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^{57}Fe NMR and spin structure of manganese ferrite

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NMR of ^{57}Fe in five $MnFe_2O_4$ single crystals with different degrees of inversion was measured in liquid He temperature. At the zero external field, two lines originating from Fe^{3+} ions on the octahedral sites are observed at 68.7 and 71.1 MHz, while the line at 72.0 MHz, the amplitude of which increases with increasing inversion, is ascribed to Fe^{3+} ions on the tetrahedral sites. Measurement in the external field shows that the spin structure is in accord with the Goodenough-Kanamori rules. This contradicts to an abnormal spin structure which Shim *et al.* [Phys. Rev. B **75**, 134406 (2007)] proposed recently on the basis of ^{57}Fe NMR measured in polycrystalline manganese ferrite. Reinterpretation of the NMR in polycrystalline compounds is given.

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I. INTRODUCTION

Manganese ferrite has a partially inverted spinel structure and its formula may be written as $(Mn_{1-y}Fe_y)_A[Fe_{2-y}Mn_y]_BO_4$, where A and B denote tetrahedral and octahedral sublattices, respectively. The inversion parameter y depends on the preparation method and on a thermal treatment; in currently prepared single crystals, $0.06 < y < 0.3$ is found;[1,2] while in the polycrystals prepared at low temperatures from the water solution, y may be as high as $y=0.52$.[3] The valency of manganese on the A sublattice is 2+ and that of iron is 3+. On the B sublattice, the valency of the Mn and Fe is less obvious, but commonly $[\{Mn^{3+}Fe^{2+}\}_yFe^{3+}_{2-2y}]_B$ is used to express corresponding valence states. It is generally accepted that the dominating exchange interaction in spinel ferrites is the antiferromagnetic $A-B$ superexchange.[4,5] The Mn^{2+} and Fe^{3+}, which occupy the A sites, have half filled $3d$ shell (electronic configuration $3d^5$ with spin $S=5/2$ and zero orbital momentum corresponding to $5\mu_B$/f.u.) and their magnetic moments are expected to point in the same direction, antiparallel to the B sublattice magnetization. The moments of the Mn^{3+} and Fe^{2+} on B sites (having four and six electrons, respectively) possess magnetic moment of $4\mu_B$. If the above given valence states are accepted, the spin magnetic moment m_s per f.u. in μ_B is connected with the inversion parameter by the relation

$$m_s = 5 - 2y, \qquad (1)$$

which was approved in a number of Mn ferrites with different y^2. Manganese ferrite is well studied experimentally[6] and recently several theoretical calculations of the exchange interactions in this compound appeared.[7–9] From these studies, it follows that the exchange interactions in the Mn ferrite comply with the standard Goodenough-Kanamori rules.[4,5] It was thus very surprising when in a recent paper Shim *et al.*[10] proposed a complex spin structure of partially inverted manganese ferrite that contradicts the Goodenough-Kanamori rules.

Shim *et al.*[10] studied the dependence of ^{57}Fe NMR on the external magnetic field B_{ext} at liquid helium temperature for a polycrystalline manganese ferrite. At zero magnetic field, the spectrum consists of two broad lines centered at ≈68.8 and 71.4 MHz. When the external magnetic field is applied, the higher frequency line splits in a less intensive line, frequency of which increases with B_{ext} and a more intensive line with decreasing frequency. The authors believe that the line, which appears at 71.4 MHz for $B_{ext}=0$, originates from $Fe^{3+}(B)$ while the one with smaller frequency comes from $Fe^{3+}(A)$. The splitting of the 71.4 MHz line in an external field then means that there are two types of $Fe^{3+}(B)$ ions with mutually antiparallel spins. Once this picture is adopted, the comparison with previous NMR experiments leads to a conclusion that on the A sites the spins of Mn^{2+} and Fe^{3+} ions should also be antiparallel.

Recently, we performed a systematic study of the ^{57}Fe NMR in the $Mn_xFe_{3-x}O_4$ system, a short summary of which will be published elsewhere.[11] In this Brief Report, the NMR spectra of five $x=1$ high quality single crystals with different inversion parameters are presented. The important information overlooked by Shim *et al.*[10] is the angular dependence of NMR of ^{57}Fe on the B sites that was measured by Kovtun *et al.*,[12] when studying the ^{17}O NMR in Mn ferrite. Combining the result by Kovtun *et al.* and our past and present measurements, we show unambiguously that the spin structure of the manganese ferrite is the one expected from the Goodenough-Kanamori rules. We also reanalyze the results of Shim *et al.*[10] and show that their incorrect interpretation of ^{57}Fe NMR spectra was caused by neglection of rather large angular dependence of the B-site Fe^{3+} ion NMR resonance frequency.

