57Fe Mössbauer study of unusual magnetic structure of multiferroic 3R-AgFeO2

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Abstract

We report new results of a 57Fe Mössbauer study of hyperfine magnetic interactions in the layered multiferroic 3R-AgFeO2 demonstrating two magnetic phase transitions at \( T_{N1} \) and \( T_{N2} \). The asymptotic value \( \beta^* \approx 0.34 \) for the critical exponent obtained from the temperature dependence of the hyperfine field \( H_{hf}(T) \) at 57Fe the nuclei below \( T_{N1} \approx 14 \) K indicates that 3R-AgFeO2 shows quasi-3D critical behavior. The spectra just above \( T_{N1} \) \( (T_{N1} < T < T^* \approx 41 \) K) demonstrate a relaxation behavior due to critical spin fluctuations which indicates the occurrence of short-range correlations. At the intermediate temperature range, \( T_{N2} < T < T_{N1} \), the 57Fe Mössbauer spectra are described in terms of collinear spin-density-waves (SDW) with the inclusion of many high-order harmonics, indicating that the real magnetic structure of the ferrite appears to be more complicated than a pure sinusoidally modulated SDW. Below \( T < T_{N2} \approx 9 \) K, the hyperfine field \( H_{hf} \) reveals a large spatial anisotropy \( (\Delta H_{anis} \approx 30 \) kOe) which is related with a local intra-cluster (FeO6) spin-dipole term that implies a conventional contribution of the polarized oxygen ions. We proposed a simple two-parametric formula to describe the dependence of \( H_{anis} \) on the distortions of the (FeO6) clusters. Analysis of different mechanisms of spin and hyperfine interactions in 3R-AgFeO2 and its structural analogue CuFeO2 points to a specific role played by the topology of the exchange coupling and the oxygen polarization in the delafossite-like structures.

Keywords: multiferroics, frustrated magnetic interactions, non-collinear spin configurations, magnetostructural phase transitions, Mössbauer spectroscopy, anisotropic hyperfine magnetic interactions

(Some figures may appear in colour only in the online journal)

1. Introduction

AMO2 delafossite-like oxides \( (A = \text{Cu}^+, \text{Ag}^+ \text{ and } M = \text{Cr}^{3+}, \text{Fe}^{3+}, \text{Co}^{3+}, \text{Ni}^{3+}) \) with triangular, geometrically frustrated spin structures attract much attention as magnetoelectric multiferroic materials [1–7]. The ferroelectricity in this class of multiferroics appears as a result of the phase transition, inducing an unusual magnetic structure that breaks the crystal symmetry. Geometrical spin frustration is one of the main origins of such a magnetic state [4]. The frustrated system, due to the vast degeneracy arising from competing magnetic interactions of transition ions, often displays non-centrosymmetric noncollinear or long-period-modulated collinear orders.

It would be useful to compare the local structural and magnetic properties of CuFeO2 and 3R-AgFeO2 oxides containing identical magneto-active Fe3+ ions but with different
diamagnetic Cu$^+$ and Ag$^+$ cations. Both of the oxides have a delafossite-like structure with the rhombohedral space group $R3m$ at room temperature. The structure consists of Fe$^{3+}$ hexagonal layers along the $c$ axis, which are separated by nonmagnetic $A^+–O^{2–}$ dumbbells ($A = \text{Cu, Ag}$) (figure 1(a)). A decrease in temperature causes a symmetry lowering from the $R3m$ space group to the monoclinic $C2/m$ [9]. According to magnetic data for CuFeO$_2$ [10] and our earlier studies of 3R-AgFeO$_2$ [11], these oxides exhibit two successive magnetic transitions at $T_{N1} \approx 14$ K, $T_{N2} \approx 11$ K (Cu) and $T_{N1} \approx 14$ K, $T_{N2} \approx 9$ K (Ag). Below $T_{N1}$, the oxides become magnetically ordered, with a sinuously modulated and partially disordered structure indexed by incommensurate propagation vectors $Q = 2\pi(0, q, 1/2)_m$ (Cu) [10] and $Q = 2\pi(−1/2, q, 1/2)_m$ [12], respectively, with the wave number $q \approx 2/5$ depending on temperature.

Despite the above similarity of the structural and thermodynamic parameters of CuFeO$_2$ and 3R-AgFeO$_2$, the magnetic ordering in these systems clearly demonstrates the difference in their magnetic ground state at low temperatures, $T < T_{N2}$. The copper ferrite has a collinear four-sublattice (4SL) ground state \( \uparrow \uparrow \downarrow \downarrow \) with a commensurate propagation vector $Q = (0, 1/2, 1/2)_m$ [10] in the monoclinic cell. At the same time, according to recent neutron diffraction experiments [9, 12], the magnetic ordering in 3R-AgFeO$_2$ at $T < T_{N2}$ is in the form of an elliptical cycloid with an incommensurate propagation wave vector $Q = 2\pi(−1/2, q, 1/2)_m$, with $q \approx 0.2026$.

Such an essential difference in the nonpolar commensurate state of CuFeO$_2$ and the polar magnetic structure of 3R-AgFeO$_2$ clearly underlines that the nonmagnetic $A$ ($= \text{Cu}^+, \text{Ag}^+$) ions play a crucial role in the magnetic exchange interactions and multiferroic behavior of the delafossite AFeO$_2$ compounds [9, 13]. The ground state spin structure and its temperature variation in the quasi-2D systems AFeO$_2$ is far from trivial, due to a competition between several interactions. First of all these are the intra-layer ($J_{ij}^{\text{(intra)}}$) and inter-layer ($J_{ij}^{\text{(inter)}}$) isotropic exchange coupling described by the Hamiltonian:

$$
\hat{H} = \sum_{ij} J_{ij}^{\text{(intra)}} S_i \cdot S_j + \sum_{ij} J_{ij}^{\text{(inter)}} S_i \cdot S_j,
$$

(1)

where $J_{ij}^{\text{(intra)}} \equiv J_0$ and $J_{ij}^{\text{(inter)}} \equiv J_{1,2,3}$ (figure 1(b)). The intra-layer exchange interactions in 3R-AgFeO$_2$ and CuFeO$_2$ are significantly affected by the substitution of the nonmagnetic $A$-site cations in spite of the common low-temperature monoclinic symmetry in both oxides. We argue that this effect can be explained to be a typical one for the edge-shared exchange-coupled clusters. Indeed, the antiferromagnetic kinetic contribution to the superexchange integral Fe$^{3+}$–O$^{2–}$–Fe$^{3+}$ ($d^6, \sigma A_{1g}$)–O$^{2–}$–Fe$^{3+}$ ($d^5, \sigma A_{1g}$) can be written as follows [14]:

$$
J_{\text{FeFe}} = \frac{2}{25U} [t_{d\sigma} + t_{d\sigma} \cos \theta] + t_{d\pi} \sin^2 \theta + t_{d\pi}(2 - \sin^2 \theta) > 0,
$$

(2)

where $\theta$ is the Fe–O–Fe bonding angle, $t_{d\sigma} > t_{d\pi} > t_{\sigma\pi} > t_{\sigma\alpha}$ are positive definite $d$–$d$ transfer integrals, $U$ is a mean $d$–$d$ transfer energy (correlation energy). For the edge-shared FeO$_6$ octahedra with the bonding angle close to 90° as in delafossite structure the strongest $\sigma$–$\sigma$ bond is invalidated and the weakened antiferromagnetic contribution starts to compete with a ferromagnetic ($J_{\text{pot}} < 0$) potential (Heisenberg) exchange giving rise to a striking sensitivity of the net exchange integral on rather small changes of structural parameters, such as superexchange bonding angles and cation–anion separations.
Furthermore, the compensation effect does promote the relative role of next-nearest-neighbors (nnn) Fe–O–Fe and next-next-nearest-neighbors (nnnn) Fe–O–O–Fe interactions (figure 1(b)).

Another characteristic feature of the topology of exchange-interactions in delafossites $AFeO_2$ is that, different from the most part of ferrites, an $O^{2-}$ ion belongs to three Fe–O–Fe bonds that make the exchange coupling to be extremely sensitive to oxygen displacements and its electric polarization thus providing paths for understanding the exotic spin-lattice coupling phenomena, specifically spin-driven bond order, in geometrically frustrated magnets [15]. The comprehensive analysis of the isotropic superexchange coupling in delafossites has to take into account a strong electric polarization of the intermediate oxygen ions.

Furthermore, specific spin structures in 3R-$A$Fe$O_2$ and CuFe$O_2$ are related with usually more weak anisotropic interactions such as a single-ion anisotropy (SIA) and Dzyaloshinskii–Moriya (DM) coupling:

$$E_{SIA} + E_{DM} = D \sum_{i} S_i^2 - \sum_{i<j} d_{ij} [S_i \times S_j],$$

where $D$ is anisotropy parameter, $d_{ij}$ is the axial Dzyaloshinskii vector. Within a linear approximation on the noncubic distortions the energy of the single-ion anisotropy in Fe$O_6$ octahedral clusters can be represented in the main coordinate system ($O_x,y,z \perp C4$) as follows:

$$E_{SIA} = \sum_i k_i \alpha_i^2 + \sum_{i<j} k_{ij} \alpha_i \alpha_j$$

where $\alpha_i$ is direction cosine of the $S_i$ spin. The anisotropy constants are proportional to components of the octahedron deformation tensor: $k_i = b_i \varepsilon_{ii}, k_{ij} = b_{ij} \varepsilon_{ii}$, where $\varepsilon_{ii} = (l_i - l_0)/l_0$, $\varepsilon_{ij} = 1/2(\pi/2 - \theta_{ij})$, $l_i$ is a cation–rth ligand separation, $l_0 = 1/3 \sum l_i$ is a mean cation–anion separation, $\theta_{ij}$ is the rth ligand–cation–rth ligand bond angle. Magnetoelastic parameters ($b_{ij},d_{ij}$) that determine the contribution of the distortions such as elongation-contraction of the cation–anion bonds and deviations of the anion–cation–anion bonding angles from $\pi/2$, respectively, were estimated earlier for Fe$O_6$ clusters in $RFEO_3$: $b_{ii} \approx 24$ cm$^{-1}$; $b_{ij} \approx 6$ cm$^{-1}$ [16]. The positive sign of the $b_{ij}$ produces an important result that the trigonal distortion along $C_3$ axis with the Fe$^{3+}$O$_6$ octahedron contraction along the axis ($\theta_{ij} > \pi/2$) makes the axis to be the easy one, while the octahedron elongation along the $C_3$ axis makes the respective perpendicular plane (1 1 1) to be the easy plane. For 3R-$AgFeO_2$ and CuFe$O_2$ with the Fe$O_6$ octahedrons contracted along hexagonal c-axis we arrive at an easy-axis type of the single-ion anisotropy with a rather large value of the anisotropy parameter $D$:

