Peculiarities of $^{57}$Fe NMR Spectrum in Micro- and Nanocrystalline Europium Orthoferrites

Anastasia Sklyarova1 · Vadim I. Popkov2 · Ivan V. Pleshakov3 · Vladimir V. Matveev4 · Helena Štěpánková1 · Vojtěch Chlan1

Received: 8 May 2020 / Revised: 3 July 2020 / Published online: 28 August 2020
© Springer-Verlag GmbH Austria, part of Springer Nature 2020

Abstract
NMR spectra of $^{57}$Fe dispersed europium orthoferrite in powder samples with micro- and nanocrystalline particles were studied for the first time. The material was synthesized by glycine–nitrate combustion, which allowed to obtain the specimens with granular diameters of 60 nm (nano-EuFeO$_3$) and 1.5 μm (micro-EuFeO$_3$). It was found out that the spectra are more complex than could be expected for a compound with a single crystallographic position of Fe$^{3+}$ ions, and it was also identified that there is a noticeable difference in samples with different fineness. Assumptions about the possible physical nature of the observed effects are made.

1 Introduction

Rare-earth orthoferrites in whole and EuFeO$_3$, in particular, are subjected to a relentless interest due to their promising properties for practical use. Being potential materials for the finding of multiferroic behavior, these ferrites undergo attention concerning their synthesis, modifications and study of their properties. Although EuFeO$_3$ is known already quite a long time and this material in the bulk state has been well studied, since the beginning of nanomaterials era, the interest to this substance has been renewed due to the potential application of its nanocrystals in photocatalytic materials, memory devices, gas sensors, etc. [1–4].

It would seem that the properties of EuFeO$_3$ are well known but there is no clear information about the magnetic moments ordering and how it changes in the different material state (bulk, nano, thin film). Previous research results show that
physical and chemical properties of ferrites may depend on the preparation route used for obtaining these materials, as it was shown for YFeO$_3$, where the spin reorientation transition was found in the hydrothermally prepared samples [5]. Moreover, some deviations on temperature curves of the magnetic susceptibility have been found for LuFeO$_3$ and EuFeO$_3$, prepared by hydrothermal method, which may indicate the existence of spin reorientation in these samples too [6], although the investigation of similar substances, prepared by other methods, contradicts the presence of spontaneous spin reorientation transition in these type of materials [7]. Concerning the magnetic structure, ABO$_3$ material shows the variety of spin orderings starting from ordinary antiferromagnetic (AFM) structure through different types of AFM, which may coexist with a weak ferromagnetism (WFM), to spiral or cycloidal distribution of spins [8–11]. Type of spin ordering depends on many factors including a synthesis route, which influences on the physical properties of obtained materials and, that is most interesting, on the magnetic structure [12, 13].

In this work, we would like to discuss some features and differences of nuclear magnetic resonance (NMR) spectra measured from nano- and microcrystalline EuFeO$_3$ powders in comparison with known facts about the magnetic structure of europium orthoferrite and some related orthoferrites.

2 Materials and Methods

2.1 Synthesis Conditions

Europium orthoferrite in form of powder was produced via glycine–nitrate combustion synthesis route followed by heat treatment in the air. A detailed description of the synthesis procedure is presented in our earlier work [14].

Reaction solution containing an equimolar amount of europium(III) nitrate and iron(III) nitrate as well as glycine was heated to boiling, after which the bulk of solvent was evaporated and formed gel-like mixture was spontaneously ignited and burned to form the brown powder. The stoichiometric expression of the reaction proceeding, in this case, is presented below:

\[
3\text{Eu(NO}_3\text{)}_3 + 3\text{Fe(NO}_3\text{)}_3 + 10\text{C}_2\text{H}_5\text{NO}_2 = 3\text{EuFeO}_3 + 20\text{CO}_2 + 14\text{N}_2 + 25\text{H}_2\text{O.}
\]  

The resulting powder was heat-treated then at 600 °C (nano-EuFeO$_3$) and 1000 °C (micro-EuFeO$_3$) for 6 h followed by thorough grinding. The obtained powders were then analyzed using a complex of physicochemical methods of analysis.

