Superparamagnetic behaviour of reentrant weak-ferromagnetic phase in haematite crystal at low temperatures

Seong-Joo Lee\textsuperscript{1}, Hyunok Jung\textsuperscript{1}, Soonchil Lee\textsuperscript{1,3} and Joonghoe Dho\textsuperscript{2}

\textsuperscript{1} Department of Physics, Korea Advanced Institute of Science and Technology, Daejeon 305-701, Korea
\textsuperscript{2} Department of Physics, Kyungpook National University, Daegu 702-701, Korea
E-mail: soonchillee@kaist.ac.kr

New Journal of Physics 11 (2009) 023020 (11pp)
Received 15 October 2008
Published 11 February 2009
Online at http://www.njp.org/
doi:10.1088/1367-2630/11/2/023020

Abstract. The present study investigates the magnetic properties of a natural haematite ($\alpha$-Fe\textsubscript{2}O\textsubscript{3}) crystal at the temperature of liquid helium using magnetometry and \textsuperscript{57}Fe nuclear magnetic resonance (NMR) methods. The magnetization curve shows that the net magnetization in the (111) plane vanishes at the Morin temperature (260 K) but weakly reappears as the temperature decreases below 40 K. A comparison of the magnetization and NMR results indicates that the spin state, direction and canting angle, at a low temperature, is identical to that in a weak-ferromagnetic state above the Morin temperature. Its volume, however, occupies only 3\% of the entire sample. The relaxation of magnetization with time, the difference of the zero-field-cooled and field-cooled magnetization, and the rise of the NMR echo intensity with increasing magnetic field exhibit the superparamagnetic behaviour of the reentrant weak ferromagnetic phase. The cluster size of the weak ferromagnetic phase is smaller than $10^2$ nm and the blocking temperature is higher than 40 K. The fact that the results from the natural crystal and pure powder are similar implies that the reentrant weak-ferromagnetic phase at a low temperature is due to the intrinsic magnetic instability of haematite.

\textsuperscript{3} Author to whom any correspondence should be addressed.
1. Introduction

Haematite ($\alpha$-Fe$_2$O$_3$) is an antiferromagnet of the corundum structure that undergoes an interesting magnetic transition around room temperature that is commonly known as the Morin transition \cite{1}. The hexagonal Fe ion layer is located between two stacked oxygen layers of the hcp structure. The spins of Fe ions in one layer, which align ferromagnetically in each layer, are antiparallel with those in the neighbouring layer. Haematite is typically indexed in the hexagonal structure but can also be indexed in the rhombohedral structure. The direction of the $c$-axis in the hexagonal structure corresponds to the [111]-direction in the rhombohedral structure. Above the Morin temperature $T_M \sim 260$ K, the spins of Fe ions antiferromagnetically align in the (111) plane with a small canting angle. Below $T_M$, however, this happens along the [111]-direction \cite{2}. As a result, haematite is in weak-ferromagnetic and antiferromagnetic states above and below the Morin temperature, respectively. In addition, a field-induced magnetic transition has been also observed in haematite \cite{3, 4}. When a strong external magnetic field is applied along the [111]-direction below $T_M$, the spins that were aligned in the [111]-direction suddenly lie in the (111) plane. This magnetic transition is frequently termed a spin-flop transition.

There have been extensive studies \cite{5–9} to investigate the interesting phenomena occurring near $T_M$. Remarkably, one \cite{9} of these studies reported that a weak-ferromagnetic state was observed in natural crystals at 4 K. Similar observations followed this initial report of another magnetic phase at a low temperature two decades later \cite{10–13}. A neutron diffraction study \cite{10} showed that the (111) peak intensity corresponding to a weak-ferromagnetic state increases in neutron-irradiated samples as temperature decreases to 4 K. It was claimed that this is due to disappearance of the Morin transition in the heavily irradiated samples. Another work \cite{11} reported that the integrated intensity of neutron diffraction increases with decreasing temperatures below 50 K; however, no detailed analysis was given. The reentrant transition from the antiferromagnetic to weak-ferromagnetic phases at low temperatures is interesting but has not been systematically studied for natural crystal or pure crystal.