$$D \approx \frac{4}{25} \cdot \frac{\pi}{360^\circ} (90^\circ - 96.6^\circ) \cdot 6 \text{cm}^{-1} \approx -0.008 \text{meV},$$

where we used experimental data for the trigonal distortion of the Fe$^{3+}$O$_6$ octahedra in 3R-$AgFeO_2$ at $T > T_N$: $\theta_{ij} = 96.6^\circ$ [12]. Interestingly, this estimate is close to experimentally found $D = -0.01$ meV in CuFe$_{1-x}$Ga$_x$O$_2$ ($x = 0.035$) [17]. However, the Fe$^{3+}$ single-ion anisotropy in CuFe$O_2$ can be as large as $D \approx -0.2$ meV with a puzzling downfall to $D \approx -0.01$ meV under a slight substitution Fe for Ga$^{3+}$ ions [17]. One of the most probable explanations for this unexpected anisotropy can be related with a markedly large and sensitive electric polarization of oxygen ions [18, 19] which seems to be a specific property of delafossite structure as compared with many other oxides. The electric field induced $O(sp)$-hybridization accompanied with an effective off-center shift of the valence $O^2$p-shell can result in a large orbital anisotropy through the anisotropic Fe 3d-O(2p) hybridization.

For so-called S-type 3d-ions (Mn$^{2+}$/4+, Fe$^{3+}$, Cr$^{3+}$, Ni$^{2+}$) with orbitally non-degenerated ground state one might use a simple formula for the Dzyaloshinskii vector for a cation(1)-anion-cation(2) superexchange bond [20–22]:

$$d(\theta) = d_{12}(\cos \theta) [r_1 \times r_2] = \frac{1}{2i} \sum d_{ij}(\cos \theta) [R_{ij} \times \rho_{ij}],$$

where $R_{ij} = R_{ij} - R_{ij}$, $\rho_{ij} = \rho_{ij} + \rho_{ij}$ are cation(1,2) bond vectors, and $\rho_{ij} \perp R_{ij}$, $r_1 = R_{ij}/l$, $r_2 = R_{ij}/l$ are respective unit vectors. The sign of the scalar parameter $d_{12}(\cos \theta)$ can be addressed to be the sign of the Dzyaloshinskii vector.

Hereafter we do not consider microscopic mechanisms of Dzyaloshinskii–Moriya coupling to be supposedly a main source of the helical ordering and multiferroicity in $AFeO_2$ delafossites and shall limit ourselves to a simplified continual Landau–Ginzburg approximation for main magnetic interactions that provides nonetheless a comprehensive description of the helical ordering in delafossites. The Landau–Ginzburg free energy ($f_{LG}$) density of the $AFeO_2$ systems can be written as follows [23]:

$$f_{LG} = \sum_i A_i (\nabla S_i)^2 - \rho \rho [\rho \nabla \rho - (\rho \nabla) \rho] + D S_i^2,$$

where the first term is an exchange interaction with an exchange stiffness constants $A_i$; the second term is the Lifshitz invariant form of the specific Dzyaloshinskii–Moriya coupling, $P$ is the spontaneous electric polarization vector, $\alpha$ is the inhomogeneous magnetoelectric interaction constant; the third term is a magnetic anisotropy term with $D$ to be the uniaxial magnetic anisotropy constant. For classical spins $S = S_0 (\sin(\cos \varphi) \sin \sin \varphi, \cos \varphi)$, the minimization of the free-energy functional $F = \int f_{LG} dV$ by the Lagrange–Euler method gives for the functions $\varphi(x, y, z)$ and $\theta(x, y, z)$ [23] as follows:

$$\cos \varphi(x, y, z) = \sin [(\pm 4 \lambda x, m)],$$

with $\varphi = \text{const}$ (ignoring the small canting out of the cycloid plane), that is, an anharmonic cycloid in which the spin component $S_i$ along $z \parallel V_{zz}$ direction is given by the elliptic Jacobi function sn(...), where $\lambda$ is the period of the cycloid, $K(m) = \frac{\pi}{2} \int_0^\pi \sin(1 - m \cos^2 \theta) \theta^{1/2}$ is the complete elliptic integral of the first kind, and $m$ is the anharmonicity parameter related to the distortion (anharmonicity) of the spiral structure. The classical distortion of the spiral corresponds to a redistribution of the spin vectors around a circle. The value of $m$ is
related to the uniaxial anisotropy $D$ as follows: when $m \to 0$ and $D = 0$, all spin directions are equivalent, giving a simple spiral that contains only one turn angle, $\Delta \theta_0$. When $m \to 1$ and $D < 0$, the spin rotation is no longer isotropic, even in the classical limit, and the spins favor the easy axis direction [23].

The Lifshitz term in (8) can be easily reproduced within so-called ‘spin-current’ mechanism of the spin-dependent electric polarization (KNB) when:

$$P \propto \sum_{ij} \{ R_{ij} \times [S_i \times S_j] \}.$$  \hspace{1cm} (9)

‘Ferroelectricity caused by spin-currents’ has established itself as one of the leading paradigms for both theoretical and experimental investigations in the field of a strong multiferroic coupling. However, the spin-current model cannot explain an emergence of ferroelectricity associated with proper crystal magnetic ordering in several multiferroics, including CuFeO$_2$, and specific features of the electric polarization induced by the cycloid structure in 3R-AgFeO$_2$ [9]. Indeed, the model stems somehow or other from exchange-relativistic effect, or Dzyaloshinskii–Moriya coupling, however, it does not take into account specific effects of the superexchange geometry. According to microscopic theory by Moskvin et al. [24, 25] the relativistic spin-dependent electric polarization for cation(1)-anion–cation(2) system can be written as follows:

$$P_{12}^{rel} = -\frac{1}{J_{12}} \mathbf{\Pi}_{12}(d_{12}[S_1 \times S_2]),$$  \hspace{1cm} (10)

where $J_{12}$ is a superexchange integral, $\mathbf{\Pi}_{12}$ is a so-called exchange-dipole moment which in general can be written as a superposition of the ‘longitudinal’ and ‘transversal’ contributions:

$$\mathbf{\Pi}_{12} = \rho_{12} \mathbf{R}_{12} + \rho_{12} \mathbf{d}_{12},$$  \hspace{1cm} (11)

where $\rho_{12}$ does not vanish only for crystallographically non-equivalent cations. In other words, the exchange-relativistic contribution to the dipole moment $P_{12}^{rel}$ is a superposition of the ‘longitudinal’ and ‘transversal’ mutually orthogonal contributions determined by the superexchange geometry, while the ‘spin-current’ factor $[S_1 \times S_2]$ does only modulate its value.

Numerous experimental findings on the electric field effect in ESR and their theoretical studies [26] can be used for a direct estimation of the single-ion contribution to the ME coupling in different multiferroics [25]. Indeed, the single-ion spin-dependent electric dipole moment widely used for many years in this field is

$$d_i = -\frac{1}{2} R_{ijk} \{ S_j, S_k \}$$  \hspace{1cm} (12)

and for $R_{ijk}$ parameters one finds numerous experimental data [26]. It should be noted that if $R_{ijk} = \delta_{ij} R_{ik}$, where vector $\mathbf{R}$ is the spin–spin bonding vector, we arrive at the expression for the spin-dependent dipole moment introduced by Arima [8] who made use of the term for explanation of the magnetoelectric polarization in CuFeO$_2$ with its proper-screw spin order.

The above physical properties, including unusual magnetic structure and magnetism, primarily depend on peculiarities of the electronic structure and crystal local surrounding of iron ions. Thus, $^{57}$Fe Mössbauer spectroscopy is one of the most powerful local methods for studying the AFMO compounds. Since the local magnetization of the iron ions induces a hyperfine field ($H_{hf}$) at $^{57}$Fe nuclei proportional to the local amplitude of the SDW via the core spin polarization mechanism, Mössbauer spectroscopy could be very useful to study the static magnetic order and low-energy spin fluctuations. Furthermore, since the basic mechanisms of the magnetic hyperfine interactions are in many respect analogous to that accepted in the theory of magnetic exchange interactions, studies of various contributions to the experimental $H_{hf}$ value can be quite useful in determining the relative importance of the various mechanisms of spin transfer within the Fe–O–Fe and Fe–Fe bonds in the AFMO structures.

While CuFeO$_2$ has been extensively investigated by Mössbauer spectroscopy [27–32], AgFeO$_2$ has been preliminarily studied only in our works [33, 34]. $^{57}$Fe Mössbauer measurements performed for 3R-AgFeO$_2$ in the paramagnetic temperature region $T > T_{N1}$ showed that all iron cations occupy unique crystallographic positions, in accordance with the crystal data [12]. Moreover, a self-consistent analysis of the complex magnetic hyperfine spectra at $T < T_{N2}$ [33] has been proposed. A reasonable fit was obtained by using the quasi-continuous variation of the hyperfine magnetic field ($H_{hf}$) amplitude, with the iron spin orientation varying in the $(bc)$ plane. It was shown [33, 34] that to obtain a good fit, an anharmonicity (bunching) of the iron spins along certain directions in the $(bc)$ plane is necessary. However, we did not discuss the origin of such anharmonicity in the context of the electronic structure of iron ions in the ferrite. Moreover, there was no information on the temperature evolution of the hyperfine Zeeman structure of Mössbauer spectra, in particular, at $T_{N2} < T < T_{N1}$ and near the critical point ($T \approx T_{N1}$), which would be very useful to clarify the nature of the magnetic phase transition.