2.2 Physico-Chemical Characterization Methods

The chemical composition and morphology of the synthesized materials were investigated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) using the Tescan Vega 3 SBN scanning electron microscope equipped with an Oxford INCA x-act x-rat spectral microanalysis device. Phase evolution was analyzed by powder X-ray diffraction (PXRD) method using Rigaku
Peculiarities of Fe NMR Spectrum in Micro- and Nanocrystal…

SmartLab 3 powder diffractometer with monochromatic CuKα radiation and ICDD PDF-2 powder database. The structural parameters and unit cell values were refined by the Rietveld method using the Rigaku SmartLab Studio software. The average crystallite size (coherent scattering area) was determined from X-ray diffraction lines broadening using the Scherrer equation.

The local magnetic properties of micro- and nano-EuFeO₃ powders have been investigated by ⁵⁷Fe nuclear magnetic resonance spectroscopy (NMR). Measurements were done using NMR spectrometer based on the Bruker Avance II console modified for magnetic materials study and the home-made probehead worked in a wide-frequency region. NMR spectra were acquired by a Carr–Purcell–Meiboom–Gill (CPMG) pulse sequence in the frequency region of 68–81 MHz with 100 kHz step. The following parameters for pulse-sequence were used: lengths of the first and the second pulses were taken of 1.5 and 3 μs, respectively, and 2049–8000 scans were accumulated at each frequency step; radiofrequency power was chosen optimal for maximizing of echo signal intensity at each measurements. Low-temperature measurements have been realized by loading NMR coil with sample inside the He dewar.

3 Results and Discussion

3.1 Structural and Morphological Features

The powder X-ray diffraction patterns of the nano-EuFeO₃ and micro-EuFeO₃ powders are represented in Fig. 1.

It is shown that the phase composition of both samples fully corresponds to the phase-pure europium orthoferrite. The PXRD pattern of the nano-EuFeO₃ powders

![PXRD pattern of the nano-EuFeO₃ and micro-EuFeO₃ powders](image)
exhibits broadened peaks in the whole Bragg-angle range, indicating that europium orthoferrite is nanostructured. The sharp and clear diffraction peaks of the micro-EuFeO$_3$ powder are also indexed well to an orthorhombic europium orthoferrite, confirming the formation of highly crystalline micropowders. In this case, the sharper and stronger diffraction peaks demonstrate the enhanced crystallinity and particle size of the micro-EuFeO$_3$ powder in relation to nano-EuFeO$_3$.

Table 1 presents Rietveld refinement results and crystal data obtained from the PXRD data. This refinement was used to calculate the cell parameters, the unit cell volume and the crystallite size of the obtained europium orthoferrites. The goodness of fit is at a good level, which confirms the reliability of the results.

The elemental analysis results of the synthesized samples of nano-EuFeO$_3$ and micro-EuFeO$_3$ show that the atomic fractions of europium (Eu) and iron (Fe) are equal to 49.5%:50.5% at. and 49.7%:50.3% at. (Fig. 2a, d), respectively, and indicate that the composition of the substances corresponds to the nominal composition of europium orthoferrite (50%:50% at.) within the error of the method (± 1% at.). No noticeable amount of any impurities of other elements were found by the results of EDX analysis of the samples under study. Then, scanning electron microscopy was used to evaluate the morphological aspects of the obtained europium orthoferrite powders (Fig. 2b, c, e, f). According to the presented results, nano-EuFeO$_3$ powder is characterized by an isometric morphology of particles with a size in the range of 40–80 nm (about 60 nm or 0.06 μm in average), which are agglomerated into foam-like micron structures that are characteristic of rare-earth elements (REE) orthoferrites in case of the synthesis by the solution combustion method [15, 16]. A similar situation is observed for the micro-EuFeO$_3$ powder with the only difference being that the characteristic sizes of the isometric particles of europium orthoferrite are about 1–2 μm (about 1.5 μm or 1500 nm in average), and they are also agglomerated into larger structures that retain the foam-like motif of the precursor observed previously [17]. Therefore, both SEM and EDX results are in a good agreement with

