1. Introduction

Magneto-electric (ME) multiferroic materials, in which both magnetic and ferroelectric ordering coexist, have attracted much attention due to the tunable magnetic properties via electric field or vice versa. Such materials also present the possibility of various applications in recording device technology or spintronics [1–3]. While searching for appropriate candidates is far from trivial, one may consider compounds with weak ferromagnetism (wFM) where the reversal of wFM by 180° using electric field has been predicted theoretically [4]. In many cases, the microscopic mechanism of wFM is either Dzyaloshinskii–Moriya (DM) interaction or single-ion anisotropy (SIA) [5–7]. In this regard, accurately measuring the...
values of such quantities in real materials is of considerable importance for future applications.

The rare-earth orthoferrites $\text{RFeO}_3$ are one of most promising model systems in this regard. The $\text{Fe}^{3+}$ ions in all of the $\text{RFeO}_3$ family undergo an antiferromagnetic transition with $T_N$ ranging from 623 K in $\text{R} = \text{Lu}$ to 738 K in $\text{R} = \text{La}$. These high transition temperatures are due to a strong nearest-neighbor exchange interaction ($J > 4$ meV) along the Fe–O–Fe bond and the large magnetic moment of $\text{Fe}^{3+}$ ($S = 5/2$). Most perovskites of ABO$_3$-type exhibit a cubic $\text{Pbnm}$ symmetry at high temperature, and a structural transition occurs upon cooling which lowers the symmetry via tilting of edge-shared BO$_6$ octahedra. $\text{RFeO}_3$ adopts the $\text{Pbnm}$ space group at this structural transition, the most frequent structure among the perovskites. Such octahedra tilting to $\text{Pbnm}$ symmetry can be described by Glazer notation: $a^- a^- c^+$ [8]. Since this structure does not break space inversion symmetry (i.e. $\text{Pbnm}$ is centrosymmetric), no net polarization in $\text{RFeO}_3$ is expected.

In the case of $\text{RFeO}_3$, the tilting of FeO$_6$ octahedra is the origin of local DM interaction in this compound (see figure 1). Competition between DM and exchange interactions results in canting magnetic moments [9]. Below $T_N$, all $\text{RFeO}_3$ adopt a canted antiferromagnetic ground state $\Gamma_4(G_a, A_b, F_z)$ with basic $G$-type antiferromagnetism along the $a$-axis, weak antiferromagnetism along the $b$-axis, and wFM along the $c$-axis as shown in figure 1(a). Such weak canted magnetic moments were extensively studied both theoretically and experimentally [10, 11]. Moskvin and Sinitsyn derived a simple formula connecting the canting of magnetic moment and the crystal properties (unit cell parameter, position of oxygen and the bond length), deducing a relation between the $A_y$ and $F_z$ [12]. This theoretical prediction was confirmed for several orthoferrites by the polarized neutron diffraction [13–15]. For $\text{YFeO}_3$, calculated value of $A_y/F_z = 1.1$ is consistent with the experimental results within errorbars. It is worth noting that in case of $\text{RFeO}_3$ with magnetic rare-earth ions, there is a magnetic ordering of $R^{3+}$ at low temperature and a spin reorientation transition of $\text{Fe}^{3+}$ at intermediate temperatures due to the interaction between $R^{3+}$ and $\text{Fe}^{3+}$ ions. Such additional interactions between the two magnetic ions sometimes induces multiferroicity below the spin reorientation transition temperature, and often results in the rotation of $\text{Fe}^{3+}$ ions by exchange-striction mechanism [16–18].

$\text{BiFeO}_3$ is the only example that is well-established to exhibit multiferoicity above room temperature. $\text{BiFeO}_3$ shares several characteristics with $\text{RFeO}_3$: it has the similar exchange interaction and the very high antiferromagnetic transition temperature $T_N$ at $\sim 650$ K [19]. However, there are also clear contrasts between these two materials such as the distinct rotation of FeO$_6$ octahedra, much of which is due to the lone pair of Bi breaking the inversion symmetry for $\text{BiFeO}_3$ unlike the other centrosymmetric $\text{RFeO}_3$. $\text{BiFeO}_3$ has the non-centrosymmetric space group $R3c$ coming from the Glazer tilting $a^- a^- a^-$. $\text{BiFeO}_3$ exhibits a large polarization with a ferroelectric transition at $T_c = 1100$ K [20]. Below $T_N$, an incommensurate spin cycloidal magnetic structure develops along the [1 1 0] direction with an extremely long period of 620 Å and is superimposed on the simple $G$-type antiferromagnetism [21]. It was also reported to have a negative magnetostrictive magnetoelastic coupling at $T_N$ [22].

