PHYSICAL REVIEW B **75**, 134406 (2007)

Abnormal spin structure of manganese ferrite investigated by ^{57}Fe NMR

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(Received 9 October 2006; revised manuscript received 5 December 2006; published 6 April 2007)

The spin structure of partially inverted $MnFe_2O_4$ is investigated using ^{57}Fe nuclear magnetic resonance (NMR). The experimental results are inconsistent with a phenomenologically deduced theoretical model predicting that Fe spins have a ferrimagnetic order where the spins in the tetrahedral (A) and the octahedral (B) sites form magnetic sublattices as in Fe_3O_4. The results show that there is an antiferromagnetic order among the Fe spins at B sites in addition to the antiferromagnetic order between the Fe spins in A and B sites. Moreover, the directions of Fe and Mn spins in A sites are antiparallel to each other, contrary to the commonly accepted assumption. We propose a model of spin structure that is also consistent with the previous ^{55}Mn NMR results. Comparison with other spinel ferrites implies that the role of Jahn-Teller ions in determining exchange interactions should be emphasized in inverted $MnFe_2O_4$.

DOI: 10.1103/PhysRevB.75.134406 PACS number(s): 75.50.Gg, 75.25.+z

I. INTRODUCTION

Iron oxide compounds of the spinel structure are ferrimagnetic or antiferromagnetic insulators having the longest history as magnetic materials. A cation in the spinel structure occupies an interstitial site of either tetrahedral (A) or octahedral (B) symmetry in the closed-packed lattice of oxygen. Since the A-B interaction is antiferromagnetic and usually stronger than the B-B and A-A interactions, a ferrimagnetic order where the spins at A and B sites form two magnetic sublattices is observed if both A and B sites are occupied by the same magnetic ions, as in magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3). In this simple case, the magnetic property is relatively well predictable within the mean-field picture and accordingly the strength of the exchange interactions can be estimated indirectly by measuring macroscopic quantities such as magnetization and susceptibility. If some of the Fe ions are replaced by other cations at A and/or B sites as manganese ferrite ($MnFe_2O_4$), however, the exchange couplings and the spin structure become complicated because the strength of the exchange interactions is influenced by chemical inhomogeneity in the sublattices, electronic valence of magnetic ions, and configuration of orbitals.[1] Macroscopic measurements cannot provide sufficient information to understand the magnetic properties of such complicated materials.

Manganese ferrite has a partially inverted spinel structure described by a formula $(Mn_{1-y}Fe_y)[Fe_{2-y}Mn_y]O_4$, where y is called the inversion parameter. The round and square brackets denote the cations locating at A and B sites, respectively. The electronic valences of Mn and Fe ions in normal manganese ferrite, $(Mn)[Fe_2]O_4$, are 2+ and 3+, respectively. In inverted $MnFe_2O_4$, the valence of Fe ions transferred from B sites to A sites remains the same as 3+. About the valence of Mn ions exchanged with Fe ions to B sites, however, there has been a controversy whether it remains the same as 2+ or changes to 3+ making the valence of nearby Fe ions at B sites change from 3+ to 2+.[2,3]

Since the valence of a magnetic ion determines its magnetic moment, the valence issue was important regarding the spin structure of $MnFe_2O_4$. Using the experimental data of saturation magnetic moment and degree of inversion, two different phenomenological models of spin structure were proposed:[4] a collinear ferrimagnetic spin order supposing the presence of Mn^{3+} and Fe^{2+} pairs in B sites and a canted ferrimagnetic spin order supposing the valence of Mn ions in B sites as 2+. Sawatzky *et al.*[3] supported the canted spin structure because Mössbauer experiments seemed to rule out the presence of Fe^{2+} ions. On the contrary, nuclear magnetic resonance (NMR) experiments supported the collinear spin structure because no evidence of spin canting was observed[5] while the spectra of Mn^{3+} and Fe^{2+} ions were clearly detected.[6] Later on, however, Dionne found that the $M(T)$ curve is not consistent with the collinear structure but explainable by the canted spin structure.[7] The main reason for this confusion seems to originate from the incorrect assignment of Mn and Fe spin directions in both models.