|                  | Nano-EuFeO$_3$ | Micro-EuFeO$_3$ |
|------------------|---------------|-----------------|
| Crystal system   | Orthorhombic  |                 |
| Space group      | Pbnm/Pnma (N. 52) |               |
| $a = \beta = \gamma$, (°)  | 90             |                 |
| $a$, (Å)         | 5.3788(2)     | 5.3767(1)       |
| $b$, (Å)         | 5.5986(4)     | 5.5983(2)       |
| $c$, (Å)         | 7.6921(5)     | 7.6888(4)       |
| $V$, (Å$^3$)     | 231.637(15)   | 231.435(7)      |
| $\rho$, (cm$^3$/g) | 7.793         | 7.800           |
| $D_0$, (nm)      | 56.9          | > 100$^a$       |
| $R_{wp}$, (%)    | 5.15          | 4.14            |
| $R_p$, (%)       | 4.00          | 3.06            |

The numbers in parentheses are the estimated standard deviations

$^a$Crystallite sizes exceed the upper threshold of the capabilities of the method for analyzing the broadening of X-ray diffraction lines
the PXRD data, confirming EuFeO₃ particles are monocrystalline in both nano- and micropowder.

Thus, the main difference between the nano-EuFeO₃ and micro-EuFeO₃ samples is in the average particle size of the europium orthoferrite particles equal to of 60 nm and 1500 nm with the same chemical and phase composition, crystal structure, morphology and particle size distribution. Therefore, the observed features and differences of the $^{57}\text{Fe}$ NMR spectra of these samples can be associated only with the influence of the size factor.

### 3.2 Local Magnetic Properties

Earlier works devoted to magnetic properties study of ABO₃ (A—rare-earth element, B = Mn, Fe) show that, with temperature changing, the Fe sublattice in this structure undergoes one or several magnetic transitions, but, concerning the rare-earth sublattice, experimental data confirming the existence of magnetic transition below 10 K and refuting one are contradicted each other [18–22]. The dependence of orthoferrite properties, including phase transitions, on preparation way is evident and the result is unpredictable, but, at the same time, magnetic structure is an important parameter in multiferroics, where magnetoelectric effect is associated with phase transitions and emerging magnetic order.

For obtaining information about the magnetic structure of micro- and nano-EuFeO₃ samples, $^{57}\text{Fe}$ NMR spectra were acquired at different temperatures starting from 4.2 K. Because it is known that EuFeO₃ has an antiferromagnetic (AFM) ordering with a weak ferromagnetism (WFM) [23], and taking into account that Fe$^{3+}$
ions occupy a single crystallographic position in it, it was assumed that a single line would be registered in the NMR spectra of this material, undergoing changes during the transition from microstructural to nanocrystalline form.

As it is seen from Fig. 3, NMR spectra of our samples have somewhat unusual shape: the spectrum of nanomaterial shows an almost single line, whereas the spectrum shape of micromaterial has a complex structure with more pronounced “shoulder”. Observed spectral shapes are in contradiction with known facts of behavior of micro and nanomaterials, where surface effects lead to the significant complication of “nano” spectrum. But in our case, the opposite picture was observed, which can be explained by the samples preparation technology as well as other possible effects described below. Also for nano-EuFeO₃ the main resonance line shows an ∼0.15 % shift to higher frequency indicating the volume magnetization grow to the same value (∼0.15 %), which is typical for nanophase.

Increasing the temperature of NMR measurements gives the further complication of micro-EuFeO₃ spectrum, Fig. 4, left panel. Between 20 and 30 K the main NMR peak starts to split and the almost separate line becomes visible by naked eye already at 50 K. This separate line remains visible up to 100 K and vanished at further temperature increasing (NMR signal of this line is not detectable at high temperature). Earlier, such temperature splitting of the main NMR line was observed in pure and substituted rare-earth orthoferrites and was bonded with the spin reorientation transition in these materials [24]. Thus, the same reason maybe adapts for the explanation of the line separation for micro-EuFeO₃.

