

Magnetic Spectra of Manganese Ferrites*

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The complex initial permeability of a series of polycrystalline manganese-rich manganese ferrites ($Mn_{1+x}Fe_{2-x}O_4$) has been measured between 20 Mc/sec and 2000 Mc/sec. Three resonances are detected; the two lower-frequency resonances, which occur below 200 Mc/sec, are associated with domain wall motion. The higher-frequency resonance, which varies between 300 and 600 Mc/sec depending on the composition, allows the calculation of an effective polycrystalline anisotropy constant, K_e . Microwave resonance measurements on single crystals of the same composition give the real anisotropy constant K_1 . Comparison of these two experiments show that $K_e \approx 2K_1$. Measurement of the magnetic moment indicates that in these compounds the Mn^{2+} ion assumes a value of approximately two Bohr magnetons instead of the expected four Bohr magnetons.

I. INTRODUCTION

IN this paper the frequency dependence of the complex initial permeability ($\mu = \mu' - i\mu''$) of a system of manganese-rich manganese ferrites, $Mn_{1+x}Fe_{2-x}O_4$, is investigated between 20 Mc/sec and 2000 Mc/sec. Considerable data¹⁻⁹ on the magnetic spectra of certain ferrites already exist, but it was evident at the beginning of this research that little systematic study had been made of a series of related ferrites in which the polycrystalline and single-crystal properties could be compared. The purpose of this paper is to discuss the resonance frequencies and effective magnetic anisotropy of manganese-rich manganese ferrites and to show the relationship between the effective anisotropy and the real magnetocrystalline anisotropy measured by microwave resonance techniques on single-crystal samples of the same composition.

The general features of this type of magnetic spectra were first synthesized by Rado.¹ Two resonances characterized by peaks in μ'' are usually observed, and these are most often attributed to domain-wall resonance at the lower frequency and to the resonance of electrons in the crystalline anisotropy field at the higher frequency. Some controversy still exists about the nature of the lower-frequency resonance. Also, in the present work, it is observed that the lower-frequency resonance is resolved into two separate resonances. For the manganese ferrites in this study the lower-frequency resonances, which are most likely domain-wall phenomena, varied between about 20 Mc/sec and 150 Mc/sec. Such resonances were first identified by Rado, Wright, Emerson,

and Terris³ in terms of the concept of domain-wall inertia suggested by Döring.¹⁰ Most of our attention in this paper will be concentrated on the electron spin-resonance peaks which occur between 300 and 600 Mc/sec. This high-frequency dispersion was predicted by Landau and Lifshitz¹¹ and first observed experimentally by Snoek.⁵ The above-mentioned resonances are superimposed on a background of absorption that extends over a very large range of frequency; this background has been attributed by Polder and Smit¹² to the resonance of electron spins in the demagnetization fields due to domain-wall configurations. This absorption should be present for frequencies as high as $\nu = \gamma H_a / 2\pi$ where H_a , the effective resonance field, is entirely due to demagnetizing effects. H_a can be as large as $4\pi M_s$, where M_s is the magnetic saturation at room temperature. Since the limiting values of this field for the manganese ferrites studied here vary from 9000 to 12 500 Mc/sec, the Smit-Polder absorption still exists at the highest frequencies in our experiments.

An effective anisotropy constant for the polycrystalline materials used in the complex initial permeability measurements may be defined in the following way. For a cubic crystal whose easy axis of magnetization is along the [111] direction,¹³ the anisotropy field, H_A , is given by

$$H_A = \frac{4}{3}(K_1/M_s), \quad (1)$$

where K_1 is the first anisotropy constant in the expression for the anisotropy energy of a cubic crystal,

$$E = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2). \quad (2)$$

K_2 is the second-order anisotropy constant and can be ignored in these materials. The α 's are the direction cosines that the magnetization vector makes with the cubic axes. The frequency for this natural spin resonance

* A preliminary report of this work was given by Pollack, Harrison, and Kriessman, *Bull. Am. Phys. Soc. Ser. II*, **2**, 128 (1957).

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¹ G. T. Rado, *Revs. Modern Phys.* **25**, 81 (1953).

² Rado, Wright, and Emerson, *Phys. Rev.* **80**, 273 (1950).

