The spin structure of maghemite investigated by $^{57}$Fe NMR

Seong-Joo Lee$^1$ and Soonchil Lee
Department of Physics, Korea Advanced Institute of Science and Technology, Taejon 305-701, Korea
E-mail: Bebop@kaist.ac.kr

New Journal of Physics 8 (2006) 98
Received 24 March 2006
Published 12 June 2006
Online at http://www.njp.org/
doi:10.1088/1367-2630/8/6/098

Abstract. Maghemite ($\gamma$-Fe$_2$O$_3$) is a ferrimagnet that has long been studied; however, its exact spin structure and hyperfine field are still controversial. Maghemite has an inverse spinel structure where magnetic Fe ions occupy either the interstitial octahedral or tetrahedral sites of the oxygen lattice. The nuclear magnetic resonance (NMR) spectrum shows double peaks in zero external field. We split these peaks clearly by applying an external magnetic field and compared the peak intensities. The result showed that the hyperfine field at the nuclear spins in the octahedral site (50.2 T) was larger than that in the tetrahedral site (49.3 T). The field dependence of resonance frequency indicates that the spins at the octahedral site are antiparallel with external field, while those at the tetrahedral site are parallel but canted by $42 \pm 10^\circ$.

Contents

1. Introduction 2
2. Experiment 3
3. Results and discussion 3
Acknowledgments 6
References 6

$^1$ Author to whom any correspondence should be addressed.
1. Introduction

For several decades, maghemite ($\gamma$-Fe$_2$O$_3$) has been used in various magnetic applications, such as magnetic recording tape and pigment [1, 2]. Therefore, study of this material also has a long history, which has recently focused on nano-size particles [3]–[5] and/or variously doped materials [6, 7] rather than the pure maghemite. It is well known that maghemite is a ferrimagnet of the inverse spinel structure similar to magnetite (Fe$_3$O$_4$). In the spinel structure, Fe ions are located at the interstitial sites of the oxygen lattice of the fcc structure. There are two different sites Fe ions can occupy: the centre of a tetrahedron (A), composed of neighbouring oxygen ions and the centre of an octahedron (B). Stoichiometrically, maghemite is represented by the formula \((8\text{Fe}^{3+})_A[40/3\text{Fe}^{3+} + 8/3\Delta]_B\text{O}_{2-}\). Thirty two oxygen ions make eight A-sites and 16 B-sites. Eight Fe ions among \(64/3\) forming a unit cell with 32 oxygen ions occupy the A-sites, and the remaining \(40/3\) Fe ions occupy the B-sites leaving \(8/3\) vacancies at the B-sites [8]. It is known that all the exchange integrals \(J_{AA}\), \(J_{BB}\) and \(J_{AB}\) of the interactions between the spins of the Fe ions are negative in the spinel structure, and therefore, the spins tend to be ordered in an antiparallel direction with neighbouring spins. Since the AB interaction is the strongest among these interactions, maghemite shows ferrimagnetism where all the A spins are antiparallel with the B spins that are also parallel to each other.

The magnetic properties of maghemite have been mainly studied using Mössbauer spectroscopy. The results of these studies, however, do not agree with one another in every detail, such as the exact hyperfine field or the exact spin structure. There have been several reports claiming that the hyperfine fields of the Fe ions located in two sublattices are the same, because only one broad peak has been observed in Mössbauer spectra obtained at room temperature [5, 6, 9, 10]. In these reports, the estimated values of the hyperfine field have varied from 47.3 to 50.0 T. Other studies have reported two different values of the hyperfine field at room temperature. One result [7] showed that the hyperfine fields of the Fe ions in the A- and B-sites were 50.0 and 50.5 T, respectively. However, another study [11] claimed that the hyperfine field at the A-site was 45.2 T, which is greater than that in the B-sites, 44.9 T. The hyperfine fields estimated by extrapolating the data obtained in the external field to zero-field were 48.8 and 49.9 T for the A-site and the B-sites, respectively [12].