In this work, we present the results of a detailed Mössbauer study of the ferrite 3R-AgFeO$_2$ in a wide range of temperatures, including both magnetic phase transitions ($T_{N1}$ and $T_{N2}$). The shape of the $^{57}$Fe Mössbauer spectra is shown to undergo significant changes when the type and character of spin ordering of the iron sublattice are changed. At $T_{N2} < T < T_{N1}$, the magnetically split spectra are fitted in terms of incommensurate spin density wave (IC-SDW) modulation [12]. In the range $T < T_{N2}$, the $^{57}$Fe Mössbauer spectra are analyzed assuming a space-modulated cycloidal magnetic structure. Such an approach allows us to reproduce, from experimental spectra, the profile of the spatial anisotropy of the hyperfine field, $H_{hf}$. In addition, we carried out a detailed analysis of the temperature dependences of hyperfine parameters, and a discussion is provided in light of the peculiarities of the electronic and magnetic states of the iron ions in 3R-AgFeO$_2$. The obtained data are compared with earlier published Mössbauer data for
the CuFeO$_2$ [27–32] and BiFeO$_3$ [35, 36] also revealing multiferroic properties.

2. Experiment

3R-AgFeO$_2$ was synthesized from a stoichiometric mixture of Ag$_2$O (99.99%) and Fe$_2$O$_3$ (99.999%). The mixture was placed in Au capsules and treated at 3 GPa and 1073–1173 K for 2 h (heating time to the desired temperatures was 10 min) in a belt-type high-pressure apparatus. After the heat treatments, the samples were quenched to room temperature (RT), and the pressure was slowly released. The samples were black dense pellets.

X-ray powder diffraction (XRPD) data were collected at RT on a RIGAKU MiniFlex600 diffractometer using CuK$\alpha_1$ radiation (2$\theta$ range of 10–80°, a step width of 0.02°, and scan speed of 1° min$^{-1}$). 3R-AgFeO$_2$ samples contained small amounts of Fe$_2$O$_3$ impurities.

Magnetic susceptibilities ($\chi = M/H$) were measured using a SQUID magnetometer (Quantum Design, MPMS-1T) between 2 and 300 K in different applied magnetic fields under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions. No dependence on the applied fields was observed, and no difference between ZFC and FCC curves was detected. Isothermal magnetization measurements were performed at 5 K between $-1 \, T$ and $1 \, T$; the M–H curves were linear with the magnetization of 0.0455 $\mu_B$ at 5 K and 1 T. Specific heat, $C_p$, was recorded from 60 K to 2 K at 0 and 90 kOe by a pulse relaxation method using a commercial calorimeter (Quantum Design PPMS).

The $^{57}$Fe Mössbauer spectra were recorded at 4.6–300 K using a conventional constant-acceleration spectrometer. The radiation source $^{57}$Co(Rh) was kept at room temperature (RT). All isomer shifts refer to the $\alpha$-Fe at RT. The experimental spectra were processed and analyzed using methods of the model fitting and reconstruction of the distribution of the hyperfine parameters corresponding to partial spectra implemented in the SpectrRelax program [37].

3. Results and discussion

3.1. X-ray diffraction data

The XRPD patterns of the synthesized samples showed the formation of the rhombohedral 3R-AgFeO$_2$ phase (space group R-3m) without traces of the hexagonal 2H-AgFeO$_2$ phase (space group P6$_3$/mmc) that differs from 3R-AgFeO$_2$ by the stacking of the (FeO$_2$) planes [2, 11]. The refined lattice parameters of 3R-AgFeO$_2$ ($a = 3.0386(1)$ Å and $c = 18.5844(4)$ Å) are in good agreement with literature data [11, 12]. In what follows, the rhombohedral 3R-AgFeO$_2$ phase will be referred without ‘3R’.

3.2. Magnetic and thermodynamic data

A discussion of the magnetic and thermodynamic properties of the AgFeO$_2$ ferrite was given in our previous paper [11] and also in a recent, detailed work [9, 12]. Here, we only present the basic magnetic parameters that characterize the quality of the samples under investigation and the data necessary for further discussion of the $^{57}$Fe Mössbauer spectra of AgFeO$_2$.

The temperature-dependence of the static magnetic susceptibility ($\chi$), measured in a field of $H_{ext} = 1 \, \text{kOe}$, is plotted in figure 2(a). At high temperatures, $70 \, \text{K} < T < 300 \, \text{K}$, the inverse susceptibility $\chi^{-1}(T)$ follows the Curie–Weiss law ($T = \Theta_{CW}/\chi$) (insert for figure 2(a)). The obtained Curie constant, $C_p = 2.73(3) \, \text{cm}^3 \cdot \text{K/mole}$, yields an effective magnetic moment $\mu_{\text{eff}} = 2.67 \cdot (C_p/\chi m)^{1/2} \approx 6.06(3) \, \mu_B$, which is slightly higher than the spin-only value $2\sqrt{S(S+1)} \mu_B$ expected for the high-spin Fe$^{3+}$ ions with $S = 5/2$ and quenched orbital moment $(L) \approx 0$. The small discrepancy may be related to the partially unquenched orbital moment for the half-filled $d^6$ system, making the effective $g_{\text{eff}}$-factor slightly higher than 2 [38].

The experimental Curie-Weiss temperature $\Theta_{CW} = -139(2) \, \text{K}$ appears to be significantly higher than the critical point $T_{N1} \approx 14(1) \, \text{K}$ of the long-range magnetic transition, deduced from specific-heat measurements $C_p(T)$ (figure 2(b)).
This finding reveals the presence of strong frustration, indicated by the high value of the ratio \( \Theta_{\text{CW}}/T_{N1} \approx 10 \), which is in complete agreement with the triangular cationic topology of the delafossite-like lattice. It should be noted the obtained ratio is higher than the \( \Theta_{\text{CW}}/T_{N1} \approx 5 \) value for CuFeO\(_2\) [10], indicating that the AgFeO\(_2\) appears to be more frustrated. In the mean-field approximation, the Curie–Weiss temperature is related to the exchange parameters by the relation \( \Theta_{\text{CW}} = \alpha \sum z_i J_i \), where \( \alpha \equiv 2 S(S + 1)/\beta k_B \) and \( z_i \) is the number of nearest neighbors of iron connected by exchange intralayer \( (J_1) \) and interlayer \( (J_2) \) coupling [39]. The Neel temperature is given in the form \( T_N = \alpha J(q) \), where \( J(q) \) is the Fourier transform of the exchange integral \( J(q) \), and \( q \) is the propagation vector representing the magnetic structure. Taking into account the almost complete coincidence of the \( T_{N1} \) values of CuFeO\(_2\) \( (T_{N1} = 16 \text{ K}) \) and AgFeO\(_2\) \( (T_{N1} = 14(1) \text{ K}) \), figure 2, the observed increase of frustration \( (\Theta_{\text{CW}}/T_{N1}) \) in the case of AgFeO\(_2\) may be ascribed to the strengthening of its own magnetic interactions.

The above results clearly demonstrate that the microscopic mechanisms for lifting the magnetic frustration within the AgFeO\(_2\) and CuFeO\(_2\) lattices, both of which have a common low-temperature monoclinic structure \( (T < T_{N1}) \), could be very different. A similar conclusion was recently drawn in the comparative analysis of the lattice distortion in these ferrites [13]. In particular, it has been shown that the \( b_m \) axis in the monoclinic basis contracts at \( T < T_{N1} \) in AgFeO\(_2\) and elongates in CuFeO\(_2\). It is important to note that all the known changes in the spin structure of the delafossite-like \( \text{AFeO}_2 \) systems occur along the \( b_m \) axis. Therefore, the nearest-neighbor (nn) exchange interactions \( (J_1) \) in the basal plane (figure 1(b)) play an essential role in the mechanisms responsible for lifting the magnetic frustration. In particular, we can speculate that the discussed [13] difference in the character of the monoclinic lattice distortion in the two ferrites is closely related to the change in the strength of the \( nn \) interaction.

The magnetism of real triangular magnets is characterized by a competition between the intra- \((J_1)\) and inter-plane \((J_2)\) interactions, and the single-ion anisotropy \((D)\), whose sign and value determine the orientation of the spin plane relative to the crystal axes. The experimental evidence that the \( b_{m} \) axis elongates in CuFeO\(_2\) [13] implies that direct AFM exchange \( (J_{\text{dir}} > 0) \) diminishes and FM superexchange \( (J_{\text{sup}} < 0) \) will dominate. This mutual cancelation leads to a weakening of the nearest interactions \( (J_1 > 0) \). As a result, the anisotropy along the hexagonal \( c_\lambda \) axis \((D < 0)\) gains importance, leading to additional frustration. According to Monte Carlo calculations [40], when \( D/|J_1| > c_{\text{crit}} = 0.317 \), the collinear \( \uparrow \uparrow \downarrow \downarrow \) (4SL) structure is expected to be stable. At the same time, in the case of AgFeO\(_2\), the \( b_m \) axis contracts, thus stabilizing AFM interactions along this axis. With increasing AFM exchange, corresponding to decreasing \( D/|J_1| < c_{\text{crit}} \), the 4SL structure eventually becomes unstable to noncollinear incommensurate phases [40]. In particular, as will be discussed the next section, the enhancement of the nearest-neighbor Fe–Fe interaction at high temperatures \( (T > T_{N2}) \) gives rise to multiple-sublattice states with maximum AFM coupling between nearest neighbors, such as a partially disordered (PD) 5 sublattice structure (5SL) with a (…↑↓↑↓-disordered…) spin sequence in the \( b_m \) direction.

3.3. Mössbauer data

3.3.1. Paramagnetic temperature range \((T > T_{N2})\). The \(^{57}\text{Fe}\) Mössbauer spectra of AgFeO\(_2\) measured in paramagnetic temperature range \( T > T_{N1} \) (figure 3) consist of a single quadrupole doublet with narrow \((W = 0.25(1) \text{ mm/s})\) and symmetrical components, indicating that all iron ions occupy in the ferrite structure equivalent crystal sites. The isomer shift \( \delta_{300 \text{ K}} = 0.37(1) \text{ mm/s} \) and quadrupole splitting \( \Delta_{300 \text{ K}} = 0.66(1) \text{ mm/s} \) correspond to the high-spin \( \text{Fe}^{3+} \) \((S = 5/2)\) in an octahedral oxygen environment with a very strong electric field gradient (EFG) at \(^{57}\text{Fe}\) nuclei [41]. In our previous study [33, 34], the main components of the EFG tensor \((V_{EFG})\) was calculated using crystal data for the high-temperature rhombohedral [42] and low-temperature \( (T < T_{N2}) \) monoclinic [42] lattices of AgFeO\(_2\). It has been shown that, in addition to monopole lattice contribution \( V_{\text{mon}} \), very large weight has dipole contribution \( V_{\text{dip}} \), arising from the induced electric dipole moments \((\mu_{\text{d}})\) of oxygen ions. The best agreement between the theoretical and experimental values of quadrupole splitting at 300 K was found for the oxygen polarizability \( \alpha_O \approx 0.83 \text{ Å}^3 \) that agrees well with the data for other oxides with the delafossite structure [18]. The calculations show that the principal component \( V_{zz} \) of the EFG tensor \( V_{EFG} \) is directed along the \( c_\lambda \) axis of the hexagonal \( \text{AgFeO}_2 \) unit cell (figure 4). The angle between the principle axis \( O_z \) of the EFG tensor and \( a_m \) axis in the \((ac)_m \) plane of the monoclinic unit cell is \(-8^\circ\), that is very close to the \( c_\lambda \) direction of the hexagonal unit cell. Thus, the symmetry lowering \( R3 \) \( m \rightarrow C2/m \) does not lead to significant changes in the values...
of the EFG gradient components and their relative orientations in AgFeO$_2$ lattice.