![Fig. 3](image)

**Fig. 3** $^{57}$Fe NMR spectra of the micro-EuFeO₃ and nano-EuFeO₃ powders acquired at 4.2 K and different RF power. All spectra are normalized to a maximal value of echo amplitude of the related sample.
Origins of satellites in the micro-sample have been analyzed using NMR signal dependence on the power of radio-frequency (RF) pulses. For both samples, the main peak and “shoulder” show the similar RF dependence in the wide power-value region and can be attributed to europium orthoferrite, but the satellite peak at \( \sim 73.5 \text{ MHz} \) shows another dependence on RF power (see Fig. 3, left panel). Based on the known equations for the behavior of echo signal versus pulse amplitude [25] and taking into account amplification coefficient, low-frequency satellite has an one and a half times lower value of anisotropy field than the main peak and may be ascribed to another unknown impurity phase, the appearing of which is not excluded by the synthesis technology. This phase should be extremely fine to become invisible on the XRD pattern.

In theory, upon the condition of homogeneous distribution of Fe atoms in orthorhombic structure, when Fe atoms occupy only one crystallographic position, \(^{57}\text{Fe} \) NMR spectrum of EuFeO\(_3\) at 4.2 K should be presented by one narrow line. And, although the NMR resonance peak of nano-EuFeO\(_3\) can be considered as a single line, it is possible to notice the presence of a weak “shoulder” as in micro-sample (Fig. 3, right panel), that excludes the simple explanation of “shoulder” by the theory of domain walls. This observation allows to propose, that other mechanisms of the appearing of complex spectrum structure should be considered, but all of them are bonded with a non-homogeneous distribution of magnetic moments in the sample volume.
One of the remarkable features of ABO$_3$ compounds, showed multiferroic properties, is a spiral or cycloid spin ordering [10]. But in orthoferrites, this ordering was found only in BiFeO$_3$ multiferroics, where the complex NMR spectrum was explained by spin-modulated magnetic structure: cycloid spin distribution [26–28]. Because of this spin distribution, low temperature NMR spectrum of bulk BiFeO$_3$ consists of wide (∼1 MHz) line with two maxima [28]. As it was shown in a number of works, this cycloida is suppressed by application of a strong external magnetic field, by producing strained thin films of this material, by substituting of Bi by rare-earth elements, and other methods [29–33]. Earlier, $^{57}$Fe MNR spectra have been obtained for La doped Bi$_{1-x}$La$_x$FeO$_3$ and it was shown that at $x = 0.3$ NMR line has only one broad peak; at $x \geq 0.9$ this peak becomes narrow and shifts to high frequencies [34]. This effect was explained by the rhombohedral-to-orthorhombic phase transition accompanied by the spin cycloid destruction. At substitution of Bi by Eu in Bi$_{1-x}$Eu$_x$FeO$_3$ ($x \geq 0.3$), the same phase transition was observed [35, 36] and it would be reasonable to expect the same behavior of NMR spectrum in the whole substitution range up to $x = 1$. However, the spectrum shape of our micro-EuFeO$_3$ sample looks rather similar to the spin distribution case, moreover, collapse of the NMR spectrum in one narrow line with the particle size reducing to nanometer range also looks rather similar to behavior of nano-BiFeO$_3$, where cycloid is not present due to the fact that the particle size is smaller than the period of ∼62 nm [37]. Nonetheless, in rare-earth element AMnO$_3$ multiferroics the coexistence of orthorhombic phase- and spin-modulated structure is not forbidden [10, 38], and even for Y-doped EuMnO$_3$ the spiral spin distribution was observed due to the formation of distortions in the orthorhombic Pbmn structure [9, 39]. But in orthoferrites, only other phases were found to be suitable for stabilization of the spin-modulated structure and similarity of our NMR spectra and spectra of BiFeO$_3$ may be formal.

Another hypothesis to explain our results is the presence of ferroelectric domain borders, which may also be responsible for the non-homogeneous distribution of magnetic moments. In this case, the observed complex spectrum shape of micromaterial is explained by the big crystallites size, which may exceed the domain size. The existence of multiferroic properties in rare-earth AFeO$_3$ orthoferrites was confirmed by a number of works [40]. In these works, the appearance of room temperature ferroelectricity in centrosymmetric ferrites was explained by two nonequivalent canted antiferromagnetic subsystems and was called “spin-canting-driven ferroelectricity” [41]. As it was mentioned above, EuFeO$_3$ has an AFM ordering with a WFM and quite satisfies the conditions of the ferroelectricity emergence. Since information on the parameters of the ferroelectric domains of the studied compound is not available in the literature now, this statement is a hypothesis.