In most Mössbauer experiments performed at low temperatures, two different values of the hyperfine field were measured. The magnitudes of the hyperfine field were about 52 and 53 T, except in one case [11]. However, a controversy remains over which hyperfine field corresponds to which sublattice even at low temperatures. Some reports [11] have claimed that the hyperfine field at the nuclear spins in the A-sites is greater than that in the B-sites, while some have claimed the opposite [6], and others have provided no indexing of the sites [9] at all.

In this study, we performed an $^{57}$Fe nuclear magnetic resonance (NMR) experiment for $\gamma$-Fe$_2$O$_3$ for various external magnetic fields at room temperature and liquid-He temperature, to determine the exact hyperfine field and the precise spin structure. NMR is a useful tool to provide information on the local spin structure of a magnetic material through the hyperfine field nuclear spins experience. As far as we know, there has been no previous NMR experiment for pure $\gamma$-Fe$_2$O$_3$. We obtained two clear peaks arising from the nuclear spins in the A- and B-sites at room temperature, and were able to assign the exact hyperfine fields to the sites by comparison of the peak areas.

One way to distinguish more clearly between the peaks of the A- and B-sites is to apply an external magnetic field, because the total fields of antiparallel spins split in opposite directions.
in an external field. Clear distinction of the peaks, in turn, provides more detailed information about the spin structure. NMR spectra were obtained as a function of an external magnetic field at liquid-He temperature. From the result of this experiment, it was confirmed that the spins at the octahedral sites are antiparallel with the external field, while those at the tetrahedral sites are parallel with the external field but canted.

2. Experiment

The sample used for this study was commercial $\gamma$-Fe$_2$O$_3$ powder whose average size was labelled as under 1 $\mu$m (KOJUNDO CHEMICAL LAB CO., LTD; Lot. No. 107927). The result of x-ray powder diffraction (XRD) measurement showed that no other form of iron oxides exists in the sample within experimental error. The $^{57}$Fe NMR spectra were obtained by the spin echo method using our home-built spectrometer. Since the spectra were broad (about 2 MHz), echo heights were measured as a function of frequency after a partial spectral excitation.

3. Results and discussion

The NMR resonance frequency $\omega$ of magnetic materials is proportional to the vector sum of the hyperfine field and external magnetic field, as follows [13]:

$$\omega = \gamma |H - A\mu|.$$  (1)

In equation (1), $H$ is the external field, $\gamma$ is the gyromagnetic ratio and $-A\mu$ is the hyperfine field generated at a nuclear spin by a magnetic moment $\mu$. Since the constant $A$ is positive for a Fe ion, the directions of the hyperfine field and the magnetic moment are opposite to each other. In the absence of an external magnetic field, the NMR frequency is simply proportional to the hyperfine field. Therefore, a zero-field NMR experiment for a sample of the spinel structure provides detailed information about the local field that the A- and B-site nuclear spins experience.

Figure 1 shows a plot of the zero-field $^{57}$Fe NMR spectrum of maghemite obtained at room temperature. The figure shows that the spectrum is composed of two peaks. The resonance frequencies obtained by the double Gaussian fit to the data are 68.1 and 69.3 MHz, which correspond to hyperfine fields of 49.3 and 50.2 T, respectively. These values are similar to those of previous Mössbauer experiments, however, the NMR results are believed to be more accurate than the Mössbauer results, because the two peaks are distinguished more clearly in the NMR spectrum.

