Spin dynamics, critical scattering and magnetoelectric coupling mechanism of Mn$_4$Nb$_2$O$_9$

Guochu Deng$^{1,**}$, Gang Zhao$^2$, Shuang Zhu$^2$, Zhenjie Feng$^2$$^{*}$, Wei Ren$^2$, Shixun Cao$^2$$^{*}$, Andrew Studer$^1$ and Garry J McIntyre$^1$

$^1$ Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation, New Illawarra Road, Lucas Heights NSW 2234, Australia
$^2$ Department of Physics, International Centre of Quantum and Molecular Structures and Materials Genome Institute, Shanghai University, Shangda Road 99, Shanghai 200444, People’s Republic of China

$^{*}$ Authors to whom any correspondence should be addressed.

E-mail: guochu.deng@ansto.gov.au and sxcao@shu.edu.cn

Keywords: magnetoelectric, spin wave, spin dynamics, inelastic neutron scattering

Abstract

The spin dynamics of Mn$_4$Nb$_2$O$_9$ were studied using inelastic neutron scattering. A dynamic model is proposed to explain the observed spin-wave excitation spectrum from Mn$_4$Nb$_2$O$_9$. The model indicates that the exchange interactions along the chain direction are weakly ferromagnetic while the exchange interactions between the neighbour chains are strongly antiferromagnetic. The antiferromagnetic interactions on the two MnO$_6$ octahedron networks are dominant in the spin dynamics of this compound. A spin gap of about 1.4 meV was observed at the zone centre, which is attributed to the weak easy-axis magnetic anisotropy of Mn$^{2+}$ ions. Magnetic critical scattering from Mn$_4$Nb$_2$O$_9$ was studied in the vicinity of its Néel temperature $T_N$ as well, indicating homogeneous development of magnetic correlations. According to the symmetry analysis and its magnetic structure, the weak magnetoelectric coupling effect in Mn$_4$Nb$_2$O$_9$ is ascribed to the uncancelled exchange striction on the two non-equivalent Mn$^{2+}$ sites.

1. Introduction

Multiferroic (MF) and magnetoelectric (ME) materials are quite unique because not only their electric polarizations response to external magnetic fields, but also their magnetizations can be controlled by applying external electric fields [1–4]. They could be potentially utilized in various devices including information-storage memories [3], multi-signal sensors, multi-field drivable actuators, and transducers for different energy conversions. The microscopic mechanism of the ME coupling effect in MF and ME materials is extremely important for understanding and improving their ME properties for applications. In the initial stage when studying MF materials started to boom, the fundamental ME coupling mechanisms in many newly-discovered MFs were not fully understood. Some explanations need to be improved. After many years, our understanding of the microscopic ME coupling mechanism has been substantially improved. The microscopic mechanisms of ME coupling can be mainly classified into three different types: (1) the magnetostriction model [4, 5], (2) the spin-current model, namely, the inverse-Dzyaloshinskii–Moriya (DM) interaction [6, 7], and (3) the spin-dependent hybridization effect [4, 8]. Different mechanisms originate from special crystal and magnetic structures of MF systems. As for the first type, for example, a collinear up–up–down–down (↑↑↓↓) magnetic structure as demonstrated in Ca$_3$(Co, Mn)O$_6$ can cause the exchange striction effect because such a magnetic structure breaks the symmetry between the Co(↑)–Mn(↑) and Co(↑)–Mn(↓) pairs, causing the bond of Co(↑)–Mn(↑) shortening and the bond of Co(↑)–Mn(↓) elongating [9]. For the second type, a non-collinear magnetic structure is requisite for the spin-current mechanism. This model has successfully explained the strong ME coupling effect in TbMnO$_3$ [10, 11]. For the last case, the hybridization between the 3$d$ orbital of the...
magnetic ion and the p orbital of oxygen is essential. In Ba₃Co₂Ge₂O₇ [12], for example, the orientations of the magnetic moments are highly dependent on the hybridized p-orbital, causing the ME effect. Even though most ME effects are caused by one or more of the three mechanisms above, it can still be difficult to discern the microscopic mechanism of the ME coupling effect for a specific MF or ME material. Careful characterization of the crystal structure, magnetic structure, and spin dynamics of a MF or ME system is necessary for a correct understanding and explanation of its ME origin.

Mn₄Nb₂O₉ (M = Fe, Co, Mn, Ni) is a family of compounds of space group P̅2₃c, with a long-range magnetic ordering at low temperature [13]. The crystal structure and the collinear magnetic structure with magnetic moments along the c axis were reported by Bertaut and his colleagues [13]. In recent years, Co₄Nb₂O₉ was discovered to demonstrate a high ME coefficient [14–16]. The origin of the ME effect in Co₄Nb₂O₉ was not clear when the property was reported. Later on, it was found that the magnetic structure of this compound is not as described in the early research work [17], and a completely new magnetic structure model was proposed by Deng et al [18]. It was reported that this magnet has a non-collinear in-plane magnetic structure with the magnetic moments lying in the ab plane [18]. This model not only resolves the inconsistency between the magnetization measurement [16] and the old magnetic structure [17], but also provides a clear understanding of the microscopic mechanism of the ME coupling effect in Co₄Nb₂O₉ [18]. It is actually caused by the inverse DM interaction, namely, the spin-current mechanism. Subsequently, there have been quite a few research works on this series of materials, e.g., Fe₄Nb₂O₉ [19], and Co₃Ta₂O₉ [20]. These compounds show many interesting phase transitions and ME properties, too.

A recent work studied the Mn doping effect in the series of (Co, Mn)₄Nb₂O₉ [21], where it was discovered that highly-Mn doped (Co, Mn)₄Nb₂O₉ has a spin-reorientation transition upon increasing the content of Mn. The Mn parent compound, Mn₄Nb₂O₉, exhibits a collinear antiferromagnetic structure with the magnetic moments aligning along the c axis below the Néel temperature Tₙ ≈ 108 K [16]. It was reported that Mn₄Nb₂O₉ also demonstrates certain ME properties. According to Fang et al [15, 22], the polycrystalline sample of Mn₄Nb₂O₉ shows a ME coefficient about 1.5 ps m⁻¹, which is less than 10% of the ME coefficient (18.4 ps m⁻¹) observed in the polycrystalline sample of Co₄Nb₂O₉. Since Mn₄Nb₂O₉ and Co₄Nb₂O₉ have the same crystal structure, the significant difference between their ME coefficients must relate to some fundamental changes in their ME coupling mechanisms. However, what causes such an enormous change is still an open question so far. According to the neutron powder diffraction results from the series of (Co, Mn)₄Nb₂O₉, the magnetic structures of the two parent compounds are completely different. This may be the key for us to reveal the secret behind the interesting ME properties of these two compounds.

