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Coexistence of ferrimagnetic and antiferromagnetic ordering in Fe-inverted zinc ferrite investigated by NMR

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The spin structure of nanocrystalline zinc ferrite synthesized via a high-energy ball milling process was investigated by nuclear magnetic resonance obtained at various external magnetic fields and temperatures. Iron inversion induced in nanosized zinc ferrite drastically changes its magnetic property. Nanocrystalline zinc ferrite shows ferrimagnetism below 460 K, while bulk zinc ferrite shows antiferromagnetism below 10 K. We found that this antiferromagnetic order coexists with the ferrimagnetic order below 10 K in nanocrystalline samples as well. A spin of Fe ion at the tetrahedral site is ferrimagnetically coupled with that at the octahedral site and the antiferromagnetism is found among the spins at the octahedral sites. The spins that participate in both of the ferrimagnetic and antiferromagnetic orderings at the octahedral site are canted.

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I. INTRODUCTION

Cations in spinel ferrites can occupy either an interstitial site of tetrahedral symmetry or octahedral symmetry within a close-packed oxygen lattice. The magnetic properties of spinel ferrites, such as transition temperature and saturation magnetic moment, strongly depend on the distribution of cations; such magnetic properties have been studied widely for several decades.[1] Zinc ferrite, $ZnFe_2O_4$, is one of the good spinel ferrites to study this effect in, because Zn is a nonmagnetic atom and, therefore, all we need to consider is the Fe distribution. Since the structure of zinc ferrite is very stable when Zn^{2+} ions occupy tetrahedral sites, the effect of cation distribution in zinc ferrite has been systematically investigated, after the discovery that some of Zn^{2+} ions are exchanged with Fe ions in nanocrystalline samples. The magnetic property of nanocrystalline zinc ferrites is very different from that of bulk zinc ferrite. Bulk zinc ferrite is antiferromagnetic below 10 K, while zinc ferrite nanoparticles show ferrimagnetic ordering at room temperature. Although it is well known that this change of magnetic property is due to the inversion of cations, the exact spin structure remains controversial.

General spinel structure can be described by a formula $(D_{1-c}T_c)[D_cT_{2-c}]O_4$, where D and T are divalent and trivalent ions, respectively, and c is called the inversion parameter. The round and square brackets denote the cations located at the center of the tetrahedral lattice of oxygen (A) and those at the octahedral (B) lattice, respectively. While bulk zinc ferrite has the normal spinel structure in which $c=0$, several experiments have reported that $c \neq 0$ in nanocrystalline zinc ferrite. The superexchange interaction between the spins at the A and B sites (A-B interaction) is stronger than those among the spins at the A site (A-A interaction) or the B site (B-B interaction), because the wave function overlaps of the cations and oxygens are different. This is the main reason why the magnetic property of zinc ferrite strongly depends on the degree of inversion.[2] Only the B-B interaction is present in normal zinc ferrite that is antiferromagnetic, while the A-B and B-B interactions compete in the inverted structure.

Néel's mean-field model predicts a collinear ferrimagnetic ordering for inverted zinc ferrites. According to the Hofmann *et al.* phase diagram of inverted zinc ferrite obtained by neutron diffraction,[3] the antiferromagnetic order changes to ferrimagnetic order near $c=0.1-0.2$. The studies using Mössbauer spectroscopy[4–6] showed that the spin structure is even more complicated when the two interactions compete. They observed spin canting that was first suggested by Yafet and Kittel as part of a general theory of spin ordering in spinel structure.[7] In spite of the various methods used to synthesize nanocrystalline samples [high-energy ball milling (HEBM), sol-gel, and producing nanoparticles in matrix], all the samples had similar grain sizes and inversion parameters. These results were not, however, sufficiently consistent to lead to a clear spin structure of inverted zinc ferrite. Goya *et al.*[4] claimed that only the spins in the B site are ferrimagnetically ordered while Chinnasamy *et al.*[5] claimed that the canted ferrimagnetic order exists both in the spins at the A site and those in the B site. Oliver *et al.*[6] made no clear statement about ordering but reported that the spin at the B site that is either parallel or antiparallel to an external field is locally canted.