³ Rado, Wright, Emerson, and Terris, *Phys. Rev.* **88**, 909 (1952).

⁴ J. L. Snoek, *Nature* **160**, 90 (1947).

⁵ J. L. Snoek, *Physica* **14**, 207 (1948).

⁶ J. B. Birks, *Nature* **158**, 671 (1946).

⁷ J. B. Birks, *Proc. Phys. Soc. (London)* **B63**, 65 (1950).

⁸ J. B. Birks, *Proc. Inst. Elec. Engrs.*, **104B** Suppl. 5, 179 (1957).

⁹ J. K. Galt, *Phys. Rev.* **85**, 664 (1952).

¹⁰ W. Döring, *Z. Naturforsch.* **3a**, 374 (1948).

¹¹ L. Landau and E. Lifshitz, *Physik. Z. Sowjetunion* **8**, 153 (1935).

¹² D. Polder and J. Smit, *Revs. Modern Phys.* **25**, 89 (1953).

¹³ All ferrites, except $CoFe_2O_4$, have negative anisotropy constants (i.e. easy axis along [111] direction). In Fe_3O_4 the easy axis changes from the [111] direction to the [100] direction at 130°K. [See L. R. Bickford, *Phys. Rev.* **78**, 449 (1950).]

is then

$$\nu = \frac{\gamma}{2\pi} H_A = \frac{2\gamma K_1}{3\pi M_s} \quad (3)$$

This relation gives the anisotropy constant in terms of the resonance frequency, but we must expect, as Rado has pointed out, that the measured resonance field is determined to some extent by the effect of demagnetizing fields in polycrystalline samples. However, in this paper, effective polycrystalline anisotropies calculated from Eq. (3) and single-crystal anisotropies determined by microwave resonance techniques are shown to be simply related.

The saturation magnetization was also measured as a function of composition; these measurements indicate that in these compounds the Mn^{3+} ion does not have the Hund's rule magnetic moment usually associated with the trivalent ionic state. This result is obtained by considering the distribution of cations among the *A* and *B* sites of the spinel lattice.

II. EXPERIMENTAL TECHNIQUES

The compounds $Mn_{1+x}Fe_{2-x}O_4$ were prepared from cp MnO_2 and Fe_2O_3 by standard ceramic techniques. The mixtures were presintered twice at $1200^\circ C$ for 24 hours. The twice-presintered powders were pressed into toroids, finally sintered at $1400^\circ C$ for 24 hours, and quenched in air from $1400^\circ C$. All the compounds were chemically analyzed after the presintering processes had been completed. In addition, some samples were analyzed after the final sintering. In these cases the composition was found to remain unchanged after the final sintering. The accuracy of the chemical analyses was better than $\pm 1\%$. These toroids were used in the measurement of the complex permeability and were inserted into a coaxial line adjacent to a short circuit termination, i.e., a position of maximum magnetic field and minimum electric field.^{1,7} They were made to fit the radial dimensions of the coaxial guide by grinding. Measurements were carried out using essentially the same experimental technique as that of Rado, Wright, and Emerson.² The real and imaginary parts of the permeability were determined by standing-wave techniques using the relations

$$\mu' = 1 + S/D, \quad (4)$$

$$\mu'' = (1/V - 1/V')(\lambda/2\pi D). \quad (5)$$

These relations are determined from the solutions of the boundary value problem for the TEM mode. The symbols have the following meanings: *S* is the shift of the position of the minimum from that of the empty wave guide; *D* is the thickness of the toroid; *V'* and *V* are standing wave ratios of the coaxial line with and without the ferrite sample, respectively; and λ is the wavelength of the electromagnetic wave in free space. The thickness of the samples was small enough so that no dimensional resonances such as those discussed by

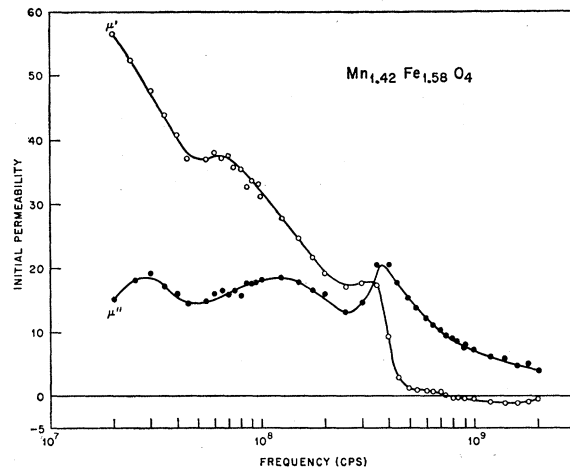


FIG. 1. The real (μ') and imaginary (μ'') parts of the initial permeability of $Mn_{1.42}Fe_{1.58}O_4$ as a function of frequency.