In this work, we study the spin dynamics and the critical scattering of the ME material Mn₄Nb₂O₉ by using inelastic neutron scattering. A spin-dynamic model has been built and used to explain the observed spin-wave dispersions. This dynamic model indicates that the antiferromagnetic interactions in the planar and buckled MnO₆ octahedron networks (see figure 1) play dominant roles, and the interactions along the c axis are ferromagnetic, but much weaker comparing to the antiferromagnetic interactions. The magnetic anisotropy of Mn in this compound demonstrates an easy-axis type, which causes a small spin gap at the antiferromagnetic zone centre. The critical scattering was measured at temperatures around the Néel temperature Tₙ and showed a significant temperature dependency in its intensity. The ME coupling mechanism in Mn₄Nb₂O₉ is discussed in detail in analogue to the case of Cr₃O₅.

2. Experiments

The Mn₄Nb₂O₉ polycrystalline sample was synthesized using a traditional solid-state reaction procedure. The powder was pressed by using a hydrostatic press into a roughly 8 mm-diameter rod about 15 cm in length for the single-crystal growth. A large Mn₄Nb₂O₉ single-crystal sample was successfully grown by using the travelling-solvent floating-zone technique in an imaging furnace (FZ-T-10000-H-VI-P-SH, Crystal Systems Corp.) in the Department of Physics at Shanghai University [23]. A high-quality part of the Mn₄Nb₂O₉ single-crystal (about 12 mm in length) was cut out for the inelastic neutron scattering experiment in this study. We performed the inelastic experiment on the cold-neutron triple-axis spectrometer Sika [24] at the Australian Centre for Neutron Scattering, Australian Nuclear Science and Technology Organisation. For this experiment, the instrument was configured in the constant-Ef mode (Ef = 5 meV) with a 60°–60°–60°–60° collimation configuration. A Be filter cooled down to 15 K was placed in front of the pre-analyser collimator to suppress the higher-order wavelength contamination. The sample was cooled down to the desired temperature using a Janis cryocooler, which was controlled by a Lakeshore 340 temperature controller. The data from Sika were analysed by the convolution fitting method involving the instrument resolution of the configuration mentioned above. The software Octave [25] and the software
Figure 1. (a) A schematic of the collinear antiferromagnetic structure of Mn₄Nb₂O₉, showing the antiferromagnetic interactions ($J_a$, $J_b$, and $J_c$) between neighbouring MnI–MnII chains and the ferromagnetic intrachain interactions ($J_d$ and $J_e$) along the c axis. The exchange interactions between different magnetic ions are marked as the dashed lines in different colours. The blue and pink spheres indicate the Mn²⁺ ions on the MnI and MnII sites, respectively. The Nb and O atoms are not shown here. (b) The planar network views of MnO₆ along the $c^*$ (top) and $b^*$ (bottom) directions. (b) The buckled network views of MnII O₆ along the $c^*$ (top) and $b^*$ (bottom) directions.

package Reslib3.4 [26] were used for the data fitting. The spin-wave excitation spectrum was simulated and fitted by using the linear spin-wave calculation package SpinW [27].

3. Results and discussions

3.1. Spin-wave excitation

The spin-wave dispersions along the $Q_H$ and $Q_L$ directions were measured in Mn₄Nb₂O₉ on Sika at the base temperature ∼1.5 K. Constant-energy scans along the $Q_H$ direction were conducted from 2 meV to 8 meV near the zone centre while constant-$Q_H$ scans were done to collect the data at higher energy near the zone boundary. The collected constant-energy and constant-$Q$ scans are plotted in figures 2(a) and (b), respectively. As shown in figure 2(a), the spin-wave excitation presents nearly a linear relationship with $Q$ in the vicinity of the zone centre. In the $Q_H$ range close to the zone boundary, the dispersion slope decreases, and the intensity drops significantly. The band-top energy is around 10.3 meV.

The dispersion along the $Q_L$ direction was measured by using energy scans, which are plotted in figure 3. As can be seen, the scan at the zone centre shows a spin gap of about 1.4 meV and an asymmetric feature. Similar asymmetric features were observed in the energy scans at the $Q_L$ positions close to the zone centre while those scans at higher $Q_L$ near the zone boundary look symmetric. The asymmetric scans are fitted by using a special asymmetric double Lorentzian convoluted with the instrument resolution [28]. The symmetric scans are fitted by using the traditional simple Lorentzian convoluted with the instrument resolution. As shown in figure 3, all the fitted results match the experimental data very well. From these data, we can see that the band top of the excitation along the $Q_L$ direction is about 5.7 meV, which is much lower than the value in the $Q_H$ direction. We could attribute this difference to the smaller exchange interaction along the c axis than in the networks roughly lying in the ab plane.

For easier visualization of the spin-wave dispersion observed in Mn₄Nb₂O₉, the constant-energy scans along the $Q_H$ direction and constant-$Q$ scans along the $Q_L$ direction are plotted as the false-colour contour maps in figures 4(a) and (b), respectively. The fitted peak positions are plotted over the contour map as the red-dot curves. From these figures, we can see that the spin-wave dispersion shows a linear relationship between energy transfer and $Q_H$ close to the zone centre. However, the spin-wave branch along the $Q_L$ direction shows an S shape. In both figures, the spin gaps are clearly visible.

