

# Cation Distributions in Ferrosinels. Magnesium-Manganese Ferrites\*

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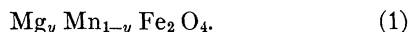
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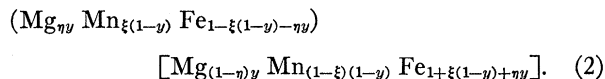
The saturation magnetization as a function of quench temperature is measured for the ferrite system  $\text{Mg}_y\text{Mn}_{1-y}\text{Fe}_2\text{O}_4$ . From these data the ionic distribution of Mg ions is evaluated and compared to the theoretical thermodynamic analysis developed in the preceding paper. The interesting quantity  $\partial u_1/\partial \eta$ , where  $u_1$  is the nonthermal energy and  $\eta$  is the fraction of Mg ions on  $A$  sites, can be evaluated from the data only if the variation of the Debye temperature with  $\eta$  can be neglected. If this assumption is made, then it is found that  $\partial u_1/\partial \eta$  is linearly dependent on  $\eta$ . The lattice constant has also been determined as a function of quench temperature.

## INTRODUCTION

IN the preceding paper,<sup>1</sup> the thermodynamic relationship between the ionic distributions and the nonthermal portion of the internal energy function has been developed. The motivation of that study was to permit empirical observations on cation distributions to be interpreted in terms of the energy function. In this paper we present the results of an experimental study of cation distributions in the mixed magnesium-manganese ferrite system, which may be represented by the chemical formula



The corresponding ionic distribution may be described by the enclosure of tetrahedrally-situated ions in parentheses, and of octahedrally-situated ions in brackets as follows:



In this formula,  $\eta$  is the fraction of Mg ions on  $A$  sites and  $\xi$  is the fraction of Mn ions on  $A$  sites.

In the analysis of the experimental data, we have used the recent result obtained from neutron diffraction that  $\xi \cong 0.80$  for manganese ferrite<sup>2</sup> and for the magnesium-manganese<sup>3</sup> compounds. Previously it had been thought that manganese ferrite was inverse.

The distribution parameter,  $\eta$ , is determined by measuring the saturation magnetization. In  $\text{MgFe}_2\text{O}_4$ , for example, since the magnetic moments of the ions on  $A$  and on  $B$  sites are aligned antiparallel by the negative  $AB$  interaction, the saturation magnetization in Bohr magnetons ( $\mu_0$ ) is given by

$$\mu_0 = 10\eta. \quad (3)$$

For a sample perfectly annealed at absolute zero,  $\eta=0$ , but as the temperature is raised, Mg ions are

thermally excited to  $A$  sites, and if the sample is rapidly quenched, these ions are "frozen" on  $A$  sites.

The pattern of our experiments is to quench samples of fixed  $y$  from various quench temperatures  $T$ , and to observe the resultant values of  $\eta$ . The empirical data, which are of the form

$$\eta = \eta(T; y), \quad (4)$$

or

$$T = T(\eta; y), \quad (5)$$

are then to be compared to the theoretical distribution function derived in paper I.

The only previous detailed empirical study of distributions as a function of quench temperature is the work of Pauthenet and Bochirol<sup>4</sup> on pure  $\text{MgFe}_2\text{O}_4$ . They found that their data were consistent with a distribution of the form

$$\eta(1+\eta)/(1-\eta)^2 = e^{-(\theta/T)}, \quad (6)$$

where  $\theta$  is a constant and equal to 1200°K. This result is somewhat surprising since comparison with Eqs. (44) and (24) of I [or (9) of this paper] indicate that the quantity  $\theta$  includes distribution-sensitive components such as the Madelung energy, and consequently should itself depend on the distribution. One obvious experimental handicap lies in the inherent difficulty in achieving true equilibrium conditions. For example, quite divergent values of  $\mu_0$  for  $\text{MgFe}_2\text{O}_4$  have been reported in the literature for similar quench temperatures, as shown in Table I. These discrepancies may be due to the relatively low sintering temperatures used for the highly refractory  $\text{MgFe}_2\text{O}_4$  and also the rate of

TABLE I. Previous values of  $\mu_0$  in Bohr magnetons for quenched samples of  $\text{MgFe}_2\text{O}_4$ .