Brockman, Dowling, and Steneck¹⁴ would occur. After grinding the toroids to fit the coaxial guide and before measuring the initial permeability, the samples were heated above the Curie point and allowed to cool slowly. This procedure caused the spin-resonance peak to become much sharper and clearer. It appears, therefore, that the internal fields caused by the stresses in the material broaden the spin-resonance peak somewhat. That these stresses do not alter the magnitude of the internal field responsible for the resonance is also in agreement with previous findings.³

The magnetic moment measurements were made by a torsion method.¹⁵ Samples in the form of very small spheres weighing 1 to 3 mg are placed in an inhomogeneous magnetic field, and the resulting force is measured by bringing the system back to a null position. The system is calibrated by measuring the force on a pure nickel standard. Magnetization data taken as a function of temperature were extrapolated from liquid nitrogen temperature to absolute zero by the formula¹⁶

$$M = M_0(1 - \alpha T^2). \quad (6)$$

III. EXPERIMENTAL RESULTS

1. Magnetic Spectra

The real ($\mu' - 1$) and imaginary (μ'') parts of the complex initial permeability of a typical sample, $Mn_{1.42}Fe_{1.58}O_4$, are plotted as a function of frequency in Fig. 1. For most of the samples studied, three resonances are observed. If the samples are placed in a remanent state, it is observed that the magnitude of the two lower-frequency peaks is considerably altered. This can be seen in Fig. 2, in which μ'' for $Mn_{1.06}Fe_{1.94}O_4$ is plotted in both the demagnetized and remanent states. However, the high-frequency peak appears to be rela-

¹⁴ Brockman, Dowling, and Steneck, Phys. Rev. **77**, 85 (1950).

¹⁵ C. J. Kriessman and S. E. Harrison, Phys. Rev. **103**, 857 (1956).

¹⁶ R. Pauthenet, Ann. Physik **7**, 710 (1952).

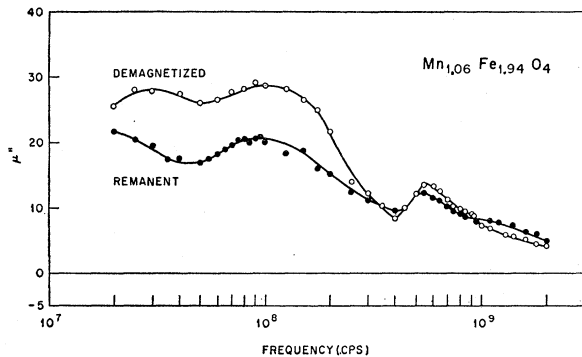


FIG. 2. The imaginary part of the initial permeability of $Mn_{1.06}Fe_{1.94}O_4$ in the demagnetized and remanent states.

tively unaffected by the change in magnetization. The frequencies at which the resonances occur for all the compositions studied are listed in Table I. For $x=1.11$ and 1.62, the middle peak appears to break up into two separate peaks. The two lower-frequency peaks occur at roughly the same frequency for all compositions. These lower-frequency peaks are observed to disappear if the sintered samples are broken up into powders in which the particle size is approximately single-domain.

As the manganese content is increased, the high-frequency peak moves systematically to lower frequencies as shown in Fig. 3.

2. Magnetic Moment and Curie Temperature

The magnetic moment *vs* temperature plots are well-behaved type-*Q* Néel curves.¹⁷ The saturation moment (μ_0) is plotted in Fig. 4 as a function of manganese content. μ_0 decreases linearly as manganese is added. The slope of the curve is 2.4 Bohr magnetons per molecule per Mn atom. The significance of this result is discussed in Sec. IV-2. The Curie point as a function of composition is shown in Fig. 5 and this also decreases linearly as the manganese content is increased.