Small angle neutron scattering experiments revealed a spin density wave (SDW) fluctuation, which is perpendicular to the spin cycloid [23]. The local wFM moment made by this fluctuation is cancelled out over the whole cycloid, giving no wFM in bulk $\text{BiFeO}_3$.

The spin-Hamiltonian of $\text{BiFeO}_3$ has been extremely well studied both theoretically and experimentally throughout many studies [24–28]. Recent study on the magnetic excitation spectra over the full Brillouin zone using inelastic neutron scattering (INS) measurements determined the values for the two exchange interactions and the DM interaction [25]. Subsequently, a detailed examination was done on the low-energy region with the observation of the unique island-like feature at 1 meV. Separately, this can also be identified as the peak-and-valley feature in the constant $Q$-cut graph at the magnetic zone center [26, 27]. By employing the full spin Hamiltonian in spin wave calculations, it was further determined that this feature originates from the interplay of the DM interaction and the easy-axis anisotropy [27].
The rare-earth orthoferrites have also been previously characterized in the literature, including studies on the spin waves of $R$FeO$_3$ with INS [29–33] and Raman spectroscopy [34–36]. Much of the focus in the INS studies was concentrated on the high energy transfer region of the excitation spectra to determine the structural and magnetic interaction strengths. For LaFeO$_3$, only powder INS spectra was reported – [34] and reproduced two characteristic features observed in the low-energy magnetic excitation spectra: (1) a finite spin wave gap of $E \sim 1$ meV (YFeO$_3$) and 2 meV (LaFeO$_3$) and (2) two distinct peaks directly above the gap, although the valleys between the two peaks are quite small. The two peaks are, as expected, most distinguishable at $Q = (101)$, signifying that the magnon branches are split at the magnetic Brillouin zone center. Figure 3 denotes the constant-energy transfer graphs of YFeO$_3$ and LaFeO$_3$ for $T = 300$ K. One can see that the magnetic signals at low energy are separated as two peaks as the energy transfer increases, implying the V-shaped dispersion of the magnetic excitation of YFeO$_3$ and LaFeO$_3$.

In order to fully explain the low-energy magnetic excitations, we employ a minimal spin Hamiltonian of $R$FeO$_3$ to model the experimental data:

$$
\mathcal{H} = J_c \sum_{\langle c \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + J_{ab} \sum_{ab \text{ plane}} \mathbf{S}_i \cdot \mathbf{S}_j + J' \sum_{\langle 00 \rangle} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{\langle 0 \rangle} \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j + K_a \sum_i (\mathbf{S}_i^2) + K_c \sum_i (\mathbf{S}_i^2),
$$

(1)
where $J_c$ and $J_{ab}$ represent the nearest-neighbor exchange constants along the $c$-axis and the $ab$ plane, respectively. In the previous INS study on YFeO$_3$ [33], these $J_c$ and $J_{ab}$ were set as same value $J$. However, we note that the difference between $J_c$ and $J_{ab}$ can reach up to 10% due to Bloch’s rule [38], especially in the case of YFeO$_3$. $J'$ denotes the exchange constant along the next-nearest neighbor bonds (see figure 1(a)). The fourth term represents the DM interactions defined on the Fe($i$)–O–Fe($j$) bonds with the antisymmetric relation: 

$\mathbf{D}_{ij} = -\mathbf{D}_{ji}$. Transition ions having a 3d$^5$ configuration such as Fe$^{3+}$ lead to $A_{1g}$ orbital symmetry. Therefore, we may assume that the DM interaction of ferrites can be given by a microscopically derived form ($\mathbf{D}_{ij} \propto \hat{x}_i \times \hat{x}_j$) [39, 40], where $\hat{x}_i$ is the unit vector connecting $i$th Fe atom and oxygen atom between $i$th and $j$th Fe atoms. This means that in the $Pbnm$ structure all DM interactions between two adjacent iron atoms may be characterized by five parameters: $\alpha_{ab}, \beta_{ab}, \gamma_{ab}, \alpha_{c}, \beta_{c}$ [41], as shown in figure 1(b). The density functional theory
(DFT) calculation on LaFeO$_3$ [42] shows good agreement with the DM vectors obtained from our structural analysis, supporting this assumption.