$T_Q(^{\circ}\text{C})$	$\mu_0$
1100	1.6 <sup>a</sup>
1200	2.2 <sup>b</sup>
1250	1.4 <sup>c</sup>

<sup>a</sup> Sakamoto, Asahi, and Miyahara, *J. Phys. Soc. Japan* **8**, 677 (1953).

<sup>b</sup> See reference 4.

<sup>c</sup> E. W. Gorter, *Phillips Research Repts.* **9**, 321 (1954).

<sup>4</sup> R. Pauthenet and L. Bochirol, *J. phys. radium* **12**, 249 (1951).

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<sup>1</sup> Callen, Harrison, and Kriessman, *Phys. Rev.* **103**, 851 (1956) preceding paper. This paper will be referred to as I.

<sup>2</sup> L. Corliss and J. Hastings (private communication).

<sup>3</sup> Nathans, Pickart, Harrison, and Kriessman (unpublished work).

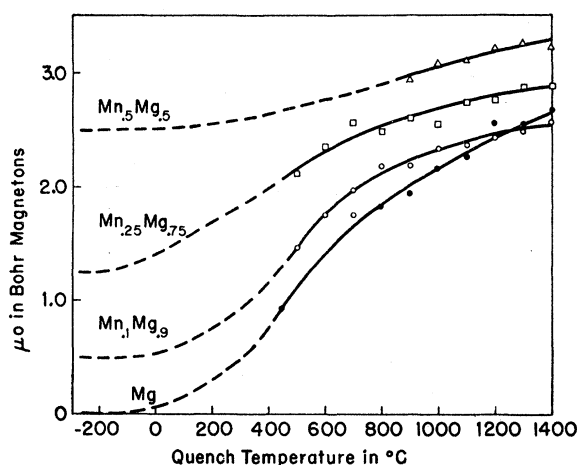


FIG. 1. Experimental values of the magnetic moment as a function of quench temperature.

quenching. We have, therefore, used higher sintering temperatures in our study and have taken special care to quench rapidly.

#### EXPERIMENTAL

The compounds  $\text{Mg}_y\text{Mn}_{1-y}\text{Fe}_2\text{O}_4$  for  $y=1.00, 0.90, 0.75, 0.50, 0.25, 0.10$ , and  $0$  were prepared from cp  $\text{MgO}$ ,  $\text{MnO}_2$ , and  $\text{Fe}_2\text{O}_3$  by standard ceramic techniques. The mixtures were presintered twice at  $1200^\circ\text{C}$  for 24 hours and then finally sintered in air at  $1400^\circ\text{C}$  for 24 hours. Samples were quenched in water from  $1400^\circ\text{C}$  and from temperatures at 100 degree intervals down to  $400^\circ\text{C}$ ; they were held at each quench temperature for at least three hours to achieve equilibrium. Many samples were held for longer times at various quench temperatures to check the achievement of equilibrium.

The magnetic measurements were made by a torsion method similar to that developed by Buehl and Wulff<sup>5</sup> and by Folen.<sup>6</sup> Samples in the form of very small spheres weighing 2 to 4 mg are placed in an inhomogeneous magnetic field. The resulting force on the sample, which is proportional to the product of the magnetization and the mass, is measured by bringing the sample back to a null position. The system is calibrated by a pure nickel standard.

Magnetization data taken as a function of temperature are extrapolated from liquid nitrogen temperature to absolute zero using the formula<sup>7</sup>

$$\sigma = \sigma_0(1 - \alpha T^n), \quad (7)$$

where  $\sigma$  is the magnetization per gram. For  $\text{MnFe}_2\text{O}_4$ ,  $n = \frac{3}{2}$ , while for the other compounds  $n = 2$  has been found to fit the data.

More than 200 samples were measured in this study. Although the experimental method is accurate to  $\pm 1\%$ ,

measurements on different samples (quenched at the same temperature) may differ by as much as  $\pm 3\%$ . This is attributed to the difficulty of obtaining complete homogeneity in these sintered and rapidly quenched materials.