A spin-dynamic model is indispensable to understand the observed spin-wave dispersions. The model can be constructed by considering the possible exchange interactions on the magnetic sublattice in Mn₄Nb₂O₉. As shown in figure 1, there are two sites (MnI and MnII) for Mn²⁺ in this compound. They are alternatively aligned along the c axis. The distances between the MnI and MnII alternate too. MnII O₆ octahedra form a nearly planar octahedron network (see figure 1(b)) in the plane perpendicular to the c axis while MnII O₆ octahedra form a buckled network (see figure 1(c)). Considering all these building
Figure 2. (a) The constant-energy scans collected from 2 meV to 8 meV are plotted as curves marked with symbols; the solid lines show the fits to the experimental data by convoluting with the instrument resolution convolution of Sika. (b) The constant-Q scans at different $Q_H$ positions close to the zone boundary $Q(1,0,1)$. The continuous curves show the fits to the experimental data presented in symbols by considering the convolution with the instrument resolution.

Figure 3. Energy scans conducted at a series of $Q_L$ positions from the antiferromagnetic zone centre $(1,0,0)$ to the zone boundary $(1,0,1)$. The excitation peak at the zone centre shows an energy gap of $\sim 1.4$ meV. The peaks shift to higher energy with the increase of $Q_L$, indicating a clear dispersive relationship. The experimental data are plotted as the symbol curves in different colours. The dashed curves show the fits to the experimental data by using an instrument resolution convolution method. The peaks at $Q_L = 0.1, 0.2, 0.3$ are fitted to an asymmetric Lorentzian peak corresponding to a damped harmonic oscillator [28] and the other peaks are fitted to a normal symmetric Lorentzian peak.

blocks, we should take into account the following interactions between the nearest-neighbour Mn$^{2+}$ ions in this dynamic model:

- the nearest Mn$\text{I}$$-$Mn$\text{I}$ interaction $J_a$ within the planar network
- the nearest Mn$\text{II}$$-$Mn$\text{II}$ interaction $J_b$ within the buckled network
- the nearest Mn$\text{I}$$-$Mn$\text{II}$ interaction $J_c$ between the planar and buckled networks
- the nearest Mn$\text{I}$$-$Mn$\text{II}$ interaction $J_d$ along the $c$ axis
- the second-nearest Mn$\text{I}$$-$Mn$\text{II}$ interaction $J_e$ along the $c$ axis

These interactions involve all the possible nearest-neighbour interactions. In addition, the magnetic anisotropies on the Mn$\text{I}$ and Mn$\text{II}$ sites are considered too. Thus, the Hamiltonian of the Heisenberg model for Mn$_4$Nb$_2$O$_9$ reads as follows:
The primary exchange interaction in Mn4Nb2O9 is the ferromagnetic interaction \( J_{e} \) steepest exchange interaction (one order of magnitude weaker than single-ion anisotropies. To simplify this model, we assume MnI and MnII to have the same magnetic anisotropy \( D \) [21]. In another Mn2 configuration with the completely quenched orbital angular momentum \( L \). It is worthwhile to mention that the magnetic anisotropy of Mn2 is much smaller than that of MnF2. In both cases, the magnetic anisotropy of Mn2 is quite weak, which is understandable because Mn2 ions in both these compounds have a 3d\( ^{2} \) electron configuration with the completely quenched orbital angular momentum \( L = 0 \).

Using the dynamic model described above, the spin-wave spectrum can be calculated by using the linear spin-wave calculation package SpinW [27]. On the basis of this package, a non-linear optimization program was coded to minimize the difference between the model and the experimental data. The optimized exchange parameters and magnetic anisotropy from this method are listed in table 1. The simulated spin-wave spectra calculated from the fitted parameters are plotted along the constant-Q scans while the contour map in \( Q \) shows no-data area. The maps in (a) and (b) use the same energy scale for the convenience of comparison. The two maps are normalized to the same intensity level as well, as indicated in the colour bar on the right.

**Figure 4.** The false-colour contour maps of the spin-wave dispersions measured from Mn4Nb2O9 along the (a) \( Q_{H} \) and (b) \( Q_{L} \) directions. The red dotted curves show the fitted peak positions from the experimental data. The contour map in (a) is plotted from the constant-energy scans while the contour map in (b) is constructed by the constant-\( Q \) scans. The pale-blue area in (b) shows no-data area. The maps in (a) and (b) use the same energy scale for the convenience of comparison. The two maps are normalized to the same intensity level as well, as indicated in the colour bar on the right.

**Table 1.** The exchange parameters of the spin-dynamic model described in the text by fitting to the experimental data.

| \( J_{a} \) (meV) | \( J_{b} \) (meV) | \( J_{c} \) (meV) | \( J_{d} \) (meV) | \( J_{e} \) (meV) | \( D \) (meV) |
|------------------|------------------|------------------|------------------|------------------|------------------|
| 3.38(15)         | 1.307(7)         | 0.202(4)         | −0.015(9)        | −0.027(5)        | −0.013(8)        |

\[
H = \frac{1}{2} J_{a} \sum_{ij} S_{i}^{z} S_{j}^{z} + \frac{1}{2} J_{b} \sum_{ij} S_{i}^{z} S_{j}^{z} + \frac{1}{2} J_{c} \sum_{ij} S_{i}^{x} S_{j}^{x} + \frac{1}{2} J_{d} \sum_{ij} S_{i}^{y} S_{j}^{y} + D \sum_{ii} (S_{i}^{z})^{2} + D_{2} \sum_{Mn_{II}} (S_{II}^{z})^{2}, \tag{1}
\]

where \( J_{a}, J_{b}, \) etc are the exchange interactions described as above, \( S_{i} \) and \( S_{j} \) are the magnetic moments on the \( i \) and \( j \) sites, which are the nearest neighbours on the different Mn sites, and \( D1 \) and \( D2 \) are the magnetic single-ion anisotropies. To simplify this model, we assume MnI and MnII to have the same magnetic anisotropy \( D \). Namely, both \( D1 \) and \( D2 \) equal \( D \).