IV. DISCUSSION

1. Magnetocrystalline Anisotropy

Since only the lower-frequency peaks are substantially altered when the magnetic state is changed from the

TABLE I. Resonance frequencies in Mc/sec as a function of composition, $1+x$.

$1+x$	f_1	f_2	f_3
1.06	29	93	570
1.11	25	80, 150	540
1.18	(25)	110	510
1.26	(40)	105	480
1.34	30	150	425
1.42	29	125	400
1.49	33	110	375
1.62	25	70, 140	300

¹⁷ L. Néel, *Ann. Physik* 3, 37 (1947).

unmagnetized to the remanent condition, it is assumed that these peaks are due to domain-wall resonance and the higher-frequency peak to the resonance of electron spins in the internal magnetocrystalline anisotropy field. These assumptions are based on the known differences in the magnetization process by domain-wall motion and by spin rotation; in domain-wall motion, the forces acting on the domain wall will be determined by the exact domain-wall configuration, i.e., by its state of magnetization. On the other hand, the forces on the spins when they rotate within a domain are determined solely by the anisotropy field which is dependent only on the crystalline field. Further experimental evidence in support of designating the lower-frequency peaks as domain-wall resonances is found in the disappearance of these peaks in finely powdered samples. This result has been previously observed by Rado¹ and is also observed in this work.

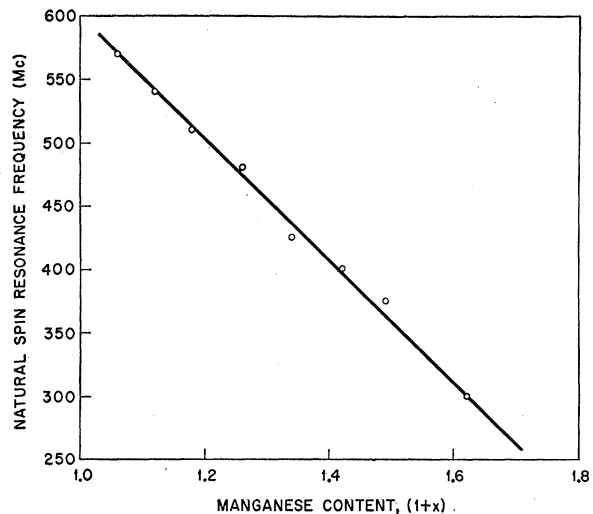


FIG. 3. The natural spin-resonance frequency obtained from initial permeability measurements plotted as a function of composition.

Since the high-frequency peak is due to the resonance of electron spins in the internal anisotropy field, an effective anisotropy constant, K_e , may be obtained by substituting the experimental resonance frequencies and magnetization data into Eq. (3). This effective constant is to be distinguished from the true anisotropy constant, K_1 .

The values of K_e determined from the natural spin-resonance experiment on polycrystalline samples are plotted as closed circles in Fig. 6 and are seen to decrease linearly with increase in Mn content. If we compare the value of K_e for pure $MnFe_2O_4$, -5.9×10^4 ergs/cm³, with the published data for K_1 obtained from a single crystal of $MnFe_2O_4$, -2.8×10^4 ergs/cm³,¹⁸ we find that $K_e \approx 2K_1$.

Single crystals identical in composition to some of the

¹⁸ Bozorth, Tilden, and Williams, *Phys. Rev.* 99, 1788 (1955).

compounds investigated in the natural spin-resonance experiments were grown by sintering disks of pressed ferrite for long periods of time. Crystals grown in this manner are small but allow their use in ferromagnetic resonance experiments in which K_1 , the true anisotropy constant, was determined. These microwave resonance experiments will be reported in detail elsewhere,¹⁹ but the values of K_1 are plotted as open circles in Fig. 6. K_1 also decreased linearly with composition; and we see that throughout the compositional range studied, K_e and K_1 are related by a constant multiplicative factor which is approximately equal to two. Also, we note that the linear dependence of K_e on composition implies that the total anisotropy of the crystal is simply the linear sum of the individual "ionic" anisotropies of each ion. This concept of "additive anisotropy" has previously been suggested for iron-rich MgFe_2O_4 by Folen and Rado.²⁰

