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Cation Distributions in Ferrospinels. Magnesium-Manganese Ferrites*

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The saturation magnetization as a function of quench temperature is measured for the ferrite system $Mg_yMn_{1-y}Fe_2O_4$. 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 η is the fraction of Mg ions on A sites, can be evaluated from the data only if the variation of the Debye temperature with η can be neglected. If this assumption is made, then it is found that $\partial u_1/\partial\eta$ is linearly dependent on η. The lattice constant has also been determined as a function of quench temperature.

INTRODUCTION

In the preceding paper,[1] 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

$$Mg_y\, Mn_{1-y}\, Fe_2\, O_4. \tag{1}$$

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:

$$(Mg_{\eta y}\, Mn_{\xi(1-y)}\, Fe_{1-\xi(1-y)-\eta y})$$
$$[Mg_{(1-\eta)y}\, Mn_{(1-\xi)(1-y)}\, Fe_{1+\xi(1-y)+\eta y}]. \tag{2}$$

In this formula, η is the fraction of Mg ions on A sites and ξ 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[2] and for the magnesium-manganese[3] compounds. Previously it had been thought that manganese ferrite was inverse.

The distribution parameter, η, is determined by measuring the saturation magnetization. In $MgFe_2O_4$, 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 (μ_0) is given by

$$\mu_0 = 10\eta. \tag{3}$$

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 η. The empirical data, which are of the form

$$\eta=\eta(T;y), \tag{4}$$

or

$$T=T(\eta;y), \tag{5}$$

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[4] on pure $MgFe_2O_4$. They found that their data were consistent with a distribution of the form

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

where θ 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 quentity θ 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 μ_0 for $MgFe_2O_4$ 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 $MgFe_2O_4$ and also the rate of

Table I. Previous values of μ_0 in Bohr magnetons for quenched samples of $MgFe_2O_4$.

T_Q(°C)	μ_0
1100	1.6[a]
1200	2.2[b]
1250	1.4[c]

[a] Sakamoto, Asahi, and Miyahara, J. Phys. Soc. Japan 8, 677 (1953).
[b] See reference 4.
[c] E. W. Gorter, Phillips Research Repts. 9, 321 (1954).

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[*] Supported in part by the Office of Naval Research.

[1] Callen, Harrison, and Kriessman, Phys. Rev. 103, 851 (1956) preceding paper. This paper will be referred to as I.

[2] L. Corliss and J. Hastings (private communication).

[3] Nathans, Pickart, Harrison, and Kriessman (unpublished work).

[4] R. Pauthenet and L. Bochirol, J. phys. radium 12, 249 (1951).

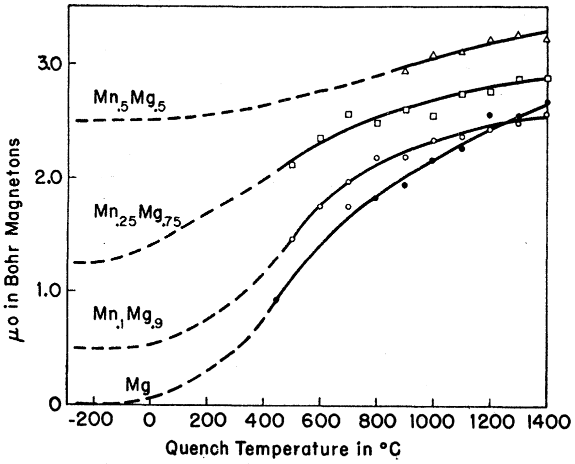

FIG. 1. Experimental values of the magnetic moment as a function of quench temperature.

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

EXPERIMENTAL

The compounds $Mg_yMn_{1-y}Fe_2O_4$ for $y=1.00$, 0.90, 0.75, 0.50, 0.25, 0.10, and 0 were prepared from cp MgO, MnO_2, and Fe_2O_3 by standard ceramic techniques. The mixtures were presintered twice at 1200°C for 24 hours and then finally sintered in air at 1400°C for 24 hours. Samples were quenched in water from 1400°C and from temperatures at 100 degree intervals down to 400°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[5] and by Folen.[6] 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[7]

$$\sigma=\sigma_0(1-\alpha T^n), \tag{7}$$

where σ is the magnetization per gram. For $MnFe_2O_4$, $n=\frac{3}{2}$, 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°C; for $y=0.25$, below 900°C; and for $y=0.10$ below 1000°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 η corresponding to these magnetic moments may be calculated from

$$\mu_0=5+(10\eta-5)y, \tag{8}$$

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°C are collected in Table II.

TABLE II. μ_0 in Bohr magnetons for all compounds quenched from 1400°C.

y	μ_0
1.00	2.67±0.05
0.90	2.56±0.07
0.75	2.88±0.03
0.50	3.22±0.04
0.25	3.93±0.05
0.10	4.29±0.04
0.00	4.79±0.05

The change in the room temperature lattice constant (a_0) with η has been determined for $y=1.00$, 0.90, and 0.75, and these data are graphed in Fig. 2. For $MgFe_2O_4$ we find a change in a_0 of 0.020 A for a change in η of about 0.20. Kingsnorth[8] has found that a_0 changes by 0.012 A between samples of $MgFe_2O_4$ quenched from 1200°C and furnace cooled.

