energy for diffusion of  $Mn^{++}$  in  $MgO$  and  $CaO$  as determined by this research is 0.55 eV and 0.79 eV.

It is observed that by combination of ionic conductivity and radioactive tracer techniques A.N. Murin<sup>3)</sup> et al. obtained a value of 0.66 eV with  $NaCl:Mn^{++}$ , and Watkins obtained a value of 0.52 eV with  $NaCl:Mn^{++}$ .

The reasons for this discrepancy are difference lattice constant of mother material cubic. Furthermore, Murin et al. state that their results must be considered preliminary for they found Ag and Al impurities in their crystals. Traces Fe and Cr were found in the crystal used in this work, and it has been shown by R.J. Maurer<sup>4)</sup> et al. that the presence of impurities materially affects measured activation energies.

This method supposedly can be used as the general method for the determination of activation energy for diffusion of transition metal in oxide crystal.

In order to increase the accuracy of this experiment, we must try to increase that of the measurement of E.S.R. signal intensity. It is possible to get the experimental error of less than 16% for signal intensity measurement, even at over estimation, by using our present apparatus.

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