Chemical analyses indicate that the nominal chemical composition is correct within the limits of the analyses. The samples were examined by x-rays for the appearance of a second phase which might occur at the lower quench temperatures. No second phases appeared at any quench temperature for  $y > 0.5$ . Second phases did appear for the following values of  $y$  at quench temperatures below those specified: for  $y = 0.50$ , below  $700^\circ\text{C}$ ; for  $y = 0.25$ , below  $900^\circ\text{C}$ ; and for  $y = 0.10$  below  $1000^\circ\text{C}$ .

The magnetic moments determined at each quench temperature are shown in Fig. 1. Because of the appearance of a second phase, data for the compounds  $y = 0.25$  and  $y = 0.10$  are not included.

Values of  $\eta$  corresponding to these magnetic moments may be calculated from

$$\mu_0 = 5 + (10\eta - 5)y, \quad (8)$$

TABLE II.  $\mu_0$  in Bohr magnetons for all compounds quenched from  $1400^\circ\text{C}$ .

$y$	$\mu_0$
1.00	$2.67 \pm 0.05$
0.90	$2.56 \pm 0.07$
0.75	$2.88 \pm 0.03$
0.50	$3.22 \pm 0.04$
0.25	$3.93 \pm 0.05$
0.10	$4.29 \pm 0.04$
0.00	$4.79 \pm 0.05$

which is independent of the position of the Mn ion if we assume that the magnetic moments of the Fe and Mn ions are both equal to 5 Bohr magnetons. The data for all compositions quenched from  $1400^\circ\text{C}$  are collected in Table II.

The change in the room temperature lattice constant ( $a_0$ ) with  $\eta$  has been determined for  $y = 1.00, 0.90$ , and  $0.75$ , and these data are graphed in Fig. 2. For  $\text{MgFe}_2\text{O}_4$  we find a change in  $a_0$  of  $0.020 \text{ \AA}$  for a change in  $\eta$  of about  $0.20$ . Kingsnorth<sup>8</sup> has found that  $a_0$  changes by  $0.012 \text{ \AA}$  between samples of  $\text{MgFe}_2\text{O}_4$  quenched from  $1200^\circ\text{C}$  and furnace cooled.

Miss Selma Greenwald of the Naval Ordnance Laboratory has kindly determined  $\eta$  for a sample of  $\text{MgFe}_2\text{O}_4$  by correlating x-ray intensities with the structure factors expected from various distributions by the method of Bertaut.<sup>9</sup> For a sample quenched from  $1400^\circ\text{C}$  she finds  $\eta = 0.28 \pm 0.03$ , which is comparable to our magnetic value of  $0.27 \pm 0.01$ .

<sup>5</sup> R. Buehl and J. Wulff, Rev. Sci. Instr. 9, 224 (1938).

<sup>6</sup> V. J. Folen (private communication).

<sup>7</sup> R. Pauthenet, Ann. phys. 7, 710 (1952).

<sup>8</sup> S. W. Kingsnorth, thesis, University of London, 1950 (unpublished).

<sup>9</sup> F. Bertaut, Compt. rend. 230, 213 (1950).

## DISCUSSION

The general distribution law has been derived in Eqs. (57) and (58) of I. For the magnesium manganese ferrites studied in this paper,  $\xi$  is a constant as discussed above. Thus we are concerned only with Eq. (62) of I, which, when the small quantity  $\partial\epsilon/\partial\eta$  is neglected, reduces to the following distribution law:

$$\frac{\eta[1.8+y(\eta-0.8)]}{(1-\eta)[0.2+y(0.8-\eta)]} = \exp\left[-\frac{1}{yRT}\left(\frac{\partial u_1}{\partial\eta} - 7RT\frac{\partial \ln c_v^{(0)}}{\partial\eta}\right)\right]. \quad (9)$$

In this equation  $u_1$  is the nonthermal contribution to the energy, which is composed of Madelung, covalent, Born repulsive and other components, and  $c_v^{(0)}$  is the lattice contribution to the low-temperature specific