From the results in table 1, we can see that the primary exchange interaction in Mn4Nb2O9 is the antiferromagnetic interaction \( (J_{b}) \) on the planar network of MnO6, and the secondary exchange interaction is the exchange interaction \( (J_{b}) \) on the buckled MnO6 network, which is also antiferromagnetic. The exchange interaction \( J_{c} \) is the inter-coupling between the two networks, which is also antiferromagnetic but one order of magnitude weaker \((\sim 0.2 \text{ meV})\). The exchange interactions \( (J_{d} \) and \( J_{e} \) along the \( c \) axis are both ferromagnetic. They are very weak, only a few hundredths of the two strong antiferromagnetic interactions. The fitting result also indicates that the magnetic anisotropy of Mn\( ^{2+} \) is a weak easy-axis type. This is consistent with the collinear magnetic structure of Mn4Nb2O9 from the neutron powder diffraction result [21]. In another Mn\( ^{2+} \)-based compound MnF2, a spin gap was observed at \( \sim 1.29 \text{ meV} \), which corresponds to the magnetic anisotropy energy about 0.11 meV [29]. The fitted anisotropy value 0.014 meV for Mn\( ^{2+} \) in Mn4Nb2O9 is even smaller than that value for MnF2. In both cases, the magnetic anisotropy of Mn\( ^{2+} \) are quite weak, which is understandable because Mn\( ^{2+} \) ions in both these compounds have a 3d\( ^{2} \) electron configuration with the completely quenched orbital angular momentum \( L = 0 \).
that the observed anisotropy in Mn₄Nb₂O₉ is still larger than the value 0.0069 meV reported for LiMnPO₄ [30]. However, the mean field calculation results shows that the dipole–dipole interaction only contribute half to the anisotropy in LiMnPO₄ [30]. The authors attributed the remaining part to higher-order orbital modifications of the ground state due to the local lattice distortion. Similar situation could happen to Mn₄Nb₂O₉ due to strong distortion and low symmetry on the two Mn sites.

Since the ferromagnetic interactions along the c axis are two orders of magnitude smaller than the main antiferromagnetic interactions, it would be interesting to consider an extreme case of the model, in which these weak interactions are completely zero in the spin-dynamic model described above. Thus, we obtain a simplified version with only the interactions on the planar octahedron network, on the buckled network, and between them. Thus, the system becomes a widely-discussed model, namely, a spin-dynamic model on the honeycomb lattices (but not completely in-plane). The difference is that there are two different honeycomb lattices in this system are linked with a weak antiferromagnetic interaction. According to the previous numerical studies [31, 32], the ground state of a honeycomb spin lattice depends on the nearest-neighbour interaction ($J_1$) and the next-nearest-neighbour interaction ($J_2$) on the hexagonal ring. When $J_2/J_1 < 1$, the system demonstrates some sort of frustration. For $J_2/J_1 \ll 1$, the system has an antiferromagnetic ground state, while the system has a spin-liquid state for $J_2/J_1$ in the range from 0.22 to 0.35 [32]. In the current case, the next-nearest interactions on both the hexagonal rings are negligible. If the two networks are decoupled from each other, this model satisfies the condition of $J_2/J_1 \ll 1$, which results in a Néel ground state, consistent with the experimental observation in this study.

It is worthwhile to compare the spin-dynamic models from both Mn₄Nb₂O₉ in this study and Co₄Nb₂O₉ in the previous study. The strong easy-plane single-ion anisotropy of Co²⁺ plays an essential role in the spin dynamics of Co₄Nb₂O₉, determining the in-plane magnetic structure. The DM interaction is another important ingredient in the model of Co₄Nb₂O₉, which causes canting of magnetic moments in the plane. In contrast, Mn₄Nb₂O₉ demonstrates the antiferromagnetic spin-dynamic feature with a weak easy-axis magnetic anisotropy. No DM interaction was observed in Mn₄Nb₂O₉ due to the 3d⁵ electronic configuration of Mn²⁺. Such a big difference between these two compounds is due to the intrinsic magnetic nature of Co²⁺ and Mn²⁺. The former has a 3d⁷ configuration with $L = 3$ while the latter has a 3d⁵ configuration with $L = 0$. Considering exchange interactions only, both of these two compounds have the strong antiferromagnetic interactions in the two networks of octahedra. They are determined by the superexchange interactions in their lattices, which is a shared feature in the spin dynamics of Mn₄Nb₂O₉ and Co₄Nb₂O₉. In another series of ME compounds, namely, LiMPO₄ (M = Ni [33], Mn [30], Fe [34]), the spin-dynamics studies show that LiMnPO₄ has no DM interaction and only very weak anisotropy in contrast to the strong canting/non-collinear magnetic structure and large spin gap in the Ni and Fe counterparts [30, 33, 34]. These two cases demonstrate the roles played by the orbital moments.

**Figure 5.** The simulated spin-wave-dispersion contour map of Mn₄Nb₂O₉ along the $Q_H$ (a) and $Q_L$ (b) directions by using the spin-dynamic model described in the text and the optimized exchange parameters fitted to the experimental data. The empty-circle curves are the fitted peak positions from the experimental data. The simulated dispersion matches the experimental data quite well.
Figure 6. The (1 0 0.1) off-Bragg peak of Mnb4O9 measured (a) at 50 K–100 K, (b) 100 K–120 K, (c) 120 K–210 K. 'G' denotes that the data points were obtained by fitting to a Gaussian. 'L' denotes that the data points were obtained by fitting to a Lorentzian. 'G + L' denotes that the data points were obtained by fitting to a sum of a Gaussian and a Lorentzian. Diffuse scattering was observed in the temperature range near $T_c$ of Mnb4O9.

3.2. Magnetic critical scattering

The magnetic critical scattering was measured at $Q (1 0 0.1)$ at a series of temperature points in the range from 50 K to 210 K through the Néel temperature of Mnb4O9. The experimental data are plotted in figures 6(a)–(c), which cover the temperatures below the phase transition, near the phase transition, and above the phase transition, respectively. As seen from the peak intensities and shapes in figure 6, at temperatures far below the Néel transition, such as 50 K and 70 K, the peaks look like a very sharp Gaussian without a broad shoulder on both sides. With temperature gradually increasing, the peaks gradually broaden and two long tails show up on both sides of the peak, which indicates a different origin. However, in the low temperature regime, the central peak intensity does not change significantly with the temperature. When the temperature approaches the Néel temperature ($\sim 108$ K), the peak intensity increases dramatically with temperature to reach a maximum intensity at 107.5 K. Then, the intensity drops gradually as the temperature rises from 107.5 K to 120 K. Near the Néel temperature, the central peak exhibits an evident long-tail feature. When the temperature continues to rise to 130 K, such a feature gradually fades away with the significant drop in intensity. Upon heating from 150 K to 210 K, the long tails become weaker and weaker while the intensity remains constant, similar to the peaks at 50 K and 70 K. It is speculated that the intense peaks with the long tails originate from the critical scattering of Mnb4O9 in the temperature range near the Néel temperature.