We performed detailed measurements of the spectra at temperatures $T > T_{N1}$, and did not find any visible anomalies in the $\delta(T)$ and $\Delta(T)$ dependences. The isomer shift $\delta(T)$ gradually increase in accordance with the Debye approximation for the second-order Doppler shift [41]. This shows that there are no any electronic and structural transitions in this temperature interval.

3.3.2. Critical spin fluctuations near $T \approx T_{N1}$. Figure 5 shows the $^{57}$Fe Mössbauer spectra of AgFeO$_2$ taken in the temperature range below $T_{N1} \approx 14$ K, including the point of the second magnetic phase transition, $T_{N2} \approx 9$ K. A Zeeman structure with broadened components is clearly observed, evidencing the existence of a continuous distribution of the hyperfine magnetic field, $H_{hf}$, at the $^{57}$Fe nuclei. As was described in [33, 44], to analyze these spectra we reconstructed the magnetic hyperfine field distribution, $p(H_{hf})$ (figure 5), assuming a linear correlation between the quadrupolar shift ($\epsilon_Q$) of the Zeeman components and the value of $H_{hf}$ [37]. From the temperature-dependences of the mean field ($\langle H_{hf} \rangle$) and dispersion $D_{\text{ph}} = \sum p(H_{hf})(H_{hf} - \langle H_{hf} \rangle)^2$ (figure 6) of the resulting distributions $p(H_{hf})$, we determined the temperature ($T^*$) at which the magnetic hyperfine structure of the spectra disappears completely. The resulting value, $T^* \approx 19$ K, appears to be somewhat higher than the Neel temperature, $T_{N1}$, determined in the magnetic and thermodynamic measurements (figure 2). This finding is related to the persistence, in a narrow temperature range $T_{N1} \leq T \leq T^*$, of short-range magnetic correlations between Fe$^{3+}$ ions, which is usually observed for quasi-layered systems with frustrated exchange interactions [43, 44]. This interpretation is discussed in detail below.

Assuming that the hyperfine field, $H_{hf}$, is proportional to the magnetization ($M_{Fe}$) of the iron sublattice at all temperatures, we can compare the experimental $H_{hf}(T)$ dependence with the critical-point behavior of the iron magnetization $M_{Fe}(T)$ at $T \rightarrow T_{N}$. We approximated, in the region near $T_{N1}$, the temperature dependence of the most probable hyperfine field $H_{hf}^{(\text{max})}$, corresponding to the maximal value of the distribution $p(H_{hf})$, by a power law [45] as follows:

$$M_{Fe}(T)/M_{Fe}(4.6\,\text{K}) \approx H_{hf}^{(\text{max})}(T)/H_{hf}(4.6\,\text{K}) = B(1 - T/T_{N})^{\beta},$$

where $H_{hf}(4.6\,\text{K}) = 485$ kOe is the value of the hyperfine field at $T = 4.6$ K, $B$ is a reduction factor which depends only on the lattice symmetry and spin value, and $\beta$ is a critical exponent. A reasonably good fit (figure 7) to a power law was obtained in the range $3 \cdot 10^{-3} \leq \tau \leq 0.57$, where $\tau \equiv 1 - T/T_N$ is the reduced temperature. The fitting leads to $B = 1.17(4)$, $T_{N} = 14.0(5)$ K, and a critical exponent $\beta = 0.28(4)$. The value of the parameter $B$ proves to be close to the theoretical value $B^0 = 1.22$ for an ideal 2D Ising magnet, while the resulting value of the critical exponent $\beta$ is significantly larger than the theoretical value, $\beta^0 = 0.125$ [45], for 2D magnetic systems. According to [45, 46], the possible reason for such a discrepancy can be related to the fact that both these values ($B$ and $\beta$) were determined outside the appropriate critical region, $0 < \tau \lesssim \tau_{\text{crit}}$, usually defined by $\tau_{\text{crit}} < 10^{-2}$. This critical region depends on the particular magnetic system and therefore, has to be determined for each case. We performed a least-squares fit to a power law to describe the experimental dependence of $H_{hf}^{(\text{max})}(T)/H_{hf}(4.6\,\text{K})$ for various temperature regions, defined by the maximum value, $\tau_{\text{max}}$, of the reduced temperature $\tau$ (by successively omitting data points). The resulting variation of

![Figure 4](image-url)
$\beta$ as a function of $\tau_{\text{max}}$ is shown in the inset to figure 7. The asymptotic behavior of $\beta$ is observed and at the same time, the critical exponent $\beta^*$ remains constant (within the error range). Therefore, a power law may yield reliable results, as observed only below $\tau_{\text{max}} \approx 0.15$. For $\tau > \tau_{\text{max}}$, to allow a direct comparison with theory, the experimental value of the exponent $\beta$ has to be adjusted while taking into consideration the selected range of reduced temperatures [45, 46] as follows:

$$\beta^* = \beta + A \nu \cdot (\tau_{\text{max}})^\nu,$$

(14)

where $\beta^*$ is the effective exponent that is related to the universal $\beta$ by $(\lim_{\tau \to 0} \beta^*) = \beta$; $A$ is the correction-to-scaling amplitude that depends on the features of the system; and $\nu$ is the universal correction-to-scaling exponent [45, 46]. This correction for the 2D Ising model ($\nu = 1, A \approx 0.21$) is presented in figure 7 (inset) by the orange, open circles. The evaluated averaged value, $\beta^* = 0.34(2)$, (the orange dashed line in the inset to figure 6) proves to be very close, but is slightly smaller than the theoretical value for 3D Heisenberg ($\beta^H = 0.365$) magnets [45].
The origin of the high critical parameter $\beta^*$ in the quasi-2D system $\text{AgFeO}_2$ is far from trivial, due to competition between several interactions such as the magnetic coupling between layers and the strength of the crystal field (single-ion anisotropy), which can lead to a range of $\beta$ values in the range $0.20 \leq \beta \leq 0.36$. The ideal 2D ($J_0 = 0$) isotropic Heisenberg system ($\zeta_{xy2} = 0$) cannot be ordered at non-zero temperatures [45]. However, any deviation from the isotropic 2D system, such as a small anisotropy ($D \neq 0$) or interlayer exchange ($J_0 \neq 0$), favors the occurrence of long-range order within the magnetic layers at $T = 0$K. Whether the order parameter of a system of weakly coupled magnetic layers shows a 2D Ising ($\beta \approx 1/8$) or a 3D ($\beta \approx 1/3$) [45] critical behavior depends on the relative strength of the anisotropy energy ($g_{hf}H_A$) and the interlayer exchange coupling $J_1$ ($\equiv J_P$) (see figure 1(b)). The asymptotic value of $\beta^* \approx 0.34$ obtained in our experiments indicates that $\text{AgFeO}_2$ shows quasi-3D critical behavior and, thus, the magnetic phase transition ($T_{N1}$) in this oxide is governed by the interlayer interaction rather than by anisotropy as follows: $U_\beta \gg |D|$. Note that this interpretation agrees with the analysis of the revised magnetic properties of the triangular $\text{CuFeO}_2$ lattice [46]. It was suggested [46] that in addition to exchange couplings within layers ($J_1 \equiv J_0$), the exchange couplings between layers ($J_1 \approx 0.3 J_0$) also play a significant role in forming the magnetic structure of delafossite-like magnets.

One can assume that the change in the character of interlayer exchange interactions when $\text{Cu}^+$ ions are replaced with $\text{Ag}^+$ is a possible reason for the observed drastic difference in the magnetic behavior of these ferrites. Further experimental and theoretical study is still required to reach a deeper understanding of critical dynamics in these low-dimensional iron-based multiferroics.

To examine the magnetic behavior of the iron sublattice at the first magnetic phase transition, we carried out a series of Mössbauer measurements just above the $T_{N1}$ temperature, $T_{N1} < T < T^*$. According to the obtained data (figure 8(a)), in addition to the paramagnetic quadrupole doublet with broadened components, it is necessary to introduce an unresolved magnetic hyperfine structure to provide a good description of the experimental spectra just above the ‘magnetic’ $T_{N1}$ temperature. Because the specific heat data (figure 2(b)) show that magnetic correlations are present in the range $T \geq T_{N1}$, we fitted the experimental spectra in the interval $T_{N1} < T < T^*$ using a stochastic relaxation model [47]. In this formalism, the magnetic hyperfine interactions are described as interactions between the nuclear magnetic moment and a randomly varying hyperfine magnetic field $H_{hf}(t)$. The time-dependent Hamiltonian for this relaxation is

$$\hat{H}(t) = \hat{H}_Q - g_a\mu_a H_{hf}^0 \sum_i I_i f_i(t),$$

where $\hat{H}_Q$ is the quadrupolar hyperfine Hamiltonian, $g_a$ is the gyromagnetic factor of the nuclear state, $\mu_a$ is the nuclear Bohr magneton, $I_i$ are the nuclear spin projection operators onto the EFG principal axes, and $f_i(t)$ is a random function of time. We assumed that the $H_{hf}(t) = H_{hf}^0 f_i(t)$ field fluctuates between the three principal directions of the EFG tensor with appropriate values $f_i(t) = \{1, 0, -1\}$ (isotropic relaxation). The lineshapes of the spectra depend on the following two parameters: a correlation time, $\tau_c$ (or frequency of the spin fluctuations $\propto 1/\tau_c$), and $H_{hf}^0$, which is the saturated hyperfine field when $1/\tau_c \to 0$ [48].