In this study, the ground spin state in nanocrystalline zinc ferrite was investigated using nuclear magnetic resonance (NMR) at various external magnetic fields and temperatures.

NMR is a useful local probe to observe microscopic spin states in ordered phases. With NMR, resonance frequency is proportional to the local field, which is the sum of the external and internal fields. The internal field at a nucleus of a magnetic ion in magnetic materials is usually much stronger than the external field. Therefore, the field generated by magnetization of a sublattice in the spinel structure can be precisely measured by zero-field NMR. We found clear evidence of the inversion of Fe ions in nanocrystalline samples and observed the ferrimagnetic state resulting from the *A*-*B* interaction. We also confirmed the coexistence of the antiferromagnetic ordering that remains among the *B* site spins at low temperature. The NMR frequency shift in the magnetic field indicates that only the *B* site spins, which participate in both the ferrimagnetic and antiferromagnetic orderings, are canted.

II. EXPERIMENT

Nanocrystalline zinc ferrite was made using HEBM from a bulk sample that was synthesized by a conventional solid state reaction method from the mixture of ZnO and Fe_2O_3. The crushed $ZnFe_2O_4$ powder was charged together with WC/Co balls into an 85 ml WC/Co bowl in air and the HEBM process was performed with a planetary ball mill at 500 rpm for 4 h. The ball-to-powder weight ratio was fixed at 20 to 1. X-ray powder diffraction (XRD) using Cu K_α radiation confirmed that the sample was single phase. Bragg peaks in the XRD pattern were broadened after mechanical treatment due to decreased grain size. Average grain size of the ball-milled sample as estimated by the Scherrer equation was 20 nm. To estimate the grain size distribution, the microstructure of the sample was investigated by a high-resolution transmission electron microscope (HRTEM) operating at 300 kV. The resulting size distribution was asymmetric with the mode of 12 nm. The average grain size was 16 nm and the deviation was about 4 nm.

Magnetization was measured using a commercial SQUID magnetometer in both the zero-field cooling and field cooling modes at 500 Oe. During the NMR experiments, the spin echo was measured with our home-built spectrometer in the temperature range of 4 to 12 K. All the ^{57}Fe NMR spectra were obtained in the field cooling mode to fully align the magnetization of each grain in the external field direction. Since the spectra were very broad, echo heights were measured as a function of frequency after a partial spectral excitation.

III. RESULTS AND DISCUSSION

Figure 1 shows the plot of the temperature dependence of the magnetic moment per Fe of nanocrystalline $ZnFe_2O_4$ obtained by a SQUID magnetometer in the zero-field cooling and field cooling modes. The sample shows a net magnetization below 460 K, which was consistent with previous measurements.[2,3] The magnetization obtained by the zero-field cooling reaches a broad peak around 150 K with increasing temperature, while that obtained by the field cooling decreases gradually, showing the hallmark of magnetic nanoparticles, i.e., the occurrence of spin blocking. The *M* vs *H* curves in the inset show that hysteresis was observed only at low temperature. The spins of nanocrystalline zinc ferrite that is superparamagnetic at room temperature become blocked at low temperatures. Clear superparamagnetic behavior of the sample at room temperature indicates that the number of multidomain particles is negligible compared with that of single-domain particles.