In the present study, the magnetization and $^{57}$Fe nuclear magnetic resonance (NMR) spectrum were measured for a natural $\alpha$-Fe$_2$O$_3$ single crystal to investigate the low-temperature magnetic state in detail. Data were also obtained from highly pure commercial powder and this result was compared with that of the natural crystal to determine whether the magnetism at a low temperature is intrinsic. Net magnetization in the (111) plane vanishes at the Morin temperature but reappears at a low temperature in both the samples. A comparison of the $M(H)$ curves and the NMR signal intensity indicates that the antiferromagnetic and the weak-ferromagnetic phases coexist at a low temperature. The time dependence of the magnetization, the temperature-dependent magnetization curves obtained in the zero-field-cooled (ZFC) and field-cooled (FC) conditions, and the field dependence of the NMR echo intensity lead to the conclusion that the weak-ferromagnetic phase at a low temperature is in a superparamagnetic state.

2. Experiment

For most of the experiments, a natural crystal was used. However, a highly pure powder was also used occasionally for comparison. The samples were commercially available natural $\alpha$-Fe$_2$O$_3$ single crystals whose dimensions were approximately $2.5 \times 5 \times 1$ mm$^3$ (MaTecK GmbH, Germany) and $\alpha$-Fe$_2$O$_3$ powder whose purity was 99.998% (Sigma-Aldrich Co.,
Figure 1. The ZFC and FC magnetizations versus the temperature for the natural crystal denoted with the (blue) solid and (red) open circles, respectively. The direction of the external magnetic field is perpendicular to the [111]-direction and the magnitude is 100 Oe. The (red) crossed circles represent FC magnetization with the direction of the external field parallel to the [111]-direction.

Inc. Cat. No. 25572-6). The result of a qualitative analysis by an electron probe micro analyzer (EPMA) showed that the natural crystal contained a small amount of impurities. The impurities detected were Sn, C, Si, Ti, Cr, Xe, Cl, K, N and Ca. Magnetization was measured from room to liquid helium temperatures using a superconducting quantum interference device (SQUID) magnetometer. The $^{57}$Fe NMR spectra were obtained by the spin echo method using a custom-built spectrometer. Echo intensities were measured as a function of frequency after partial spectral excitation in external fields from 0 to 7 T.

3. Results and discussion

Figure 1 shows the temperature dependences of the ZFC and FC magnetizations of the natural crystal. These are denoted as solid and open circles, respectively. The external magnetic field is 100 Oe and its direction is perpendicular to the [111]-direction. The temperature-dependent magnetization $M(T)$ obtained with external field pointing along the [111]-direction (crossed circles) is also plotted for comparison. When the external field is perpendicular to the [111]-direction, the Morin transition is clearly observed in the temperature range of 250–200 K. The broad Morin transition is one of the characteristics of natural crystals containing small amounts of impurities, including Sn, Ti and Cr ions. The transition temperature of the natural crystal sample is high compared to those in previous works [2]. A comparison of $M(T)$ in the (111) plane with that in the [111]-direction shows that the net magnetization is in the (111) plane. The most interesting feature in this figure is that the magnetization increases again as the temperature decreases below 40 K, which is more clearly seen in the FC magnetization in the inset. The distinctive difference between the ZFC and FC magnetizations is discussed later.
Figure 2. Magnetization versus external magnetic field for the natural crystal obtained at 300 K ((blue) open symbols) and 5 K ((red) solid symbols). The circles and rectangles represent cases in which the direction of the external field is parallel with and perpendicular to the [111]-direction, respectively. Solid lines are guides for the eye.