The observed coexistence of magnetic and paramagnetic subspectra close to the $T_{N1}$ point was interpreted as follows: antiferromagnetic clusters are possibly created in $\text{AgFeO}_2$ layers by 2D spin correlations in the paramagnetic region near the temperature $T_{N1}$. A similar behavior has been previously

![Figure 6](image-url)

**Figure 6.** Temperature dependences of the average value of the hyperfine field ($H_{hf}$) and dispersion $D_{hf}(\text{ex})$ (inset) of the distributions $p(H_{hf})$.

![Figure 7](image-url)

**Figure 7.** Reduced hyperfine field $H_{hf}^{\text{max}}(T)/H_{hf}^{\text{max}}(4.6\,\text{K})$ as a function of the reduced temperature (red solid line corresponds to fit to the power law given by equation (13)). Inset: variation of critical exponents $\beta$ and $\beta^*$ with maximum reduced temperature $T_{max}$ (logarithmic representation). Blue dashed line corresponds to fit with parameters $\nu = 1$ and $A \approx 0.36$ (see (equation (14))) and orange dashed line corresponds to the average $\beta^*$ value.
observed for many low-dimensional systems [49]. It was shown that well above $T_N$, each spin relaxes in the local, rapidly fluctuating exchange field produced by its uncorrelated neighbors at the rate $1/\tau_c$, typically as large as $\sim 10^{11} - 10^{12}$ s$^{-1}$, thus resulting in a paramagnetic hyperfine structure (singlet or quadrupole doublet). As $T_{N1}$ is approached, the correlation length $\xi$ increases, i.e. small clusters of spins with a short-range order are formed, and these act as a single unit for which the magnetization relaxes slowly, as in superparamagnetic particles [50]. Thus, at $T \rightarrow T_{N1}$, where the system orders, both quantities $\tau_c$ and $\xi$ increase, and the characteristic frequency of the spin fluctuations decreases (inset to figure 8(b)). Such a critical slowing down of $1/\tau_c$ is expected to be more important in low-dimensional systems [49]. At $T \rightarrow T_{N1}$, the correlation length diverges and long-range order sets in. Although the magnetization of the crystal as a whole remains zero, it is possible to find increasingly large regions in which there is a net magnetization. From the fits of the spectra, we extracted the paramagnetic fraction ($I_{\text{par}}$) at different temperatures. Figure 8(b) clearly shows that above $T_{N1}$, this paramagnetic fraction begins to increase sharply at the expense of the magnetic sub-spectrum, reaching a steady value of 100% at $T^* \approx 21$ K. This behavior is consistent with superparamagnetism or superferromagnetism [50], i.e. the formation of nanosized magnetic domains with the randomly flipping direction of the magnetization under the influence of temperature. The relative temperature range $(T^* - T_N)/T_N$ of the dynamic critical region over which a slowing of the spin correlations time ($\tau_c$) occurs should be influenced by the ordering dimensionality, which is defined by $\beta$ (equation (14)). To verify the validity of this assumption, it would be interesting to compare the Mössbauer data for AgFeO$_2$ with those of other local resonance methods, such as NMR or ESR, sensitive to spin dynamics in the iron sublattice.

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Figure 8. (a) $^{57}$Fe Mössbauer spectra (experimental hollow dots) of 3R-AgFeO$_2$ recorded just above the Neel temperature ($T \approx T_N$). Solid lines are simulation of the experimental spectra as the superposition of magnetic (orange area) and paramagnetic (blue line) subspectra (see text). (b) Temperature variation of the fraction of paramagnetic component. Inset: temperature dependence of the relaxation rate ($1/\tau_c$) associated with the 2D spin correlations.
3.3.3. Magnetic ‘Intermediate’ temperature range 

\(T_{N2} < T < T_{N1}\). According to recent neutron diffraction data [12], at \(T_{N2} \leq T \leq T_{N1}\), AgFeO2 has a collinear, sinusoidally modulated spin structure with the propagation wave vector \(Q\) along the monoclinic \(b_m\) axis. We assumed that the hyperfine field distribution \(p(H_{hf})\) observed in this temperature range (figure 5) is related to incommensurate spin-density-waves (SDW), in which iron ions at different iron sites, \(x_n\), along the SDW propagation carry different values of magnetic moments \((\mu_{Fe})\). Assuming that the magnetic hyperfine field \(H_{hf}(x_n)\) at each particular iron position is parallel and proportional to the magnetic moment, \(\mu_{Fe}\), the modulation of the hyperfine field can be defined in terms of a Fourier series as [51]

\[
H_{hf}(x_n) = \sum_{l=0}^{N} h_{2l+1} \sin [(2l + 1)q x_n],
\]

where \(h_{2l+1}\) represents the amplitude of the \(i\)-th \((i = 2l + 1)\) harmonic, \(q\) is the wave number of the SDW, \(x_n\) is the relative \(n\)th position of the iron ions along the direction of SDW propagation (for commensurate SDW, \(x_n = nb_m\), and \(n\) denotes the number of iron atoms in the direction of the \(b_m\) axis). The spectra were fitted as a superposition of Zeeman subspectra, with hyperfine field values according to equation (16) for discrete \((qx_n)\) values in the range \(0 \leq qx_n \leq \pi/2\) [51].

An analysis of the experimental Mössbauer spectra using only a fundamental harmonic, \(h_1\) (sine-modulation), did not yield a good fit (the blue dashed line in figure 9(a)). Thus, the \(^{57}\)Fe Mössbauer spectra can be described in terms of spin-density-waves (SDW) but with the inclusion of many high-order harmonics, \(h_{2l+1} (l \neq 0)\) (the red solid line in figure 9(a)). This observation indicates that the real magnetic structure of the AgFeO2 ferrite in the intermediate temperature range,
T_{N2} \leq T < T_{N1}$, appears to be more complicated than the early, supposedly purely sinusoidally modulated SDW [12] (the blue dashed lines on the distributions $p_{SDW}(H_{hf})$ and modulations $(H_{hf})_{q}(\chi)$ of the hyperfine magnetic field in figure 9(b)). One of the most probable reasons why neutron diffraction measurements could not detect that the magnetic structure in the range $T_{N2} < T < T_{N1}$ is a square wave modulated, can be related to the fact that the magnetic peaks associated with the higher harmonics of the fundamental sine wave are too weak to be observed from the neutron experiments. We obtained a series of least-squares ($\chi^2$) fits of the spectra, with harmonic amplitudes ($h_{2l+1}$) as the variable parameters. The number of Fourier components ($z$) in the fitting was increased until the experimental lineshape was satisfactorily reproduced. The good fits, shown in figure 9(a), were obtained with six ($0 \leq l \leq 6$) Fourier components. The introduction of more components, i.e. $l \geq 7$, did not result in a significant decrease of $\chi^2$.

The observed slight asymmetry of the spectra (figure 9(a)) has been described assuming a linear correlation of the isomer shift, $\delta_0 + (\partial\delta/\partial H_{HF})H_{HF}$, and quadrupole shift, $\varepsilon_Q = \varepsilon_0 + (\partial\varepsilon/\partial H_{HF})H_{HF}$ with the hyperfine field, $H_{HF}$ [37]. Such correlations may be caused by an incommensurate modulation induced by magnetoelastic coupling with the SDW. A similar conclusion has been drawn from synchrotron x-ray diffraction experiments on a CuFeO$_2$ crystal, in which cooperative displacements of oxygen ions along the $b_m$ axis are induced in the partially distorted (PD) phase, as a result of magnetostriction [52]. It is interesting that the $^{57}$Fe Mössbauer spectra of the CuFeO$_2$ ferrite with the PD magnetic structure have very a similar profile to those of AgFeO$_2$ recorded at 'intermediate' temperatures (figure 9(a)). Using the results of the above fitting, we calculated the average values of polar (\(\vartheta(T)\)) and the average hyperfine field (\(H_{HF}(T)\)), we estimated the mean values of \(\delta(T)\) and \(\varepsilon_Q(T)\) for each spectrum in the interval $T_{N2} \leq T \leq T_{N1}$. The $\langle \delta_{10-18s}(T)\rangle \approx 0.53$ mm s$^{-1}$ values thus obtained show good agreement with the data, $\delta_{10} = 0.43(1)$ mm s$^{-1}$, for temperatures above $T_{N1}$ (accounting for the second-order Doppler shift). In contrast, the $\varepsilon_Q(T)$ values (see inset of figure 10) appear to be significantly smaller than the quadrupole shift $\varepsilon_Q(\Delta/2) \approx 0.33$ mm s$^{-1}$ for $T > T_{N1}$. Taking into account that according to our calculations, monoclinic distortion of the AgFeO$_2$ lattice does not lead to significant changes in the values of the EFG components, the observed reduction of the $\varepsilon_Q(T)$ can be related to its angular dependence on the relative orientation of the principal axis, OZ, of the EFG tensor and $H_{HF}$. If $H_{HF} \parallel eQV_{zz}$ and the first-order quadrupole shift, $\varepsilon_Q(3/2, m) = (3/2, m)_{\parallel} H_{HF} 3/2, m)$, the energy level, $3/2, m$ is given by [53]

$$\varepsilon_Q = (-1)^{m+1/2} \sqrt{3} eQV_{zz}^{par} \left[ 3 \cos^2 \vartheta - 1 + \eta \sin^2 \vartheta \cos 2\varphi \right],$$

(17)\n
where $m$ are magnetic quantum numbers; $eQV_{zz}^{par}$ is the quadrupole splitting constant, which equals that in the paramagnetic state ($T > T_S$) if there is no distortion of the crystal lattice at $T_S$, and shows temperature-independent behavior below and above $T_N$; $\vartheta$ and $\varphi$ are the polar and azimuthal angles of the hyperfine field, $H_{HF}$, in the principal axes of the EFG tensor. Because the Fe$^{3+}$ ions occupy sites with a nearly axial symmetrical EFG tensor ($V_{xx} \approx V_{yy}$) in the AgFeO$_2$ structure, the parameter of asymmetry, $\eta$, was taken to be zero. Thus, we assumed that the spectral shape does not depend on the azimuthal angle $\varphi$. Taking the experimental values of $\varepsilon_Q(T)$, we calculated the average values of polar $\vartheta(T)$ for each temperature in the interval $T_{N2} \leq T \leq T_{N1}$. Figure 10 shows clearly that the obtained $\vartheta(T)$ values are well correlated with the $\varphi(T)$ corresponding to the relative orientation of the SDW magnetization and the $c||OZ$ axis deduced from ND data for AgFeO$_2$ [12].