4 Conclusions

In conclusion, the described NMR study of micro- and nano-powders of EuFeO$_3$ shows the appearing of new properties in europium orthoferrites produced by glycine–nitrate combustion method. Obtained results point to possible spin
reorientation transition in the absence of an external field and the appearing of ferroelectric properties in the samples. We believe that further thorough investigation of obtained effects may give important information about the mechanism of multiferroic properties formation in rare-earth orthoferrites.

Acknowledgements The research was supported by OP RDE project no. CZ.02.2.69/0.0/0.0/16_027/0008495, International Mobility of Researchers at Charles University.

References

1. X. Niu, W. Du, W. Du, Sens. Actuators B 99, 399–404 (2004)
2. X. Niu, H. Li, G. Liu, J. Mol. Catal. A 232, 89–93 (2005)
3. D.I. Khomskii, J. Magn. Magn. Mater. 306, 1–8 (2006)
4. Y. Dwivedi, S.C. Zilio, J. Nanosci. Nanotechnol. 14, 1–20 (2014)
5. M. Shang, Ch. Zhang, T. Zhang, L. Yuan, L. Ge, H. Yuan, Sh. Feng, Appl. Phys. Lett. 102, 062903 (2013)
6. Zh. Zhou, L. Guo, H. Yang, Q. Liu, F. Ye, J. Alloys Compd. 583, 21–31 (2014)
7. A. Bombik, H. Böhm, J. Kusz, A.W. Pacyna, J. Magn. Magn. Mater. 234, 443–453 (2001)
8. J. Hemberger, F. Schrettle, A. Pimenov, P. Lunkenheimer, V.Yu. Ivanov, A.A. Mukhin, A.M. Balbashov, A. Loidl, Phys. Rev. B 75, 035118 (2007)
9. Y.J. Choi, C.L. Zhang, N. Lee, S.-W. Cheong, Phys. Rev. Lett. 105, 097201 (2010)
10. Y. Tokura, Sh. Seki, Adv. Mater. 22, 1554–1565 (2010)
11. M. Fiebig, T. Lottermoser, D. Meier, M. Trassin, Nat. Rev. Mater. 1, 1–15 (2016)
12. S. Radhakrishnan, J. Rangarajan, K. Baerner, J. Nanophotonics 8, 083086 (2014)
13. N.T. Huynh, D.L. Minh, Adv. Mater. Sci. Eng. 2012, 1–6 (2012)
14. K.D. Martinson, I.S. Kondrashkova, V.I. Popkov, Russ. J. Appl. Chem. 90, 980–985 (2017)
15. V.I. Popkov, O.V. Almisheva, V.N. Nevedomskyi, V.V. Sokolov, V.V. Gusarov, Nanosyst. Phys. Chem. Math. 6, 866–874 (2015)
16. O.V. Komova, V.I. Simagina, S.A. Mukha, O.V. Netskina, G.V. Odegov, O.A. Bulavchenko, A.V. Ischenko, A.A. Pochtar, Adv. Powder Technol. 27, 496–503 (2016)
17. V.V. Zvereva, V.I. Popkov, Ceram. Int. 45, 1380–1384 (2019)
18. N.I. Steblevskaya, M.A. Medkov, M.V. Belobelekskaya, JILRST 2, 45–47 (2013)
19. Z.M. Stadnik, E. de Boer, Solid State Commun. 50, 335–337 (1984)
20. M. Sivakumar, A. Gedanken, D. Bhattacharya, Y. Yeshurun, W. Zhong, Y.W. Du, I. Felnner, I. Nowik, Chem. Mater. 16, 3623–3632 (2004)