In figure 2, the field dependence of the magnetization $M(H)$ of the natural crystal as obtained by the SQUID magnetometer is plotted. The open and solid symbols represent the data obtained at 300 and 5 K, respectively, and the circles and rectangles represent cases in which the direction of the external field is parallel with and perpendicular to the [111]-direction, respectively. At 300 K, the saturation magnetization of the weak-ferromagnetic phase estimated by extrapolating the linear region of the experimental data to zero field is 0.38 emu g$^{-1}$ (see the inset in the right bottom corner). The saturation magnetization $M_S$ is related to the canting angle $\theta$ through

$$M_S = (5\mu_B)(2 \sin \theta N_A/m),$$

where $5\mu_B$ is the magnetic moment of the Fe$^{3+}$ ion, $N_A$ is Avogadro’s number and $m$ is the formula mass of haematite. The canting angle estimated from equation (1) and the measured value of the saturation magnetization is 0.06°, which is fairly similar to the previous result [2]. The inset in the upper left corner of figure 2 shows that magnetic hysteresis exists in the (111) plane at 5 K, though the saturation magnetization is only approximately 0.01 emu g$^{-1}$.

The results of the $M(T)$ and $M(H)$ measurements indicate the existence of the weak-ferromagnetic phase below a reentrant temperature $T_R$ of nearly 40 K. The Dzialoshinskii–Moria (DM) interaction [5, 6] predicts that the spins tend to align in the (111) plane when haematite shows weak ferromagnetism. Therefore, the spins are believed to be antiferromagnetically aligned in the (111) plane below $T_R$, as above $T_M$. One of the reasons why the saturation magnetization below $T_R$ is much weaker than that above $T_M$ is that the sample is not entirely in the weak-ferromagnetic state. In an external magnetic field parallel to the [111]-direction, the $M(H)$ curve measured at 5 K (solid circles) is clearly different from that measured at 300 K (open circles). When the external field increases in parallel with the [111]-direction, the magnetization at 5 K remains low initially but starts to increase rapidly near 30 kOe until
Figure 3. (a) The ZFC and FC magnetization versus the temperature for the highly pure powder denoted with the (blue) solid and (red) open circles, respectively. The direction of the external magnetic field is perpendicular to the [111]-direction and the magnitude is 100 Oe. (b) Magnetization versus external magnetic field obtained at 300 and 5 K as denoted by the (blue) open circles and (red) solid circles, respectively.

Figure 3 shows the $M(T)$ and $M(H)$ values of the highly pure commercial powder obtained by the SQUID magnetometer. For the polycrystalline powder sample, there is essentially no significant difference between the ZFC and FC $M(T)$ curves. The Morin transition, the temperature range of which is narrower than that of the natural crystal, was found to be close to 250 K, and the net magnetization increases slightly as the temperature decreases below 20 K. Although magnetic hysteresis is clearly observed in the $M(H)$ curve obtained at room temperature in figure 3(b), it is relatively weak at low temperatures. However, the $M(T)$
Figure 4. NMR frequency ((blue) crossed circles) and normalized spin echo amplitudes plotted as a function of the temperature for the natural crystal. The (black) open circles represent the raw echo intensity data, whereas the (red) solid circles denote the corrected data for the temperature dependence of the nuclear magnetization and the spin–spin relaxation. The solid line represents the normalized $FC M(T)$ in figure 1.

and $M(H)$ measurements indicate the existence of a low-temperature weak-ferromagnetic phase in the highly pure commercial powder, implying that the phase transition at $T_R$ may be an intrinsic property of haematite. However, the shapes of the ZFC and FC $M(T)$ curves are very similar and the reentrant transition temperature $T_R$ is lower than that in the natural crystal.

To obtain microscopic information regarding the magnetic state at a low temperature, $^{57}$Fe NMR value for the natural crystal was measured. The NMR resonance frequency $\omega$ of magnetic materials is proportional to the vector sum of the hyperfine field and external magnetic field, as

$$\omega = \gamma |H - A\mu|,$$

where $H$ is the external field, $\gamma$ is the gyromagnetic ratio and $-A\mu$ is the hyperfine field generated at a nuclear spin by the electronic magnetic moment $\mu$. As the constant $A$ is positive for Fe ions, the directions of the hyperfine field and the magnetic moment are opposite to each other.