Using the results of the above fitting, we calculated the distribution $p_{SDW}$. Figure 9(b) shows a comparison between the hyperfine field distribution $p_{SDW}(H_{HF})$ and a similar distribution $p(H_{HF})$ of hyperfine fields, $H_{HF}$. An important feature of both distributions is the presence of several humps (figure 9(b)), which may be related to different Fe$^{3+}$ magnetic sublattices or a domain structure. The appearance of higher harmonics can be qualitatively understood within the Hamiltonian (1), which includes the main contributions of competing exchange interactions for the nearest neighbors, $J_{nn}$, and next-nearest neighbors, $J_{nnn}$, respectively (see figure 1(b)). We speculate that the observed profile of SDW and the distribution $p_{SDW}(H_{HF})$ (figure 8(b)) can be understood using the domain wall or 'soliton' model [54, 55]. Such an analysis has been performed in [54] for a simple 3D Ising spin system with competing $J_{nn}$ and $J_{nnn}$ interactions, which exhibits modulated phases. It has been shown that when $U_{nn}$ is small, the ground state is non-distorted SDW, but when $U_{nn}/J_{nn}$ $\approx 0.5$, this state becomes marginally stable with respect to the domain-wall formation. The ground state is infinitely degenerate, corresponding to all possible ways to introduce domain
walls. In general, the regularly spaced solitons build a soliton lattice with a soliton density that depends on the value of $U_{\text{mip}}/u_{\text{mip}}$ [54, 55]. It must be noted that near $T_N$, the spin structure is almost sinusoidal, whereas, at lower temperatures, it contains a significant number of higher harmonics.

It should be noted that we cannot exclude another explanation for the observed $p(H_{\text{sd}})$ distributions with several maxima (figure 9(b)), which is based on the assumption of phase separation into magnetic and para- or superparamagnetic phases. Such an explanation was supposed earlier for the CuFeO$_2$ ferrite with the modulated, partially disordered (PD) magnetic structure in the range $T_{N_2} < T < T_{N_1}$ [56]. In inelastic neutron scattering experiments, a quasi-elastic magnetic scattering was observed in the PD phase, suggesting strong thermal spin fluctuations [56]. The same PD phase was recently found in the metallic triangular antiferromagnetic Ag$_2$CrO$_2$ using a muon-spin rotation and relaxation study ($\mu^+\text{SR}$) [57]. The $\mu^+\text{SR}$ spectra of this 2D oxide were fitted by a combination of a cosine oscillation corresponding to a static but inhomogeneous internal field at the muon sites and two relaxing non-oscillatory signals for fluctuating Cr$^{3+}$ moments. This result reflects the dynamic character of the PD state, in which the distorted Cr$^{3+}$ spins are fluctuating too rapidly to be observed by $\mu^+\text{SR}$.

3.3.4. Low-temperature range, $4.6 \, \text{K} < T < T_{N_2}$

The highly asymmetric profile of the experimental spectra at low temperatures below $T_{N_2} = 8.9 \, \text{K}$ (figure 5) reflects a high degree of correlation between the values of the magnetic hyperfine field and quadrupole shift ($\xi_0$) of the Zeeman components. According to [11], below $T_{N_2}$, the magnetic moments of Fe$^{3+}$ ions form an elliptic cycloid with a period of ~500 Å, which propagates along the [0 1 0] direction in the hexagonal lattice. This change in the character of magnetic ordering within the iron sublattice of AgFeO$_2$ induces non-zero electric polarization [11]. The complex hyperfine magnetic structure for the AgFeO$_2$ ferrite significantly differs from the single magnetic sextet in the CuFeO$_2$ ferrite, which has the same delafossite-like structure and which is characterized by collinear magnetic ordering $\uparrow\downarrow\uparrow$ [10], excluding any spontaneous electric polarization [1, 10]. At the same time, a similar hyperfine magnetic structure was observed for the perovskite-like ferrite BiFeO$_3$, possessing a non-collinear magnetic structure of the cycloid type [35, 36]. Thus, we observed the inhomogeneous line broadenings of the Mössbauer spectra for AgFeO$_2$ reflect non-collinear spatially modulated spin ordering, which is one of the most important intrinsic features of ‘improper’ multiferroics.

As described in detail in previous work [33, 34], for a model fitting of the Mössbauer spectra in the $T < T_{N_2}$ range, we used a procedure similar to that applied earlier for the analysis of the $^{57}$Fe Mössbauer [33–37] and NMR [58] spectra of the multiferroic BiFeO$_3$. It was taken into account the dependences of the quadrupole shift $\xi_0(\theta)$ (equation (17)) and hyperfine field $H_{\text{hf}}(\theta) = H_{\text{c}} \cos^2 \theta + H_{\text{s}} \sin^2 \theta$ on the polar angle $\theta$ between the direction of $H_{\text{hf}}$ and the principal axis $V_z$ of the EFG tensor, which coincides, according to our calculations, with the hexagonal axis (figure 4). In the expression for the anisotropy of hyperfine field $H_{\text{hf}}(\theta)$, the $H_{\text{c}}$ and $H_{\text{s}}$ parameters are the values of $H_{\text{hf}}$ oriented along and perpendicular to the principal axis $V_z$ (figure 11(a)).

The anharmonicity (bunching) of spatial distribution of Fe$^{3+}$ magnetic moments, which results from magnetic anisotropy in the ($zx$) plane of spin rotation (figure 10(b)), was described using Jacobian elliptic function (equation (8)). The best description of the spectra was obtained by using sufficiently high values of the anharmonicity parameter $m \approx 0.75$, which remains almost constant in the temperature range $T < T_{N_2}$ (figure 12). Anharmonicity is related to the constant $\kappa = N S^2 D/V$ of the uniaxial anisotropy as follows [23, 58, 59]: $\kappa = 16mAK^2(m)/\lambda^2$, where $K(0.78) = 2.21$, and $\lambda \approx 500 \, \text{Å}$ [11]. Taking into account that $A \approx NS^2(b_0)^2(J_1)/V$ with the monoclinic unit cell parameter $b_0 = 3.03 \, \text{Å}$ [11] we estimated the value $D/I_{J_1} \approx 16mAK^2(m)(b_0)^2/\lambda^2 \approx 2.2 \cdot 10^{-3}$ that appears to be substantially smaller than the critical value $(D/I_{J_1})_{\text{crit}} \approx 0.27$, below which the collinear $\uparrow\downarrow\uparrow$ 4SL phase of CuFeO$_2$ is not energetically stable and is replaced by more stable complex noncollinear (CNC) spin structures [60]. Below the second critical value of $(D/I_{J_1})_{\text{crit}} \approx 0.08$, the cycloid-like structure has a lower energy than the CNC phase [60]. As an example, we can refer to the CuFe$_{0.965}$Ga$_{0.035}$O$_2$ system, in which $(D/I_{J_1}) \approx 0.04$ [6], exhibiting a helicoidal magnetic structure and multiferroic behavior. As discussed in [6], this reduction of the $(D/I_{J_1})$ ratio must be one of the reasons for the disappearance of the collinear 4SL magnetic ground state. If the exchange stiffness constant to estimate as follows: $\alpha \approx 3/2(\kappa H_{\text{sd}}/R_{\text{Fe-Fe}})$, we arrive at an estimation of the single-ion anisotropy parameter $D$ as $D = \sim 0.017 \, \text{meV}$, that is twice as much as our theoretical prediction $(\sim 0.008 \, \text{meV})$ for trigonally distorted FeO$_6$ octahedra in AgFeO$_2$ given nonpolarized oxygen ions. One of the most probable explanations both for this deviation and an unexpected spread of the anisotropy parameters in ferro-delafossites can be related with a markedly large and sensitive covalent contribution of the electrically polarized oxygen ions [18, 19], which seems to be a specific property of delafossite structure as compared with many other oxides. All the above estimations may be useful in explaining the possible reasons for the different character of magnetic ordering in the two delafossite-like CuFeO$_2$ and AgFeO$_2$ ferrites.

To visualize the effect of the uniaxial anisotropy, which results in the distortion of the circular cycloid, on $H_{\text{hf}}$, the dependences $H_{\text{hf}}(\omega) \propto \sin[(\pm 4 K(m)/\lambda)\omega], \omega$ and $H_{\text{hf}}(\omega) \propto -\cos[(\pm 4 K(m)/\lambda)\omega], \omega$ in terms of the Jacobi elliptic functions for the easy-axis anisotropy ($D > 0$) are shown together with $\sin(q\omega)$ in figure 13. It is clearly observed that, in spite of the very small value of the single-ion anisotropy, the both projections $H_{\text{hf}}^{(1)}$ and $H_{\text{hf}}^{(0)}$ are significantly deviated from harmonic behavior. Another manifestation of anisotropy is the dependence of the $\Delta H(\omega)$ angles between neighboring iron spins along the cycloid propagation (see figure 11(a)). Without easy-axis anisotropy ($D = 0$), the $\Delta \theta$ angle defining the relative orientation of spins for the given wave vector is constant, $\Delta \theta = qa$. However, for the case of easy-axis anisotropy, the cycloid with $\theta_0$ no longer describes
the minimal energy of spin arrangement, due to the admixture of higher-order harmonics. The anisotropy tends to align the spins along the easy axis (OZ), thereby distorting the originally perfect cycloid into one with modulated rotation angles \( \Delta \theta(x) = \Delta \theta_0 + \xi(x) \) (where \( \xi(x) \) depends on the value of \( \frac{D}{\langle J \rangle} \)). In figure 13, the non-uniform population density of spin angles \( \rho(\theta) \propto 4K(m)/\lambda(1 - m\cos^2 \theta)^{1/2} \) peaks at 90° and 270° because the iron spins prefer to align along ±OZ directions.

The approximated saturation value of the hyperfine field, \( H_{hf}(T=0) \approx 484 \) kOe, is anomalously low for high-spin ferric ions in octahedral oxygen coordination, for which \( H_{hf}(0) \) is usually approximately 540–568 kOe (figure 14), corrected for covalence effects [61]. This ~10% spin reduction cannot be explained only by covalency effects and may be partially attributed to zero-point spin reduction, which has been predicted to be large in low-dimensional antiferromagnets [62]. However, our estimations of the zero-point spin fluctuations (not shown) point to a very small contribution to the reduction of the \( H_{hf}(0) \) value for AgFeO₂.