21. T.N. Stanislavchuk, Y. Wang, Y. Janssen, G.L. Carr, S.-W. Cheong, A.A. Sirenko, Phys. Rev. B 93, 094403 (2016)
22. S. Artyukhin, M. Mostovoy, N.P. Jensen, D. Le, K. Prokes, V.G. de Paula, H.N. Bordallo, A. Maljuk, S. Landsgeesel, H. Ryll, B. Klemke, S. Paeckel, K. Kiefra, K. Lefmann, D.N. Argyriou, Nat. Mater. 11, 694–699 (2012)
23. H. Xu, X. Hu, L. Zhang, Cryst. Growth Des. 8, 2061–2065 (2008)
24. A.S. Karnachev, Yu.I. Klechkin, N.M. Kotvun, A.S. Moskvich, E.E. Solov’ev, JETP 51, 592–602 (1980)
25. V.I. Chizhik, Y.S. Chernyshev, A.V. Donets, V. Frolov, A. Komolkin, M.G. Shelyapina, Magnetic Resonance and Its Applications (Springer International Publishing, Cham, 2014), pp. 1–782
26. I. Sosnowska, T. Peterlin-Neumaier, E. Steichele, J. Phys. C 15, 4835–4846 (1982)
27. I. Sosnowska, M. Loewenhaupt, W.F. David, R.M. Ibberson, Phys. B 180–181, 117–118 (1992)
28. A.V. Zaleskii, A.K. Zvezdin, A.A. Frolov, A.A. Bush, JETP Lett. 71, 465–468 (2000)
29. B. Andrzejewski, A. Molak, B. Hilczer, A. Budzia, R. Bujakiewicz-Korońska, J. Magn. Magn. Mater. 342, 17–26 (2013)
30. B. Xu, B. Dupé, C. Xu, H. Xiang, L. Bellaiche, Phys. Rev. B 98, 184420 (2018)
31. R.S. Fishman, J.T. Haraldsen, N. Furukawa, Sh. Miyahara, Phys. Rev. B 87, 134416 (2013)
32. A. Agbelele, D. Sando, C. Toulouse, C. Paillard, R.D. Johnson, R. Rüffer, A.F. Popkov, C. Carré- téro, P. Rovillain, J.-M. Le Breton, B. Dkhil, M. Cazayous, Y. Gallais, M.-A. Méasson, A. Sacuto, P. Manuel, A.K. Zvezdin, A. Barthélémy, J. Juraszek, M. Bibes, Adv. Mater. 29, 1602327 (2017)
33. I.O. Troyanchuk, M.V. Bushinsky, D.V. Karpinsky, O.S. Mantytskaya, V.V. Fedotova, O.I. Proch- nenko, Phys. Status Solidi B 246, 1901–1907 (2009)
34. A.V. Zalesskii, A.A. Frolov, T.A. Khimich, A.A. Bush, Phys. Solid State 45, 141–145 (2003)
35. X. Zhang, Y. Sui, X. Wang, Y. Wang, Zh. Wang, J. Alloys Compd. 507, 157–161 (2010)
36. P.C. Sati, M. Kumar, S. Chhoker, M. Jewariya, Ceram. Int. 41, 2389–2398 (2015)
37. T.-J. Park, G.C. Papaefthymiou, A.J. Viescas, A.R. Moodenbaugh, S.S. Wong, Nano Lett. 7, 766– 772 (2007)
38. M. Kenzelmann, A.B. Harris, S. Jonas, C. Broholm, J. Schefer, S.B. Kim, C.L. Zhang, S.-W. Cheong, O.P. Vajk, J.W. Lynn, Phys. Rev. Lett. 95, 087206 (2005)
39. I.S. Lyubutin, S.A. Pikin, J. Phys. Condens. Matter 25, 236001 (2013)
40. I.H. Lone, J. Aslam, N.R.E. Radwan, A.H. Bashal, A.F.A. Ajlouni, A. Akhter, Nanoscale Res. Lett. 14, 142 (2019)
41. J.-H. Lee, Y.K. Jeong, J.H. Park, M.-A. Oak, H.M. Jang, J.Y. Son, J.F. Scott, Phys. Rev. Lett. 107, 117201 (2011)

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.