The well-behaved dependence of the effective anisotropy, K_e , on composition leads us to believe that the spin-resonance frequency is determined mainly by the

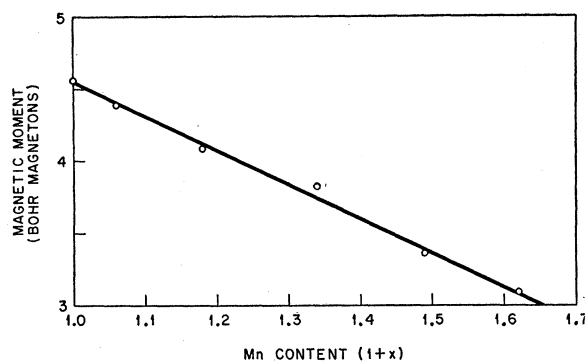


FIG. 4. The magnetic moment in Bohr magnetons plotted as a function of composition.

crystalline anisotropy and not by demagnetization fields, since demagnetization effects depend on the random grain structure of each individual polycrystalline sample and do not in general result in the regular dependence shown in Fig. 6. Both the real and the effective magnetic anisotropies when plotted as a function of composition extrapolate to zero at approximately $x=0.8$. This is the composition at which a second crystalline phase is detected by x-ray diffraction. The second phase is the tetragonal Mn_3O_4 phase with a slightly smaller c/a ratio (1.04 compared to 1.16 for Mn_2O_4). The two-phase compound is produced for $x=0.8$ if the compound is slowly cooled. If quenched in air, the diffraction lines of the cubic spinel phase appear. However, even in the quenched samples, the diffraction lines are considerably broadened and indicate that a small amount of second phase has been formed.

¹⁹ Harrison, Belson, and Kriessman (to be published).
²⁰ V. J. Folen and G. T. Rado, Bull. Am. Phys. Soc. Ser. II, 1, 132 (1956).

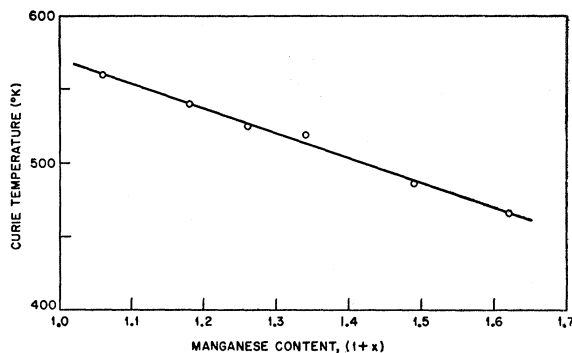


FIG. 5. The Curie temperature plotted as a function of composition.

We conclude that the effective internal field responsible for the natural spin-resonance is proportional to the anisotropy field. Even though the actual value of the anisotropy measured in the magnetic spectra work is larger than the real magnetocrystalline anisotropy, the real anisotropy field has not been obscured by the polycrystallinity of the sample.

Since the data on the system $\text{Mn}_{1+x}\text{Fe}_{2-x}\text{O}_4$ suggest that $K_e=2K_1$ within experimental error, we have investigated K_e for two simple ferrites, MgFe_2O_4 , and NiFe_2O_4 . The data for K_e are listed in Table II, and it again turns out that K_e is just about twice the value of K_1 determined from microwave resonance experiments. There remains however, the fact that other natural spin-resonance data²¹ on NiFe_2O_4 and on certain magnesium ferrites²² yield values of K_e not equal to twice K_1 ; in these data the ratio K_e/K_1 lies between one and