II. EXPERIMENT

The single crystals used in this study were grown by pulling the optically heated floating zone through the sintered polycrystalline rods (of ~5 mm in diameter) as described elsewhere.[13] The wet chemical analysis of the iron and manganese contents determined in the final single crystals were within ±3% to the original compositions of the polycrystal-

TABLE I. Inversion parameter y_{nom} determined by Jirák *et al.* (Ref. 1) and the magnetic moment per f.u. of five single crystals used in this study.

Sample	1	2	3	4	5
y_{nom}	0.06	0.13	0.19	0.21	0.24
m_s (μ_B)	4.84	4.74	4.63	4.58	4.52

line rods. The inversion parameters y of these samples were determined earlier by Jirák *et al.*[1] using the neutron scattering and their values are given in Table I. The magnetic moments m_s were found to be in fair agreement with Eq. (1) and are also listed in Table I.

^{57}Fe NMR spectra were measured by the spin-echo method using the phase-coherent pulse spectrometer with an averaging technique and the Fourier transformation. The signal-to-noise ratio was significantly improved by using the Carr-Purcell pulse sequence. The excitation conditions were selected so that only the nuclei in the domains contribute to the signal and the correction for the finite spin-spin relaxation time was made. In Fig. 1, the ^{57}Fe NMR spectra, of the five compounds at zero external field and liquid helium temperature, are displayed.

III. DISCUSSION

The local symmetry of the A site in the spinel structure is cubic and the nuclear spin of the ^{57}Fe nuclei is 1/2. As a result, the single NMR frequency of ferric ion on the A site is independent of the magnetization direction. The situation on the B sites is different: the local symmetry is trigonal with the C_3 axis parallel to one of the cube diagonals.[4] There are four such diagonals; thus, for general direction of the magnetization, four NMR lines appear. Corresponding resonance frequencies are given by

$$f_{res} = f_0 + f_1(1 - 3\cos^2\theta_i), \quad i = 1,2,3,4, \tag{2}$$

where f_0 and f_1 are parameters and θ_i is the angle that magnetization makes with the trigonal axis of the ith type of the B site.

Kovtun *et al.*[12] measured angular dependence of the resonance frequency of ^{57}Fe located on the B sites, with magnetization confined to the (110) plane. In Fig. 2, corresponding experimental points are displayed. We used Eq. (2) to fit the experiment (full curves in Fig. 2) and resulting values of the parameters are f_0=70.074 MHz and f_1=0.878 MHz.

The easy direction for the magnetization of the Mn ferrite is [111]. As seen from Fig. 2, for $\vec{M}\parallel[111]$ two NMR lines originating from Fe^{3+} on the B sites are expected. The line B_1 corresponds to the sites for which the local trigonal axis ζ is parallel to $\vec{M}\parallel[111]$. Sites with $\zeta\parallel[\bar{1}\bar{1}1],[\bar{1}1\bar{1}],[1\bar{1}\bar{1}]$ give rise to line B_2 and the intensity ratio of B_1 and B_2 lines is thus 1:3. As seen in Fig. 1, the centers of these lines are at $f(B_1)$=68.67 MHz and $f(B_2)$=71.11 MHz. The difference $f(B_2)-f(B_1)$=2.44 MHz gives a value of anisotropy parameter f_1 equal to 0.914 MHz, which agrees well with the value deduced from the results of Kovtun *et al.*[12] B_1 and B_2 lines in our measurements are shifted to lower frequencies by 0.4 MHz, which is expected. The measurement of the angular dependence was performed in the external field $\vec{B}_{ext}$=0.5 T, which is parallel to the magnetic moment of the B sublattice and it will induce a negative shift of the NMR frequency of ^{57}Fe nuclei on the B sublattice as compared with our zero field measurement on single crystals—see Fig. 1.

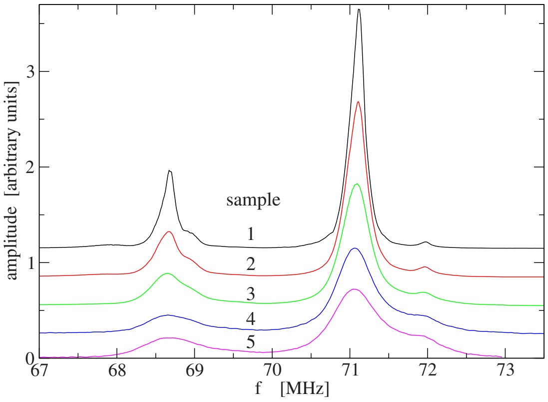

FIG. 1. (Color online) ^{57}Fe NMR spectra of the five MnFe$_2$O$_4$ single crystals (Table I) at zero external field and liquid helium temperature. For better clarity, the spectra were displaced vertically.