In figure 4, the temperature dependences of the NMR frequency (crossed circles) and the normalized spin echo amplitudes (open circles) obtained in a zero external magnetic field are plotted. Given that the NMR frequency is proportional to the magnetic moment in a zero external field, as shown in equation (2), the temperature dependence of the NMR frequency simply follows that of the magnetic moment of a single Fe ion. The resonance frequency decreases from 73.55 to 71.23 MHz as the temperature increases from liquid helium to room temperature. These frequencies correspond to hyperfine fields of 53.24 and 51.56 T, respectively. The hyperfine fields are very close to the values measured in the Mössbauer experiment [4] in the weak-ferromagnetic state. In the Mössbauer study, the hyperfine field changed to 0.827 T [7], crossing the Morin transition; however, this discontinuity was not observed in the present NMR result. The resonance frequency observed at a low temperature is also similar to a previous NMR work that reported a weak signal [9].
Figure 5. The $^{57}$Fe NMR spectra of the natural crystal obtained in various external magnetic fields at 4.2 K. The direction of the field is perpendicular to the [111]-direction.

The signal intensity at a low temperature reported here is significantly large. It is even larger than that at room temperature, as seen in the figure. Remarkably, the temperature-dependent NMR intensity also shows a clear increase below 40 K as well as a broad Morin transition at 200–250 K. The NMR intensity generally depends on the spin–spin relaxation time ($T_2$) and the temperature as $1/T$. $T_2$ was measured in the entire temperature range, which varied between 0.8 and 10 ms. The solid circles in figure 4 represent the normalized NMR intensity with respect to the value at 284 K after a correction for the temperature dependence of the nuclear magnetization and of $T_2$. The solid line in figure 4 is a replica of the normalized $M(T)$ obtained in the FC condition in figure 1. The temperature dependence of the NMR echo intensity is similar to the FC $M(T)$ curve over the entire temperature range. The macroscopic magnetization is proportional to the product of a magnetic moment and its volume. The ratio of the saturation magnetizations obtained along the (111) plane at 300 and 5 K is $1:0.03$. This difference in the saturation magnetization values comes from the difference of the magnetic moments and/or their volumes. The ratio of the corrected NMR echo intensities obtained at room temperature and at a low temperature is also $1:0.03$. The NMR echo intensity is dependent on the number of nuclei giving that signal, which is proportional to the volume of the weak-ferromagnetic phase in this case, as the NMR frequency and therefore the magnetic moment are nearly constant over the entire frequency range. Therefore, it is not the magnitude of the magnetic moment but the volume of the weak-ferromagnetic phase that results in the differences in the magnetization values at a low temperature and at room temperature. Consequently, it was found that at a low temperature, approximately 3% of the spins align in the (111) plane with a small canting angle. The rest of the spins align in the [111]-direction antiferromagnetically.

To investigate the magnetic state at a low temperature in more detail, the NMR spectra in an external magnetic field up to 7 T of the natural crystal (figure 5) were observed. Both
Figure 6. (a) The $^{57}$Fe NMR frequency versus the external magnetic field at 4.2 K ((red) solid circles) and at room temperature ((blue) open circles). The solid lines represent the theoretical curves of the frequency shift. (b) Normalized spin echo intensity versus the external magnetic field at 4.2 K ((red) solid circles) and at room temperature ((blue) open circles).

The resonance frequency and the signal intensity changed with the application of the external field. In the weak-ferromagnetic state of haematite, the direction of the magnetic moment that aligns in parallel with external field is nearly perpendicular to the spin direction. Therefore, the direction of the hyperfine field that is parallel with the spin direction is also nearly perpendicular to the external field direction. Hence, the frequency shift due to the external field is very small. From equation (2), the frequency shift can be expressed by

$$\omega = \frac{\gamma}{\sqrt{H^2 + H_{hf}^2 - 2HH_{hf}\sin \theta}},$$

where $\theta$ is the canting angle of the spins and $H_{hf}$ is the hyperfine field. The shift of the NMR frequency versus the external magnetic field obtained at a low temperature is plotted in figure 6 together with the data obtained at room temperature for comparison. The NMR signal intensity decreases as the external field increases in general and was observed only up to 1 T above $T_M$ in previous studies [8, 9], in contrast with the present study. The solid lines represent the
theoretical prediction of equation (3) with a canting angle $\theta = 0.06^\circ$. The lines fit well with the experimental data both at room temperature and at a low temperature. This is clear microscopic evidence that the magnetic structures at low and room temperatures are identical.