In general, the critical scattering from a magnetic system can be described as the sum of a Lorentzian, a squared-Lorentzian and background:[35]

$$I(Q) = \frac{A}{Q^2 + \kappa^2} + \frac{B}{(Q^2 + \kappa^2)^2} + BG,$$

where $A$, $B$ are peak intensities, $\kappa = \xi^{-1}$, where $\xi$ is the correlation length, and BG the background.

In the formula above, the Lorentzian contribution is attributed to the conventional Ornstein–Zernike form of magnetic critical scattering [36], while the squared-Lorentzian contribution is due to the magnetic clusters caused by inhomogeneities due to defects or impurities [35, 36]. In order to fit the data in this experiment properly, we have tried to fit the peaks to only a Gaussian, only a Lorentzian, only a squared-Lorentzian, the sum of a Lorentzian and a Gaussian, and the sum of a Lorentzian and a squared-Lorentzian. All these peak functions were convoluted with the instrument resolution during the fitting procedures. We found that the data below 100 K and above 130 K can be well fitted by a single Gaussian. The data from 90 K to 100 K can be well fitted by the sum of a Gaussian and a Lorentzian. The same method applies to the data between 120 K to 130 K. In the vicinity of $T_N$, namely, from 100 K to 120 K, the data can be almost perfectly fitted by a single Lorentzian. The squared-Lorentzian or the sum of a Lorentzian and squared Lorentzian do not improve the fitting results. See figure S1 (https://stacks.iop.org/NJP/24/083007/mmedia) in the supplemental materials. All these fittings indicate that there are some Gaussian residuals in the data set, which could be attributed to the Bragg tail since the scans were conducted not far away from the Bragg peak. This can be clearly seen at both low and high temperature ends. However, the Gaussian contribution is relatively weak in the vicinity of the phase transition. The fitting to a single Lorentzian is better than the fitting from a squared-Lorentzian, which indicates the magnetic critical scattering should be mainly attributed to the Ornstein–Zernike form of scattering rather than the scattering from the magnetic clusters [36]. This means that the sample is quite homogeneous and pure. This is quite normal for single crystals grown by the travelling-solvent
The fitted $\kappa$ values at different temperatures from the experimental data shown in figure 5. The black squares show the Gaussian + Lorentzian fittings to the experimental data at low temperatures. The blue triangles show the fitted values by fitting to the sum of a Gaussian and a Lorentzian. The red dots show the fitted values using a single Lorentzian function. The pink and blue lines are the guides to eyes. (b) The fitted Gaussian (the upper panel) and Lorentzian (the lower panel) amplitudes of the peaks at different temperatures from the different fitting methods. In the lower panel, the Lorentzian amplitude shows a strong peak at 107.5 K, around $T_N$, see the dotted red line. The dashed red line is a guide to eyes. In the upper panel, the Gaussian peak intensity, corresponding to the Bragg intensity, gradually decreases on heating in the temperature range below $T_N$. The dashed red curve in this range is fitted to the power law as described in the text. The horizontal dashed line above $T_N$ is a guide to eyes, showing residual intensity in the paramagnetic phase. All the parameters in this figure are produced by fitting the experimental data to the as-mentioned peak functions convoluting to the instrument resolution.

3.3. Mechanism of magnetoelectric coupling in Mn$_4$Nb$_2$O$_9$

As discussed in the previous papers [18, 21], Mn$_4$Nb$_2$O$_9$ has a collinear magnetic structure with the magnetic moments along the c axis, which is completely different from the in-plane magnetic structure of Co$_2$Nb$_2$O$_6$. We already concluded that the ME coupling effect in Co$_2$Nb$_2$O$_6$ can be explained by the inverse DM interaction because of its non-collinear in-plane magnetic structure. This explains the strong ME coupling in Co$_2$Nb$_2$O$_6$. However, Mn$_4$Nb$_2$O$_9$ has a collinear spin configuration with magnetic moments aligning along the c axis. Furthermore, Mn$^{2+}$ ions in Mn$_4$Nb$_2$O$_9$ have a 3d$^7$ electron configuration with the orbital angular momentum $L = 0$, which excludes the spin-orbital coupling in this compound. Therefore, the DM interaction does not play any role in the ME coupling mechanism of Mn$_4$Nb$_2$O$_9$. No analogue can be applied between Mn$_4$Nb$_2$O$_9$ and Co$_2$Nb$_2$O$_6$ to explain the ME coupling mechanism in the former. Therefore, it is still an open question what the origin of the ME coupling mechanism is in Mn$_4$Nb$_2$O$_9$. Considering that Mn$_4$Nb$_2$O$_9$ has a collinear magnetic structure, the most possible microscopic ME mechanism is magnetostriction, which is widely observed in the so-called up–up–down–down collinear floating-zone method because this method intrinsically has a purifying function similar to the zone-melting purification procedure [37].