In this study, the Fe spin structure of $MnFe_2O_4$ was investigated by a ^{57}Fe NMR experiment. NMR is a useful local probe to examine the microscopic spin structure of magnetic materials. Most of the previous NMR experiments were focused on Mn ions and the absence of experimental information on the spin state of Fe ions led to the misunderstandings described above. One of the main results is that the spin direction of Fe ions in A sites is opposite to that of Mn ions in the same sites, contrary to the assumption commonly adopted in phenomenological models. Another surprising result is that the spectrum shows evidence for not only an antiferromagnetic order between the Fe spins at A and B sites but also an antiferromagnetic order among the Fe spins at B sites. This cannot be explained by Néel's mean-field theory based on the simple assumption that the effect of the substitution of other magnetic cations for Fe is only a slight change in the magnetic moment and exchange interactions. Based on these results, we propose a more accurate model of spin structure in inverted $MnFe_2O_4$. Comparison with the NMR experiments for nickel ferrite implies that Jahn-Teller ions play a role in determining the exchange interactions in $MnFe_2O_4$.

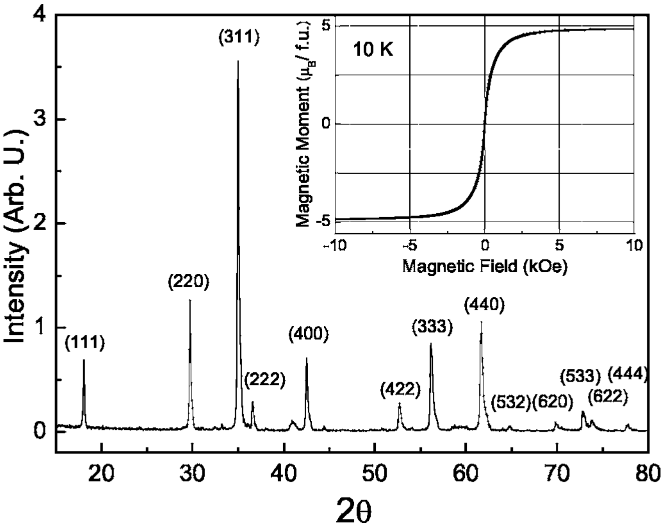

FIG. 1. The powder XRD pattern of polycrystalline $MnFe_2O_4$ obtained at room temperature. The inset is the *M-H* curve measured at 10 K.

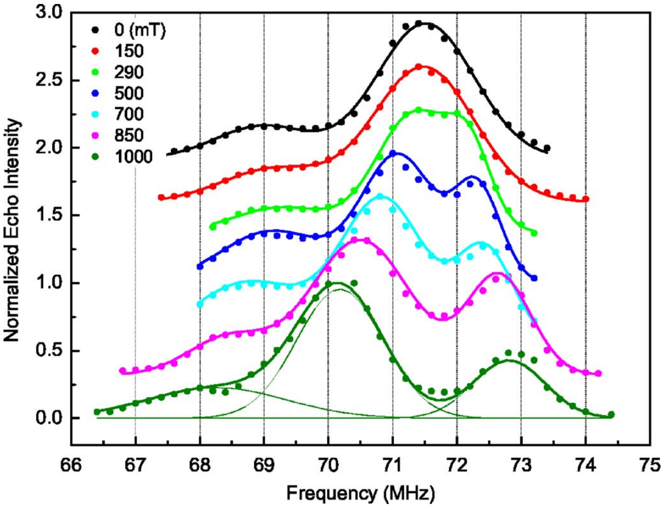

FIG. 2. (Color online) The ^{57}Fe NMR spectra of Mn ferrite obtained with various external magnetic fields and at 4.2 K. The solid lines represent multiple Gaussian fits.