Since the area of a peak in an NMR spectrum is proportional to the number of the nuclei giving that signal, it is possible to assign the peak frequencies to the hyperfine fields at the A- and B-sites by comparing the areas of the two peaks. According to the stoichiometric formula of $\gamma$-Fe$_2$O$_3$, the ratio of the numbers of $^{57}$Fe ions at the A- and B-sites is 0.6 : 1. The ratio of the areas of the lower and higher frequency peaks estimated by double Gaussian fit to the data in figure 1 is 0.62 : 1. Therefore, the lower frequency peak represents the hyperfine field at the A-sites, and the higher frequency peak represents the hyperfine field at the B-site. In $\gamma$-Fe$_2$O$_3$, all Fe ions have the same valency of +3, and therefore, the magnetic moment at either the A-site or the B-site is equal to $5\mu_B$. The reason why the two hyperfine fields are different, even though

New Journal of Physics 8 (2006) 98 (http://www.njp.org/)
the magnetic moments are the same, is that the covalent bonding of a Fe ion is stronger in a tetrahedral site than in an octahedral site. Since the hyperfine field of an Fe ion tends to decrease with increasing covalent bonding [12, 14], the hyperfine field is weaker in a tetrahedral site than in an octahedral site.

We applied an external magnetic field to distinguish more clearly between the two peaks and to investigate the spin structure of the sublattices. Figure 2 shows the NMR spectra measured for various external fields at liquid-He temperature. At zero-field, the resonance frequencies increase to 71.8 and 73.0 MHz, from 68.1 and 69.3 MHz at room temperature, respectively. This increase is due to an increase of the average magnetic moment in thermal equilibrium with a decreasing temperature. The spectrum remains almost unchanged until 0.3 T, but the two peaks become overlapped at 0.58 T. As the external field is further increased, these peaks begin to split again until they are clearly separated at 2 T.

In a ferrimagnetic material like maghemite, the larger magnetization aligns parallel with the external field and the smaller one aligns antiparallel. The hyperfine field is antiparallel with the magnetization and is much stronger than a usual external magnetic field. Therefore, the hyperfine field and external field are antiparallel to each other at the sublattice of the larger magnetization. In addition, the NMR resonance frequency, which is proportional to the vector sum of the hyperfine field and the external field, decreases with an increasing external field. In contrast, the hyperfine field and external field are parallel with each other at the sublattice of the smaller magnetization, and the resonance frequency increases with an increasing external field. Figure 2 clearly shows that the peak corresponding to the tetrahedral site shifts to the higher frequency side with an increasing field, whereas the peak corresponding to the octahedral site shifts to the lower frequency side. This means that the magnetic moments at the tetrahedral site and the octahedral site are antiparallel and parallel with external field, respectively. The magnetization of the B-site sublattice is larger than that of the A-site sublattice, even though the magnetic moments of the two sublattices are the same, because there are more Fe ions in the B-site.

Figure 1. The zero-field NMR spectrum of maghemite obtained at room temperature. The dashed lines represent a double Gaussian fitting curve.
The change of $^{57}$Fe NMR spectra with the application of an external magnetic field at 4.2 K.

Since the gyromagnetic ratio $\gamma$ is negative, the spins at the octahedral sites are antiparallel with the external field, while those at the tetrahedral sites are parallel.

Figure 3 shows a plot of the resonance frequency versus the external field for the A- and B-sites. The solid circles represent the resonance frequency of the A-site, and the open circles, the B-site. In both cases, there is almost no change in the resonance frequencies until the external field reaches 0.3 T, after which they vary linearly. The resonance frequency remains unchanged for the low field until the magnetic moments rotate to the direction of the external field overcoming the anisotropy field that is estimated to be about 0.3 T from the data in figure 3. When the external field is increased more than this, the magnetic moments become parallel or antiparallel with the external field, and the resonance frequencies vary in proportion to the external field as expected from equation (1). In this case, the slope of the graph simply represents the gyromagnetic ratio of $^{57}$Fe ions. The solid line is the line with the slope value of the gyromagnetic ratio of $^{57}$Fe ions, 1.3815 MHz T$^{-1}$. This theoretical curve seems to fit well with the experimental data of the B-site.