The fitted parameters, $\kappa$, and the amplitudes of the fitted Gaussian and Lorentzian peaks, are plotted against temperature in figures 7(a) and (b), respectively. As shown in figure 7(a), the fitted $\kappa$ values from the two methods are plotted together. Considering all these $\kappa$ values in the full temperature range, we can draw two lines which cross at $T_N \sim 108.3$ K (see the red and blue lines). This point somehow is very close to the reported transition temperature $T_N$. Figure 7(b) shows the intensities for the fitted Gaussian and the Lorentzian peaks at different temperatures. Below $T_N$, the intensity of the Gaussian peak can be fitted to the power law: $I = I_0((T_N - T)/T_N)^{-2\beta}$. The fitting yields $T_N = 104.77 \pm 3.4$ and $\beta = 0.147 \pm 0.03$. The fitted transition temperature is slightly lower than the temperature mentioned above. The critical component $\beta$ value is closer to the reported value of 0.129 for the 2D Ising model [38]. As we know from the dynamic model discussed above, the exchange interactions in the networks, roughly in the ab plane, play the most important roles in the spin dynamics of this compound, which is consistent with this 2D-like value for the critical component. The intensities of the Lorentzian peaks are plotted in the lower part of the right figure. The dotted red curve shows the peak intensities fitted to a single Lorentzian. This curve shows a nearly symmetric shape around the Néel temperature $T_N$, which decays quickly on both sides, indicating the short-range correlation gradually developed when cooling to $T_N$ from above and gradually fades away when continuously cooling below $T_N$ due to the formation of the long-range order. It also means that the critical fluctuation dies out when the temperature moves away from $T_N$. The fitted $\kappa$ values in figure 7(b) can be used to calculate the correlation length of the magnetic structure, which reaches a maximal value ($\sim$50 Å) at the phase transition temperature.
magnetic structure [1, 4], as mentioned in the introduction. However, Mn$_4$Nb$_2$O$_9$ has no such a special magnetic configuration. How to explain the ME coupling mechanism in this compound is still elusive.

Even though Cr$_2$O$_3$ is the first ME compound ever discovered, the ME mechanism in Cr$_2$O$_3$ has been intensively studied experimentally and theoretically until recent years. From the theoretical point of view, there are several possible contributions to the ME coupling effect in Cr$_2$O$_3$, including the electric-field-induced exchange interaction, the electric-field-induced single-ion anisotropy change, the electric-field-driven g-factor shift, and the spin-orbital coupling (namely, antisymmetric exchange coupling). Hornreich and Shtrikman discussed all these possibilities and compared the simulated results to the measured ME coupling coefficient data in Cr$_2$O$_3$ [39]. They found that the two-ion exchange coupling is the predominant contribution to the ME coupling coefficient in the parallel direction while the ME coupling property in the perpendicular direction was ascribed to the electric-field dependent single-ion anisotropy. In both the parallel and perpendicular cases, the contributions from the electric field g-factor effect and the antisymmetric coupling are much weaker than the exchange coupling effect and single-ion anisotropy effect. Recently, the first-principle studies by two theoretical groups further clarified the origin of the ME coupling mechanism in Cr$_2$O$_3$. Mostovoy et al [40] confirmed that the spin fluctuation play critical roles in the ME property of Cr$_2$O$_3$, and the ME coupling effect is mainly ascribed to the exchange interaction. The relativistic interaction can explain the non-zero ME coupling at zero Kelvin. Malashevich et al [41] also theoretically studied the ME contribution in the perpendicular and parallel directions in Cr$_2$O$_3$, and found the orbital contribution to the longitudinal direction is small. Even though the sign changing effect of the ME coupling coefficient at the temperature approaching zero is still elusive, the ME coupling effect in Cr$_2$O$_3$ below $T_N$ has been well studied from the experimental and theoretical points of view. These studies in Cr$_2$O$_3$ provide in-depth insight into the ME mechanism in magnetic insulators with collinear magnetic structures. On the basis of Cr$_2$O$_3$ studies, we could discuss the ME coupling mechanism in Mn$_4$Nb$_2$O$_9$ since there are many similar features between Mn$_4$Nb$_2$O$_9$ and Cr$_2$O$_3$.

Despite that Mn$_2$Nb$_2$O$_7$ and Cr$_2$O$_3$ have different crystal and magnetic structures, and different magnetic ions, there are still some similarities between these two compounds. First of all, Mn$_4$Nb$_2$O$_9$ has a hexagonal crystal structure just as Cr$_2$O$_3$. In figure S2 in the supplemental materials, we compare the crystal structure of Mn$_2$Nb$_2$O$_7$ and Cr$_2$O$_3$. These two compounds have very similar crystal structure except the absence of inversion centre of the former from the symmetry point of view. Secondly, the magnetic structure of Mn$_2$Nb$_2$O$_7$ has the same magnetic point group 3$m'$ as Cr$_2$O$_3$ according to the symmetry analysis. Therefore, Mn$_4$Nb$_2$O$_9$ has in the same ME coefficient tensor just as Cr$_2$O$_3$:

$$
\alpha = \begin{bmatrix}
\alpha_{11} & 0 & 0 \\
0 & \alpha_{11} & 0 \\
0 & 0 & \alpha_{33}
\end{bmatrix}.
$$

The last but not the least, the MnO$_6$ octahedra have the similar distortions as the CrO$_6$ in Cr$_2$O$_3$. Each MnO$_6$ octahedron is formed with a large and a small triangle. In both compounds, these octahedra link in an up–down–up–down pattern (see figure 8). Such a special structure is essential to the large ME response to external electric or magnetic fields, which will be discussed in detail later. With the three similarities described above, we could consider the ME coupling mechanism in Mn$_4$Nb$_2$O$_9$ carefully as done for Cr$_2$O$_3$. In Cr$_2$O$_3$, at least four potential micro-mechanism have been considered to contribute to the ME coupling: the field-induced single-ion anisotropy change, the field-induced exchange interaction, the field-induced g-factor shift, and the antisymmetric exchange coupling (namely, the DM interaction). Considering the electron configuration of Mn$^{2+}$ and Cr$^{3+}$, we found that the orbital angular momentum of Mn$^{2+}$ is completely quenched, which excludes the possible contribution of the DM interaction. Due to the same reason, the single-ion anisotropy of Mn$^{2+}$ is highly suppressed. Therefore, we do not need to consider the contribution of the antisymmetric exchange effect and the field-induced single-ion anisotropy effect. The theoretical and experimental studies in Cr$_2$O$_3$ have confirmed that the exchange interaction makes the dominant contribution to the longitudinal ME effect. In Mn$_2$Nb$_2$O$_7$, all the orbital-induced contributions such as DM interaction, g-factor contribution, can be excluded. From the analysis above, the only possible origin of the ME coupling effect in Mn$_2$Nb$_2$O$_7$ is the exchange striction, namely, magnetostriction. Since exchange striction is very sensitive to bond lengths and angles, its responses to the external fields are highly dependent on the local configuration of the magnetic ions, such as the distortion of octahedra.