In addition to the B_1 and B_2 lines, the third line at 72.0 MHz is detected. The amplitude of this line increases with increasing inversion parameter y (i.e., with the number of A sites occupied by iron) and it is thus natural to attribute this signal to Fe^{3+}(A) ions. As the spins of Fe^{3+}(A) ions are antiparallel to the magnetization and thus also to $\vec{B}_{ext}$, the resonance frequency of this line should increase linearly with increasing B_{ext} once the sample is fully magnetized. This behavior was indeed observed.[11]

The spectra in Fig. 1 may be decomposed in three lines B_1, B_2, and A using a Gaussian broadening. The integrated

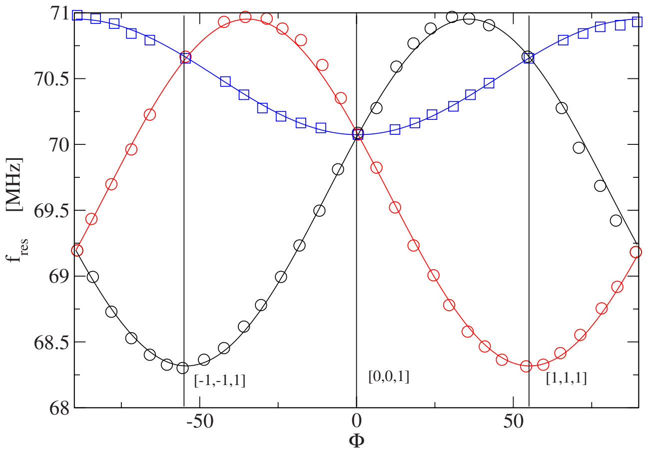

FIG. 2. (Color online) Angular dependence of the NMR frequency f_{res} of Fe^{3+} ions on the B sites. Φ is the angle between the magnetization and [001] direction. Symbols are the experimental data taken from Fig. 3 of Ref. 12, and full curves are our fits to Eq. (2) with f_0=70.074 MHz and f_1=0.878 MHz.

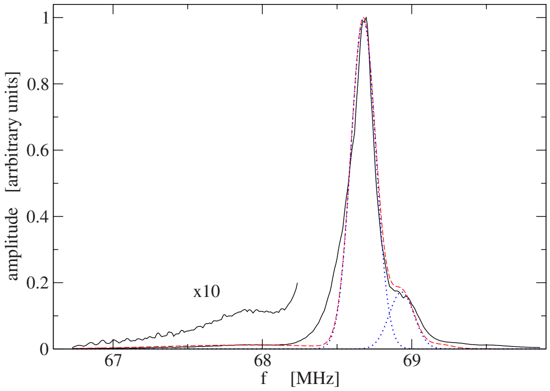

FIG. 3. (Color online) B_1 line of $y_{nom}=0.06$ single crystal. Full curves correspond to the experiment, dotted curves to the main and satellite lines, and the dashed curve is their sum. Part of the spectrum is multiplied by 10 to show the resonance of ^{17}O nuclei.

area $\mathcal{I}$ under each line should be proportional to the number of resonating nuclei, which allows an independent estimation of the inversion parameter

$$\frac{y_{\mathrm{NMR}}}{2-2y_{\mathrm{NMR}}}=\frac{\mathcal{I}(A)}{\mathcal{I}(B)}. \tag{3}$$

Comparison of y_{NMR} with the nominal one shows that the inversion is underestimated by NMR. This is clearly seen for samples with small inversion, where the lines are well separated—y estimated from Eq. (3) are 0.03 and 0.07 for crystals with nominal inversions 0.06 and 0.13. For higher inversion, the disagreement is smaller, but the decomposition is burdened by the large overlap of the lines and their clearly nonsymmetrical shape. A possible explanation of the disagreement is the $\mathrm{Fe}^{3+}(A)$-$\mathrm{Fe}^{2+}(B)$ cross relaxation. The localized, octahedrally coordinated Fe^{2+} ion has considerable orbital momentum. As a consequence, its nuclear spin relaxes very fast and it cannot be detected by NMR. Occurrence of Fe^{3+} on the A sublattice, occupied otherwise by Mn^{2+}, represents an extra positive charge, while $\mathrm{Fe}^{2+}(B)$ brings an extra negative charge to the B sublattice. For this reason, there should be an attractive $\mathrm{Fe}^{3+}(A)$-$\mathrm{Fe}^{2+}(B)$ interaction, leading to a nonrandom distribution of $\mathrm{Fe}^{3+}(A)$-$\mathrm{Fe}^{2+}(B)$ pairs. Assuming that the cross relaxation is effective, the ferric ions trapped in such a pair will not contribute to the NMR signal. As the inversion increases, the number of $\mathrm{Fe}^{2+}(B)$ becomes bigger and, as a consequence, the extra negative charge starts to delocalize. The delocalization causes gradual disappearance of the orbital momentum and thus the $\mathrm{Fe}^{2+}(B)$ relaxation rate decreases and the cross relaxation becomes ineffective.