In figure 6(b), the NMR echo intensities versus the external magnetic field obtained at a low temperature (solid circles) and at room temperature (open circles) are plotted. The echo intensity decreases as the field increases at room temperature. The radio-frequency (RF) field necessary to generate the maximal echo height, in contrast, increases as the external field increases. These are the typical signal and RF field enhancement effects observed in NMR for ferromagnetic or ferrimagnetic materials in an external field. It is well known that both enhancement effects decrease as the field increases in ordinary magnets. The NMR echo intensity at liquid helium temperature, however, increases as the external field increases to 5 T and then decreases as the field increases further. The RF field generating the maximal echo intensity continues to increase as the external field increases to 5 T and then becomes saturated. The echo intensity obtained at 5 T is nearly three times as large as that obtained at a zero field. The intensity peak in a finite external magnetic field at 4.2 K may be due to the competition between the decrease of the RF enhancement effect and the volume expansion of the weak ferromagnetic phase embedded in the antiferromagnetic matrix as the field increases. A more plausible explanation is the superparamagnetic behaviour of the small-size cluster of the weak ferromagnetic phase. Such unusual signal enhancements with external field have been observed in several superparamagnets. The NMR signal increased as the external field increased to 9 kOe in a $^{59}$Co NMR experiment with a nanosized Co/NaY sample [14]. The authors explained that the signal of a superparamagnet increases because the spins in nanoparticles are blocked and then behave ferromagnetically in an external magnetic field. Another observation was made in a $^{101}$Ru NMR experiment with a Sr$_2$RuGdO$_6$ powder sample [15]. In this experiment, a new peak corresponding to the superparamagnetic phase in the antiferromagnetic matrix emerged as the field increased at 1.3 K. The observation of superparamagnetic behaviour in the weak ferromagnetic state at a low temperature by NMR is consistent with the observation of the difference between the FC and ZFC magnetizations in figure 1, which is one of the typical phenomena found in superparamagnets.

Another experimental evidence of superparamagnetic behaviour at a low temperature was obtained through the time dependence of magnetization. Figure 7 shows normalized magnetizations $M(t)$ for the natural crystal obtained at 300 K (open circles) and at 10 K (solid circles). Although the magnetization at 300 K remains constant with time, the magnetization at 10 K increases approximately 5% as the time increases from 10 to $10^4$ s and continues to increase, even after $10^4$ s. This long-term relaxation and the difference between the ZFC and FC magnetizations are typically observed in spin glasses as well as in superparamagnets. Considering that geometrical magnetic frustration cannot occur in the crystal structure of haematite, it is difficult to imagine that the sample exhibits spin glass behaviour though cluster glass behaviour is occasionally observed in some materials with impurities [16]. Moreover, the NMR signal enhancement has been observed in superparamagnets but not in spin glasses. Therefore it is believed that the reentrant weak-ferromagnetic phase at low temperature is in the superparamagnetic state.

The NMR signal is generally unobservable in the superparamagnetic state above the blocking temperature because spin fluctuation is so fast that a spectrum becomes too broad to be detected. Therefore, the lower bound of the superparamagnetic blocking temperature $T_B$ can be estimated by the highest temperature where the NMR signal is clearly observed, which
Figure 7. The time dependence of the normalized ZFC magnetization curve for the natural crystal obtained at 10 K ((red) solid circles) and at 300 K ((blue) open circles). The external magnetic field was 100 Oe.

is approximately 40 K in this case. The size of the weak-ferromagnetic phase embedded in an antiferromagnet matrix should be smaller than the single domain size of nanoparticles, which is nearly $10^2$ nm for Fe$_3$O$_4$ and γ-Fe$_2$O$_3$ [17].

For comparison, the same NMR experiments were repeated for the pure commercial powder. The spectra were observed not only at room temperature but also at low temperature, as with the natural crystal. The resonance frequencies of the natural crystal and pure powder in a zero field are identical within an acceptable level of experimental error. As the easy axes are randomly distributed in the powder sample, broader spectra than those of the natural crystal were obtained in the external field. The signal intensity decreased monotonically as the field increased at both temperatures. A comparison of the results of the two samples obtained by the NMR and SQUID experiments implies the possibility that the weak-ferromagnetic state at the low temperature is due to an intrinsic instability, which may be enhanced by the effects of the defects and/or impurities.