II. EXPERIMENT

$MnFe_2O_4$ used in this study is commercially available polycrystal powder of 99.9% purity synthesized by KOJUNDO Chemical. Other ferrites studied for comparison, Fe_3O_4 and $NiFe_2O_4$, were synthesized by conventional solid-state reaction processing in air. As shown in Fig. 1, x-ray powder diffraction data collected using Cu K_α radiation confirmed that the samples have single phase of $MnFe_2O_4$. Magnetization was measured at 10 K by a commercial superconducting quantum interference device magnetometer. The *M-H* curve in the inset of Fig. 1 indicates that the saturated magnetic moment amounts to $4.85\mu_B$ per formula unit. ^{57}Fe NMR spectra were obtained using our homebuilt spectrometer. We used a closed-cycle cryogenic system to reach low temperature and an electromagnet for external magnetic field. In NMR experiments, spin echoes were measured at liquid helium temperature for various external fields. In a spin-echo pulse sequence $(90°\text{-}\tau\text{-}180°)$, the τ and 90° pulse widths were fixed as 80 μs and 0.5 μs, respectively. Since the spectra were broad, the echo height was measured as a function of frequency after a partial spectral excitation. At each frequency the NMR probe was tuned carefully with an impedance analyzer to avoid artificial effects.

III. RESULT AND DISCUSSION

The zero-field NMR spectrum reflects the hyperfine field that a nucleus in a magnetic material experiences. In the presence of an external magnetic field, NMR detects the direction of the local magnetic moment relative to external field. This is because the NMR resonance frequency is proportional to the total local field as[8]

$$f = \frac{\gamma}{2\pi}|\mathbf{H} - A_0\mathbf{M}|, \tag{1}$$

where **M** is magnetization and **H** is external magnetic field. The gyromagnetic ratio of a nucleus, $\gamma/2\pi$, is 1.38 MHz/T for ^{57}Fe. The hyperfine coupling constant A_0 is positive for most of the transition metal ions including Fe. Since the total magnetic field in Eq. (1) is a vector sum of the hyperfine field and external field and the former is generally much greater than the latter, the frequency shift due to the external field *H* is given as $-(\gamma/2\pi)H\cos\theta$ in first-order approximation, where θ is the angle between the magnetization of a sublattice and the external field. Therefore, the NMR resonance frequency shift obtained as a function of external field gives information on the direction of the magnetization.

The top graph of Fig. 2 is the zero-field ^{57}Fe NMR spectrum of $MnFe_2O_4$ obtained at 4.2 K. Double Gaussian peaks, one centered at 68.8 MHz and the other at 71.4 MHz, are clearly observed in the figure. The corresponding hyperfine fields are 49.8 T and 51.7 T, respectively. These two peaks represent the hyperfine fields that the nuclei of Fe^{3+} ions in the magnetic sublattices of *A* and *B* sites experience. The difference between the hyperfine fields of the two sites stems from the difference in the covalence of bonding between an Fe ion and the neighboring oxygens. Since this bonding is more covalent in the *A* site than in the *B* site, the hyperfine field of a Fe ion at the *A* site is expected to be slightly lower than that at the *B* site,[9] assuming identical chemical valences. Therefore, the left and right peaks in the spectrum come from *A* and *B* sites, respectively.

The relative population of ions in *A* and *B* sites is determined by the inversion parameter *y*. Previously reported values such as the degree of inversion vary from 0 to 0.5 depending on the method of thermal treatment.[10] Then the number of Fe ions at the *B* site is several times bigger than that at the *A* site and the intensity of the Fe NMR signal coming from the *B* site is also expected to be several times larger than that coming from the *A* site. Therefore, the small and large peaks in the top panel of Fig. 2 correspond to *A* and *B* sites, respectively, and this interpretation is consistent with the hyperfine field analysis discussed above.