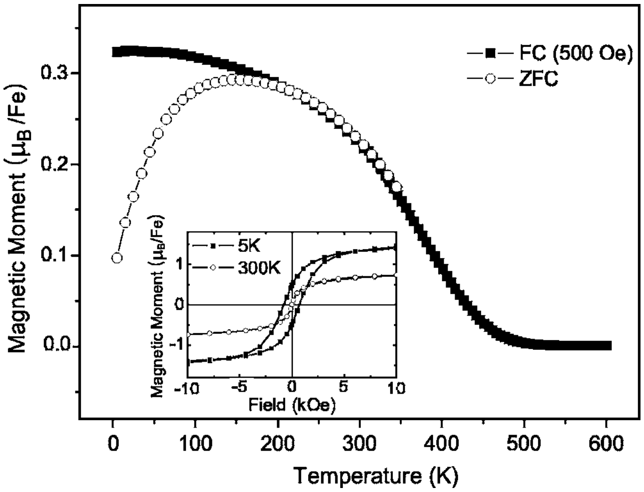

FIG. 1. Magnetic moment per Fe of zinc ferrite high-energy ball milled for 4 h plotted as a function of temperature. The open circles represent zero-field cooling and the closed circles represent field cooling at 500 Oe. The inset shows hysteresis curves.

The NMR spectrum reflects the local magnetic field that a nucleus of a magnetic atom encounters via hyperfine interaction. The local field depends on the magnetic moment of the atom and the bonding with neighboring atoms. The ^{57}Fe NMR spectrum of nanocrystalline zinc ferrite obtained at 4.2 K varies with the external magnetic field, as shown in Fig. 2. In the zero field, clear double Gaussian peaks are observed, one (HP) centered at 71.8 MHz and another peak (LP) at 69.4 MHz. The corresponding hyperfine fields are 51.9 T and 50.2 T, respectively, which are similar to the results of the Mössbauer measurements. The double peaks indicate that there are two different local environments around the Fe atoms, which must be the *A* and *B* sites. This double-peak feature of the ions located both in the *A* and *B* sites has been reported in several spinel ferrites.[8,9] Calculation of the hyperfine field predicts the local field in the *A* site is slightly lower than that in the *B* site because the degree of covalency of bonding in the *A* site is greater than in the *B* site.[10] Therefore, LP and HP are the NMR signals coming from the *A* and *B* site Fe ions, repectively, and the top graph of Fig. 2, which represents the zero-field, provides an evidence of inversion of Fe ions occurred during HEBM.

The relative directions of local magnetic moments can be determined by applying a magnetic field. The resonance frequency of the NMR spectrum that is proportional to the total magnetic field at a nucleus is given by[11]

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

where **M** is the magnetization of a sublattice and **H** is the external magnetic field. The gyromagnetic ratio of the

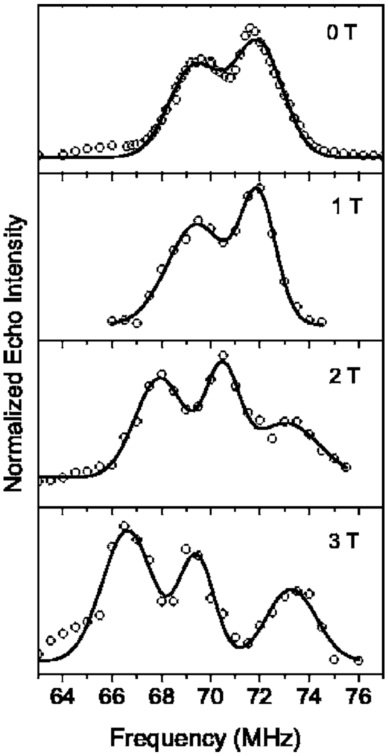

FIG. 2. NMR spectra of nanocrystalline zinc ferrite obtained at various external magnetic fields (0 T, 1 T, 2 T, and 3 T) and 4.2 K. Solid lines are guides for the eye.