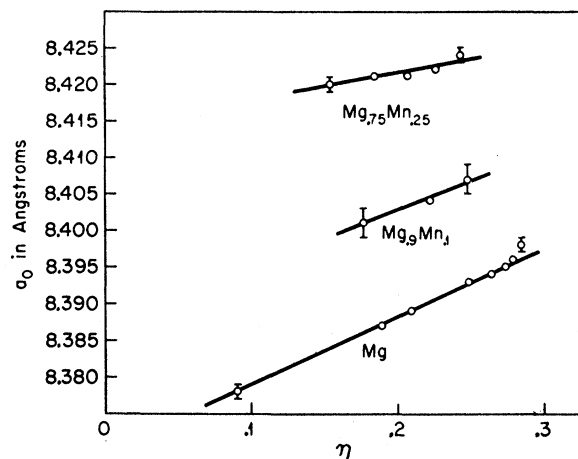


FIG. 2. Lattice constant as a function of the fraction of Mg ions on A sites.

heat. The partial derivatives in Eq. (9) are to be carried out at constant temperature and constant  $y$ , and are to be evaluated at some arbitrary low fiducial temperature. The partial derivatives of  $u_1$  and  $c_v^{(0)}$  are then temperature-independent.

In order to apply Eq. (9) it would be necessary to have specific heat measurements as well as magnetic moment measurements. In the absence of the former, we have arbitrarily adopted the simple assumption that the low-temperature specific heat is fairly insensitive to the distribution of the Mg ions. The second term in the exponent of Eq. (9) is then negligible.

Thus we may now evaluate the quantity  $(1/R) \times (\partial u_1/\partial\eta)$  from Eq. (9) by substituting the experimental values of the quench temperature,  $T$ , and the distribution parameter calculated from Eq. (8). These values for  $\text{MgFe}_2\text{O}_4$  and  $\text{Mg}_{0.75}\text{Mn}_{0.25}\text{Fe}_2\text{O}_4$  are plotted in Fig. 3. It is apparent that  $(1/R)(\partial u_1/\partial\eta)$  is a linear

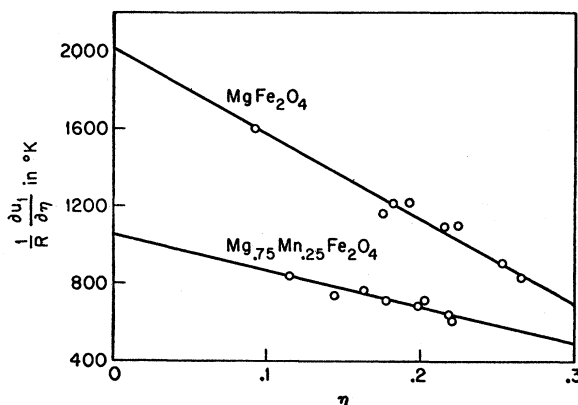


FIG. 3. Calculated values of  $(1/R)(\partial u_1/\partial\eta)$  plotted as a function of  $\eta$  for  $\text{MgFe}_2\text{O}_4$  and  $\text{Mg}_{0.75}\text{Mn}_{0.25}\text{Fe}_2\text{O}_4$ .

function of  $\eta$  and may be written

$$\frac{1}{R} \frac{\partial u_1}{\partial\eta} = \theta_0 - \theta_1\eta. \quad (10)$$

This implies that the energy may be expressed as

$$u_1(\eta, y) = u_0(y) + R[\theta_0(y)\eta - \frac{1}{2}\theta_1(y)\eta^2]. \quad (11)$$

An  $\eta^2$  term in  $u_1(\eta, y)$  may be attributed to several of the contributions to the energy. For example, the Madelung energy is proportional to the product of the average charge on the A and B sites, and since each of these charges is linearly dependent on  $\eta$ , this product will contribute an  $\eta^2$  term to the total energy.