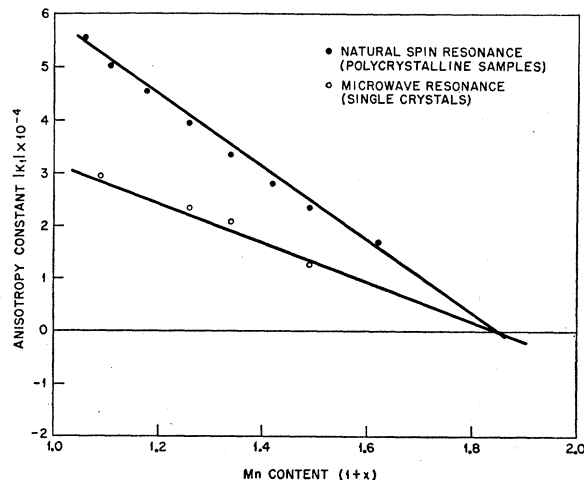


FIG. 6. The effective anisotropy constant, K_e , calculated from the natural spin resonance observed in initial permeability measurements (plotted as closed circles), and the real anisotropy constant, K_1 , obtained from microwave resonance experiments (plotted as open circles), both as functions of composition. The anisotropy constants are in units of ergs/cm^3 .

²¹ Yager, Galt, Merritt, and Wood, Phys. Rev. 80, 744 (1950).
²² Rado, Folen, and Emerson, Proc. Inst. Elec. Engrs. 104B, Suppl. 5, 198 (1957).

TABLE II. Values of K_1 (from microwave resonance measurements) and K_e (natural spin resonance, initial permeability measurements), in ergs/cm³.

Ferrite	K_1	K_e
NiFe ₂ O ₄	-6.0×10^4 ^a	-1.2×10^5 ^d
MgFe ₂ O ₄	-3.9×10^4 ^b	-8.0×10^4 ^d
Fe ₃ O ₄	-1.1×10^5 ^c	-2.1×10^5 ^e

^a See reference 21.

^b H. Belson and C. J. Kriessman (unpublished data).

^c L. R. Bickford, Phys. Rev. **78**, 449 (1950).

^d C. J. Kriessman and S. E. Harrison (unpublished data).

^e See reference 7.

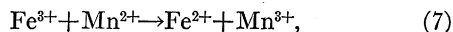
two. Closer examination of these data indicates that these materials for which K_e/K_1 does not equal two are quite porous, and that in these samples the demagnetization fields determine the resonance fields. Thus we expect that $K_e=2K_1$ is a general relation only for samples in which the density is close to the true density of the material, and that the ratio K_e/K_1 will be dependent on density. The density of all of our samples is at least 98% of the x-ray density, and we assume that in this type of sample the crystalline anisotropy alone determines the effective resonance field.

2. Magnetic Moment of Mn_{1+x}Fe_{2-x}O₄

We have seen in Fig. 4 that the magnetic moment decreases linearly as the Mn content increases. It is interesting to consider this variation of magnetic moment in the light of recent work on the ionic distribution of these compounds and to compare the experimental with the theoretically predicted variations.

Stoichiometric manganese ferrite (MnFe₂O₄) is a predominantly normal spinel. From neutron diffraction studies, Corliss and Hastings²³ have determined that about 0.8 of the Mn²⁺ ions in MnFe₂O₄ are on *A* sites. Further evidence for the strong preference of MnFe₂O₄ to be a normal spinel is found in the work of Kriessman and Harrison.¹⁵ In this last reference the magnetic moment as a function of quench temperature and composition is determined for Mg_yMn_{1-y}Fe₂O₄ (0 ≤ *y* ≤ 1.0). It was shown that a plot of the maximum fraction of Mg²⁺ ions on the *A* sites as a function of composition will approach zero at *y* = 0 if MgFe₂O₄ is combined with a normal spinel or ½ if combined with an inverse spinel. This method does not determine the exact degree of inverseness or normality, but it does qualitatively and clearly establish the predominant nature of the ionic distribution as has been shown for both MnFe₂O₄¹⁵ and NiFe₂O₄.²⁴

The distribution of cations in MnFe₂O₄ is shown in the first line of Table III. The manganese ions on the *B* sites are assumed to be in the divalent state. The occurrence of Fe²⁺ on the *B* sites, which in a stoichiometric compound would imply the electron transfer



²³ L. Corliss and J. Hastings, Phys. Rev. **104**, 328 (1956).