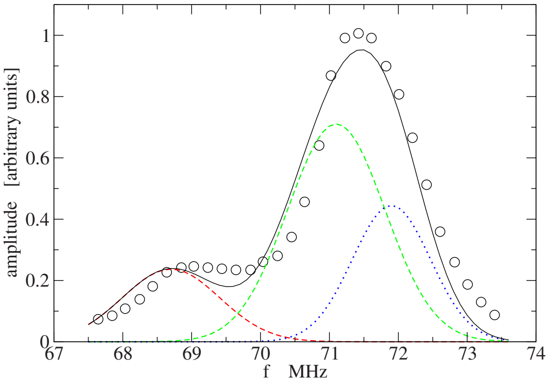

FIG. 4. (Color online) NMR of ^{57}Fe in $\mathrm{MnFe_2O_4}$ polycrystal at zero external magnetic field. Circles correspond to the experiment (Ref. 10), dashed and dotted curves are contributions of B- and A-site ferric ions, and the full curve is their sum.

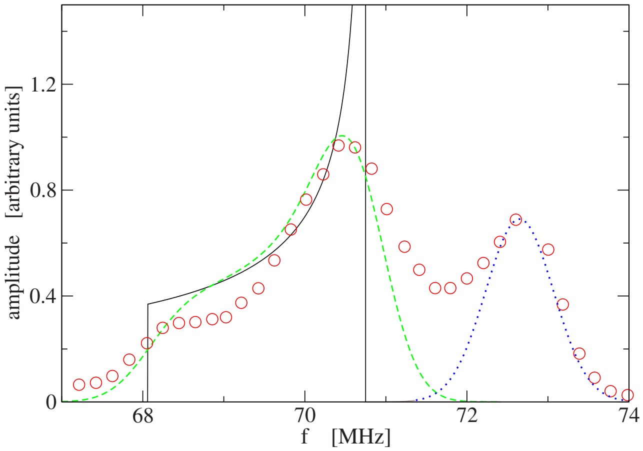

FIG. 5. (Color online) NMR of ^{57}Fe in $\mathrm{MnFe_2O_4}$ polycrystal at $B_{ext}=0.85$ T. Circles correspond to the experiment (Ref. 10), the full curve is the contribution of $\mathrm{Fe}^{3+}(B)$ ions obtained from Eq. (4), and the dashed curve is its convolution with the Gaussian distribution. Dotted curve is the signal from $\mathrm{Fe}^{3+}(A)$ ions. The ratio of integrated areas $\mathcal{I}(A)/\mathcal{I}(B)$ corresponds to $y_{\mathrm{NMR}}=0.42$ deduced from the zero field spectrum (Fig. 4).

For small inversion, the disorder in the system is not large and the NMR lines are narrow. This makes it possible to observe a satellite structure, especially for the B_1 line, which is well isolated. In Fig. 3, the B_1 line is displayed for the crystal with the smallest inversion. The signal is decomposed on the main line and a satellite line having the same width. The satellite most probably corresponds to those $\mathrm{Fe}^{3+}(B)$ ions that have five Mn and one Fe neighbor on the A site. The inversion parameter deduced from the ratio $\mathcal{I}(\mathrm{sat})/\mathcal{I}(\mathrm{main})$ equals to 0.028, close to the value deduced from $\mathcal{I}(A)/\mathcal{I}(B)$. Comparison between the experimental and fitted spectra reveals a possible unresolved satellite at ~68.4 MHz. It could correspond to $\mathrm{Fe}^{3+}(B)$ ions with one $\mathrm{Mn}^{3+}(B)$ neighbor. Interestingly, we also detected the NMR signal of ^{17}O nuclei at ~67.96 MHz. This corresponds well to the frequency determined by Kovtun *et al.*[12]