Normalized values of the local DM vectors of YFeO$_3$ and LaFeO$_3$ shown in Table 1. We note that the in-plane DM vectors defined in different basal planes, e.g. $D_{41}$ and $D_{52}$, are different along the $b$-axis. The result of combining all contributions of adjacent ions is that every Fe$^{3+}$ ion feels a different DM interaction, therefore global DM interactions cannot be as expected defined in this space group. This is an assumption contrary to those used in previous studies on YFeO$_3$ [33, 34].

The two last terms of equation (1) denote the easy-axis ($K_B, K_C < 0$) SIA terms to stabilize the G-type antiferromagnetic order along the $a$-axis and the wFM along the $c$-axis, respectively. With respect to the spin wave theory, SIA is the origin of the spin wave gap at the Brillouin zone center. It is worth noting that the most generalized form of the spin Hamiltonian also includes the symmetric anisotropic exchange interaction, i.e. two-ion anisotropy (TIA). Such TIA terms are formulated as the form $\sum y \Omega_y S_y$, where $\Omega_y$ denotes $3 \times 3$ symmetric matrix. This is characterized by eight different parameters related to its $Pbnm$ symmetry. This anisotropy, however, seems to be small with the order of $D'^2/J$ [43], and would add unnecessarily too many parameters to our model Hamiltonian. The TIA mostly affects the spin wave gap at the zone center, like the SIA. In that sense, this TIA can be neglected and therefore will not be discussed further in this study.

After combining all contributions from the oxygen environments, the four-sublattice magnetic ground state $\Gamma_4(G_a, A_b, F_c)$ of the RFeO$_3$ can be stabilized [42]. In spherical coordinates, the four spins can be defined using two spin canting angles $\theta$ and $\phi$, which are related to the weak ferro- and antiferromagnetic moment, respectively.

$$
\begin{align*}
S_1 &= S (-\cos \theta \cos \phi, -\cos \phi \sin \phi, \sin \phi) \\
S_2 &= S (\cos \theta \cos \phi, \cos \phi \sin \phi, \sin \phi) \\
S_3 &= S (-\cos \theta \cos \phi, \cos \phi \sin \phi, \sin \phi) \\
S_4 &= S (\cos \theta \cos \phi, -\cos \phi \sin \phi, \sin \phi). 
\end{align*}
$$

(2)

Since the spin cantings are very small ($\sim 0.5^\circ$) for RFeO$_3$, we can ignore terms higher than second order with respect to the spin–orbit coupling $\lambda_{SO}$ to obtain the relationship between spin canting angles and the spin Hamiltonian parameters from the ground state energy [13]:

$$
\begin{align*}
\theta &= \frac{2\beta_{ab} + \beta_c}{4J_{ab} + 2J_c + K_c - K_a}, \\
\phi &= \frac{2\gamma_{ab}}{4J_{ab} - 8J' - K_a}.
\end{align*}
$$

(3)

Using this Hamiltonian of RFeO$_3$, we tried to find the best fit parameters that reproduce the experimental result well.