Miss Selma Greenwald of the Naval Ordnance Laboratory has kindly determined η for a sample of $MgFe_2O_4$ by correlating x-ray intensities with the structure factors expected from various distributions by the method of Bertaut.[9] For a sample quenched from 1400°C she finds $\eta=0.28\pm0.03$, which is comparable to our magnetic value of 0.27 ± 0.01.

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[5] R. Buehl and J. Wulff, Rev. Sci. Instr. **9**, 224 (1938).
[6] V. J. Folen (private communication).
[7] R. Pauthenet, Ann. phys. **7**, 710 (1952).
[8] S. W. Kingsnorth, thesis, University of London, 1950 (unpublished).
[9] 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, ξ 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 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.

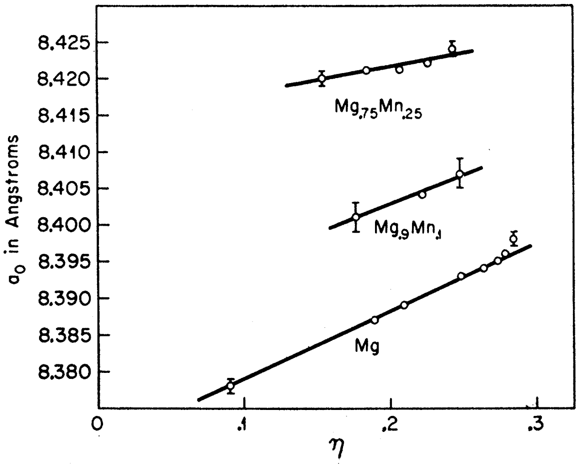

FIG. 2. Lattice constant as a function of the fraction of Mg ions on A sites.

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 $MgFe_2O_4$ and $Mg_{0.25}Mn_{0.75}Fe_2O_4$ are plotted in Fig. 3. It is apparent that $(1/R)(\partial u_1/\partial\eta)$ is a linear function of η and may be written

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

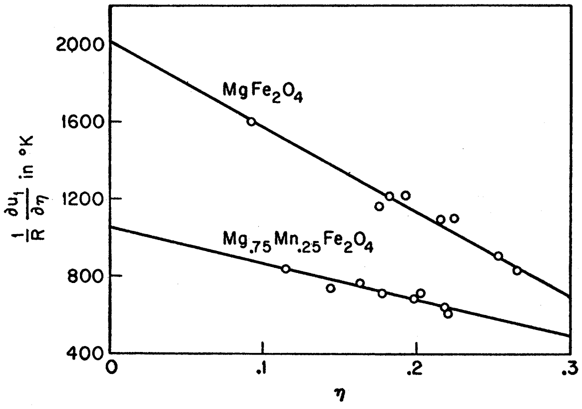

FIG. 3. Calculated values of $(1/R)(\partial u_1/\partial\eta)$ plotted as a function of η for $MgFe_2O_4$ and $Mg_{0.75}Mn_{0.25}Fe_2O_4$.

This implies that the energy may be expressed as

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

An η^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 η, this product will contribute an η^2 term to the total energy.

The values of θ_0 and θ_1 deduced for the other compounds are tabulated in Table III. To interpret the variation in θ_0 and θ_1 with y, it is necessary to give physical meaning to θ_0 and θ_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 θ_0 and θ_1 in °K.

y	θ_0	θ_1
1.00	2020	4350
0.90	1445	2220
0.75	1050	1820
0.50	600	0

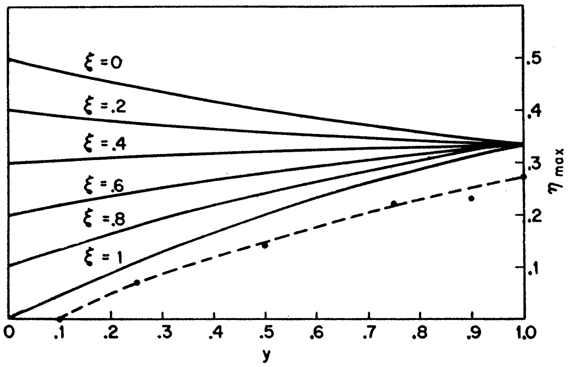

FIG. 4. η_{max} for the various values of ξ plotted as a function of y. The experimental values of η for samples quenched from 1400°C are also shown (dashed line).

tetrahedral sites, then the nonthermal energy, or work, required for the transfer of the first Mg ion is θ_0/y. We see from Table III that θ_0 is largest for $MgFe_2O_4$ 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. θ_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 ξ in the spinel structure. We define η_{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

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

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

ACKNOWLEDGMENTS

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