IV. NMR IN POLYCRYSTALS

In zero external field, the magnetization in the domains is along the easy [111] direction and the NMR spectra of a single crystal and polycrystal should be the same, providing the system is the same. We thus fitted the NMR spectrum of polycrystalline $\mathrm{MnFe_2O_4}$ as given by Shim *et al.*[10] by fixing the resonance frequencies of the three NMR lines at values obtained from our single crystal spectra: $f(B_1)=68.7$ MHz, $f(B_2)=71.1$ MHz, and $f(A)=72.0$ MHz and varying their linewidths and the inversion parameter y. The Gaussian halfwidths thus obtained equal to 0.34 MHz for B lines and 0.40 MHz for the A line, while the inversion parameter determined from Eq. (3) equals to 0.42. As seen in Fig. 4, the agreement of experimental and calculated spectra is fair.

If an external magnetic field is applied, the situation is different. In a polycrystalline system, for B_{ext} sufficiently large to saturate it magnetically (for $MnFe_2O_4$ corresponding B_{ext} is ≈ 0.3 T) and assuming that the crystallites are randomly oriented, an averaging over all possible orientations is necessary in order to obtain the form of the NMR spectra. Due to the cubic symmetry of the A sites, the NMR frequency is isotropic in this case and such averaging does not influence the $Fe^{3+}(A)$ signal. For the B site, local symmetry of which is trigonal the amplitude $\mathcal{A}$ of the normalized signal at frequency f is given by[14]

$$\mathcal{A}(f) = \frac{\sqrt{3}}{12 f_1 \sqrt{\left[1 - \frac{f - f_0}{f_1}\right]}}. \tag{4}$$

To compare this theoretical signal with the experiment, a convolution with the broadening function should be made. We take the anisotropy parameter $f_1 = 0.914$ MHz deduced from our measurements and assume that the broadening function has the Gaussian character. As seen in Fig. 5, an example of the spectrum taken at $B_{ext}=0.85$ T, this procedure qualitatively explains the form of the signal obtained by Shim *et al.*

V. CONCLUSIONS

Analysis of the NMR spectra of five $MnFe_2O_4$ single crystals shows that the spin structure of this ferrite is the one expected and it complies with the Goodenough-Kanamori rules. The incorrect interpretation of the experimentally obtained spectra of the polycrystalline sample by Shim *et al.* was caused by considering the low frequency tail of the B-site Fe^{3+} ion signal to be a third resonance line.

ACKNOWLEDGMENTS

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[1] Z. Jirák, Z. Šimša, J. Šimšová, V. Roskovec, S. Vratislav, and V. A. M. Brabers, *Proceedings of ICM-73* (Nauka, Moscow, 1974), Vol. V, pp. 260–264.

[2] Z. Šimša and V. A. M. Brabers, IEEE Trans. Magn. **MAG-11**, 1303 (1975).

[3] H. Yasuoka and A. Hirai, J. Phys. Soc. Jpn. **22**, 174 (1967).

[4] J. Goodenough, *Magnetism and the Chemical Bond* (Wiley, New York, 1963).

[5] P. W. Anderson, *Solid State Physics* (Academic Press Inc., New York, 1963), Vol. 14, p. 99.

[6] R. Vautier and M. Paulus, in *Mn-Fe^{3+} Spinels (Mn Ferrites) and Mn-Fe^{3+} Spinels with Substitutions*, Landölt-Bornstein, New Series, Vol. 12, edited by K.-H. Hellwege (Springer-Verlag, Berlin, 1980), pp. 122–160.

[7] D. J. Singh, M. Gupta, and R. Gupta, Phys. Rev. B **65**, 064432 (2002).

[8] Xu Zuo, B. Barbiellini, and C. Vittoria, J. Magn. Magn. Mater. **272-276**, 306 (2004).

[9] G. F. Dionne, J. Appl. Phys. **99**, 08M913 (2006).

[10] Jeong Hyun Shim, Soonchil Lee, and B. I. Min, Phys. Rev. B **75**, 134406 (2007).

[11] V. Chlan, V. Procházka, H. Štěpánková, B. Sedlák, P. Novák, Z. Šimša, and V. A. M. Brabers, J. Magn. Magn. Mater. (to be published).

[12] N. M. Kovtun, A. M. Kotelva, and A. A. Shemyakov, JETP Lett. **45**, 320 (1987).

[13] V. A. M. Brabers, Ber. Dtsch. Keram. Ges. **47**, 648 (1970).

[14] G. E. Pake, J. Chem. Phys. **16**, 327 (1948).