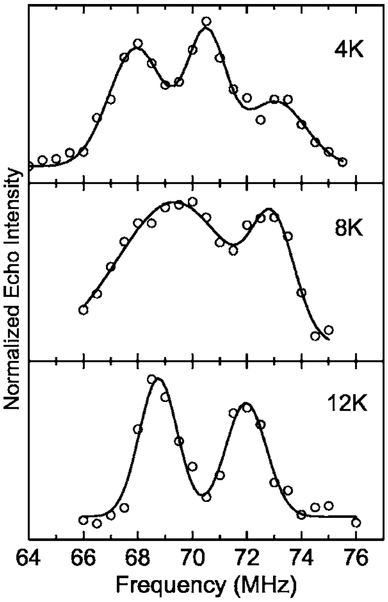

FIG. 3. NMR spectra of nanocrystalline zinc ferrite obtained at 2 T for various temperatures. Solid lines are guides for the eye.

nucleus is γ. $\gamma/2\pi$ is 1.38 MHz/T for ^{57}Fe, and A_0 is a constant proportional to the hyperfine interaction constant. The NMR frequency of an ion located at a sublattice, whose magnetization is parallel to the external magnetic field, shifts to a lower frequency with increasing field for positive A_0 as in our case.

The spectrum obtained at 1 T in Fig. 2 is almost identical to that of the zero field, and the central frequencies remain unchanged. This is because magnetization does not rotate to the external field direction until the field becomes large enough to overcome the magnetic anisotropy field. Figure 2 shows that LP shifts downward with an increasing external field over 1 T, but HP splits into two peaks: one (HP1) shifting downward with an increasing external field and another (HP2) shifting upward. Therefore, the magnetic moments of LP and HP1 are parallel to the external field, while that of HP2 is antiparallel. The peaks LP and HP are produced by the spins at the *A* and *B* sites, and the *A*-*B* and *B*-*B* interactions couple spins antiferromagnetically. Therefore, the experimental results indicate that the antiferromagnetic coupling among the spins at the *B* site represented by HP1 and HP2 coexists with the antiferromagnetic or ferrimagnetic coupling between the spins at the *A* and *B* sites represented by LP and HP2, respectively. The antiferromagnetic order in the *B* site has the same origin as the antiferromagnetism observed in bulk zinc ferrite, i.e., the *B*-*B* interaction. The tendency of this ordering should be strong at the *B* site spins whose neighboring *A* sites have mostly Zn ions so that the *B*-*B*interaction is dominant.

The foregoing claim is supported by comparison of the transition temperatures of the antiferromagnetic orders in bulk and nanocrystalline zinc ferrites. The Néel temperature of bulk zinc ferrite, which has Fe ions only at the *B* sites, is 10 K. Figure 3 shows the NMR spectra of nanocrystalline zinc ferrite obtained at various temperatures for a fixed field of 2 T. At 4 K, three peaks (LP, HP1, and HP2) are clearly observed. When the temperature increases to 8 K, LP and HP1 merge into one broad peak; at 12 K, the HP1 peak completely disappears, and the spectrum shows only two simple Gaussian peaks whose broadenings are similar to those at 4 K. The disappearance of HP1 over 10 K strongly supports the idea that HP1 and HP2 represent the antiferromagnetically ordered state due to the *B*-*B* interaction as in bulk zinc ferrite.

After the antiferromagnetic long range order in the *B* site vanishes over 10 K, only the ferrimagnetic or antiferromagnetic order represented by HP2 and LP remains. Since magnetization is nonzero at this temperature, the ordering is ferrimagnetic. This ordering is due to the strong *A*-*B* interaction, as in other ferrites. The NMR frequency shifts of LP and HP2 at 12 K relative to those at 4 K imply that the ferrimagnetic order is influenced by the antiferromagnetic order and the overall spin structure is not a simple mixture of two well-defined separate orders.