The rest of the graphs in Fig. 2 show the spectra obtained in the presence of an external magnetic field. It is most no-

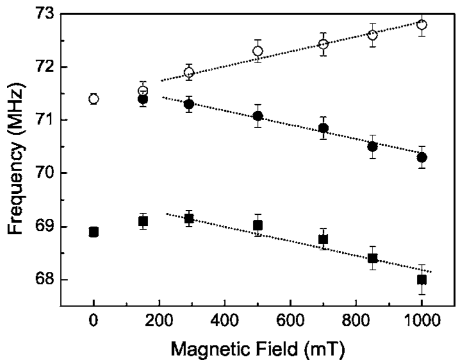

FIG. 3. The ^{57}Fe resonance frequency of the A site (squares) and B site (circles) vs external magnetic field obtained at 4.2 K. Dotted lines represent the theoretical fit of Eq. (1).

ticed that the B-site peak splits into two, one moving downward and the other moving upward with increasing field, while the A-site peak keeps its shape shifting downward. Equation (1) predicts that the resonance frequency shifts downward with increasing external field when the local magnetization is parallel with external field and upward when antiparallel. Therefore, the splitting of the B-site peak implies an antiferromagnetic order in B sites. The spins at B sites are antiferromagnetically ordered among themselves with their directions collinear with the direction of the spins at A sites that are also ordered in one direction. The largest peak in the middle moves downward with increasing external field, meaning that the majority magnetic moments are the Fe ions in B sites aligned parallel with external field as expected. Since the A-site peak shifts in the same direction with the majority peak, the magnetic moments of Fe ions transferred to A sites in inverted $\mathrm{MnFe_2O_4}$ are parallel with the majority magnetic moments in B sites. Therefore, the direction of majority Fe^{3+} spins in B sites and the spins in A sites are antiparallel with external field, while the minority spins in B sites are parallel.

The exact canting angle of the magnetization of a sublattice with respect to the direction of the external field, θ, can be estimated from Fig. 3, which displays the center frequencies of three peaks as a function of external field. The dotted lines represent the theoretical curves expected when the spins are collinear with the external field; that is, the slopes of the dotted lines are $\mp\gamma/2\pi$ ($\theta=0°$ or $180°$). All three curves fit relatively well to the experimental data at high fields, and therefore the canting angle is negligible within experimental error. The frequency shift of the B-site peak is somewhat unusual; the frequency increases slightly up to about 300 mT and then decreases. This unusual response to the external field may be related to domain wall motion, but complete understanding is absent for now.

The spin directions of these Fe^{3+} ions are depicted in Fig. 4, which illustrates the overall spin structure derived from the results of the present and previous experiments. In the figure, directions of spins were drawn for an external magnetic field pointing downward and the magnitude of the spin of each ion was represented by the length of each arrow. The thicker arrows represent majority spins and Fe′ represents the minority Fe ions in B sites. The result of previous Mn NMR experiment[5] showed that the direction of the majority Mn^{2+} spins in A sites is parallel with the external field, which we could confirm through our Mn NMR experiment. The fact that no evidence of spin canting of either Mn or Fe ions has ever been found in NMR experiments leads us to reject the model of the canted spin structure.

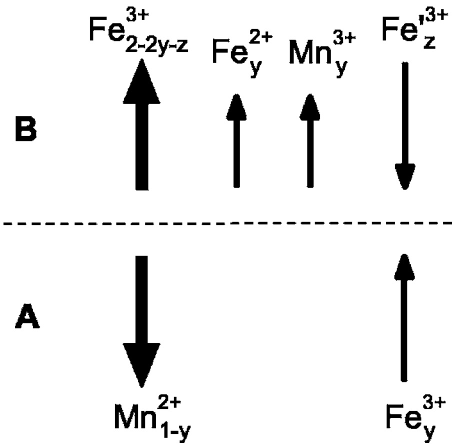

FIG. 4. The spin structure of manganese ferrite deduced from the present and previous NMR experiments. The longer arrows represent spin $S=5/2$ and shorter ones $S=2$. The thicker arrows represent majority spins in A and B sites. The subscripts represent the amounts per unit formula. The presently obtained spin direction of Mn^{2+} is consistent with the previous report of Ref. 5.