However, this is not the end of the story. Exchange interactions widely exist in magnetic materials. However, only a small number of magnetic materials are MF/ME materials because most of the exchange-induced ME coupling effect cancelled out due to the opposite responses from neighbour magnetic ions in the lattice. On the other hand, Mn$^{2+}$ has a larger magnetic moment than Cr$^{3+}$. Why does Mn$_4$Nb$_2$O$_9$ demonstrate a similar ME coefficient as Cr$_2$O$_3$?
Looking at the crystal structure of Mn$_4$Nb$_2$O$_9$, there are two different MnO$_6$ octahedra: Mn$^{I}$O$_6$ and Mn$^{II}$O$_6$. These octahedra have three oxygen ions on the top, forming a triangular face, and three oxygen ions on the bottom, forming another triangular face. These triangular faces are roughly perpendicular to the $c$ axis. There are three different triangular faces in total: one for the octahedron Mn$^{I}$O$_6$, one for the octahedron Mn$^{II}$O$_6$, and another one shared by two neighbouring octahedra Mn$^{I}$O$_6$ and Mn$^{II}$O$_6$ (denoted as $\Delta_A$). The shared triangle is the smallest one with the edge O–O distance $\sim$ 2.94 Å. The Mn$^{I}$O$_6$ triangle has the edge length 3.32 Å (denoted as $\Delta_B$), and the Mn$^{II}$O$_6$ one has the edge length 3.37 Å (denoted as $\Delta_C$). Along one Mn$^I$–Mn$^{II}$ chain in the unit cell, the triangles form an order like $\Delta_C | \Delta_A | \Delta_B | \Delta_C | \Delta_A | \Delta_B | ...$, where | indicates the shared triangles, || indicates the separated triangles. The schematics in figure 8 show the details about this configuration. The neighbour Mn$^I$–Mn$^{II}$ chains have just the reverse order.

The asymmetric octahedral arrangement of Mn$_4$Nb$_2$O$_9$ is reminiscent of the crystal structure of Cr$_2$O$_3$. Cr$_2$O$_3$ has the similar configuration of the CrO$_6$ octahedra, which were denoted as $[+]$ and $[-]$ in the discussion by Siratori et al [42] Such a structure is essential for the ME coupling effect in Cr$_2$O$_3$. The structure of Cr$_2$O$_3$ is built by octahedra with two different end triangles along the $c$ axis, one end is larger than the other. Since Cr$_2$O$_3$ forms an up–down–up–down magnetic structure along the $c$ axis (see figure S3 in the supplemental materials), an external electric field will cause different displacements of Cr$^{3+}$ ions and different changes of the magnetization on the two sites. For example, if an electric field pointing down is applied, the Cr$^{3+}$ ions on the up octahedra (namely, the octahedron with large triangle at the bottom) with up moments change more than the octahedra with down moments due to the crystal-field effect. Such inequivalent responses from Cr$^{3+}$ ions to external fields cannot cancel and consequently causes the magnetization variation and corresponding ME coupling [42]. The ME coupling effect in Mn$_4$Nb$_2$O$_9$ comes from a similar effect. When applying an electric field along the $c$ axis, the magnetic Mn$^{2+}$ ions would like to displace along the direction of the electric field in the octahedra. However, the Mn$^{2+}$ ion displacement in each octahedra will be different because of the asymmetric shapes of the octahedra. The ions would move a larger distance to the large triangle than towards the small triangle due to the local crystal fields if the external field is driving in that way.

In one chain, two Mn$^{I}$ octahedra align the same direction along the $c$ axis, while the two Mn$^{II}$ octahedra in the neighbouring chains align in the opposite direction. The Mn$^{II}$ octahedra have just an opposite situation. As for the four Mn$^I$ in the unit cell, two shift a larger distance and the other two shift a short distance. The same for the Mn$^{II}$ ions. If the octahedra Mn$^{I}$ and Mn$^{II}$ were identical, all the displacement
effects, e.g., the induced magnetization changes, would cancel out (see figure 8). However, the octahedra for \( \text{Mn}_1 \) and \( \text{Mn}_II \) are slightly different. The neutron powder diffraction experiment indicates the \( \text{Mn}^{2+} \) magnetic moments on these two sites are different, too. Thus, the external-field-induced magnetization changes cannot cancel. Eventually, we could observe the ME coupling effect due to the subtle difference between \( \text{Mn}_1 \) and \( \text{Mn}_II \). This explains the weak ME effect in \( \text{Mn}_4\text{Nb}_2\text{O}_9 \).

Zheng et al measured the ME coupling coefficients from a single crystal sample of \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) recently, and explained its ME coupling mechanism to be the same as the mechanism in \( \text{Cr}_2\text{O}_3 \) except the orbital contribution [43]. However, they did not pay attention to the fact that the non-equivalent \( \text{Mn}_1 \) and \( \text{Mn}_II \) sites play the critical role for the ME coupling effect in \( \text{Mn}_4\text{Nb}_2\text{O}_9 \). While in \( \text{Cr}_2\text{O}_3 \), the consistency between the magnetic structure and the \[ \pm \] octahedra guarantees the ME effect in this compound. For another isostructural compound, \( \alpha-\text{Fe}_2\text{O}_3 \) has a slightly different magnetic configuration, resulting in the completely cancellation of the ME effect [42]. See figure S3 in the supplemental materials. From the crystal and magnetic structures of \( \text{Mn}_4\text{Nb}_2\text{O}_9 \), if the non-equivalence is removed, \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) will lose its ME coupling effect just as \( \alpha-\text{Fe}_2\text{O}_3 \). \( \text{Mn}^{2+} \) ions have much larger magnetic moments than \( \text{Cr}^{3+} \). However, \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) does not demonstrate much larger ME coefficient than \( \text{Cr}_2\text{O}_3 \) [43]. This also supports the conclusion that the ME coupling effect is from the non-equivalent \( \text{Mn}_1 \) and \( \text{Mn}_II \) responses, as discussed here.