Quantitative estimation of the frequency shift with an external magnetic field provides information on spin canting. The resonance frequency in Eq. (1) is proportional to the total field, that is, the vector sum of the external field and the hyperfine field. In the first order approximation, the frequency shift with external field is given as $\gamma H \cos\theta/2\pi$, where θ is the canting angle of the magnetization of a sublattice from the direction of the external field, because the hyperfine field is generally much greater than the external field. Figure 4 displays the central frequency of each peak as a function of external field. The dotted lines represent the theoretical curves expected in the spin structure collinear with external magnetic field, that is, the lines that each have

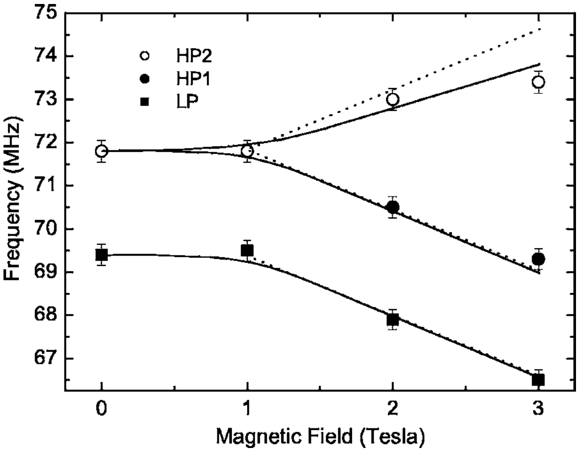

FIG. 4. The dependence of NMR frequency of each peak (LP, HP1, and HP2) at 4.2 K on external magnetic field is displayed. Dotted lines represent the theoretical curves of the collinear spin states and the solid lines are guides for the eye.

a slope of $\pm\gamma/2\pi$. The LP and HP1 peaks follow these theoretical lines well, indicating that they are collinear with the external field. The slope of HP2, in contrast, is smaller than γ. The canting angle of the spins corresponding to HP2, which was roughly estimated from linear fitting of the experimental data over 1 T, is $54^\circ \pm 10^\circ$. The spins producing HP2 interact with the *A* site spin via the *A*-*B* interaction and the other *B* site spins via the *B*-*B* interaction. Therefore, the two interactions compete at the spins of HP2 and this is believed to be the reason why only the spins corresponding to HP2 are canted. The canting angle of the spins in the *B* site depends on the number of nearest-neighbor Zn ions in the *A* site and the ratio of the *A*-*B* to *B*-*B* interaction strengths.[12] Since ferrimagnetism in zinc ferrite is observed only in nanocrystalline samples, it is possible that the nanometer scale influences not only the macroscopic magnetic property of zinc ferrite but also the spin canting angle.

IV. CONCLUSION

Fe ions are located only at the *B* site in bulk zinc ferrite. Some Fe ions are inverted to the *A* site when the crystal size of zinc ferrite is reduced to the order of nanometers, irrespective of the method of synthesis. A striking physical property change induced by the inversion of Fe ions is the change in magnetic order, from antiferromagnetism to ferrimagnetism. In this study, the spin structure of nanocrystalline zinc ferrite, that is synthesized by the HEBM process, was investigated. Direct experimental evidence that inversion occurred in nanocrystalline zinc ferrite during the HEBM process was provided by the zero-field NMR spectrum. Analysis of the NMR data obtained under various external fields lead to our conclusion that a ferrimagnetic order with a transition temperature of 460 K coexists with an antiferromagnetic order with a transition temperature of 10 K. We showed that the antiferromagnetic order found in nanocrystalline zinc ferrite has the same origin of interaction as that of bulk zinc ferrite, i.e., the *B*-*B* superexchange interaction. The *B*-*B* interaction induces the antiferromagnetic coupling among the spins in the *B* site, and the *A*-*B* interaction induces the ferrimagnetic coupling between the spins in the *A* site and those in the *B* site. The spin structure, including spin canting, in nanocrystalline zinc ferrite has been controversial. We showed that only the spins that participate in both the ferrimagnetic and antiferromagnetic orderings in the *B* site are canted. This is consistent with theory that predicts spin canting when two interactions compete.

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