4. Conclusion

The results of $M(T)$ and $M(H)$ measurements show that haematite undergoes two magnetic phase transitions as the temperature decreases from room to liquid helium temperature. These are a transition from the weak-ferromagnetic to antiferromagnetic phases around 260 K and another transition from the antiferromagnetic phase back to the weak-ferromagnetic phase around 40 K. A comparison of the magnetization and NMR results indicates that the weak-ferromagnetic state at a low temperature is identical to the weak-ferromagnetic state above the Morin temperature; i.e. the spins are aligned in the (111) plane and canted by $0.06^\circ$, generating a weak-ferromagnetic state. The reentrant weak-ferromagnetic phase at a low temperature, however, occupies only about 3% of the entire sample volume. It is thought that nano-sized clusters of the weak-ferromagnetic phase are embedded in the antiferromagnetic matrix, occupying the rest of the volume. The relaxation of magnetization with time, the difference in
the ZFC and FC magnetizations, and the rise of the NMR echo intensity as the field increases indicate the superparamagnetic behaviour of the local weak-ferromagnetic phase. The size of the weak-ferromagnetic phase is smaller than \(10^2\) nm and the blocking temperature is higher than 40 K.

The reentrant weak-ferromagnetic state is also found with highly pure powder through its magnetization and by the NMR. However, the magnetic properties of the weak-ferromagnetic state were weaker to a certain extent in the pure powder than in the natural crystal. For example, the saturation magnetization is smaller, the reentrant transition temperature is lower, the difference of the ZFC and the FC measurements is smaller, and the RF enhancement behaviour in NMR is different. The weak-ferromagnetic state at a low temperature appears to be due to the intrinsic magnetic instability of haematite, which is enhanced by the effects of impurities and/or defects.

Acknowledgments

This work was supported by the SRC/ERC program of MOST/KOSEF (R11-2000-071), a grant (R01-2006-000-10369-0) from the Basic Research Program of KOSEF and by a Korea Research Foundation grant (KRF-2008-314-C00127).

References

[1] Morin F J 1950 Phys. Rev. 78 819
[2] Cornell R M and Schwertmann U 1996 The Iron Oxides: Structure, Properties, Reactions, Occurrence and Uses (Weinheim: VCH)
[3] Kaneko T and Abe S 1965 J. Phys. Soc. Japan 20 2001
[4] Pankhurst Q A, Johnson C E and Thomas M F 1986 J. Phys. C: Solid State Phys. 19 7081
[5] Dzialoshinskii I E 1957 Sov. Phys. JETP 5 1259
[6] Moriya T 1960 Phys. Rev. 120 91
[7] Tobler L, Kündig W and Savić I 1981 Hyperfine Interact. 10 1017
[8] Matsuura M, Yasuoka H, Hirai A and Hashi T 1962 J. Phys. Soc. Japan 17 1147
[9] Anderson D H 1966 Phys. Rev. 151 247
[10] Zheltbaev A K and Donbaev K M 1986 Hyperfine Interact. 28 623
[11] Baruchel J, Clark G, Tanner B K and Watts B E 1987 J. Magn. Magn. Mater. 68 374
[12] Zheltbaev A K, Donbaev K M and Ablanov M B 1990 Phys. Status Solidi b 157 K55
[13] Donbaev K M, Zheltbaev A K and Mukusheva M K 1993 Phys. Status Solidi b 176 219
[14] Zhang Y D, Hines W A, Budnick J I, Zhang Z and Sachtler W M H 1994 J. Appl. Phys. 76 6576
[15] Han Z H, Mohottala H E, Budnick J I, Hines W A, Klamut P W, Dabrowski B and Maxwell M 2006 J. Phys.: Condens. Matter 18 2273
[16] Dho J, Kim W S and Hur N H 2002 Phys. Rev. Lett. 89 027202
[17] Leslie-Pelecky D and Rieke R 1996 Chem. Mater. 8 1770