4. Conclusion

The spin dynamics of \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) were studied by using inelastic neutron scattering on the cold-neutron triple-axis spectrometer Sika. A spin-dynamic model was proposed and fitted to the experimental dispersions of \( \text{Mn}_4\text{Nb}_2\text{O}_9 \), which indicates that the antiferromagnetic interactions in the planar and buckled networks between nearest neighbour Mn--Mn cations dominate the dynamic behaviour of this system. The intrachain interactions along the \( c \) axis are weak ferromagnetic. \( \text{Mn}^{2+} \) ions demonstrate a weak easy-axis magnetic anisotropy. The magnetic critical scattering was measured, giving the correlation length of this system near the transition temperature. The ME coupling effect observed in \( \text{Mn}_4\text{Nb}_2\text{O}_9 \) can be explained by the exchange striction mechanism as observed in \( \text{Cr}_2\text{O}_3 \) due to the asymmetric crystal-field effects caused by the distorted octahedra around \( \text{Mn}_1 \) and \( \text{Mn}_II \). Differently, however, no orbital contribution plays role in the ME coupling in \( \text{Mn}_4\text{Nb}_2\text{O}_9 \). The non-equivalent responses on the \( \text{Mn}_1 \) and \( \text{Mn}_II \) sites are the key for the bulk ME coupling effect without complete cancellation.

Acknowledgments

This work is partially supported by the National Natural Science Foundation of China (NSFC, Nos. 12074242 and 11774217). We thank the Australian Centre for Neutron Scattering for the allocation of beam time on Sika (P6415). We also thank Taiwan National Synchrotron Radiation Research Centre for the financial support to the Sika operation.

ORCID iDs

Guochu Deng https://orcid.org/0000-0001-8807-9427
Zhenjie Feng https://orcid.org/0000-0001-5870-5159
Shixun Cao https://orcid.org/0000-0002-3915-2621

References

[1] Fiebig M 2005 J. Phys. D: Appl. Phys. 38 R123–52
[2] Cheong S-W and Mostovoy M 2006 Nat. Mater. 6 13–20
[3] Scott J F 2007 Nat. Mater. 6 256
[4] Tokura Y, Seki S and Nagaosa N 2014 Rep. Prog. Phys. 77 076501
[5] Choi Y J, Yi H T, Lee S, Huang Q, Kiryukhin V K and Cheong S-W 2008 Phys. Rev. Lett. 100 047601
[6] Katsura H, Nagaosa N and Balatsky A V 2005 Phys. Rev. Lett. 95 057205
[7] Sergienko I A and Dagotto E 2006 Phys. Rev. B 73 094434
[8] Yamauchi K, Barone P and Picozzi S 2011 Phys. Rev. B 84 165137
[9] Kaushik S D, Rayaprol S, Saha J, Mohapatra N, Siruguri V, Babu P D, Patnaik S and Sampathkumaran E V 2010 J. Appl. Phys. 108 084106
[10] Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y 2003 Nature 426 55
[11] Kenzelmann M et al 2005 Phys. Rev. Lett. 95 087206
[12] Murakawa H, Onose Y, Miyahara S, Furukawa N and Tokura Y 2010 Phys. Rev. Lett. 105 137202
[13] Bertaut E F, Corliss L, Fornat F, Aleonard R and Pauthenet R 1961 J. Phys. Chem. Solids 21 234
[14] Kolodiazhnyi T, Sakurai H and Vittayakorn N 2011 Appl. Phys. Lett. 99 132906
[15] Fang Y et al 2014 Sci. Rep. 4 3860
[16] Cao Y et al 2017 Sci. Rep. 7 14079
[17] Khanh N D, Abe N, Sagayama H, Nakao A, Hanashima T, Kiyanagi R, Tokunaga Y and Arima T 2016 Phys. Rev. B 93 075117
[18] Deng G et al 2018 Phys. Rev. B 97 085154
[19] Maignan A and Martin C 2018 Phys. Rev. B 97 161106
[20] Lee N et al 2020 Sci. Rep. 10 12362
[21] Deng G et al 2019 J. Phys.: Condens. Matter 31 235801
[22] Fang Y, Zhou W P, Yan S M, Bai R, Qian Z H, Xu Q Y, Wang D H and Du Y W 2015 J. Appl. Phys. 117 17B712
[23] Cao Y, Xiang M, Feng Z, Kang B, Zhang J, Guiblin N, Ren W, Dkhil B and Cao S 2017 RSC Adv. 7 13846
[24] Wu C-M, Deng G, Gardner J, Vorderwisch P, Li W-H, Yano S, Peng J-C and Imamovic E J. Instrum. 11 P10009.
[25] Eaton J W, Batement D, Hauberg S A and Wehbring R 2020 GNU Octave Version 6.1.0 Manual: A High-Level Interactive Language for Numerical Computations https://gnu.org/software/octave/doc/v6.1.0/ A
[26] Zheludev A 2007 Reslib3.4c
[27] Toth S and Lake B 2015 J. Phys.: Condens. Matter 27 166002
[28] Deng G and McIntyre G J unpublished.
[29] Yamani Z, Tun Z and Ryan D H 2010 Can. J. Phys. 88 771–97
[30] Toft-Petersen R et al 2012 Phys. Rev. B 85 224415
[31] Fouet J B, Sindzingre P and Lhuillier C 2001 Eur. Phys. J. B 20 241–54
[32] Bishop R F and Li P H Y 2012 Phys. Rev. B 85 155135
[33] Toft-Petersen R et al 2011 Phys. Rev. B 84 054408
[34] Toft-Petersen R et al 2013 Phys. Rev. B 92 024404
[35] Tian W et al 2009 Phys. Rev. B 80 134422
[36] Collins M F 1989 Magnetic Critical Scattering (Oxford: Oxford University Press)
[37] Pfann W G 1952 JOM 4 747
[38] Ibarra-García-Padilla E, Malanche-Flones C G and Poveda-Cuevas F J 2016 Eur. J. Phys. 37 065103
[39] Hornreich R and Shtrikman S 1967 Phys. Rev. 161 506
[40] Mostovoy M, Scaramucci A, Spaldin N A and Delaney K T 2010 Phys. Rev. Lett. 105 087202
[41] Malashevich A, Coh S, Souza I A and Vanderbilt D 2012 Phys. Rev. B 86 094430
[42] Siratori K, Kohn K and Kita E 1992 Acta Phys. Pol. A 81 431
[43] Zheng S H et al 2020 Appl. Phys. Lett. 117 072903