²⁴ C. J. Kriessman and S. E. Harrison, Bull. Am. Phys. Soc. Ser. II, **1**, 189 (1956).

does not seem to be energetically possible, since the third ionization potential for manganese is three electron volts greater than the third ionization potential for iron. McClure²⁵ has recently calculated the thermodynamic stabilization energy of the transition ions in the sites of the spinel lattice due to the crystal field splitting of the *d*-shell energy levels. According to these calculations, the crystal field stabilization lowers the energy of the Fe²⁺ and Mn³⁺ ions by about two electron volts with respect to the Mn²⁺ and Fe³⁺ ions in the octahedral sites. This still leaves a requirement of one electron volt for the formation of Fe²⁺, which is prohibitively large. Nevertheless, this hypothesis of electron transfer has been suggested²⁶ as a possible explanation for the discrepancy between the experimentally determined magnetic moment (4.6 Bohr magnetons) and the value of 5 Bohr magnetons expected in a spinel consisting of Mn²⁺ and Fe³⁺. However, in the small compositional range where Fe²⁺ and Fe³⁺ could exist, (i.e., while Mn²⁺ is present on the *B* sites), the final conclusions are not altered by the possibility of this electron transfer. When *x* increases from *x* = 0 to *x* = 0.2, then all the *A* sites are occupied by Mn²⁺ ions and further increases in *x* merely result in the replacement of Fe³⁺ ions by Mn³⁺ ions, as indicated in the second and third lines of Table III.

This change in the distribution of the magnetic ions will be accompanied by a variation in the magnetic moment with composition. For the purpose of discussion let us consider *x* > 0.2, in which case the magnetic moment (μ_0) in Bohr magnetons per molecule is

$$\mu_0 = 2\mu_{\text{Fe}^{3+}} - \mu_{\text{Mn}^{2+}} - x(\mu_{\text{Fe}^{3+}} - \mu_{\text{Mn}^{3+}}). \quad (8)$$

This equation predicts a linear decrease in the magnetic moment as *x* increases. The curve of Fig. 4 shows the expected linear variation of the magnetic moment. However, the slope of the line gives the value of $\mu_{\text{Mn}^{3+}} \approx 2$ Bohr magnetons (the exact value varies over a small range which is dependent on the value of $\mu_{\text{Fe}^{3+}}$) instead of the anticipated value of 4 Bohr magnetons, which is derived from the spin-only magnetic moment. There are several possibilities that may explain this surprising result. One explanation may be derived from a comparison of the strength of the crystalline field and exchange splittings. The crystalline electric field in a cubic crystal splits the five atomic levels into two degenerate levels, a doublet and a triplet. In the *A* site the doublet has a lower energy whereas in the *B* sites the

TABLE III. Ionic distribution of magnetic ions in manganese ferrites, Mn_{1+x}Fe_{2-x}O₄.

Composition	<i>A</i> sites	<i>B</i> sites
<i>x</i> = 0	Mn _{0.8} ²⁺ Fe _{0.2} ³⁺	Mn _{0.2} ²⁺ Fe _{1.8} ³⁺
0 < <i>x</i> < 0.2	Mn _{0.8+x} ²⁺ Fe _{0.2-x} ³⁺	Mn _{0.2-x} ²⁺ Fe _{1.8+x} ³⁺ Mn _{<i>x</i>} ³⁺
0.2 < <i>x</i> < 0.8	Mn ²⁺	Mn _{<i>x</i>} ³⁺ Fe _{2-x} ³⁺

²⁵ D. S. McClure, J. Phys. Chem. Solids (to be published).

²⁶ E. W. Gorter, Proc. Inst. Elec. Engrs. **104B** Suppl. 5, 228 (1957).

triplet is lower. In addition to the crystalline field splitting there is also the exchange splitting which sets the five states of the electrons of one spin at a higher energy than those of the other spin. This distribution of energy levels is shown schematically in Fig. 7. If the exchange energy splitting is greater than the crystalline field splitting, as in Fig. 7(a), then the magnetic moment of Mn^{3+} will be equal to 4 Bohr magnetons. If, however, the exchange energy is not greater than the crystalline field splitting, the distribution of the electrons over the energy states is that shown in Fig. 7(b), which predicts a magnetic moment of 2 Bohr magnetons in close agreement with the experimental result. It should be pointed out that McClure²⁵ has shown that the crystalline field splitting for Mn^{3+} in the octahedral site is substantially larger than the splittings for other transition elements.