The slope of the line fitting the experimental data of the A-site in the linearly changing region is, however, smaller than the gyromagnetic ratio. This phenomenon is observed when spins are canted. The hyperfine field of the canted spins, which is parallel or antiparallel with the spin direction, is not parallel with the external field. Since the hyperfine field is generally much greater than the external field, the frequency shift is approximately given by

$$\Delta \omega = \gamma H \cos \theta,$$  

(2)
Figure 3. The $^{57}$Fe NMR resonance frequency of the A-site (solid circles) and B-site (open circles) versus the external magnetic field at 4.2 K. The lines represent a linear fit to the data in the linearly changing region.

where $\theta$ is the canting angle. The linear fit to the data of the A-site (the dotted line) gives the slope of 1.03 MHz T$^{-1}$, and the canting angle estimated from equation (2) is $42 \pm 10^\circ$. This result is different from the conclusions of the previous reports claiming that both the A-site and B-site spins are canted and that the canting angles are 20$^\circ$ and 22$^\circ$, respectively [1], and 12$^\circ$ and 23$^\circ$, respectively [6].

In summary, from the $^{57}$Fe NMR spectra, we have accurately estimated the hyperfine fields of the Fe ions at the A- and B-site of maghemite as 49.3 and 50.2 T at room temperature, respectively, and 52.0 and 52.8 T at 4.2 K, respectively. The NMR spectrum change from application of an external magnetic field showed that the spins at the octahedral sites were antiparallel with the external field, while those at the tetrahedral sites were parallel but canted by $42 \pm 10^\circ$.

Acknowledgments

This work was supported by the SRC/ERC program of MOST/KOSEF (R11-2000-071) and a grant (R01-2006-000-10369-0) from the Basic Research Program of the KOSEF.

References

[1] Morrish A H and Haneda K 1983 J. Magn. Magn. Mater. 35 105
[2] Cornell R M and Schwertmann U 1996 The Iron Oxides (Weinheim: Verlagsgesellschaft mbH) p 4
[3] Dormann J L, D’Orazio F, Lucari F, Tronc E, Prené P, Jolivet J P, Fiorani D, Cherkaoou R and Noguès M 1996 Phys. Rev. B 53 14291
[4] Serna C J, Bødker F, Mørup S, Morales M P, Sandiumenge F and Veintemillas-Verdaguer S 2001 Solid State Commun. 118 437
[5] Vollath D, Szabó D V, Taylor R D, Willis J O and Sickafus K E 1995 Nanostruct. Mater. 6 941
Greenwood N M and Gibbs T C 1971 Mössbauer Spectroscopy (London: Chapman and Hall) p 241

New Journal of Physics 8 (2006) 98 (http://www.njp.org/)
[6] Helgason Ö, Greneche J, Berry F J, Mørup S and Mosselmans F 2001 J. Phys.: Condens. Matter 13 10785
[7] da Costa G M, De Grave E and Vandenbergh R E 1998 Hyperfine Interact. 117 207
[8] Waychunas G A 1991 Rev. Mineral. 25 11
[9] Murad E 1998 Hyperfine Interact. 111 251
[10] Vandenbergh R E, Barrero C A, da Costa G M, Van San E and De Grave E 2000 Hyperfine Interact. 126 247
da Costa G M 1995 PhD Thesis University of Gent
[11] Cornell R M and Schwertmann U 1996 The Iron Oxides (Weinheim: Verlagsgesellschaft mbH) p 124
da Costa G M, De Grave E, Bryan A M and Bowen L H 1994 Hyperfine Interact. 94 1983
[12] Armstrong R J, Morrish A H and Sawatzky G A 1966 Phys. Lett. 23 414
[13] Turov E A and Petrov M P 1972 Nuclear Magnetic Resonance in Ferro- and Antiferromagnets (Jerusalem:
Israel Program for Scientific Translations)
[14] Watson R E and Freeman A J 1961 Phys. Rev. 123 2027