To discuss other possible reasons for the observed reduction of the \( H_{hf}(0) \) value, we took into account the fact that the \( H_{hf} \) hyperfine field is the vector sum of several contributions [61, 63]:

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**Figure 11.** (a) Directions of the principal EFG axes for the iron sites (the angle \( \vartheta \) gives the orientation of the hyperfine field \( H_{hf} \) in the (cb) plane, varying continuously between 0 and \( 2\pi \); the symbol \( H_{t} \) denotes hyperfine field component at \( ^{57}\text{Fe} \) along the c-axis, while \( H_{\perp} \) stands for the iron hyperfine field component along the b-axis) (b) (left site) Polar diagram demonstrating evolution of the spin structure from harmonic distribution (no uniaxial anisotropy, i.e. \( D \approx 0 \)) to squared modulation (very hard uniaxial anisotropy) and (right site) corresponding modulation of the projection \( H_{hf}^{\perp}(\vartheta) \) on the c axis along the q direction. (c) Polar diagrams corresponding to the isotropic, \( H_{t} = H_{\parallel} \) (circular polarization) and anisotropic \( H_{t} \neq H_{\perp} \) (elliptical polarization) hyperfine magnetic fields.
The anharmonicity parameter $m$ (see equation (8)), $H_0$ and $H_1$ contributions and the isotropic part $H_a (\equiv 1/3 H_0 + 2/3 H_1)$ of the hyperfine magnetic field at $^{57}$Fe nuclei extracted from least-squares fits of the Mössbauer spectra.

![Figure 12](image)

**Figure 12.** Temperature dependence of the anharmonicity parameter $m$ (see equation (8)), $H_0$ and $H_1$ contributions and the isotropic part $H_a \equiv (1/3 H_0 + 2/3 H_1) \approx 9.1 \text{kOe}$ of the hyperfine magnetic field on $^{57}$Fe nuclei from six equivalent $^{57}$Fe nuclei extracted from least-squares fits of the Mössbauer spectra.

The existence of the angular dependence of the $H_{\text{STHF}}$ field has been shown experimentally in several studies of rare earth (R) orthoferrites $\text{RFEO}_3$ [63, 64]. In these perovskite-like compounds, there is no direct overlap of iron orbitals, so one can neglect the direct $\text{Fe}–\text{Fe}$ hyperfine field. Thus, the calculations of Moskvin et al. [65] for the $\text{RFEO}_3$ ferrites have shown that $H_a \approx 9.1 \text{kOe}$ and $H_{\text{STHF}} \approx 8.95 \text{kOe}$, which is in accordance with the work [63]. Using the average value of $h_{\text{STHF}} = 8.95 \text{kOe}$, we evaluated $(H_{\text{F}} + H_{\text{conv}} + H_{\text{STHF}}) = 564 - 6 \times h_{\text{STHF}} = 494 \text{kOe}$. This value, corresponding to the hyperfine field at $^{57}$Fe sites in the ‘free’ ($\text{FeO}_6$) octahedra, is used as a reference value (figure 14) in our subsequent calculations.

In the delafossite-like structure of the $\text{CuFeO}_2$ ferrite, each iron cation is surrounded by six nearest Fe$^{3+}$ neighbors lying in the hexagonal $(h_0,h_0)$ plane (figure 1). Below $T_{N2}$, $\text{CuFeO}_2$...
demonstrates a collinear four-sublattice magnetic structure with two of the six nearest Fe$^{3+}$ cations have the same spin direction as central iron cation [40]. The remaining four Fe$^{3+}$ neighbors have the opposite spin direction (the middle part of figure 14). As a result, in the immediate surrounding of the central iron cation, there are two pairs of mutually compensated Fe$^{3+}$ spins that give a resultant zeroth contribution to the experimental value of the hyperfine field $H_{hf} \approx 515$ kOe. In this case, the difference $\Delta H_{hf} \equiv H_{hf} - (H_F + H_{cov}) = 515 - 494) = 21$ kOe corresponds to the positive partial contribution of two Fe$^{3+}$ neighbors (figure 14). Taking into account the fact that the spin angle for the Fe-O-Fe bonds is approximately 90°, we can neglect the transferred contributions $h_{\text{dip}}$ (according to [65], the tiny positive field, $H_{s}$, can be compensated by the strong negative contribution of potential $s-d$ exchange at $\theta \approx 90°$). Therefore, the experimental difference $\Delta H_{hf}$ is equal to the direct contributions of the two nearest iron neighbors as follows: $h_{\text{dip}} = \Delta H_{hf} + \Delta H(0) \approx 24$ kOe, and $h_{\text{dir}} \approx 12$ kOe.

AgFeO$_2$ exhibits noncollinear magnetic order (see lower part of figure 14), in which among six nearest iron neighbors of the central iron cation, there are two pairs with compensated spins, giving a total contribution of zero to the $H_{hf}$ field. As a result, the $H_{hf}$ value for the AgFeO$_2$ ferrite can be presented as $H_{hf} \approx (H_F + H_{cov}) - 2h_{\text{dip}} \cos \xi$, where the angular part $\cos \xi$ is a measure of deviation from the collinear structure, $\xi = 2\theta q$ (figure 14). Taking into account that for the AgFeO$_2$ magnetic structure below $T_{N2}$ the incommensurate propagation wave vector $q = 0.2026$, we obtain $\xi \approx 74.25°$. Substituting $(H_F + H_{cov}) = 494$ kOe, $h_{\text{dir}} = 12$ kOe, and $\cos \xi = 0.271$, we obtain $H_{hf} = 488$ kOe, which is in very good agreement with our experiment $H_{hf}(T \rightarrow 0) \approx 484$ kOe (slight difference of these values may be associated with zero-point spin reducton $\Delta H(0)$). This result suggests that the observed difference between the $H_{hf}$ values for AgFeO$_2$, CuFeO$_2$, and RF$_2$O$_3$ ferrites is mainly related to their local magnetic structure, whereas the magnetic dimensionality plays a minor role.

3.3.5. Origin of anisotropic hyperfine magnetic fields in AgFeO$_2$. According to our calculations, $V_{zz} > 0$, that is the maximum value of quadrupole shift $e_{Q}(\hat{d})$ is attained at $\hat{d} = 0°$ (figure 3). Taking into account the positive value of the correlation coefficient $\partial e_{Q}(\hat{d})/\partial H_{hf} \approx +1.6 \times 10^{-4}$ mm/s/kOe [33, 34], one may conclude that maximum hyperfine field $H_{hf}$ is attained for the spins of Fe$^{3+}$ ions that are directed along the $V_{zz}(H_0)$ axis, i.e. $H_0 > H_1$, similar to the elliptical polarization (figure 11(c)). Note that a similar characteristic of hyperfine field anisotropy ($H_{hf} > H_1$) is observed in NMR spectra for BiFeO$_3$ ferrite having a similar noncollinear magnetic structure of the cycloid type [35, 36]. The analysis of the spectra below $T_{N2}$ [33, 34] shows the strong anisotropy of hyperfine field $H_{hf} = 499(1)$ kOe and $H_1 = 476(1)$ kOe (at 4.7 K), in addition, the difference $\Delta H_{hf} = (H_{hf} - H_1)$ increases with the temperature (see figure 12).

Assuming that a hyperfine coupling tensor, $\tilde{A}$, specifying the coupling between the nuclear spin and the electronic spin ($S_{fe}$), is diagonal with respect to the principal axes of the EFG tensor with axial symmetry, the hyperfine field $H_{hf}$ can be written as follows [59, 66],

$$H_{hf} = \tilde{A} \cdot S_{fe} = iA_{xx}S_x + jA_{yy}S_y + kA_{zz}S_z$$

$$= A_i (iS_i + jS_j) + A_qS_q,$$  \tag{20}

where $S_{x, y, z}$ are projections of the Fe spin moment on the principal axes of the EFG tensor; $A_{xx} = A_{yy} \equiv A_1$ and $A_{zz} \equiv A_3$ are the values of the components of the hyperfine coupling tensor $\tilde{A}$ corresponding to the orientation parallel and perpendicular to the principal axis $O$, of the EFG tensor. The expression (20) clearly suggests that the observed anisotropy of the hyperfine field can be analyzed in terms of anisotropy of the hyperfine coupling tensor $\tilde{A}$ and anisotropy of iron magnetic moment. In this formalism it is assumed $A_1 = S_{fe} \sin \theta \cos \varphi$, $A_3 = S_{fe} \cos \theta$ and $A_2 = S_{fe} \sin \theta$, where $\theta$ and $\varphi$ are the polar and azimuthal angles of the iron magnetic moments except in the case of alignment along the $c_0$ axis, or in the $(ab)$ plane. In other cases, the angle $\vartheta$ which the $H_{hf}$ field makes with the principal $O$ axis (see figure 3) can be written as tan$\vartheta = (A_1/A_3)\tan \theta$, and the magnitude of the hyperfine field will be given by $H_{hf} = S_{fe}(\overline{A}_1 \cos^2 \theta + \overline{A}_3 \sin^2 \theta)^{1/2}$. However, taking into account that $H_{hf}(H_F \approx 1$, in first order, only the component $\tilde{A} \cdot S_{Fe}$ parallel to the spin direction will affect the magnitude of the $H_{hf}$ field, we can rewrite the expression for $H_{hf}(lls_{Fe}) = A_1S_{fe}\cos^2 \theta + A_3S_{fe}\sin^2 \theta$, that is similar to the expression for the hyperfine field anisotropy $H_{hf}(\vartheta)$ [33–37, 58].

Both principal $A_1$ and $A_3$ components include isotropic ($\overline{A}_1^{iso} = A_1^{iso}$) term, related to the Fermi contact hyperfine field due to the polarization of the inner ns electrons by exchange interaction with the unpaired spins of the d electrons, and anisotropic ($\overline{A}_1^{anis} = A_1^{anis}$) terms. Usually the anisotropy of the hyperfine tensor $\tilde{A}$ for the Fe$^{3+}$ ions having a spherically symmetric $d^6$ configuration is related to a distant dipole contribution $A_0^{dip} = \mu FeD_{ih}$ where $D_{ih}(i = z, x)$ are the principal components of the lattice sums and $\mu Fe$ are the projections of the magnetic moment of iron onto corresponding principal axes of the EFG tensor. Using the structural data for AgFeO$_2$ [13, 37] we arrive at $D_{iz} = -0.223 \AA^3$ and $D_{ix} = 0.112 \AA^3$ that corresponds to maximal value of $H_{min} = 5$ kOe that appears to be distinctly smaller than the experimental values ~30 kOe. Therefore, the observed anisotropy of hyperfine coupling in AgFeO$_2$ ferrite cannot be explained using only the dipole contribution $H_{dip}$.