First, an initial set of parameters was chosen under several constraining conditions. As the Hamiltonian contains many parameters: $J_z, J_{ab}, J', D_{41}, D_{52}, K_c$ and $K_a$, utilizing all the reasonable initial and constraining conditions is important for determining a reliable set of best fit parameters. Therefore, starting with the previously reported exchange coupling constants $J_1 = 4.77$ and $J_2 = 0.21$ meV derived from high energy INS experiment [33], $J_z, J_{ab}$ and $J'$ were refined. Since only the $J_1$ value of LaFeO$_3$ has been previously reported [32], we made the assumption that the $J_1/J_z$ ratio of LaFeO$_3$ is similar with that of YFeO$_3$. This assumption combined with the ratio of $T_N$ of both compounds, yields $J_z = J_{ab} = 5.47$ and $J' = 0.24$ meV for LaFeO$_3$. We also used in our analysis the canting angle $\theta$ as derived from polarized neutron diffraction results [13] and magnetization measurements along the $c$-axis [44]. To obtain the consistency between the spin canting angles and the spin Hamiltonian parameters, equation (3) was used as one of the constraint conditions.

Secondly, with the chosen initial parameters fitting was performed by a bounded non-linear least squares fit to the experimental data set. Due to the presence of the constraint condition (equation (3)), fmincon programming solver implemented in MATLAB was used. During the non-linear fit, the theoretical magnon dispersion curve and dynamic structure factor $S(Q, \omega)$ have been calculated. We note that the derivation of the analytic form of the dispersion is not easy as the size of Hamiltonian matrix is $8 \times 8$. We used the SpinW software package [45] to diagonalize the spin Hamiltonian in the Holstein–Primakoff approximation.

Since the neutron intensity obtained from the triple axis spectrometer is convoluted with the instrumental 4D resolution ellipsoid in the momentum-energy space, the theoretically derived dynamic structure factor should also be convoluted with the resolution ellipsoid for direct comparison with experimental data. The total INS intensity measured by the triple axis spectrometer is given by [46]:

$$
\begin{align*}
I(Q_0, \omega_0) \approx R_0 \int d^3Q d\omega S(Q, \omega) \\
\times \exp \left[ -\frac{1}{2} \Delta \varphi / M(Q_0, \omega_0) \Delta \varphi' \right].
\end{align*}
$$

(4)

where $Q_0 = k_i - k_f$ represents the momentum transfer to the sample, $\hbar \omega = E_i - E_f$ is the energy transfer, $\Delta \varphi \equiv (Q - Q_0, \hbar(\omega - \omega_0))$, and $M$ is a $4 \times 4$ matrix defining a 4-dimensional resolution ellipsoid. Based on the geometry of the SIKA beamline and information of the sample, $M$ matrices were calculated via a Cooper-Nathans method in the Reslib library [46]. Uniformly sampled $41 \times 41 \times 41$ $q$-points within the ellipsoid were used for a convolution function in the Reslib library. Finally, the convoluted intensity $I(Q, \omega)$ was compared with the experimentally obtained $\text{Im}[\chi(Q, \omega)]$ until we get satisfactory convergence of the parameter.

Throughout the above process, the set of parameters that best explain the data was determined. In figures 3, 4(d) and (e), the overall $V$-shapes of the spin-dispersions are modelled accurately by calculations for both compounds. The splitting of magnon branches at the zone center are not as noticeable in the INS data (figures 4(a) and (b)). But nevertheless it is fully

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**Table 1.** Normalized components of local DM vectors of YFeO$_3$ and LaFeO$_3$.  

|          | $\alpha_{ab}$ | $\beta_{ab}$ | $\gamma_{ab}$ | $\alpha_c$ | $\beta_c$ |
|----------|----------------|--------------|---------------|------------|-----------|
| YFeO$_3$ | 0.517          | 0.488        | 0.703         | 0.346      | 0.938     |
| LaFeO$_3$| 0.554          | 0.553        | 0.623         | 0.191      | 0.982     |
consistent with theoretical dispersion curves. The constant-$Q$ cuts in figures 2(b) and (d) show this consistency more clearly, especially given the tendency for the convoluted $I(Q, \omega)$ to have slightly higher energies due to instrumental resolutions than the calculated energies of the two low-lying magnon branches. For example, the two measured peak positions at $Q = (101)$ for YFeO$_3$ are at $\sim 1.7$ and $2.4$ meV, whereas the theoretically calculated magnon energies are at $\sim 1.2$ and $2.42$ meV. We note that the calculated energies of magnon branches at the magnetic zone center are consistent with Raman data ($\sim 1.4$ and $2.2$ meV) [34].