The values of  $\theta_0$  and  $\theta_1$  deduced for the other compounds are tabulated in Table III. To interpret the variation in  $\theta_0$  and  $\theta_1$  with  $y$ , it is necessary to give physical meaning to  $\theta_0$  and  $\theta_1$ . If  $n$  is the number of Mg ions on A sites (per formula unit), then

$$n = \eta y, \quad (12)$$

and we note that from Eq. (10)

$$\frac{\theta_0}{y} = \frac{1}{R} \left( \frac{\partial u_1}{\partial n} \right)_{\eta=0}, \quad (13)$$

$$\frac{\theta_1}{y} = \frac{1}{R} \left( \frac{\partial u_1}{\partial n} \right)_{\eta=0} - \frac{1}{R} \left( \frac{\partial u_1}{\partial n} \right)_{\eta=1}. \quad (14)$$

If we consider a ferrite sample in which all the Mg ions are on octahedral sites, and if we proceed to transfer them quasistatically, one by one, to the

TABLE III. Values of  $\theta_0$  and  $\theta_1$  in  $^\circ\text{K}$ .

$y$	$\theta_0$	$\theta_1$
1.00	2020	4350
0.90	1445	2220
0.75	1050	1820
0.50	600	0

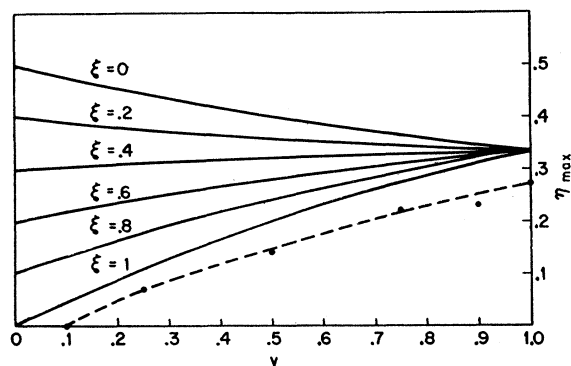


FIG. 4.  $\eta_{\max}$  for the various values of  $\xi$  plotted as a function of  $y$ . The experimental values of  $\eta$  for samples quenched from 1400°C are also shown (dashed line).

tetrahedral sites, then the nonthermal energy, or work, required for the transfer of the first Mg ion is  $\theta_0/y$ . We see from Table III that  $\theta_0$  is largest for  $\text{MgFe}_2\text{O}_4$  and decreases as Mn is added. One possible explanation of this is that the Born repulsion energy decreases as the size of the structure increases due to the addition of the large Mn ions, thus enabling the Mg ions to be transferred more easily to the smaller  $A$  sites.  $\theta_1/y$  may be interpreted from Eq. (14) as the difference in the work required for the transfer of the first and last Mg ions. This difference in work approaches zero as  $y$  decreases. This is expected because as the number of Mg ions decreases, the work necessary to transfer the first and the last becomes more nearly equal.

The magnetic data, considered as a function of composition, give some useful information about the

value of  $\xi$  in the spinel structure. We define  $\eta_{\max}$  as the maximum fraction of Mg ions which can migrate to  $A$  sites. This is the fraction consistent with maximum disorder and is given by

$$\eta_{\max} = [1 + \xi(y-1)] / (2+y). \quad (15)$$

This equation is plotted as a function of  $y$  in Fig. 4. In the case of a normal spinel ( $\eta=1$ ),  $\eta_{\max}$  decreases to zero as  $y$  decreases, while for an inverse spinel ( $\eta=0$ ),  $\eta_{\max}$  increases to a value of 0.5. The experimental trend of  $\eta_{\max}$  can be established from the values of  $\eta$  obtained at the highest quench temperature, 1400°C, and these values are also plotted in Fig. 4. The experimental values of  $\eta_{\max}$  decrease to zero as expected for a normal ferrite. Thus, this plot of  $\eta_{\max}$  vs  $y$  gives a semiquantitative method for determining the degree of inversion. The decrease in the experimental values of  $\eta_{\max}$  appears to resemble the theoretical curve for  $\xi=0.8$  in agreement with the neutron diffraction work discussed previously.

#### ACKNOWLEDGMENTS

We wish to thank Miss Selma Greenwald of the Naval Ordnance Laboratory for having made x-ray studies of the ionic distributions in  $\text{MgFe}_2\text{O}_4$ . Our gratitude is also due Dr. L. R. Maxwell, of the same laboratory, who checked some of our magnetization measurements.

Assistance with the experimental details of this work was given by the following: J. Coleman, magnetic measurements; R. Moore and R. Smith, fabrication of samples; and W. McCann, x-ray measurements.