Previous NMR experiments[6,11] show clearly the presence of Mn^{3+} and Fe^{2+} ions in B sites, which we could also confirm through the Mn and Fe NMR. Therefore, the formula for inverted $\mathrm{MnFe_2O_4}$ can be described by $(\mathrm{Mn}^{2+}_{1-y}\mathrm{Fe}^{3+}_{y})[\{\mathrm{Mn}^{3+}\mathrm{Fe}^{2}\}_{y}\mathrm{Fe}^{3+}_{2-2y}]\mathrm{O}_4$. The spin directions of Mn^{3+} and Fe^{2+} ions are, however, hard to determine by measurement of the spectral shift with external field because their spectra are much broader than those of Mn^{2+} or Fe^{3+}. The directions of these spins illustrated in Fig. 4 were chosen to fit better the spectral areas of the peaks in Fig. 2 and the saturation magnetization value of $4.85\mu_B$ per formula unit (the inset of Fig. 1) along with the degree of inversion. From Fig. 4, the magnetic moment per formula unit is given as $M(\mu_B)=5-10z+8y$, where y and z can be estimated from the relative areas of three peaks in the NMR spectrum at 1 T in Fig. 2. The best Gaussian fit of the NMR spectrum intensity with three components after ω^2 correction gives $y=0.37$ and $z=0.31$.

Since our result of the observation of local spin states is much different from Néel's assumption of an antiferromagnetic arrangement of spins, the spin structure we derived from experiment is also different from the previous collinear spin model based on Néel's assumption. Compared with the previous model, the spin structure in Fig. 4 shows two peculiar features. One is the fact that there is antiferromagnetic order among the Fe^{3+} spins (Fe^{3+} and Fe'^{3+}) in B sites. The more striking fact is that the order between Mn and Fe spins in A sites is antiferromagnetic. This highly abnormal spin structure implies that the exchange interactions in inverted $\mathrm{MnFe_2O_4}$ are much more complicated than the existing mean-field theory has assumed. The change of the NMR

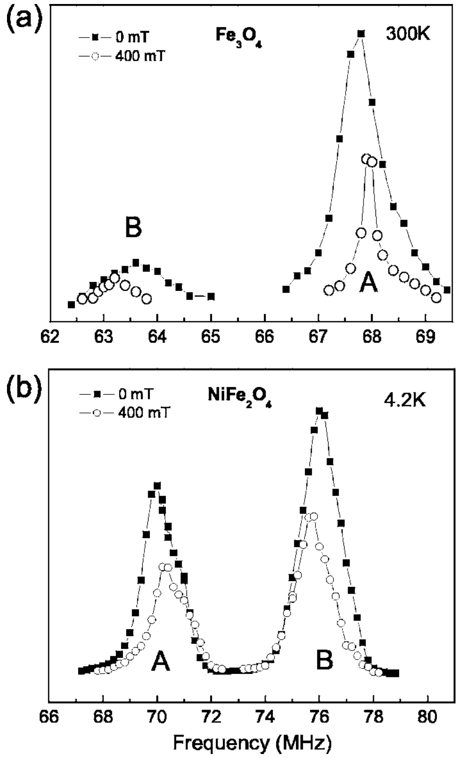

FIG. 5. The ^{57}Fe NMR spectra of (a) magnetite (Fe_3O_4) obtained at room temperature and (b) nickel ferrite ($NiFe_2O_4$) obtained at 4.2 K for zero external field and 400 mT.

spectrum in the presence of an external field is indeed very similar to that of partially inverted zinc ferrite ($ZnFe_2O_4$).[12] Physical situations, however, are completely disparate because Mn ions in $MnFe_2O_4$ have magnetic moment, while Zn ions in $ZnFe_2O_4$ have not. Though microscopic understanding is missing at this moment, some hints about the actual exchange interactions can be obtained by comparison with similar systems.