In order to obtain a more quantitative estimate of the value of the magnetic moment of Mn^{3+} from the experimental results plotted in Fig. 4, it is necessary to determine the magnetic moments of Mn^{2+} and Fe^{3+} utilizing the recent neutron diffraction results of Corliss and Hastings.²³ According to their measurement of the magnetic moment (4.6β per $MnFe_2O_4$ molecule) and the distribution of Mn^{2+} ions, $\mu_{Mn^{2+}}$ and $\mu_{Fe^{3+}}$ are related by the following expression:

$$4.6\beta = 1.6\mu_{Fe^{3+}} - 0.6\mu_{Mn^{2+}}. \quad (9)$$

This equation does not allow the spin-only values of 5 Bohr magnetons for Mn^{2+} and Fe^{2+} to be used. One obvious possibility is to postulate the value of 5β for Mn^{2+} , which gives a magnetic moment of 4.8β for $\mu_{Fe^{3+}}$ and 2.4β for $\mu_{Mn^{3+}}$. The value of 4.8β for $\mu_{Fe^{3+}}$ seems difficult to justify since even a partial covalent binding of the Fe^{3+} ions in the B sites seems rather unlikely. However, the alternative presented by taking $\mu_{Fe^{3+}} = 5\beta$ seems physically to be much more questionable than the previous assumption since $\mu_{Mn^{2+}}$ would then equal 5.8β . The analysis of the neutron diffraction data²³ gives a value of 4.6 Bohr magnetons for each site. This is obtained from the neutron scattering factors. This result may, as a third alternative, be interpreted as $\mu_{Mn^{2+}} = \mu_{Fe^{3+}} = 4.6$.

These values of magnetic moment suggest that there is a small orbital contribution to the total magnetic moment, i.e., the orbital moment may not be completely quenched.

Van Vleck²⁷ has pointed out that in ions which are in S states (i.e., Mn^{2+} and Fe^{3+}) there may be a small amount of incipient $j-j$ coupling, not enough to distort appreciably the g factors from their Russell-Saunders values, but sufficient to impart a slight amount of orbital angular momentum to the S states. In any case it seems

²⁷ J. H. Van Vleck, Phys. Rev. 44, 208 (1932).

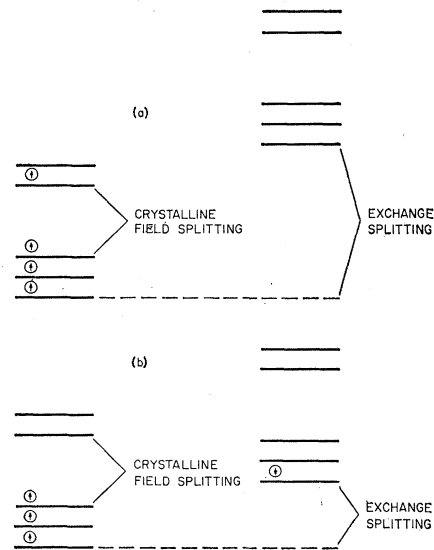


Fig. 7. Schematic distribution of energy levels for the octahedral site in a spinel. In (a) the exchange splitting is larger than the crystalline field splitting; while in (b) it is smaller.

unlikely that the residual amount of orbital moment would be identical for A and B sites.

Of the three possible sets of values of $\mu_{Mn^{2+}}$ and $\mu_{Mn^{3+}}$ mentioned above, we prefer the first set which gave $\mu_{Mn^{3+}} = 2.4$ because it appears at the moment to be the least objectionable. The choice of the exact numerical values of the magnetic moment of these ions is made for the sake of definiteness and does not influence the results or conclusions discussed in this paper.

V. SUMMARY

From the measurements of the natural spin-resonance of $Mn_{1+x}Fe_{2-x}O_4$ we have found that an effective anisotropy constant can be determined which is very closely equal to twice the magnetocrystalline anisotropy. This will allow determination of the magnetocrystalline anisotropy constant without the necessity of using a single crystal. From the variation of the magnetic moment with composition and a comparison with the ionic distribution, it appears that the magnetic moment of Mn^{3+} does not correspond to the spin-only moment of four Bohr magnetons. Instead the value for $\mu_{Mn^{3+}}$ is found to be approximately two Bohr magnetons.

ACKNOWLEDGMENTS

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