The best fit parameters are given in table 2 together with the spin canting angles. In our work, the values obtained for the DM interactions for YFeO$_3$ are quite different compared to those of Hahn et al [33]. We point out two possibilities for this discrepancy:

(i) The spin Hamiltonian used in [33] does not include DM interaction along the c-axis. Since the magnitude of $D_{ab}$ and $D_c$ is similar in $R$FeO$_3$, they should be considered together.

(ii) The canting angles $\theta$ and $\phi$ of YFeO$_3$ used in [33] are much less than the known values ($\sim 0.5^\circ$). Underestimation of the DM vectors is therefore inevitable since they are proportional to the canting angles (equation (3)).

The ratio between DM interaction and exchange interaction, $D/J$, is a criterion that indicates the competition between them. A rough estimate for the spin canting angle is given by $\tan^{-1}(D/J)$, and so one can find an approximate value for $D/J$ from equation (3). For LaFeO$_3$ the value we obtain for $D/J$ is $\sim 0.026$, which is larger than the values obtained from DFT calculations ($\sim 0.018$ in [42], 0.021 in [47]). It is also noteworthy that the canting angles of YFeO$_3$ and LaFeO$_3$ are remarkably similar, which is quite unexpected because they have significantly different values for their respective FeO$_6$ octahedra rotation angles. In case of YFeO$_3$, the ratio between canting angles $\theta/\phi \sim 1.137$ is consistent with previous theoretical and experimental results [12–15].

Having said that, the low-energy magnetic excitations of YFeO$_3$ and LaFeO$_3$ have several common features with that of BiFeO$_3$ (see figures 4(c) and (f) and 5) such as the shoulder-like signal seen below the modes dispersing from the zone center. This feature has been shown to be the result of competition between the three different terms in the Hamiltonian: exchange interaction, DM interaction and SIA. Of course, there is room for this feature to manifest itself in several ways depending on the details. In $Pbnm$, centrosymmetry and local DM vector constrain $R$FeO$_3$ to have the commensurate 4-sublattice magnetic structure, resulting in the simple V-shape dispersion curves with two of four magnon branches.

\begin{table}
\centering
\caption{Best fit parameters and spin canting angles used in this work and compared to other work on YFeO$_3$.}\\
\begin{tabular}{lllllllll}
\hline
 & $T_N$ (K) & $J_c$ & $J_{ab}$ & $J'$ & $D_{ab}\parallel$ & $D_{ab}\perp$ & $K_a$ & $K_c$ & $\theta$ (°) & $\phi$ (°) \\
\hline
YFeO$_3$ (our work) & 644 & 5.02 & 4.62 & 0.22 & 0.1206 & 0.1447 & -0.0091 & -0.0025 & 0.51 & 0.58 \\
YFeO$_3$ ([33]) & 644 & 4.77 & 4.77 & 0.21 & 0.079 & - & -0.0055 & -0.00305 & 0.30 & 0.18 \\
LaFeO$_3$ (our work) & 738 & 5.47 & 5.47 & 0.24 & 0.130 & 0.158 & -0.0124 & -0.0037 & 0.52 & 0.46 \\
\hline
\end{tabular}
\end{table}
as shown in figure 3. In contrast, all local DM interactions in R3c can be effectively expressed as a global DM interaction along two directions, [1 1 0] and [0 0 1]. Thus, a spin cycloid structure can be stabilized. Furthermore, SDW fluctuations and anharmonicity add more complexity to the structure, making the magnon branches to become more complex. All of these effects combined lead to the distinct behavior of the susceptibility of BiFeO3, which has indeed been observed [27]. However, both YFeO3 and LaFeO3 do not show any clear temperature dependence in R3c. With the careful quantitative examination of the magnon behavior in these three compounds, we have shown how the relationships between the DM interaction, J, and SIA serves as the underlying mechanism driving the spin dynamics. Our study provides a guide for future work on other perovskite systems, in particular with regard to the delicate balance among DM, J and SIA. The values of the magnon mode splitting in most of the other RFeO3 compounds is currently available in the literature [29, 32–34]. Exploiting the relations between these parameters will play a key role in any future implementation of technological applications which utilize Fe3+-based perovskites.

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