The interaction in magnetic insulators is a sum of direct-exchange and superexchange interactions, and the latter dominates in the spinel structure. In spinel ferrites, three antiferromagentic couplings compete to determine the spin structure: the *A*-*A*, *A*-*B*, and *B*-*B* interactions. Usually, the *A*-*A* interaction is negligible compared with the other two and the *A*-*B* interaction is stronger than the *B*-*B* interaction. When both the *A*-*B* and *B*-*B* interactions are present or only the *A*-*B* interaction is active, the usual ferrimagnetic ordering appears as in Fe_3O_4. The structure of Fe_3O_4 is expressed by a formula $(Fe^{3+})[Fe^{2+}Fe^{3+}]O_4$. Figure 5(a) is the NMR spectrum of Fe_3O_4 obtained at room temperature—i.e., above the Verwey transition temperature. The spectrum also shows double peaks coming from *A* and *B* sites. Contrary to $MnFe_2O_4$, the peak corresponding to the *B* site is observed at a lower frequency than that corresponding to the *A* site, because the average valence in the *B* site is reduced from 3+ to 2.5+ above the Verwey transition temperature due to rapid hopping of an excess electron between the Fe^{3+} and Fe^{2+} ions.[13] The spectral change of Fe_3O_4, having ferrimagnetic ordering, in the presence of an external magnetic field is clearly different from that of $MnFe_2O_4$. Two peaks shift in opposite directions with external field but keep their shapes unchanged and never split. Therefore, the magnetic moments at *A* and *B* sites are aligned antiparallel to each other. The main difference of $MnFe_2O_4$ from Fe_3O_4 is the inhomogeneity of chemical species and their electronic valence states in *A* and *B* sites. However, comparison with nickel ferrite ($NiFe_2O_4$) below shows that not only the inhomogeneity of chemical species and their valence states, but also the electronic configuration of each magnetic ion in sublattices influences the exchange interactions.

$NiFe_2O_4$ has the inverse spinel structure: that is, all Ni^{2+} ions occupy *B* sites, and a half of Fe ions occupy *A* sites and the other half *B* sites ($(Fe^{3+})[Ni^{2+}Fe^{3+}]O_4$). Figure 5(b) is the ^{57}Fe NMR spectrum of $NiFe_2O_4$ obtained at 4.2 K. Two clearly separated peaks are also observed in the spectrum, where the low-frequency peak comes from the spins of the *A* site and the high-frequency peak from those of the *B* site, as in $MnFe_2O_4$. The peaks shift in opposite directions with the external field maintaining their shapes, and no splitting is observed even at 400 mT as in Fe_3O_4. This means that $NiFe_2O_4$ also has a ferrimagnetic order composed of two magnetic sublattices of *A* and *B* sites in spite of the substitution of Ni ions for Fe ions in the *B* site.

Compared with Fe_3O_4 and $NiFe_2O_4$, the most notable feature of $MnFe_2O_4$ in an electronic configuration is that Mn^{3+} and Fe^{2+} in *B* sites are Jahn-Teller ions in contrast to Mn^{2+}, Fe^{3+}, and Ni^{2+}. The octahedral symmetry of *B* sites will be broken by the lattice distortion due to these ions, and this is believed to generate spectral splitting in the *B*-site peak (Fig. 2). Understanding how these factors affect the exchange interactions to generate the abnormal spin structure of $MnFe_2O_4$ needs further study. A real situation should be more carefully reflected in theoretical investigations including various valence states of magnetic ions and the associated Jahn-Teller distortion at *B* sites.

In conclusion, the results of a ^{57}Fe NMR experiment for partially inverted $MnFe_2O_4$ reveal that there is an antiferromagnetic order among the Fe spins in *B* sites in addition to the antiferromagnetic order between the Fe spins in *A* and *B* sites usually observed in spinel ferrites. Since no evidence of spin canting of either Mn ions or Fe ions is observed, all Fe and Mn spins are aligned collinear. The directions of Mn and Fe spins in *A* sites are antiparallel to each other, contrary to the commonly accepted assumption that they are parallel. The observation of spin directions can end the controversy about the spin structure of inverted $MnFe_2O_4$ that originated mainly from a misunderstanding about the spin direction of each magnetic ion. The abnormal spin structure of inverted $MnFe_2O_4$ cannot be understood within the mean-field picture, but requires a more detailed study of exchange interactions. Comparison with the other ferrites of the same structure seems to indicate that the Jahn-Teller ions play a crucial role in determining the spin structure of inverted $MnFe_2O_4$.

ACKNOWLEDGMENTS

This work was supported by the SRC/ERC program of MOST/KOSEF (Grant No. R11-2000-071) and a grant (No. R01-2006-000-10369-0) from the Basic Research Program of the KOSEF.

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