The local anisotropic $\tilde{A}^{anis}$ coupling tensor is usually expressed as a superposition of spin and orbital terms:

$$\tilde{A}^{anis} = \tilde{A}^{spin} + \tilde{A}^{orb},$$  \tag{21}

where for one $d$-electron

$$A_0^{spin} = \frac{2\mu_B^2\mu_e}{21} \left( \frac{1}{r^3} \right) \langle 3l_i j_i - l_i^2 \delta_{ij} \rangle,$$  \tag{22a}
\begin{equation}
A_{ij}^{\text{orb}} = 2\mu_B \left( \frac{1}{r^3} \right) (\hat{g}_i - g_\| \epsilon_{ij}),
\end{equation}

where \( \langle 1/r^3 \rangle \) is the average value of \( r_\| \) for the 3d orbitals, \( g_\| \approx 2 \) is the spin-\( g \)-factor, \( \mu_B \) the Bohr magneton, \( \hat{g}_i \) the \( \hat{g} \)-tensor. The first term is produced by the dipolar interaction of the \( d \)-electron spins with the nucleus, and does not vanish only when the \( d \) orbitals are such that the spin density is aspherical. This term is related to the electronic part of the EFG, \( V_{\text{el}} \), which arises from an aspherical charge density, and usually represented as \( \bar{\Delta}^{\text{spin}} \approx \gamma_{i\beta} \bar{V}_{i\beta} \) \( (V_{ijkl})_d \) \cite{67}. For isolated high spin \( \text{Fe}^{3+} \) ions having spherical 3d electron distribution or for ideal \( \text{FeO}_6 \) octahedra with orbital singlet ground 3d-state \( ^6\text{A}_{1g} \) the \( \bar{\Delta}^{\text{spin}} \) term turns into zero. However, specific feature of the high spin 3d\( ^6 \) configuration for \( \text{Fe}^{3+} \) ions is that these have the only \( ^6\text{A}_{1g} \) term with maximal spin \( S_{\text{Fe}} \) contribution into effective magnetic moment. The orbital term \( \bar{\Delta}^{\text{orb}} \) is worth noting a close relation of the \( \bar{\Delta}^{\text{spin}} \) with the same as \( \text{AgFeO}_2 \) delafossite-like structure, has revealed an almost isotropic \( g \)-factor \( (g_\| \approx 2) \) at low temperatures, that seems to rule out the presence of significant orbital contribution to the \( A^{\text{anis}} \) coupling constant, though the non-zero value of single-ion anisotropy

\begin{equation}
D \approx -0.02-0.03 \text{ meV} \end{equation}

implies small non-zero anisotropy \( g_\| - g_\perp \approx 0.001 \) and \( H^{\text{orb}} \approx 2 \text{ kOe} \). Thus, the main contribution to the anisotropy of the hyperfine coupling tensor should be related with a local intra-cluster \( \text{FeO}_6 \) spin-dipole term whose magnitude first depends on the cation-anion covalence effects. Similarly to single-ion anisotropy for weakly distorted \( \text{FeO}_6 \) octahedra with nonpolarized ligand one may introduce a simple linear parameterization for the \( \bar{\Delta}^{\text{spin}} \) tensor in the principal axes system \((Ox,y,z\|C4)\) as follows:

\begin{equation}
A_{ij}^{\text{spin}} = a r_{ij} e_{ij},
\end{equation}

where \( e_{ij} \) are the components of the octahedron deformation tensor (see Introduction). For \( \text{FeO}_6 \) octahedra with equal cation-ligand separation as in \( \text{AgFeO}_2 \) and \( \text{CuFeO}_2 \) one may use another parameterization approach, based on the so-called superposition model, as follows:

\begin{equation}
A_{ij}^{\text{spin}} = \frac{1}{2} \sum_{n=1}^{6} 3x_{nn} x_{nn} - \delta_{ij},
\end{equation}

where \( x_{nn}, x_{nn} \) are the Cartesian coordinates of the cation—ninth ligand bond. For trigonally distorted octahedron in the coordinate system with \( O \| \text{C}_3 \) we arrive at a simple relation:

\begin{equation}
A_{zz}^{\text{spin}} = 3a(3\cos^2 \theta_h - 1),
\end{equation}

where \( \theta_h \) is the polar angle of the cation-ligand bond. It is worth noting that the contribution turns into zero for the critical angle \( \theta_h = \theta_{\text{crit}} = \cos^{-1}(1/\sqrt{3}) \approx 55^\circ \). The above parameterization does not work for \( \text{FeO}_6 \) octahedra with polarized ligands characterized by nonzero electric dipole moment due to a shift of the valent electron shell, or a local \( s-p \) hybridization. In such a case one may use the superposition model for the dipole-induced EFG \cite{33,34} considering that \( A_{ij}^{\text{spin}} \propto V_{ij}^{\text{dip}} \). Assuming that all the six ligand dipoles in the trigonally distorted \( \text{FeO}_6 \) octahedra are oriented parallel \( O \| \text{C}_3 \) with an ‘antiferromagnetic’ ordering of the three ‘upper’ and three ‘bottom’ dipoles, respectively, we arrive at a rather simple relation

\begin{equation}
A_{zz}^{\text{spin}} = b \sum_{n=1}^{6} (3\cos \theta_h + 5\cos 3\theta_h) d_{nn}(n),
\end{equation}

where \( d_{nn}(n) = \pm 1 \) for positive and negative orientation of the dipole, respectively. To demonstrate the workability of this simple two-parameter model we will assume its applicability both to \( \text{AgFeO}_2 \) and \( \text{BiFeO}_3 \) considering the geometrical factor to be the only cause for different anisotropy of the local fields: \( H_{\text{anis}} = H_{\|} - H_{\perp} = 30 \text{ kOe} \) \( (\text{AgFeO}_2) \), \( 5 \text{ kOe} \) \( (\text{BiFeO}_3) \). We find our simple model points to a leading contribution of the dipole-induced term. Furthermore, it does uncover the origin of a strong difference in \( \Delta H_{\text{anis}} \) for \( \text{AgFeO}_2 \) and \( \text{BiFeO}_3 \). In the delafossite \( \theta_h > \theta_{\text{crit}} \) and the both terms work with the same sign, while in \( \text{BiFeO}_3 \) \( \theta_h < \theta_{\text{crit}} \) and we arrive at a partial compensation of the two contributions. For further investigation both of the origin and magnitude of the anisotropic magnetic interactions in 3R-\( \text{AgFeO}_2 \) the
measurements that can directly probe the electronic states of Fe$^{3+}$ and O$^{2-}$ ions, such as x-ray-absorption and x-ray photoemission spectroscopy, optical spectroscopy, and $^{17}$O NMR study are required.

4. Conclusions

In summary, we have carried out detailed $^{57}$Fe Mössbauer measurements on polycrystalline samples of 3R-AgFeO$_2$ that allowed us to elucidate different unconventional features of the electronic and magnetic structure, as well as spin and hyperfine interactions in this delafossite as compared with its analogue CuFeO$_2$.

The ferrite exhibits very strong magnetic frustration ($\Theta_{CW}/T_N$), which can be related to the strengthening of the AFM contribution in the nearest-neighbor Fe–Fe exchange interactions ($J^{11}$) in the basal plane. The asymptotic value, $\beta' \approx 0.34$, for the critical exponent obtained from Mössbauer measurements indicates that 3R-AgFeO$_2$ shows quasi-3D critical behavior. Mössbauer measurements just above the $T_{N1}$ temperature $T_{N1} < T < T \approx 19 K$ show unresolved magnetic hyperfine structure, indicating the occurrence of short-range magnetic correlations; small clusters of iron spins are created, for which the magnetization relaxes slowly, as in superparamagnetic correlations. The $^{57}$Fe Mössbauer spectra can be described in terms of SDW but with the inclusion of many high-order harmonics, indicating that the real magnetic structure of the ferrite in this intermediate temperature range appears to be more complicated than the previously supposed purely sinusoidally modulated SDW.

The line broadenings and spectral asymmetry at $T < T_{N2}$ arise from the spatial modulation of the electric hyperfine interactions and the intrinsic anisotropy of the magnetic hyperfine field at the $^{57}$Fe$^{3+}$ sites along the cycloid propagation vector. The model fitting shows a high degree of the anharmonicity in the cycloid ($m \approx 0.78$), which is related to rather large magneto-crystalline single-ion anisotropy. Comparison of the theoretical estimations within conventional models that imply nonpolarized oxygen ions and different experimental data points to a markedly large and sensitive covalent contribution of the electrically polarized oxygen ions which seems to be a specific property of delafossite structure as compared with many other oxides. We argue that such oxygen dipoles calculated self-consistently provide a large and decisive contribution to the EFG tensor for Fe nuclei while conventional monopole (or point charge) and electronic contributions partially compensate each other.

The hyperfine field, $H_{hf}$, reveals a puzzlingly large anisotropy with $H_{hf} = (H_{||} - H_{\perp}) \approx 30$ kOe that cannot be related to only the dipole contribution from the magnetic neighbors or conventional orbital contribution $\propto g_L - g_\perp$. This anisotropy is shown to be related with a local intra-cluster FeO$_6$ spin-dipole term that implies a conventional contribution of the cation-anion covalence effects induced by nonpolarized oxygen ions and even larger contribution of the polarized oxygen. We propose a simple two-parametric formula to describe the dependence of $H_{hf}$ on the distortions of the FeO$_6$ octahedra. A variety of different results evidencing a specific role of the oxygen polarization in ferro-delafossites seems to be one of the main outcomes of the paper. The very large difference between the $H_{hf}$ values observed for AgFeO$_2$ and CuFeO$_2$ ferrites is mainly related to their local magnetic structure, whereas the magnetic dimensionality plays a minor role.

Our study shows once more that Mössbauer spectroscopy is not only an useful tool to probe the local crystal structure and magnetic interactions of the iron cations in delafossites but a technique that is capable to uncover novel unexpected effects.

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